

Université catholique de Louvain Institute of Condensed Matter and Nanosciences Division of Bio and Soft Matter

Nanostructured Organic Radical Cathodes from Self-assembled Nitroxide-containing Block Copolymers

Guillaume Hauffman Supervisor: Professor J.-F. Gohy

> Thesis submitted in fulfilment of the degree of Doctor in Sciences

Louvain-la-Neuve 2015-2016



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"Quand vous avez éliminé l'impossible, ce qui reste, même improbable, doit être la vérité." Sherlock Holmes Le signe des quatre, Sir Arthur Conan Doyle

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List of abbreviations and symbols

χ	Flory-Huggins parameter
ΔG_m	Free energy of mixing
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
3DOM	Three-dimensional electrodes
4-oxo-TEMPO	4-Oxo- $2,2,6,6$ -tetramethylpiperidine- N -oxyl
Ð	Dispersity
\mathbf{AC}	Activated carbon
AFM	Atomic force microscopy
AGET	Activator generated by electron transfer
AIBN	Azobisisobutyronitrile
ARGET	Activator regenerated by electron transfer
ATRP	Atom transfer radical polymerization
BCC	Body centered cubic spheres
BCP	Block copolymer
Bpy	Bipyridine
C_{\parallel}	Parallel cylinders
C_{\perp}	Perpendicular cylinders
CB	Carbon black
CGC	Critical gel concentration
CMC	Carboxy methyl cellulose
CMC	Critical micellization concentration
CMT	Critical micellization temperature
CNTs	Carbon nano-tubes
CRP	Controlled radical polymerization
CTA	Chain transfer agent
Cu ⁰ -RDRP	Copper(0) mediated reversible-deactivation radical poly-

	merization
CV	Cyclic voltammetry
D_{eq}	Domain size at equilibrium
DEC	Diethyl carbonate
DLS	Dynamic light scattering
DMC	Dimethyl carbonate
DMF	N, N-Dimethylformamide
DNA	Deoxyribonucleic acid
dNbpy	4,4'-Dinonyl-2,2'-dipyridyl
DP	Degree of polymerization
E_i	Initiator efficiency
E	Reduction potential
E_0	Standard reduction potential
EBiB	Ethyl α -bromoisobutyrate
EC	Ethylene carbonate
EPR	Electron paramagnetic resonance
Equiv.	Equivalents
ESR	Electron spin resonance
FRP	Free radical polymerization
GTP	Group transfer polymerization
HEX	Hexagonally packed cylinders
ISET	Inner-sphere electron transfer
ISL	Intermediate segregation limit
ITO	Indium tin oxide
IUPAC	International union of pure and applied chemistry
L_{\parallel}	Parallel lamellae
$L_{\perp}^{"}$	Perpendicular lamellae
LAM	Lamellae
Li-ion	Lithium-ion
LiTFS	Lithium trifluoromethanesulfonate
\bar{M}_n	Number average molar mass
M_p	Molar mass of the highest peak
$\bar{M_w}$	Weight average molar mass
\bar{M}_z	Z average molar mass
MCF	Mesocellular carbon foam
MEMs	Microelectromechanical systems
MWCNTs	Multi walls carbon nano-tubes
MWCO	Molecular weight cut-off
N	Total degree of polymerization
NimH	Nickel metal hydride
NMP	Nitroxide mediated polymerization
NMR	Nuclear magnetic resonance

OCV	Open circuit voltage
ODT	Order-disorder transition
ORB	Organic radical battery
OSET	Outer-sphere electron transfer
PAA	Poly(acrylic acid)
PAn	Polyaniline
PAzPMA	Poly(3-azidopropyl methacrylate)
PDI	Polydispersity index
PDMS	Poly(dimethylsiloxane)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PGMA	Poly(glycidyl methacrylate)
PMDETA	N, N, N', N', N'', N''-Pentamethyldiethylenetriamine
PMMA	Poly(methyl methacrylate)
PNB	Polynorbornene
\mathbf{PS}	Polystyrene
\mathbf{PTFE}	Polytetrafluoroethylene
PTMA	Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate)
PTMPM	Poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate)
PVDF	Polyvinylidene fluoride
R_c	Radius of the core
R_{a}	Radius of gyration
$\vec{R_h}$	Hydrodynamic radius
R_m	Radius of the micelle
\mathbf{RAFT}	Reversible addition-fragmentation chain transfer
RFB	Redox flow battery
ROMP	Ring opening metathesis polymerization
ROP	Ring opening polymerization
SARA-ATRP	Supplementary activator and reducing agent atom trans-
	fer radical polymerization
SBS	Polystyrene-b-polybutadiene-b-polystyrene
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SET-LRP	Single-electron transfer living radical polymerization
SI-ATRP	Surface initiated atom transfer radical polymerization
SOC	State of charge
SQUID	Superconducting quantum interference device
SSL	Strong segregation limit
SWCNTs	Single wall carbon nano-tubes
$TBAClO_4$	Tetrabutylammonium perchlorate
TBAF	tert-n-Butylammonium fluoride
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy

TEMPO-OH	4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy
THF	Tetrahydrofuran
TMPM	2,2,6,6-Tetramethylpiperidin-4-yl methacrylate
TsCl	Tosyl chloride
UV-vis	Ultraviolet–visible spectroscopy
VGCF	Vapor grown carbon fibres
WSL	Weak segregation limit
Z	Aggregation number

CHAPTER 1

Introduction

Abstract

This introduction deals with two different concepts that can appear unrelated to the unadvertised reader. Indeed, self-assembly of block copolymers and batteries seem at first unrelated. Although, this thesis focuses on the development of new cathodic organic materials, based on block copolymer self-assemblies, for the development of a new generation of nanostructured secondary batteries. Consequently, in a first part, the focus is made onto block copolymers: from their synthesis, which has become more accessible thanks to the development of controlled radical polymerization techniques, to the self-assembly properties of such high value materials. Indeed, block copolymers can self-assemble in thin films and in solution, leading to the formation of nanostructured materials. These properties have been widely employed in a wide range of applications from nanotechnologies to life sciences. In a second part, the development of primary and secondary batteries over the past decade is briefly reviewed. Indeed, chemical storage appears to be the most efficient way to obtain nomad electrical energy.

1.1 Polymers and block copolymers

The Oxford dictionary on-line defines a polymer as "A substance" which has a molecular structure built up chiefly or completely from a large number of similar units bonded together." Therefore a polymer is a macromolecule made of the repetition of smaller molecules covalently linked together and named monomers. Polymers are characterized by a degree of polymerization (DP) corresponding to the number of repeating units forming the polymer. The DP can be determined by dividing the molar mass of the polymer by the molar mass of the repeating unit.^[1] Since a polymeric sample is usually constituted of a distribution of chains with different lengths, a molar mass distribution is used in order to describe the relation between the number of moles of each polymer chain length (N_i) and the molar mass (M_i) of that species. Depending of the used statistical method, different average molar masses can be obtained: number average molar mass (\bar{M}_n) , weight average molar mass (\bar{M}_w) and Z average molar mass (\bar{M}_z) (Equations 1.1). The ratio between \bar{M}_w and \overline{M}_n gives the molar mass dispersity D_M ,¹ measuring the distribution of molar masses in a polymer sample. A $D_M = 1$ corresponds to the ideal case where all polymer chains have the same size. Proteins are a natural example of a polymer with a \mathcal{D}_M of 1.

$$\bar{M}_n = \frac{\sum M_i N_i}{\sum N_i} \qquad \bar{M}_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \qquad \bar{M}_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i}$$
(1.1)

A homopolymer is constituted of only one monomer species and a copolymer is composed of two or more different monomer species. Different types of copolymer exist depending on the monomer species arrangement along the chain: statistical (or random) copolymers, gradient copolymers, alternating copolymers and block copolymers, corresponding to copolymers where the monomer species are respectively disposed: randomly, with a gradient, alternatively and sequentially (Figure 1.1).

Block copolymers can take different architectures depending on block disposition (Figure 1.2).^[4] Due to the covalent bond between the blocks constituting the copolymer, block copolymers present several advantages over other copolymer types. When the constituting blocks are immiscible, a phase separation limited in space occurs, giving block copolymers the possibility to form ordered nanostructures (Section 1.3). Due to they self-assembly properties, block copolymers have attracted a great interest

 $^{^1}According$ to IUPAC, the term dispersity and its symbol $\mathcal D$ should be preferred over the term polydispersity index and its acronym PDI. $^{[2]}$



Figure 1.1: Types of copolymers with two different monomer species.^[3]

over the past decade. In bulk, block copolymers can be used as thermoplastic elastomers. In thin films, the range of applications spans from filtration membranes to nanotemplates.^[5] Self-assembly can also occur in solution by using a selective solvent to form micelles and vesicles.^[6] Micelles and vesicles are used in medicine as drug delivery vehicles and in chemistry as nano reactors.^[5,7] The variety of shapes and structures available for block copolymers added to the variety of monomer species with radically different properties allow block copolymers to be used in a wide range of applications.^[4,8,9]



Figure 1.2: Typical architectures of block copolymers.

1.2 Synthesis of block copolymers

Block copolymers were initially produced by living anionic polymerization, which consists of adding monomers to an anionic chain carrier. Anionic polymerization, as cationic polymerization, is a living polymerization belonging to the chain growth polymerization class. The *International Union of Pure and Applied Chemistry* (IUPAC) defines a living polymerization as "A chain polymerization from which chain transfer and chain termination are absent."^[1] (Figure 1.3) i.e. monomers will add to the reactive chain end until their full consumption. Moreover, the addition of monomers to the system will restart and continue the chain growth. Usually, living systems also present a fast initiation step compared to the propagation, allowing all chains to grow at the same time. Unfortunately, living anionic polymerization presents some drawbacks such as the extreme reactivity of the anionic species toward interfering electrophiles, making the technique difficult to handle.^[10]



Figure 1.3: Chain growth polymerization steps. Where * is an active center e.g. a cation, an anion or a radical. Reproduced from Ref.^[11]

In the 1990's controlled radical polymerization (CRP) techniques were developed, allowing the synthesis of well-defined polymers and block copolymers with a wide range of architectures.^[12] A controlled radical polymerization presents a radical chain carrier. CRP is similar to living polymerization but presents minimized steps of chain transfer and chain termination (Figure 1.3). Of course, radicals are highly active species and can side react during the polymerization process. Moreover transfer and termination processes compete with the propagation step, leading to uncontrolled polymer size with broad dispersity. In order to limit these undesired steps, CRP are based on an equilibrium between active species, i.e. growing radicals, and dormant species, i.e. the reversibly deactivated propagating radicals (Figure 1.4). Such equilibrium is largely displaced to the dormant form, leaving a very low concentration of radical species at a given time. Indeed, the kinetic equations reveal that the propagation rate is proportional to the radical concentration in the system (Equation 1.2). On the other hand, the termination rate is proportional to the square of the radical concentration in the system (Equation 1.3). Therefore, a decrease of the radical concentration at a given time will proportionally decrease the propagation rate but will decrease more dramatically the termination rate.



Figure 1.4: CRP main equilibrium between an active radical (P_n^{\bullet}) and its dormant form $(P_n - X)$. M stands for monomers and X stands for the controlling agent.

$$R_p = k_p[M][P^{\cdot}] \tag{1.2}$$

$$R_{ter} = k_{ter}[P^{\cdot}][P^{\cdot}] \tag{1.3}$$

Different methods of CRP have been developed depending on the implementation of the active/dormant equilibrium. The mostly used methods are:

- NMP: nitroxide mediated polymerization.
- RAFT: reversible addition-fragmentation chain transfer.
- ATRP; atom transfer radical polymerization.

Both NMP and ATRP are based on a reversible encapsulation of the active radical. The cap is a stable nitroxide radical in NMP and an halogen in ATRP. RAFT is based on a free radical polymerization mechanism (FRP), usually initiated by Azobisisobutyronitrile (AIBN), where a chain transfer agent (CTA) is added to the system. The active radical undergoes a degenerative transfer to the CTA, forming a dormant chain and releasing another polymer chain, previously added to the CTA, which will come back to its active form (Figure 1.5).

$$\begin{pmatrix} P_n \\ M \end{pmatrix} + \begin{matrix} X \\ Z \end{matrix} \stackrel{X \\ Z \end{pmatrix} \stackrel{X \\ Z \end{pmatrix} \stackrel{X \\ Z \end{pmatrix} \stackrel{X \\ Z } \stackrel{X \\ Z \end{pmatrix} \stackrel{X } \stackrel{X } \stackrel{X } \stackrel{X } \stackrel{X } \stackrel{X } \stackrel{X$$

Figure 1.5: RAFT main equilibrium. An active chain add to the CTA, forming a dormant species and releasing a dormant chain previously added to the CTA.

1.2.1 Atom transfer radical polymerization

ATRP is a powerful and widely used CRP technique, allowing the polymerization of a wide range of monomer types such as styrenic, acrylate, methacrylate, acrylamide and methacrylamide and the formation of a wide range of architectures.^[13]

Simultaneously developed in 1995 by Professor Krzysztof Matyjaszewski^[14–16] and Professor Mitsuo Sawamoto,^[17] ATRP is based on the establishment of a reversible equilibrium between an active and a dormant species. This equilibrium is based on the reversible reduction of the halide chain end, generating the propagating radicals. The reduction is catalysed by a metal-ligand complex formed by the association of copper bromide (CuBr) or copper chloride CuCl salt with a bidentate or tridentate nitrogen ligand e.g. bipyridine (bpy). Several transition metals are available but copper is the most widely used due to its efficiency in term of cost and versatility.^[18]

Figure 1.6 shows the mechanism of ATRP catalysed by a copper halide (Cu^IX). The initiation step consists in the formation of a free radical (\mathbb{R}^{\bullet}) via the reduction of an initiator i.e. an alkyl halide (\mathbb{R}^{-X}). The reduction is catalysed by a Cu^IX/L metal ligand complex. During the catalysis, the metal Cu^I is oxidized into Cu^{II} and the halogen is transferred from the initiator to the metal-ligand complex, forming Cu^{II}X₂/L. The free radical \mathbb{R}^{\bullet} reacts with the first monomeric unit, initiating the polymerization. During the propagation step, the active chain is growing by adding monomers. CuX₂/L transfers an halogen to the growing chain, leading to the dormant species $\mathbb{R}_n - X$ and the Cu^I catalyst form. The inactive dormant chain is reduced by the Cu^IX/L, regenerating the active growing chain and allowing the monomer addition. Such oxydoreduction cycles continue all over the polymerization process, allowing a control of the polymerization reaction by drastically decreasing the termination and transfer reactions thanks to the reduced concentration of radicals present in solution.

This section presents the basis of the ATRP and the interested reader is encouraged to take a look in the literature to understand all the factors influencing the control in ATRP and all the potential of this technique for well-defined polymer synthesis.^[13,19–21]



Figure 1.6: Mechanism of ATRP catalysed by copper halides. X stands for an halogen, usually a bromide or a chloride.

Over the years, Matyjaszewski has developed different variants of the ATRP process. In reverse ATRP, a conventional free radical initiator is used in combination with a Cu^{II} complex, generating *in situ* the I–X initiator and the Cu^{I} complex.^[22] In AGET-ATRP,² a classical ATRP initiator and a Cu^{I} complex are added to the reaction. The Cu^{I} complex is generated *in situ* by adding a non-radical forming reducing agent, e.g. ascorbic acid, to the solution.^[23,24] Both reverse-ATRP and AGET-ATRP present the advantage to generate *in situ* the more air sensitive Cu^{I} . ARGET ATRP³ is similar to AGET-ATRP but in ARGET-ATRP the reducing agent constantly regenerates the Cu^{I} species from Cu^{II} species irreversibly formed during termination processes.^[25,26] Therefore, in ARGET-ATRP the copper catalyst concentration can be decreased to a few ppm and the reaction can be performed in the presence of air.^[24] eATRP consists in using an electric current to reduce Cu^{II} in Cu^{I} and *vice versa*.^[27]

²Activator Generated by Electron Transfer (AGET).

³Activator ReGenerated by Electron Transfer (ARGET).

1.2.2 SARA-ATRP or SET-LRP?

A last variant of ATRP consists in using a mix of Cu^0 and Cu^{II} as catalytic system. Since 2006, Professor Matyjaszewski (SARA-ATRP)^[28,29] and Professor Haddleton (SET-LRP)^[30,31] are under discussion about the involved mechanism.^[32-35]

In supplementary activator and reducing agent atom transfer radical polymerization (SARA-ATRP), Professor Matyjaszewski postulates that Cu^0 acts as a supplemental activator and a reducing agent of Cu^{II} via an inner-sphere electron transfer (ISET) mechanism, (re)generating the main activator Cu^{I} through comproportionation (Figure 1.7.a).^[34]

In single-electron transfer living radical polymerization (SET-LRP), Professor Haddleton postulates that alkyl halides are activated by Cu^0 via an outer-sphere electron transfer (OSET) process, generating Cu^{I} species. Cu^{I} is instantaneously disproportionated into Cu^{0} and Cu^{II} and doesn't participate to the alkyl halides activation. The dormant species are activated by Cu^{0} and active species are deactivated by Cu^{II} . A minimal amount of comproportionation maintains a suitable concentration of Cu^{0} activator (Figure 1.7.b).^[36–38]

Since both mechanisms are similar and differ only about the species involved into the alkyl halides activation, we will not take part into the discussion about the correct mechanism and the generic term of copper(0) mediated reversible-deactivation radical polymerization (Cu⁰-RDRP) will be employed for both SET-LRP and SARA-ATRP processes.



Figure 1.7: The mechanism of SARA-ATRP (a) and SET-LRP (b). Bold arrows indicate major reactions contributing to the polymerization process. Solid arrows indicate supplemental reactions. Dashed arrows indicate unessential reactions that can be neglected. Reproduced from Ref.^[35]

1.3 Self-assembly of block copolymers

As previously mentioned, block copolymers can self-assemble in solid state and in solution to form periodic nanostructures. IUPAC defines self-assembly as "spontaneous and reversible organization of molecular entities by noncovalent interactions".^[39] They clarify that "self-assembly is a process in which a system of pre-existing components, under specific conditions, adopts a more organized structure through interactions between the components themselves". In the case of block copolymers, the phase separation occurs due to the mutual immiscibility of the blocks. Since the blocks are linked together the phase separation process is limited in space, leading to a microphase separation, i.e. the formation of periodic nanostructures. Therefore a wide range of nanostuctures can be observed as illustrated in Figure 1.8. These self-assembly properties of block copolymers have been widely studied over the past decades leading to applications in a variety of fields from medicine,^[7,40,41] to engineering.[42,43]



Figure 1.8: Typical self-assembled structures obtained from block copolymers in bulk, thin film and solution. In bulk: body centered cubic packed spheres (BCC), hexagonal packed cylinders (HEX), gyroid, simple lamellar (LAM). In thin films: lamellar perpendicular (L_{\perp}) or parallel (L_{\parallel}) to the surface, cylindrical perpendicular (C_{\perp}) or parallel (C_{\parallel}) to the surface and spherical. In solution: spherical micelles, cylindrical micelles and vesicles. Reproduced from Ref.^[44]

1.3.1 Self-assembly in bulk

Phase separation in bulk has been widely studied.^[12,45-53] Phase separation behavior of block copolymers in bulk is governed by the χN parameter. χ is the Flory-Huggins interaction parameter and N is the total degree of polymerization. Roughly, N represents the entropy of the system and χ the enthalpic contribution to the phase separation.

$$\chi \propto \frac{1}{T} \tag{1.4}$$

Indeed, from a thermodynamic point of view, the phase separation will be spontaneous when the free energy of mixing (ΔG_m) is disadvantaged, i.e. $\Delta G_m > 0$ with:

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{1.5}$$

where ΔH_m is the enthalpy of mixing and ΔS_m is the entropy of mixing.^[54]

In a mixing, the entropy is generally favored since the mixing increases disorder ($\Delta S_m > 0$). On the opposite, the enthalpy term does not favor the mixing ($\Delta H_m > 0$). Consequently phase separation is favored, i.e. the mixing is unfavored (ΔG_m), when the entropic gain of mixing ($\Delta S_m > 0$) doesn't balance the enthalpy of mixing term (ΔH_m):

$$T\Delta S_m < \Delta H_m \tag{1.6}$$

This is often the case for polymers, since the constrains on chain configurations imply a low entropic contribution. Therefore, phase separation in block copolymers is favored when the DP increases and when the temperature decreases (equation 1.4).

Another factor influencing the phase separation in block copolymers is the composition of the polymer, i.e. the volume fraction f_A of the blocks. For a block copolymer A-B, f_A corresponds to the volume fraction of A. In consequence $f_A = 0$ corresponds to a homopolymer of B and $f_A = 1$ corresponds to a homopolymer of A. The χN value at which phase separation occurs for a given f corresponds to the order-disorder transition (ODT). By plotting χN as a function of f_A a phase diagram predicting the different accessible morphologies is obtained. The theoretical phase diagram of PS-*b*-PI block copolymers is illustrated in Figure 1.9. When both blocks have the same volume fraction, i.e. $f_A = 0.5$, a lamellar structure is observed. $f_A = 0.5$ corresponds to the minimum value of χN where the ODT occurs ($\chi N = 10.5$ in this example). Below that value the blocks are miscible. Above that value the phase separation occurs. Three regimes of phase separation exist depending on the value of χN :^[47-49,53]

- $\chi N \simeq 10 12$ Weak segregation limit (WSL).
- $12 \lesssim \chi N \lesssim 100$ Intermediate segregation limit (ISL).
- $\chi N > 100$ Strong segregation limit (SSL).

Figure 1.10 represents the evolution of structure and composition profiles from a WSL to a SSL regime. For a $\chi N \ll 10$ no phase separation is observed and the composition profile is homogeneous. For a SSL with $\chi N \gg 10$, the phase separation is well defined and the composition profile corresponds to a strongly microphase segregated pattern.



Figure 1.9: Theoretical phase diagram of PS-*b*-PI block copolymers with the main morphologies accessible and the corresponding volume fractions (*f*). BCC, HEX and LAM stand respectively for body centered cubic packed spheres, hexagonal packed cylinders and simple lamellaes. Adapted from Ref.^[55–57]

Depending on the regime, the domain size at equilibrium can be predicted.^[58]

- For SSL regime: $D_{eq} \sim N^{2/3} \chi^{1/6}$.
- For WSL regime: $D_{eq} \sim N^{1/2} \chi^0$.

Symmetric block copolymers $(f_A \simeq 0.5)$ form lamellar structures, alternating the layers of the constituting blocks. When the block copolymers become asymmetric, other morphologies are obtained in order to minimize the interaction surface. Since curved surfaces are energetically



Figure 1.10: Evolution of structure with the combined parameter χN for a symmetric diblock copolymer with f = 0.5. When $\chi N \sim 10$, small variations in system entropy ($\sim N^{-1}$) or energy ($\sim \chi$) lead to ordered ($\chi N \geq 10$) or disordered ($\chi N \leq 10$) states. A homogeneous composition profile ϕ_A versus r results when entropic factors dominate ($\chi N \ll 10$), whereas a strongly microphase segregated pattern characterizes the limits where energetic factors prevail ($\chi N \gg 10$). Adapted from Ref.^[51]

more favorable, curved phases are formed. For $0.2 \leq f_A \leq 0.3$ cylindrical structures (cylindrical micro-domains of A inside a matrix of B) are obtained. For lower values of f_A spherical micro-domains of A inside a matrix of B are observed. Of course by increasing f_A the opposite structures are achieved, i.e. micro-domains of B inside a matrix of A (Figure 1.9). Therefore, the morphology can easily be tuned by changing the composition and the chain length of block copolymers, leading to tailor-made nanostructured materials.^[41,56,58-64]

Finally, it's generally admitted that a narrow dispersity is mandatory for obtaining long-range ordered microphase separation. However this thought begins to be re-examined.^[65] For example Mahanthappa *et al.* have obtained microphase separation with lamellar and cylindrical morphologies for PS-*b*-PMMA presenting a broad dispersity up to 1.7.^[66]

1.3.2 Self-assembly in thin films

Thin films can be obtained using various techniques such as spincoating, dip-coating or drop casting. The self-assembly of block copolymer in thin films is similar to the self-assembly in solid state excepted that the thickness of the polymer layer is lower than 1 μ m. Important factors such as the Flory-Huggins parameter χ , the total degree of polymerization N and the volume fraction f_A are still influencing the self-assembly process. However, due to the film thickness, some factors negligible in bulk are playing an important role in thin films.

Interface effects

One additional factor which plays a role in thin film self-assembly is the interfacial interaction. Two interfacial interactions are distinguished:

- Film/substrate interface, corresponding to the interfacial tension $\gamma_{substrate}$.
- Film/air or film/superstrate interface, corresponding to the interfacial tension γ_{air} and $\gamma_{superstrate}$.

Usually micro-domains are oriented parallel to the surface due to the preferential interaction of one block with one interface (Figure 1.11.a).^[12] ^[67,68] In order to obtain micro-domains perpendicular to the surface the interactions of both blocks with the surface need to be the same. This requirement can be met as the interfacial tensions (γ) between the blocks and the surface are equal (Figure 1.11.b). This phenomenon has been demonstrated by Hawker *et al.*^[69] They demonstrate that without control of the film/air interface a parallel orientation of lamellar micro-domains is obtained. Indeed, the PS block interacts preferentially with the air due to its lower surface energy. However by deposing a non preferential surface on the top of the polymer film, the lamellaes are oriented perpendicular to the surface. A surface coated with a random copolymer using the same monomeric units than the self-assembled block copolymer was used as non preferential surface.

How to control the phase separation of block copolymer thin films

Techniques used for the formation of thin films generally imply a kinetic process leading to nanostructured thin films with defects and a lack of long-range ordering. In some cases no nanostructuration is observed after thin film formation. In order to increase the phase separation, reduce the defects and improve the long-range order, different techniques of annealing are employed. Indeed, the annealing process allows the polymer chains to move and reorganize, enabling them to reach a more stable state, and a better phase separation. The main annealing



Figure 1.11: Influence of the interfaces on the orientation of lamellar micro-domains for an AB diblock copolymer. a. with preferential interactions, b. without preferential interactions. $\gamma =$ interfacial tension. Reproduced from Ref.^[70]

processes employed are thermal annealing and solvent annealing. Thermal annealing consists in heating the sample above the T_g and below the T_{ODT} of the constituents.^[71] Solvent annealing consists in swelling the polymer film with solvent vapors or super critical CO₂ in order to allow polymer chains to reorganize.^[72] Ober *et al.* have reported solvent annealing of poly(2-hydroxyethyl methacrylate)-*block*-poly(methyl methacrylate) (PHEMA-*b*-PMMA) by using mixtures of selective solvents.^[73]

The thickness of the swollen film is a key parameter for controlling the thin film morphology. Indeed, as demonstrated by simulations and experiments, an incommensurability between the natural period of the copolymer and the film thickness rises the chain stretching that can induce an orientation of the microdomains perpendicular to the surface.^[74-78] Thanks to this, perpendicular oriented domains can be obtained even in the presence of preferential interfacial interactions.^[77] Knoll *et al.* have solvent annealed a triblock copolymer of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) in chloroform. The annealing process introduces variations in the film thickness and atomic force microscopy (AFM) pictures reveal a variation of morphology as a function of the film thickness (Figure 1.12).^[67]

Another factor influencing the final morphology during a solvent annealing is the solvent evaporation rate.^[79-81] Indeed, the solvent evap-



Figure 1.12: Influence of the film thickness onto the morphology. a,b: tapping-mode AFM phase pictures of two SBS films with different initial thickness after solvent annealing. A change of morphology as a function of film thickness is observed (c). d. Simulation profile of the same triblock copolymer film. Reproduced from Ref.^[67]

orating from the swollen film induces a gradient of concentrations into the film (Figure 1.13). The gradient goes from the most concentrated, i.e. the substrate, to the less concentrated, i.e. the surface. The transition from the disordered to the ordered state is driven by the decrease of solvent concentration. This transition extends through the film to the substrate following the opposite direction of the solvent gradient, leading to a perpendicular orientation of the micro-domains.

Some more exotic processes have been developed in order to ameliorate the phase separation and increase the micro-domains ordering of block copolymer thin films:

- Electric field: thanks to the difference of dielectric constant of the copolymer blocks, the micro-domains orient parallel to the electric field lines.^[82,83]
- Templated self-assembly onto nanopatterned surfaces: a structured substrate orients the morphology thanks to the preferential chemical affinity of one block to the template.^[4,56,84,85]
- Epitaxy: In the case of copolymers with a crystallizable sequence, domain orientation is driven by the preferential interaction of the



Figure 1.13: Schematic representation of micro-domains ordering via the application of a solvent concentration gradient onto a block copolymer thin film. r is the film thickness and ϕ_s the solvent gradient. Reproduced from Ref.^[80]

crystal growth onto the surface of another crystal. The growth follows one crystallographic direction of the crystalline substrate.^[86]

Applications

Block copolymer thin films have been widely studied in academic and industrial areas due to they many interesting features such as:

- Self-assembly properties leading to a variety of morphologies.
- Small amount of material required for their fabrication.
- Physical properties different from the material bulk properties.

Block copolymer thin films are used in a wide range of applications like filtration membranes, $^{[41,87-89]}$ nanotemplates $^{[43,56,59,90,91]}$ and memory devices. $^{[92]}$ Their range of applications has already largely been described into different reviews. $^{[5,41,56,59]}$

1.3.3 Self-assembly in solution

The self-assembly of block copolymers in solution is driven by the affinity of the polymer to the solvent. A distinction is made between a non-selective and a selective solvent. A non-selective solvent corresponds
to a solvent in which all the blocks constituting the copolymer are soluble. Then the polymer chains adopt a random-coil conformation and no phase separation is observed. A selective solvent is a thermodynamically good solvent of one block and a precipitant of the other one. The dissolution of the block copolymer into a selective solvent leads to the formation of micelles. The insoluble blocks associate to form the core of the micelle while the soluble ones form the corona, surrounding and stabilizing the core in solution (Figure 1.14).^[6,93–96] Another method allowing the preparation of micelles consists of dissolving the copolymer into a non selective solvent. The selective solvent is then added dropwise to the solution, inducing the precipitation of one polymer block. Finally the non selective solvent is removed from the solution.



Figure 1.14: Schematic representation of a micelle in solution. Reproduced from Ref.^[44]

In solution, micelles are generally in dynamic equilibrium with the unimers. So a polymer chain can transit from one state to the other depending on the core polymer characteristics. When the core is made of a poorly solvated block, e.g. polystyrene, a suppression of the equilibrium is observed and the micelle is kinetically frozen. Another way to kinetically freeze the micelle is by cross-linking of the polymer core or corona.^[94,97,98]

An important factor influencing the micellization of block copolymers is the polymer concentration. The critical micellization concentration (CMC) is the minimal concentration of copolymers in solution, at a given temperature, where the first micelle is formed. Below the CMC copolymers are present as unimers in solution and no micelles are observed. Above the CMC, the concentration of unimers stays constant and the formation of micelles is observed (Figure 1.15). This definition of the CMC is theoretical since it is almost impossible to precisely determine the exact concentration at which the first micelle is formed. In practice, the CMC corresponds to the concentration at which a sufficient number of micelles is formed in order to be detected by a given method.^[99] By increasing the concentration, the formation of a micellar gel can be observed. At this point, the micelles are ordering themselves into lattices. The critical gel concentration (CGC) is consequently the minimal concentration of copolymer in solution, at a given temperature, where the gel is observed. As previously mentioned, the micellization and therefore the CMC are temperature dependent. Indeed, the unimers/micelles equilibrium is a thermodynamic equilibrium and is for that reason influenced by the temperature. Likewise to CMC a critical micellization temperature (CMT) can be defined as the temperature, at a given polymer concentration, where micelle formation is observed.



Figure 1.15: Schematic representation of the critical micelle concentration (CMC) and the critical gel concentration (CGC) in a block copolymer solution. Reproduced from Ref.^[100]

As expected the block copolymer composition has an influence over the structure of micelles. Depending on the length of the block constituting the core two limiting cases may be observed:

- Star-like micelles with a small core compared to the corona (Figure 1.16.a).
- Crew-cut micelles with a large core compared to the corona (Figure 1.16.b).

The micellization process is characterized by important parameters. The aggregation number (Z) indicates the aggregation of a given number of block copolymer chains. The core is defined by a radius R_c , and the overall micelle by a radius R_m (Figure 1.16.b). Other ways to define the

dimensions of micelles are the radius of gyration R_g , which characterizes the mass distribution of the micelles around the mass centre of the particles, and the hydrodynamic radius R_h , which corresponds to "the radius of an equivalent sphere, experiencing during its Brownian motion in solution a friction f identical in magnitude to that of the scattering particle analysed in dynamic light scattering".^[101,102]



Figure 1.16: Schematic representation of: a. "starlike" micelle, b. "crewcut" micelle. R_c and R_m are indicated in b. Reproduced from Ref.^[6]

Similarly to the self-assembly in solid state, key parameters that control R_c , R_m and Z are the degree of polymerization of the polymer blocks N_A , N_B and the Flory-Huggins parameters χ . Indeed, the free energy of a micelle is determined by three factors:

- The interfacial energy of the core/shell interface.
- The stretching energy of the block chains.
- The repulsion among coronal chains.

Micellization in organic solvents

According to excellent reviews on micelles formed in organic media, the micellization in organic solvents can usually be considered as an enthalpy-driven process.^[98,103,104]

In organic solvents, compared to aqueous media, two types of block copolymers can be employed. Those with two hydrophobic blocks and those with one hydrophobic block and one hydrophilic block, forming respectively "classic" micelles and "reverse" micelles, i.e. micelles with a hydrophilic core surrounded by a soluble hydrophobic corona. In organic media the more general terms solvophilic and solvophobic can be employed to designate respectively a block soluble in the solvent and a block insoluble in the solvent.

Double-hydrophobic block copolymer micelles are mainly controlled by the solvent and its interactions with the copolymer. Therefore, changing the organic solvent make possible to tune the micellization of such copolymers. For that reason R_h , R_c , Z and other parameters are expected to drastically change in function of the solvent employed, as demonstrated by Pitsikalis *et al.* for PS-*b*-PMMA block copolymers dissolved into ethylacetate or methylacetate. Both solvents are selective solvents of the PS block. However, unimolecular micelles were observed in ethylacetate whereas larger aggregates were observed in methylacetate.^[97]

Self-assembly of amphiphilic block copolymers into organic solvents leads to reverse micelles. The corona is made of hydrophobic blocks and the core is made of the hydrophilic ones, e.g. PEO,PMMA and PAA.^[98,105-108]

Morphologies of micelles

Similarly to the self-assembly in the solid state, micelles can take different morphologies: spherical micelles, cylindrical micelles and polymersomes (vesicles). A simple approach allowing the prediction of selfassembled structures has been proposed by Discher *et al.* and is based on the mass fraction of the hydrophilic block ($f_{hydrophilic}$) to the total mass of the copolymer:^[109]

- Spherical micelles: $f_{hydrophilic} > 45\%$.
- Cylindrical micelles: $f_{hydrophilic} < 50\%$.
- Polymersomes (vesicles): $f_{hydrophilic} \sim 35\%$.
- Inverted microstructures (e.g. large compound micelles):

 $f_{hydrophilic} < 25\%$

Of course numerous factors such as the preparation method, the presence of salts inside the solution, the starting selective solvent and others can influence the micellization. As a consequence this general rule should be seen as a trend-line.

Micelles are mainly used in solution as drug delivery systems for medical purpose [7,40,93,110-113] Other applications are nanoreactors [114] and templates for nanoparticles synthesis. [90,115,116]

1.4 Batteries

The industrial and technological development of the past century has brought new needs for energy production. Energy is usually powered via electricity, mainly obtained by converting fossil fuel or nuclear energy into heat. The heat is next converted into electrical energy and sent through the grid in order to supply all needing devices and equipments. This process, beside its low energy efficiency, involves a permanent connection to the grid. Therefore two main reasons to store energy come up:

- The energy produced now needs to be available later.
- The energy needs to be carried up with you.

Examples of the former include storing energy produced by green and renewable processes, e.g. wind powered and sun powered energy. Examples of the latter include portable applications like computer, cell phones, electric cars and pacemakers. Over the past decades electrochemical power sources have appeared to be the most efficient way to store energy.^[117]

An electrochemical power source is a system capable of producing electrical energy from chemical energy. Two kinds of electrochemical cells can be distinguished: the galvanic cell and the electrolytic cell. A galvanic cell involves a spontaneous reaction, i.e. $\Delta G < 0$, when the electrodes are connected via a conductor. An electrolytic cell involves a non-spontaneous reaction, $\Delta G \geq 0$, and an external potential needs to be applied in order to drive the electrochemical reaction.

Electrochemical cells are divided into two compartments composed of an electrode immersed into an electrolyte solution, kept apart by a separator. The electrodes are the sites where the chemical reactions occur. They are sorted into two types: the anodes (-), giving up electrons, and the cathodes (+), receiving electrons. The electrolyte is a solution containing dissolved chemical species with a net electrical charge called ions. The compartments are kept apart by a separator which allows ion mobility. During the discharge, the electrons move spontaneously from the anode (-) to the cathode (+). By convention the current flows in the opposite direction than the electrons. The reaction occurring at the cathode is the reduction, i.e. electrons are added to an atom or molecule. The reaction occurring at the anode is the oxidation, i.e. electrons are removed from an atom or molecule. A molecule that is reduced is called an oxidant and a molecule that is oxidized is called a reductant. The reactions occurring at the electrodes are named half redox reactions. Each half redox reaction possesses an electrochemical potential (E) which measures the tendency of the the chemical species to acquire electrons, i.e. to be reduced. It is measured in volts (V) relatively to the hydrogen ions to hydrogen potential (H⁺/H₂). Indeed H⁺/H₂ was chosen as a reference and it's half-cell potential was set at 0.00 V by convention. The Daniel cell is a good example of an electrochemical cell (Figure 1.17). It is based on the redox reactions between copper and zinc for a standard potential of 1.1 V (0.34 - (-0.76)) (Equation 1.7).

$$\operatorname{Zn} \longrightarrow \operatorname{Zn}^{2+} + 2 e^{-} \qquad \operatorname{E}^{0}_{\operatorname{Zn}^{2+}/\operatorname{Zn}} = -0.76V \ vs \ \mathrm{H}^{+}/\mathrm{H}_{2}$$
(1.7)

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
 $E^0_{Cu^{2+}/Cu} = +0.346V \ vs \ H^+/H_2$ (1.8)

A simple galvanic cell usually produces a low cell voltage from 0.5 to 4 V. By plug-in several cells together a battery is obtained. Galvanic cells connected in series increase the voltage of the battery and galvanic cells connected in parallel increase the capacity of the battery. Two types of battery are available: primary and secondary batteries. Primary batteries are non rechargeable, i.e. the electrochemical reaction is irreversible. Therefore the battery is useless after discharge and can not be reused. On the opposite, secondary batteries are based on reversible electrochemical reactions and can be reused several times. By applying an external electrical energy, the electrochemical process involved is reversed and energy is stored into the cell.

1.4.1 The history of batteries

On 20 March 1800, professor Alessandro Volta wrote a letter to the prestigious Royal Society of London, describing the first primary battery. It was made of alternating disks of zinc and silver paired together and separated by a leather moistened with an aqueous solution of sodium chloride. A superposition of one zinc disk, one leather with electrolyte and one silver disk corresponds to one galvanic cell. Therefore the Volta battery is constituted of zinc-electrolyte-silver elementary cells connected in series (Figure 1.18). Since the dynamo will be invented by Gramme 70 years later, the Volta battery is the historically first sustained source of electrical current. In 1834 Faraday proposed the battery science terminology still in use today: electrode, anode, cathode, electrolyte, ion,



Figure 1.17: Schematic representation of the Daniel cell. The active components, i.e. zinc metal and copper ions, are separated. Reproduced from Ref.^[118]

anion and cation. The Daniel cell was developed in 1836 and marks the beginning of modern battery technology.

One big advance in primary technology was the development of alkaline cells, i.e. alkaline electrolyte in place of aqueous one. They have been developed and improved from 1881 with the zinc-copper oxide wet cell invented by Felix Lalande and Georges Chaperon to 1912 when alkaline zinc-manganese dioxide dry cells were described. However they were not commercially available since 1949. Alkaline zinc-manganese dioxide finally found an important commercial success when Union Carbide Corporation started to produce them in the standard cylindrical shapes and sizes still used today. Figure 1.19 retraces the key developments in primary batteries until nowadays.^[118]

1.4.2 Secondary batteries

Rechargeable batteries are really interesting devices since they can be employed multiple times before being discarded. One of the most known example of secondary battery is the lead acid one, developed in the late nineteenth and still in use today (Scheme 1.1, chemical reaction 1.9). Astonishingly, lead acid batteries have allowed the development of electric



Figure 1.18: Schematic representation of the Volta silver zinc battery, A stands for silver and Z for zinc. Reproduced from Ref.^[118]



Figure 1.19: Primary battery evolution. Reproduced from Ref.^[118]

cars. In 1900, 40% of automobiles where powered by batteries since the gasoline cars were considered unreliable and noisy. It is interesting to notice that gasoline cars have been developed over one century for finally coming back to electrically powered cars these days. Nickel-cadmium (NiCd) batteries (Scheme 1.1, chemical reaction 1.10) have widely been employed during the nineties, before being almost completely replaced by nickel metal hydride (NimH)(Scheme 1.1, chemical reaction 1.11) and Li-ion batteries.^[119] NiCd batteries present two drawbacks: the presence of an important memory effect⁴ and the use of toxic cadmium metal. During the last decade, despite a higher price, Li-ion batteries have

⁴A memory effect is the situation in which a battery loses its maximum capacity when it is repetitively charged after being only partially discharged.

overwhelmed NiCd and NimH batteries due to a higher energy density (Figure 1.20). Indeed, lithium is the lightest and less dense metal and presents the lowest redox potential ($E_{Li^+/Li}^0 = -3.05V \ vs \ H^+/H_2$).

$$Pb + PbO_2 + 2 H_2SO_4 \xleftarrow{\text{discharge}}_{\text{charge}} 2 PbSO_4 + 2 H_2 O$$
(1.9)

$$\operatorname{Cd} + 2\operatorname{Ni}(O)\operatorname{OH} + 2\operatorname{H}_2O \xrightarrow[\text{charge}]{\text{discharge}} \operatorname{Cd}(OH)_2 + 2\operatorname{Ni}(OH)_2$$
 (1.10)

$$MH + Ni(O)OH \xrightarrow[charge]{discharge} M + Ni(OH)_2$$
(1.11)

Scheme 1.1: Battery reactions of different secondary batteries lead-acid, nickel-cadmium and nickel-metal-hydride.



Figure 1.20: Comparison of the different battery technologies in terms of volumetric and gravimetric energy densities. Reproduced from Ref.^[120]

Li-ion Batteries

The characteristic features of Li-ion batteries is that lithium is used on both electrodes of the battery for electrochemical reactions. Li-ion primary batteries, using lithium metal as anodic material, were initially developed due to they high energy density. However, their development was a challenging task. Indeed, lithium metal tends to form dendrites during charging, leading to a loss of active lithium (i.e. a loss of capacity), short-circuits and a risk for fire (1.21, a).^[121] In order to overcome these limitations, lithium metal has been replaced by carbon materials. Lithium ions intercalate into the carbon, taking advantage of the lithium high density while avoiding limitations and safety concern of lithium metal. Indeed, graphite anodes present a potential of 0.1 - 0.2V vs Li⁺ / Li.^[122]

Li-ion positive electrodes are constituted of lithium containing metal oxides or phosphate compounds. Different types of positive electrodes are available:^[123,124]

- Lithium-cobalt oxide (LiCoO₂).
- Lithium-manganese oxide (LiMn₂O₄).
- Lithium-iron phosphate (LiFePO₄).
- Lithium-mixed metal oxides (LiNi_{0.8}Co_{0.2}O₂,

 $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$).

Li-ion electrolytes are lithium salt (e.g. LiPF₆) dissolved into a mixture of carbonated solvents (ethylene carbonate (EC), dimethyl carbonate (DMC)).^[125-127] Li-ion batteries are based on intercalation/extraction processes. Lithium ions (Li⁺) switch and intercalate from one electrode to the other one during the charge/discharge process (1.21, b). The example of a Li-ion battery made of a carbon anode and a LiCoO₂ cathode will be discussed in more details.

During the electrochemical reduction of the negative electrode (charge process), Li^+ ions are reduced to form metal lithium intercalated into graphitic layers (Scheme 1.2, chemical reaction 1.12). An amount of x Li intercalates per C₆ unit of carbon. The value of x is included between 0 and 1. During the discharge process, i.e. the electrochemical oxidation of the negative electrode, the reverse process occurs: Li is extracted from the carbon electrode and Li⁺ ions are released into the electrolyte solution.^[127,128]

A similar process occurs at the positive electrode. During charging Li^+ ions exit LiCoO₂ and intercalate during discharging (Scheme 1.2, chemical reaction 1.13). The value of x is comprised between 0 and 1. LiMn₂O₄ and LiFePO₄ present a three-dimensional structure in place



Figure 1.21: Schematic representation of Li-ion batteries. a. Rechargeable lithium metal battery. The negative electrode shows a SEM picture of growing dendrites. b. Li-ion battery. 0 < x < 1. Reproduced from Ref.^[120]

of a layered structure. However the intercalation process is similar and Li^+ ions intercalate into the space available between the atoms of the structure.^[127,128]

Even if Li-ion batteries have dominated the market over the past decade, they are facing issues such as the cost, safety, environmental concern and raw materials availability.^[117,121,126] Indeed cathode materials, especially rare earth metals such as cobalt, need to be obtained from ores by mining natural resources. Therefore, extraction and manufacture of raw materials require an increasing amount of energy. From an environmental point of view, more renewable batteries are needed since actual Li-ion batteries present a high carbon footprint and their recycling is a challenging task.^[129,130] In order to overcome these limitations,

$$C_6 + x \operatorname{Li}^+ + x \operatorname{e}^- \xleftarrow{\text{anode}} \operatorname{Li}_x C_6$$
 (1.12)

$$\operatorname{LiCoO}_2 \xleftarrow{\operatorname{catnode}} \operatorname{Li}_{1-x} + \operatorname{Li}_{1-x} \operatorname{CoO}_2 + x \operatorname{Li}^+ + x \operatorname{e}^-$$
(1.13)

(1.14)

$$C_6 + \text{LiCoO}_2 \xrightarrow[\text{charge}]{\text{charge}} \text{Li}_x C_6 + \text{Li}_{1-x} \text{CoO}_2$$
 (1.15)

Scheme 1.2: Redox reactions occurring in Li-ion Batteries. From top to bottom: negative electrode reaction, positive electrode reaction and overall battery reaction. With 0 < x < 1.

different alternatives such as Li-air, aluminum-air, sodium-ion, and organic radical batteries are currently investigated, each system presenting several advantages over the current Li-ion batteries.

Organic batteries

Organic batteries based on polymeric materials are currently developed as alternatives to Li-ion batteries. Using organic compounds as electrode materials presents several advantages over their inorganic counterparts such as their flexibility, rapid charge/discharge processes, the absence of resources-limited transition metal compounds and the potentially unlimited organic resources available. Moreover, they are potentially low cost and recyclable. Unlike inorganic electrodes, a high temperature annealing is not required. Therefore a low CO₂ footprint is expected. The concept of an organic battery is not new and the basis of polymer battery research can be tracked back in the 70s with the discovery of the reversible oxidation of poly(acetylene).^[131] The successful development of intercalation materials in Li-ion batteries combined to the slow development of conductive materials as rechargeable cathodes has convoluted the interest over these materials.

Organic batteries can be classified into three major classes:

- Organosulfur compounds.
- Carbonyl compounds.
- Stable radical compounds.

Organosulfur compounds Organosulfur compounds are molecules bearing disulfide bonds which undergo electrodimerization/scission following the redox reaction:

$$RSSR + 2e^- + 2Li^+ \leftrightarrow 2LiSR$$

The first class of organosulfur compounds consists of polymers bearing disulfide bonds in the backbone (Figure 1.22, 1-3). By varying the organic backbone from electro-donating alkyl groups (Figure 1.22, 1) to electron-withdrawing aryl groups (Figure 1.22, 2,3), the open circuit voltage varies from 2.3 to 3.0 V vs Li⁺/Li. Such systems are capable of delivering high energy density but require high temperatures (up to 80-130 °C) to operate due to the low redox reaction rate. Blends of organosulfur polymers with electrocatalysts, e.g. polyaniline (PAn), allow room temperature operation. The biggest drawback facing main-chain disulfides polymers is the solubility in common electrolytes of thiolate ions obtained after the thiolate reduction. In consequence, most systems use solid or gel electrolytes.^[132-134]

In order to overcome dissolution problems, a second generation of organosulfur electrodes with disulfide bonds on the side chain of the polymer was developed (Figure 1.22, 4,5).^[135] In order to increase the capacity by increasing the sulfur content in the polymer, a third generation called polysulfides was developed. Such polymers bear polysulfides bonds (Figure 1.22, 6,7). They are synthesized via elemental sulfur or inorganic polysulfide salts. They present a non-stoichiometric character and need elemental analysis in order to determine the sulfur content. Since the reduction of organopolysulfides generates S_x^{2-} anions, a rapid capacity fading in ether electrolytes is observed. However contrary to elemental sulfur, organopolysulfides exhibit a good capacity retention in carbonated electrolytes.^[132,133,136,137]

Finally, a fourth class of organosulfur compounds has recently been developed (Figure 1.22, 8,9). Thioethers (p-type organosulfur polymers) form stable cationic radical species via a reversible electron-extraction process:

$$RSR + X^{-} \longleftrightarrow RS^{+}RX^{-} + e^{-}$$

Where X^- is the counter ion provided by the electrolyte. They present the advantage to not undergo disulfide bond cleavage.^[132,133,138,139]



Figure 1.22: Examples of organosulfur polymer structures.

Carbonyl compounds Carbonyl compounds are common organic functions. In the presence of the appropriate stabilizing group (R), the carbonyl can undergo a reversible one-electron reduction, leading to the formation of a radical mono-anion (Figure 1.23). Small molecules bearing carbonyl groups present the same drawback than other organic battery materials, i.e. the solubility in the electrolyte. One approach to overcome this limitation is to enhance their polarity via the formation of salts (Figure 1.24, molecules 10-14). Another approach to reduce solubility of small molecules bearing carbonyl groups is the use of polymeric carbonyl compounds (Figure 1.24, molecules 15-18). Depending on their structures, carbonyl compounds can be divided into three main classes:

• Quinones: guinones and their derivatives are reduced in the range of 3 to 2 V vs. Li^+/Li and are employed as cathode, thanks to their high redox potentials. The formation of polyquinones is difficult due to both the radical scavenging properties of quinones and their electrophilic center. The appropriate polymerization technique needs therefore to be selected carefully.

- Imides: polyimides are redox-active polymers based on the reduction of phthalimides to the corresponding anion radicals. Despite a possible two electrons redox process, forming the dianion, only the first redox stage is usually employed in charge storage applications. Indeed, the second reduction leads to the decomposition of the redox-active structure whereas the first reduction is fully reversible. Imides are reduced in the range of 2 to 1.5 V vs. Li⁺/Li and find application as cathode in lithium-ion or sodium batteries.
- Conjugated carboxylates: organic conjugated carboxylic acids undergo a reversible two electrons redox reaction. A conjugated aromatic system stabilizes the resulting dianion. Conjugated carboxylates are reduced in the range of 1 to 0.5 V vs. Li⁺/Li and can be employed as anode in lithium-ion and sodium batteries.

Thanks to the variety of carbonyl structures available, the cell potential can easily be tailored depending on the targeted application, as illustrated in Figure 1.25. Their rapid reaction kinetics, their structural diversity and their high theoretical capacity make carbonyl compounds promising materials for organic lithium-ion batteries and sodium-ion batteries.^[132,133,140]

$$\begin{array}{c} O \\ R \\ \hline R \\ \hline R \\ \hline e^{-}, -Li^{+} \\ \hline O \\ O \\ \hline \hline O \\ \hline O \\ \hline \hline \hline O \\ \hline \hline \hline$$

Figure 1.23: Mechanism for reversible reduction of general carbonyl compounds (up) and quinone (down). Reproduced from Ref.^[132]

Stable radical compounds Organic radicals are unstable highly active molecules. However organic radicals can be stabilized, leading to species presenting a long life time at ambient conditions. Stabilization is achieved via sterical protection of the unpaired electrons or via resonance structures involving unpaired electrons. Different structures presenting stable organic radicals are now available, as illustrated in Figure 1.26.^[141] The stable radical can be centered onto different atoms such as



Figure 1.24: Examples of carbonyl compounds.

carbon, nitrogen or oxygen. Polymer analogues of stable organic radicals have been widely studied as active electrode materials for organic radical batteries.^[142] Indeed, these materials present interesting properties such as stable cell voltage, good processability and short charging times. Organic radical batteries are essentially based onto polymers bearing stable nitroxide functions and their particular case will be discussed in more details in the next chapter (Chapter 2).



Figure 1.25: Overview of the discharge cell potential and the theoretical capacity of the three major organic carbonyl material classes. Reproduced from Ref. $^{[140]}$



Figure 1.26: Stable radical molecules.

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CHAPTER 2

Nitroxide based organic radical batteries

Abstract

Stable nitroxides are a particular class of molecules. Thanks to their stable unpaired electron, they present interesting and unique properties. Nitroxyl radicals are used for a wide range of applications from organic chemistry synthesis to medicine. This chapter starts by presenting a rapid overview of their applications. Next the focus is made onto the development of organic radical batteries based on nitroxyl radicals. Then the preparation of ORB is investigated. Afterwards the methods and strategies for the synthesis of nitroxyl radicals containing polymers are investigated from PTMA homopolymers to more complex architectures such as well defined block copolymers. Finally different applications of organic radical polymers in the frame of energy are presented.

2.1 Stable radicals

Nitroxides are radicals derived from hydroxylamines by removal of the hydrogen atom from the hydroxy group and are most of the time isolable.^[1] They have the structure illustrated in Figure 2.1 where R1 and R2 substituents can be primary, secondary or tertiary alkyl groups. However the presence of an α -hydrogen to the nitroxide should be avoided since it results in a loss of stability due to a disproportionation reaction, leading to the formation of a nitrone and a hydroxylamine (Figure 2.2). Organic radicals are usually really unstable and highly reactive compounds. The stability of nitroxides comes from their resonance structures and the steric hindrance brought by bulky substituent groups. One of the most representative and studied nitroxide compound is the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). TEMPO is a stable and commercially available nitroxide presenting a remarkable persistence. Indeed it can be stored as an orange solid powder for years.^[2,3]



Figure 2.1: Nitroxide resonance structures.

Pathway a: hydrogen atom abstraction



Pathway b: single atom electron transfer

Figure 2.2: Proposed disproportionation mechanisms for α -hydrogen nitroxides: a, direct hydrogen atom abstraction; b, single electron transfer from head-to-tail dimer. Reproduced from Ref.^[4]

Nitroxide bearing molecules can not be characterized by ¹H NMR due to their paramagnetic character. Therefore three different methods are usually employed in order to analyse organic molecules bearing stable radicals: ¹H NMR after quenching radicals via hydrazine^[5,6], superconducting quantum interference device (SQUID) and electron spin resonance (ESR). A SQUID is a very sensitive magnetometer used to measure very low magnetic fields (as low as 5×10^{-18} T). ESR¹ is a spectroscopy technique allowing to study materials bearing unpaired electrons. The electron spins are aligned via a constant applied magnetic field in a similar manner than nuclei in NMR. The magnetic moment of electrons is larger than the one from nuclei in consequence of the electron-nuclei mass difference. Therefore for an identical magnetic field, a higher electromagnetic frequency is required for ESR than NMR in order to obtain a spin resonance absorption. ESR measurements are classically made with microwaves in the range of 9-10 GHz for a constant magnetic field of 3500 G.^[7–10]

Nitroxides present two redox potentials. Nitroxyl radicals can be oxidized into oxoammonium cation or reduced into aminoxyl anion. The former redox potentials is reversible and easily observed. The latter one is less described in literature and not always observed. These redox processes make stable nitroxide bearing molecules good candidates for the fabrication of organic electrode materials, as it will be discussed later.

In addition to their redox properties and their use as electrode materials, nitroxyl radicals present a wide variety of properties and subsequent applications.^[2,3]

- Organic chemistry:
 - \Rightarrow Organocatalyst for oxidation.^[11-16]
 - \Rightarrow Trapping of C-centered radicals.^[17-19]
- Polymer synthesis
 - \Rightarrow Radical capping in NMP.^[20-23]
- Biochemistry
 - \Rightarrow Spin probe for medical imaging.^[24-27]
 - \Rightarrow Therapeutic drugs. The properties of nitroxide to modify oxidative stress and redox status of tissues allow them to be used

¹Also named electron paramagnetic resonance (EPR)

as treatment for a large variety of diseases such as cancer and hypertension. [3,28,29]

2.2 Nitroxide bearing polymers as electrode materials

Despite their redox properties nitroxides are too soluble in battery electrolytes to be used directly as electrode materials in organic radical batteries. In order to overcome solubility issues, polymers bearing nitroxyl radical side groups were synthesized.

Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) is a methacrylate bearing a TEMPO group. It was first studied as cathode material by Hasegawa at al.^[30] and further developed in 2002 by Nishide and Suga.^[31,32] PTMA is used in blends with conductive carbons, e.g. carbon black, and a binder, e.g. poly(vinylidene fluoride) (PVDF). The system was originally studied with a lithium anode, leading to the first organic radical battery (ORB) and is now a thoroughly studied standard model.^[30,32-45] Depending on the anode involved, different terminologies can be employed: lithium organic batteries (Li-ORB) for a Li anode and all organic radical battery (org-ORB) for a polymer radical anode.^[46] As cathodic material PTMA presents a flat charge/discharge voltage profile at 3.5 V (vs. Li^+/Li) with a theoretical capacity of 111 mAhg⁻¹ and a good cycling stability up to 1000 cycles.^[32,41,44,47] The flat voltage profile is a prerequisite for battery applications in order to deliver a constant voltage, and was absent in previous organic electrodes made of conductive polymers. When used with a lithium anode, PTMA thus presents a cell voltage of 3.5 V which is comparable to commercial lithium ion batteries employing metal oxide cathodes (e.g. $LiCoO_2$) and presenting a cell voltage of 3.6 V, making thus PTMA a good alternative as cathode material in Li-ion batteries. During the charge process, the nitroxyl radical is oxidized into an oxoammonium cation, leading to a p-doping of the polymer (Figure 2.3). As previously mentioned, the nitroxyl radical can be reversibly reduced into the aminoxyl anion, leading to an n-doped polymer (Figure 2.3).^[31] Modern applications often require short charging times. Conventional batteries are charged at a current corresponding to a C-rate between 0.1 C to 0.5 C. The C-rate is the current needed to charge or discharge a battery in one hour. 1 C corresponds to a full charge in one hour.^[48] Therefore a C-rate between 0.1 C to 0.5 C corresponds to a charging time of respectively 10 and 2 hours. ORBs, thanks to the fast kinetics of the one electron transfer redox reaction, can be charged at C-rates between 10 C to 100 C, i.e. a full charge in a few minutes.^[34,43,49] A C-rate up to 2400 C, i.e. a charging time of 1.5 s, was even reported.^[50] These rapid charging rates are related to the molecular structure of the radical polymer. For example, TEMPO groups demonstrated a charge transfer rate of the order of 10^{-1} cm s⁻¹ whereas, in comparison, organic dissulfides showed a charge transfer rate of the order of 10^{-8} cm s⁻¹.^[45,51] The mechanism by which the charge transport occurs through the polymer is not perfectly known. It has been proposed that an electron self-exchange process between the stable pendant radical groups occurs through a series of oxidation-reduction reactions. In electrolyte supported systems, this transport is guided by a gradient in radical density. For a solid state device, the charge transport is thought to occur through an electric field driven mechanism.^[51] In both cases the fast charge transport within the polymer matrix is possible thanks to the close spatial proximity of radicals. [52,53] Indeed, in order to allow the charge transport to occur, radicals need to be in close proximity. For PTMA, an effective charge transfer length of 0.55 nm was predicted by molecular dynamic simulations. It was also demonstrated that 85% of the charge transfer occurs via interchain transport.^[54]



(p-type)

Figure 2.3: Redox behavior of nitroxyl radicals.

Thanks to organic and polymer chemistry, different nitroxide structures and polymer backbones are available (Figure 2.4). Indeed, the charge storage capacity of a nitroxide polymer depends on the number of electrons stored per repeating unit (usually one) and the molar mass of the monomer (Equation 2.1). Therefore it can be tuned via molecular design. Lighter is the monomer and higher is the theoretical capacity.^[46,55]

$$C_t(mAhg^{-1}) = \frac{n \times F(Cmol^{-1})}{M_w(gmol^{-1})}$$
(2.1)

Anode

0

Aminoxyl anion

(n-type)

Where C_t , n, F and M_w stand respectively for the theoretical capacity, the number of electrons transferred during the redox process per monomer unit, the Faraday constant and the molar mass of the monomer unit.



Figure 2.4: Variety of stable radicals and polymer backbones employed in ORB. * with those specific groups no battery was built. Reproduced from Ref.^[46]

Even if TEMPO is the most common nitroxide bearing moiety, some other structures have been developed. A change in the stable nitroxide radical leads to a change of potential. Therefore the cell voltage can be shifted by changing the nitroxide radical employed. For example the presence of electron withdrawing groups on the structure decreases the potential, leading to n-type, i.e. anodic, electrodes (Figure 2.4).^[56]

Polystyrene derivatives bearing NO groups (poly(nitroxylstyrenes)) were studied as cathode materials. Poly(4-(N-tert-butyl-N-oxylamino)-styrene), i.e. a polystyrene bearing one nitroxide function, showed a reversible redox wave at 0.74 V vs Ag/AgCl. Poly(3,5-di(N-tert-butyl-N-oxylamino)styrene), i.e. a polystyrene bearing two meta substituted nitroxide functions, reveals an irreversible anodic peak at 1.0 V vs Ag/AgCl.

The instability was attributed to the lack of a stabilizing *para*-substitutent on the nitroxide radical. Finally, a poly(nitroxylstyrene) ortho-substituted with a trifluoromethyl group (poly(4-(*N*-tert-butyl-*N*-oxylamino)--3-trifluoromethylstyrene)) shows a reversible redox wave at -0.76 V on the cathodic side, corresponding to a n-type polymer (Figure 2.4).^[57] Nishide et al. reported n-type redox active radical polymers. They prepared org-ORB constituted of poly(galvinoxylstyrene) anode and poly-(TEMPO-substituted norbornene) (bearing two NO per units). The system demonstrates a plateau voltage at 0.66 V for a charge capacity of 32 mAhg⁻¹.^[58] Such org-ORB are promising materials for flexible organic batteries.^[59] Surprisingly, some nitroxide polymers can present both anodic and cathodic behavior. Poly(4-(nitronylnitroxyl)styrene) and polynorbornenes containing nitronyl nitroxide radical were developed as bipolar redox polymers, showing n-type and p-type behaviors.^[60-62]

Nitroxide can undergo two redox reactions. Most of the studies focus onto the oxidation of NO into oxoammonium cation and some works have developed the reduction of nitroxyl radicals into aminoxyl anion. However both redox processes are rarely observed together. TEMPOcontaining DNA was developed by Masuda et al. 192% of the theoretical capacity for single-electron process was obtained, indicating a two-electrons process.^[63] This phenomenon was also observed for cellulose polymers^[64] and PTMA/graphene composites.^[47] The advantage to stabilize the aminoxyl anions is obvious since it double the battery's capacity. In consequence, stabilisation of the second redox process of nitroxide bearing polymers is a promising tool for increasing ORB capacity.

Some polymers like polynorbornene can present two TEMPO, i.e. two nitroxides, per monomer unit.^[58,65-69] The spatial proximity of the NO has an important impact onto the electrochemical behavior of these polymers. Indeed the two TEMPO substituents can present different orientations. In endo,endo and exo,exo orientations the NO are spatially distant from 10 Å. In these configurations, the polymer presents only half of the theoretical capacity. Whereas with exo,endo configuration, the NO distance is higher and full theoretical capacity is obtained. Therefore it is assumed that the spacial proximity of TEMPO groups influences in a negative manner the electrochemical process.^[69] TEMPO bearing acetylene backbones with up to four TEMPO per monomer unit were reported.^[70-72] However such complicated structures are difficult to synthesize and present no advantages compared to PTMA since their theoretical capacity is similar and some times even lower than the latter (e.g. four substituted acetylene presents a theoretical capacity of 106 $mAhg^{-1}$). Moreover, in a similar manner than multi-substituted polynorbornenes, only a fraction of the theoretical capacity is observed in practice due to spatial proximity of the NO functions.^[70]

2.3 Organic radical cathodes preparation

The preparation process for the formation of organic radical electrodes is a key factor for the final performances of the system. The electrochemical active polymer needs to swell into the battery electrolyte solution while its dissolution needs to be avoided. Moreover, due to the lack of conductivity, polymers need to be mixed with some carbon additives. In order to achieve these requirements, nitroxide polymers are usually mixed with conductive carbon and binder. Typical blends are composed of 10-30 wt.% of active polymer, 10-20 wt.% of binder and 60-80 wt.% of conductive carbon, even if cathodes with up to 80 wt.% of polymer have been reported.^[73] In consequence to the addition of redox inactive species, the theoretical capacity of the ORB is lower than the theoretical capacity of the polymer alone. During the manufacturing, the electrode thickness needs to be carefully controlled. Song et al. have demonstrated that an increase of the electrode thickness leads to an increase of electrode/electrolyte resistance interface and polarization of the cell. [37]

Due to the insulating character of organic radical polymers, different carbon additives were investigated over the years in order to promote the electrical conductivity inside the blended electrode and to obtain the best performances. Vapor grown carbon fibers $(VGCF)^{[32,41,74,75]}$ and carbon black $(CB)^{[30,34-37,40]}$ are the most employed conductive carbons. However, VGCFs appear more efficient than carbon black since electrodes presenting higher content of active polymers were prepared using VGCFs. Indeed, fibres form an interconnected network allowing a better electrical conductivity than carbon particles for the same carbon content. A mixture of carbon black with 60 wt.% of PTMA presented a high ohmic resistance and therefore low discharge performances.^[35] While Nakahara et al. have fabricated cathodes containing 80 wt.% of organic radical polymer (poly(4-vinyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl) (PTVE)) and 15 wt.% of VGCF. Such high polymer content was reached thanks to a new water-based slurry preparation method.^[73] Cairns et al. have developed Al-laminated film packaged ORBs where a mix of PTMA, carboxy methyl cellulose (CMC), PTFE and VGCF was coated onto aluminium foil.^[39] Mesocarbon microbeads were used as anode. The 100 mAh ORB obtained displayed good rate properties and cyclic performances, demonstrating the industrial potential of ORBs.

Another carbon additive employed in ORBs is the mesocellular carbon foam (MCF). MCF was filled with PTMA and coated with polyethylene glycol (PEG) leading to nanocomposite cathodes. The system exhibited good capacity retention even at high temperature (50 °C) thanks to the protective effect of PEG.^[76] Graphene appears to be a good candidate too as conductive support, allowing good retention capacity and long cycle life.^[47] Carbon nano-tubes (CNTs) were also used as conductive materials. PTMA wrapping around single wall carbon nano-tubes (SWNTs) allows quantitative charge-storage capacity at high C rate for a very low amount of conductive materials (4 wt.%).^[77,78] More recently, wrapping of polyacetylene bearing TEMPO groups around CNTs was investigated.^[79] CNT-arrays blended with PTMA were developed since CNT-array provide continuous conduction pathways compared to conventional CNT. High retention capacity was observed during fast charge/discharge processes. The discharge capacity was 63 mAhg^{-1} at 100 C and 98% of capacity was retained after 100 cycles.^[80]

Rather than changing the employed additives, some works have focussed onto the preparation method. Micro-fibrous polymer films were fabricated by electrospinning of a mixture of PTMA, PVDF and carbon black. These electrodes demonstrated excellent electrochemical performances, even at high C rate (50 C), ascribed to the fast ion transport promoted by the nanostructure obtained. The mechanical integrity and flexibility were both increased in the resulting material (Figure 2.5).^[81,82]

Some hybrid systems combining inorganic materials and organic polymers were developed. Xia and Li demonstrated a cathode based on PTMA mixed with activated carbon (AC). In this example, AC is used as electronic conducting support and active material, leading to a hybrid capacitor.^[83] Gohy et al. published a hybrid supercapacitor-battery. PTMA is mixed with LiFePO₄ (a classic metal-oxide employed in Li-ion batteries) leading to a hybrid cathode presenting enhanced power and allowing a full charge in less than 5 minutes.^[84] During the fast charging process, a thermodynamically unstable configuration is generated. High potential PTMA⁺ co-exists with low potential LiFePO₄. This configuration drives an internal charge transfer equilibration. The PTMA⁺ discharged by charging the LiFePO₄ (Figure 2.6).

As already mentioned, addition of conductive carbon to PTMA is necessary due to the lack of conductivity of the polymer. Therefore a



Figure 2.5: Schematic representation of: a) the micro-fibrous PTMA electrodes and photography of: b) a rolled-up micro-fibrous electrode. Adapted from Ref.^[82]

conductive polymer backbone presents some interest. This was achieved by using polythiophene backbones. Unfortunately, some backbone oxidation due to the presence of NO functions, known as catalysts for alcohol oxidations, was observed.^[85,86]

Binders generally employed for the formation of ORB are non electrochemical active materials, decreasing the theoretical capacity. In consequence some researches focus onto the suppression of these additives. One strategy consists of grafting the nitroxide polymer onto the current collector or the conductive carbon. Moreover, grafting polymers is another way to overcome solubility issues in electrolyte. 4-carboxy-TEMPO and 3-carboxy-PROXYL were reacted with residual hydroxyl group of ethyl cellulose or cellulose acetate to form free radical-containing cellulose derivatives.^[64] Nitroxide polymer brushes grafted onto silica nanoparticles were fabricated via surface initiated ATRP (SI-ATRP). The grafting avoids polymer dissolution and allows the fabrication of binder free electrodes presenting good charge/discharge capacity and cyclability.^[87] PS microspheres were grafted with PMMA-b-PTMA block copolymers via SI-ARGET-ATRP for oxidation catalysis applications.^[88] SI-ATRP was also employed for the preparation of flexible nitroxide polymer brushes attached onto conducting flexible substrates.^[89] PTMA brushes should not be too thick to avoid the problem of the difficult oxidation of bottom PTMPM segments (see section 2.4 about the synthesis of PTMA). Moreover, an increase of oxidation time led to over-oxidation at the top of PTMA brushes.^[90] SI-ATRP is not limited to spherical particles or flat



Figure 2.6: Schematic representation of the fast charge - relaxation process. The green and black half-cylinders are indicative of the stored charge respectively in PTMA and LiFePO₄. The relative position of the red disk indicates the polarization of the constituents in the hybrid electrode. Reproduced from Ref.^[84]

surfaces and was performed onto three-dimensionally ordered macroporous (3DOM) substrates (Figure 2.7). The three-dimensional electrodes present a large surface area decreasing the ion diffusion and the concentration polarization. Furthermore, the highly porous and interconnected structure improves the rate capabilities.^[91]

Several works have investigated the grafting of nitroxide polymers onto multi walls carbon nanotubes (MWCNTs). Two different methods of grating are available. The "grafting from" method consists of initiating the polymerization from the surface. The "grafting to" method consists of attaching polymers to the surface via functionalized chainends. Geckeler et al. used both methods to prepare MWCNTs grafted with polynorbornenes bearing nitroxide radicals (Figure 2.8). According to this study the "grafting to" method leads to a better capacity.^[92] In another study, PTMA was grafted onto MWCNTs by SI-ATRP. The electrode was fabricated via a filtration method, leading to buckypaper flexible electrodes.^[93] Due to the alteration of the carbon nanotube surface during the grafting process, MWCNTs are preferred to SWCNTs. Indeed the inner walls remain intact and their conduction properties are preserved.

Electrolytes employed in Li-ion batteries are usually carbonate mix-


Figure 2.7: Schematic representation of the three-dimensionally ordered macroporous nitroxide polymer brushes electrode. Reproduced from Ref.^[91]

tures loaded with lithium salts. Therefore the vast majority of the works using PTMA as cathode was performed using these electrolytes. Indeed, the second electrode is generally made of metallic lithium or lithium intercalation species, e.g. carbon. However, nitroxide bearing polymers were also studied in aqueous media, using poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether) (PTVE), i.e. a hydrophilic backbone bearing a TEMPO group, with a zinc counter electrode.^[94] PTMA displays a one-electron redox capability even in aqueous media. Such aqueous systems, thanks to the high electrical conductivity of the electrolyte, combined with the hydrophilic backbone present ultrafast charging. A charging of 3 mC cm⁻² in 3 seconds was reported.^[50] Using an aqueous electrolyte, Nishide et al. reported poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) (PTMAm), a poly(acrylamide) bearing TEMPO, as a new electrode active polymer for ORB.^[95]

The electrochemical behavior of PTMA in ORB using ionic liquid as electrolyte was also investigated (Figure 2.9). Actually, ionic liquids present a high polarity, preventing the dissolution of PTMA in the electrolyte. Cells using ionic liquid electrolytes demonstrate good capacity retention, 94.5% after 200 cycles, and 84% of the discharge capacity at 1 C.^[96]



Figure 2.8: Schematic illustration of the radical polymer-grafted MW-CNT via: (a) the grafting to method, (b) grafting from method, (c) no grafting. Reproduced from Ref.^[92]



Figure 2.9: Ionic liquid structures employed in organic radical batteries: a) lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and B) N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI). Reproduced from Ref.^[96]

2.4 Synthesis of polymers bearing stable nitroxyl radical functions

Polymers bearing stable nitroxides are not commercially available and need therefore to be synthesized. Thanks to polymer chemistry, a variety of different syntheses methods is accessible. Two strategies were employed for the synthesis of nitroxide bearing polymers. The first one consists in the polymerization by radical polymerization methods of a free secondary amine precursor, followed by its oxidation into nitroxyl radical. The second one is the direct polymerization of nitroxide containing monomers by radical non-sensitive polymerization methods (Figure 2.10). a. Polymerization of NH precursor followed by its oxidation



Figure 2.10: Strategies available for PTMA synthesis. a. Polymerization of a precursor followed by its oxidation. b. Direct polymerization of NO containing monomers.

PTMA is a widely studied model. It can be prepared by free radical polymerization of its secondary amine precursor TMPM (2,2,6,6-tetramethylpiperidin-4-yl methacrylate) followed by its subsequent oxidation into PTMA.^[30,32,34-37,40,41] The oxidation was firstly performed using mCPBA, leading to high oxidation rates, up to 90 %. [30,32,36,83] In order to reach a full conversion, another oxidation pathway was developed by using H_2O_2 with NaWO₄ catalyst.^[37,76,97] This synthesis strategy can be enlarged to other monomers. Polyallene with pendant TEMPO groups were synthesized by FRP and $H_2O_2/NaWO_4$ oxidation.^[98] For applications where well defined PTMA (i.e. low dispersity) are not required, FRP is the easiest way to process. Indeed the TMPM precursor is commercially available and FRP is easy to handle. FRP is usually performed in organic solvents. However melt polymerization of TMPM is also possible, either alone or directly mixed with carbon (Figure 2.11). This process leads to a more environmental friendly set-up thanks to the absence of organic solvents. Moreover by performing the melt polymerization with a blend of monomers and carbon, an homogeneous electrode is obtained, leading to superior cycling stability and higher power.^[99]

In 2012, Schubert et al. investigated controlled radical polymerization techniques (NMP, ATRP and RAFT) of secondary amine bearing



Figure 2.11: Schematic representation of the solvent-free meltpolymerization of TMPM with in situ incorporated carbon. Reproduced from Ref.^[99]

monomers. NMP appeared to be not suitable for TMPM polymerization and its acrylate counterpart. Due to termination reactions after 15 to 20% of conversion, ATRP was ruled out as suitable technique for TMPM polymerization. Finally, RAFT was retained as the most suitable technique for the preparation of well defined PTMA.^[100] RAFT polymerization of TMPM was also investigated by Boudouris et al., leading to well defined PTMA (D < 1.2) with molar masses between 5000 and 24000 kg mol⁻¹ and an oxidation yield comprised between 65 to 73%.^[101] More recently, we demonstrated the successful polymerization of TMPM by ATRP.^[102] These results will be analyzed in more details in Section 4 of this manuscript. Finally, controlled radical polymerization of TMPM by SET-LRP was demonstrated.^[103] PTMA and PTMA-*co*-PAzPMA (poly(3-azidopropyl methacrylate)) random copolymers were polymerized in a controlled manner.

Interestingly, free radical polymerization of NO bearing monomers can be performed provided that the oxidation of the monomer into oxoammonium cation and formation of the oxoammonium salt is performed prior the polymerization process.^[104]

Different direct polymerizations of NO bearing monomers were investigated. Among others, classic living polymerization techniques were studied. 2,2,6,6-tetraethylpiperidinyloxy-vinylether was polymerized by cationic polymerization despite the costly preparation of the vinylether monomer.^[73,105] Anionic polymerization of 4-methacryloyloxy-2,2,6,6tetramethylpiperidin-1-oxyl (TMA) was performed using methyl methacrylate-capped 1,1-diphenylhexyllithium (DPHLi/MMA) as initiator. ^[106,107] However the stringent conditions needed for this method make it difficult to handle. Therefore, group transfer polymerization (GTP) was explored as an alternating method. The first work on GTP indicated a lack of control with dispersity up to 3.^[108] The second report demonstrated lower dispersity values (D = 1.5). Moreover an influence of the tacticity on the electrochemical properties was observed.^[109] It appeared that syndiotactic and heterotactic triads present distinct redox waves, observed respectively at 0.37 V and 1.6 V vs. Fc^+/Fc . Ring opening polymerization (ROP) of polyethers bearing stable NO such as PTMA and PROXYL (2,2,5,5-tetramethyl-2,5-dihydro-1-H-pyrrol-1oxyl-3-yl) was studied.^[110] Such ionophoric polyether backbones present the advantage to promote solvated counter ions propagation. Ring opening metathesis polymerization (ROMP) was investigated for the synthesis of norbornenes and 7-oxanorbornene substituted with PROXYL or one to two TEMPO. [58,65-69,111,112] The polymerization of 2,2,5,5tetramethyl-3-oxiranyl-3-pyrrolin-1-oxyl was performed by anionic coordinated ring opening polymerization. The polymer is made of a polyethylene backbone bearing PROXYL groups. Such minimized monomer structures lead to a gain of capacity (147 mAhg^{-1}) compared to PTMA (111 mAhg⁻¹).^[78,113,114] Nakano et al. have employed silicone polymer backbone. The TEMPO-substituted silicone was polymerized by platinum- or rhodium- catalyzed reactions. However, despite an excellent cycling stability, only 47 to 69% of the theoretical capacity were recovered.^[115]

Crosslinking can be required to avoid dissolution of NO polymers in battery electrolytes. Indeed, changing the electrolyte solvent for a non solvent of the polymer is not a good approach since the polymer needs to swell in order to make available the electrochemical active functions. Crosslinking can be performed in-situ by adding multifunctional monomers inside the polymerization media^[99,108,116] or by post treatment. Photocrosslinking by a bis(azide) crosslinker was studied by Suga et al., leading to an insoluble TEMPO-substituted polynorbornene film.^[65] Oxidation of the amine precursor into PTMA is not always complete, especially when using mCPBA. Therefore a PTMA network can be formed by employing an epoxy crosslinker in combination with the remaining secondary amines. This approach was successfully used in inkjet printing. The crosslinking process was initiated after inkjet printing by thermal treatment, thanks to the thermal stability of PTMA up to 200°C, allowing the formation of printed organic radical cathodes.^[42]

2.4.1 Block copolymers for nanostructured organic radical cathodes

The recent developments in controlled radical polymerization techniques for the polymerization of TMPM and other nitroxide bearing structures enable the development of well-defined PTMA with controlled molar mass and dispersity ($\mathcal{D}_M < 1.5$).^[100–102] Surprisingly, only a few reports have investigated the possibilities opened by the CRP of TMPM for the formation of diblock copolymers with a stable nitroxide radical containing block and the subsequent self-assembly study. PGMA-*b*-PTMA (PGMA = poly(glycidyl methacrylate)) block copolymers were synthesized by ATRP of the TMPM precursor and its subsequent oxidation. The GMA block presents epoxide functions that were used to graft the resulting block copolymers onto ITO substrates.^[117] The grafted copolymer layer, with a thickness up to 5 μm on ITO demonstrated a good capacity storage (120 mC cm⁻²) and a sufficient charge diffusion $(10^{-10}cm^2s^{-1})$.

2.4.2 Self-assembly in solution

Self-assembly of block copolymers in solution leads to micellar structures. Amphiphilic block copolymers bearing stable nitroxyl radicals were used to form micelles in aqueous media (Figure 2.12). Such micelles find interest as ESR probe for *in vivo* medical imaging. Indeed, the nitroxide functions are protected into the micellar core while the ESR signal remains detectable.^[118] Micelles with nitroxide containing core were also developed in the frame of nanomedicine and drug delivery. Micelles were obtained via self-assembly of amphiphilic PEG-*b*-PRAS (poly(aminomethyl-styrene) containing nitroxyl radicals) block copolymers. The core of the micelles is pH-sensitive, allowing the disintegration of the micelles in response to a low pH environment.^[29,119–122] We reported the formation of electrochemical active micelles with PTMA as corona for ORB applications.^[123] This work will be presented and discussed in Chapter 5.

2.4.3 Self-assembly in thin films

Self-assembly of block copolymers allows the formation of nanostructured thin films. Nishide et al. used PS-*b*-PEO block copolymer selfassembled templates as active layers for organic nonvolatile memory.^[124] In this example nitroxides are not present in the block copolymer himself but are rather loaded in the form of a TEMPO-substituted ionic liquid into the PEO phase. The resistive behavior of the resulting non volatile



Figure 2.12: Synthesis and self-assembly of MPEG-*b*-PTAm and MPEG-*b*-PLA-*b*-PTAm. Reproduced from Ref.^[118]

memory device can be modulated by changing the structure and orientations of the block copolymer nanodomains.

Boudouris et al. reported the possibility to form thin films with tailored morphologies from polydimethylsiloxane-block-PTMA (PDMS-b-PTMA) diblock copolymers using solvent vapor annealing in CHCl₃.^[125] In 2014, Nishide and Suga published the synthesis of pendant radicaland ion-containing block copolymers. The self-assembled thin films exhibit different morphologies from spheres to inverse spheres and were used as active layer into a diode-structured thin-film device, combining the redox-active radicals of one block to the charge-compensating ions of the other one (Figure 2.13).^[6] More recently, Ober et al. described the formation of cylindrical morphologies using block copolymers with a block of PTMA and different blocks of fluorinated and non-fluorinated methacrylates. They demonstrated that phase separation after thermal or solvent annealing only occurs for block copolymers with fluorinated blocks.^[126] We reported further advance with respect to control of PTMA-b-PS diblock copolymer self-assembly in thin films.^[127] Chapter 6 of this manuscript will be dedicated to these results.



Figure 2.13: Chemical structure of a pendant radical- and ion-containing block copolymer and the resulting diode-structured thin film device. Reproduced from Ref.^[6]

2.5 Organic radicals for energy applications

Nitroxide bearing polymers are mainly used as electrode materials for Li-ORB or org-ORB.^[34–36,43] However some other applications have been developed around this electrochemically active polymer. As mentioned into the previous section, nitroxyl radical bearing molecules can be involved in the formation of organic resistive memory devices.^[6] Memory devices with a sandwiched structure demonstrating non-volatile, bistable and rewritable memory performances were developed by Nishide et al.^[33,128,129] The PTMA layer was employed as a p-dopable material (Figure 2.14).



Figure 2.14: Memory device structure based on PTMA and $PMMA/AgBF_4$ layers and the chemical structure of PTMA. Reproduced from Ref.^[128]

PTMA was also investigated as anodic interfacial modifying layer in inverted organic photovoltaic devices, improving the short-circuit current density and the open-circuit voltage.^[130] PTMA was used as transparent conducting layer, thanks to its transparency in the visible spectrum due to its non conjugated backbone. PTMA served as counter electrode into an organic electrochromic cell. The PTMA layer and the electrochromic layer, i.e. a polyion complex composed of poly(decyl viologen) and poly(styrene sulfonate), were spin coated onto ITO substrates.^[131] The device presented a battery behavior associated with coloration / decoloration process.

Redox flow batteries

Redox flow batteries (RFBs) are secondary batteries where the redox species, rather than solid, are in solution in the electrolyte and stored in separated external tanks. The liquid cathode is named the catholyte whereas the liquid anode is called the anolyte. During the functioning, catholyte and anolyte are pumped through the electrochemical engine. generating electricity (Figure 2.15). Power and energy capacities can be scaled independently. Indeed, energy capacity depends on the tank size whereas power depends on the electrodes surfaces.^[132] Electrodes are generally composed of porous structures like carbon felt or carbon nanotubes, allowing a compromise between a good electrode permeability and a high active area. Electrochemically active species are separated by ion exchange membranes such as Nafion membranes. Two categories of RFBs can be distinguished: true RFBs, where all the species storing energy are fully dissolved in solution at all time and hybrid-RFBs, where at least one of the chemical species storing energy is a solid during the charge. Figure 2.15 illustrates a true RFB where vanadium is used both as cathode (\mathbf{V}^{III-II}) and anode (\mathbf{V}^{IV-V}) . Examples of hybrid-RFBs are zinc-bromide and zinc-chloride systems where Zn^{2+} is reduced to $Zn^{0}_{(s)}$ during the charge. RFBs present certain advantages over classic batter ies: the virtually unlimited capacity by simply using larger tanks, and the absence of self-discharge. Indeed, the electrochemically active species are stored separately. Moreover, RFBs can be left completely discharged for long periods of time and very deep discharges doesn't affect the cell morphology. Some disadvantages of RFBs are the low power density and energy density making RFBs more suitable for stationary applications than mobile ones. Another problem is the Nafion membranes which are really expensive and can represent up to 40 % of the price.^[133] Finally the use of organic or corrosive acid electrolytes and metal species as active materials make the RFB unsuitable for domestic and large scale applications due the long term access problematic to metals like lithium and vanadium.



Figure 2.15: Schematic representation of a RFB energy storage system: RFB stack and electrolyte tanks are separated. Reproduced from Ref.^[132]

In this context, TEMPO-based electrolytes were developed since they offer a high redox potential and a high solubility in battery electrolytes. Indeed, these two properties are key parameters for an electrode to achieve high energy density in redox flow batteries.^[134] PTMA was grafted onto polynorbornene (PNB) via a grafting-through approach, leading to radical-crowded PNB-g-PTMA bottlebrush polymers. Macromonomers composed of PTMA chains with norbornene chain-end were synthesized by anionic polymerization. The macromonomers were then polymerized by ROMP using a Grubbs third-generation catalyst. The subsequent polymer brushes were used as cathode materials in a flow cell system. Indeed, bottlebrush polymers present tunable molecular dimensions and a low viscosity in comparison to their linear counterpart, designating them as new candidates for redox active polymers for redox flow batteries.^[107]

Schubert et al. have developed a polymer-based RFB using environmentally benign sodium chloride solution as electrolyte and cheap, commercially available filtration membranes, advantageously replacing the



Figure 2.16: Schematic representation of the PNB-g-PTMA bottlebrush polymers synthesis. Reproduced from Ref.^[107]

highly corrosive acid electrolytes and expensive Nafion membranes usually employed in RFBs technologies.^[133] Copolymers employed as active materials are made of two components: a redox-active unit and an unit enhancing the water solubility to prevent precipitation of the polymer during the charge/discharge process. PTMA was used as cathode electrochemically active species and a polystyrene derivative bearing viologen units as anode electrochemically active species (Figure 2.17). Nafion membrane was replaced by a more cheaper size-exclusion membrane like dialysis one. This work is a first step toward economical energy-storage devices using safe, metal-free and all-organic raw materials.



Figure 2.17: **a.** Schematic representation of a polymer-based RFB consisting of two electrolyte tanks and an electrochemical cell. The anolyte and catholyte are separated by a semipermeable size-exclusion membrane. **b.** Fundamental electrode reactions of electrochemically active moieties, i.e. TEMPO and viologen. Reproduced from Ref.^[133]

2.6 Conclusion

After the introduction dedicated to general concepts involved in this manuscript, the aim of this chapter was to focus more precisely onto the recent developments in organic radical batteries based on polymers bearing nitroxyl radicals. After an overview of the general characteristics and applications of stable nitroxide molecules, the focus was made onto polymers bearing stable nitroxide as electrode materials for organic radical batteries. Then the preparation of such ORB was investigated. The syntheses strategies and methods for the formation of organic radical polymers were developed. Finally, an overview of electronic and energy applications involving organic NO radical polymers was presented.

While the research primarily focused onto the development of organic radical cathodes based on mixtures of PTMA with carbon in order to replace inorganic cathodes in lithium ion batteries, the recent researches tend to go further by combining the properties of block or statistical copolymers to the redox properties of nitroxide polymers in order to create a new generation of systems which find applications in different fields such as medical imaging and energy storage.

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CHAPTER 3

Objectives

Abstract

The aim of this thesis is the development of nanostructured organic radical cathodes. The general frame and the objectives of the project are presented in this chapter. In short, the first objective is the synthesis of block copolymers bearing an electrochemical active moiety. Next, two kinds of nanostructured electrodes will be examined: micelles resulting from the self-assembly of copolymers in solution and nanostructured thin films with electrochemical active nanodomains. Finally, the development of another block copolymer with two electrochemical active moieties will be discussed.

3.1 The project

As previously mentioned in Chapter 1, a new class of organic radical battery has emerged recently as an alternative to conventional Li-ion batteries.^[1,2] In this context, PTMA is one of the most studied cathode polymers for the fabrication of ORBs. It consists of a methacrylate bearing a TEMPO group. The stable nitroxide radicals present on the polymer can be reversibly oxidized into an oxoammonium cation, leading to the charged form of the polymer. The redox potential of PTMA is 3.6 V vs Li/Li⁺.^[3,4] Due to the well documented redox behavior of PTMA and the commercial availability of its secondary amine precursor, we decided to focus on this particular redox polymer for the development of our nanostructured radical cathodes. PTMA is usually blended with conductive carbons and polymer binders to form the cathode. [5-10]Indeed, conductive carbon is needed since PTMA is not a conductive material and a binder is necessary to keep the cathode integrity over the charge/discharge cycles. However, the presence of these additives lowers the capacity of the system.

This project takes place in a miniaturization concept for organic radical batteries. Indeed, Prof. Song et al. demonstrated that when fabricating a PTMA cathode, the PTMA layer wraps around the carbon with a thickness lower than 100 nm.^[7] It can therefore be assumed that by decreasing the cathode thickness, the need of conductive carbon can be overcome. Another problem encountered with PTMA is its solubility in battery electrolytes. Our strategy consists in combining the self-assembly properties of block copolymer thin films with the redox properties of PTMA to create nanostructured organic radical cathodes. On one hand, the second block of the block copolymer will act as an anchor, avoiding PTMA dissolution and maintaining the structural integrity of the cathode. On the other hand, the thickness of the thin film electrode will make it possible to design cathodes without carbon additives. As a first approach and as a proof of the concept, PS will be used as the second polymer block. Indeed, PS is insoluble in battery electrolytes and electrochemically inactive. PS could later be replaced by an electrochemically active block or by an ionic conducting block. Even so, it is important to start this study by working with PS since it is a well documented polymer that will not interfere with the PTMA redox process, making it a good standard model for later more intricate systems.

Another interesting feature of block copolymers is their self-assembly

property to form micelles in solution. The formation of micelles will be investigated with the PTMA-*b*-PS block copolymers and can found applications in redox flow batteries.

3.2 The objectives

The goal of this thesis is to create nanostructured organic radical cathodes. In this context, the synthesis of PTMA-*b*-PS block copolymers will be investigated. The self-assembly of the synthesized block copolymers will be next studied in both solution and bulk. The electrochemical properties of the materials will be measured at each step of the project (Figure 3.1). Finally, the last part will focus onto the replacement of the electrochemically inactive PS by an electrochemically active PS derivative.



Figure 3.1: Schematic representation of the aim of the project: the development of nanostructured organic radical cathodes by self-assembling block copolymers in solution and in bulk.

3.2.1 Synthesis of PTMA-*b*-PS block copolymers

The first objective is the synthesis of PTMA-*b*-PS block copolymers. Even if some groups reported the direct polymerization of TMA by techniques such as anionic or group transfer polymerization,^[11–13] PTMA is mainly obtained by free radical polymerization of a secondary amine precursor (TMPM), followed by its oxidation.^[4,14,15] However, FRP doesn't allow the formation of block copolymers. A controlled radical polymerization of TMPM needs therefore to be developed. We decided to focus onto ATRP which is a versatile technique allowing the polymerization of a wide range of monomers from methacrylates to styrenes. The synthesis strategy consists in three steps. First the polymerization of TMPM by ATRP, followed by the polymerization of the PS block using the PTMPM as a macroinitiator and finally the oxidation of TMPM into PTMA (Figure 3.2). Since the polymerization of styrene by ATRP and the oxidation of TMPM using either mCPBA or H_2O_2 in the presence of NaWO₄ are well referenced in the literature, the main challenge of this part will be the development of the ATRP of TMPM. A wide variety of polymers presenting different ratios of PTMA and different chain lengths needs to be synthesized in order to get a library for the self-assembly study. Indeed, the polymer length and the PTMA ratio will vary depending on the targeted application.



Figure 3.2: Scheme of the synthetic strategy for the formation of PTMA*b*-PS block copolymers.

3.2.2 Self-assembly study

One of the main objective of this study is the development of nanostructured organic radical cathodes. By employing block copolymers, two kinds of self-assembly can be performed: in solution or in solid state, e.g. thin films. Both of these aspects will be investigated, leading to different structures and applications.

In solution, the formation of micelles will be investigated. The key feature for the self-assembly in solution is the difference of solubility of the blocks into the battery electrolyte (EC/DEC/DMC, 1:1:1 in volume with 1M LiTFS). PTMA is soluble in this specific electrolyte whereas PS is insoluble. In consequence, micelles with a core of PS and a corona of PTMA are expected. Two methods will be employed to study the micellar objects: DLS and AFM. Micelles in solution can be characterized by DLS whereas dried micelles deposited onto a surface can be measured by AFM. Polymers with around 30 wt% of PS will be employed in order to maximize the amount of electrochemical active PTMA.

In the solid state, PTMA-b-PS will be self-assembled onto surfaces in order to obtain nanostructured thin films. As previously mentioned in the introduction (Chapter 1), different morphologies are accessible depending on the volume fraction (f) of the constituting blocks. Cylindrical morphology with cylinders of PTMA perpendicular to the surface will be targeted. Indeed, this morphology presents a continuous PS matrix which can be crosslinked, avoiding any dissolution of the polymer film into the electrolyte, while perpendicular cylinders crossing the entire film will allow a good continuity between the current collector and the liquid electrolyte. In order to reach this morphology copolymers with a volume fraction of PTMA of around 0.2 - 0.3 will be employed. In order to increase the phase separation and obtain the desired morphology, different annealing conditions such as solvent and thermal annealing will be investigated. AFM will be employed to obtain information about the morphology of our polymer films.

3.2.3 Electrochemical characterization

The electrochemical properties of our systems will be investigated at each step of the project. After synthesis of the block copolymers it will be important to check that PS doesn't interfere with the redox behavior of PTMA. The micelles will be analyzed directly in solution such as in redox flow batteries and also in the solid state by immobilizing them onto a carbon nanotubes mat. Since commonly employed electrochemical cells such as Swagelock cells, are not suitable for thin film characterization, a suitable electrochemical system will specifically be developed to analyze polymer thin films.

3.2.4 Replacement of the PS block

As already mentioned, PS is a first approach for the fabrication of nanostructured organic radical cathodes and will be further replaced by a more interesting polymer. The last part of this work will investigate the possibility to replace the PS block by an electrochemical active PS derivative, i.e. a PS bearing stable nitroxide radicals. The corresponding monomer will need to be synthesized and its polymerization by controlled radical polymerization techniques will be performed. Finally its incorporation into a block copolymer with a PTMA block will be studied for the further fabrication of thin films.

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CHAPTER 4

Synthesis of nitroxide-containing block copolymers for the formation of organic radical cathodes

Abstract

This chapter focuses on the synthesis of poly(2,2,6,6)-tetramethylpiperidinyloxy-4-yl methacrylate)-block-polystyrene (PTMA-b-PS) copolymers by atom transfer radical polymerization (ATRP) in order to obtain the materials further employed for the self-assembly studies. PTMA-b-PS block copolymers are obtained via a three step synthesis. Since nitroxide containing monomers can not been polymerized by ATRP, a precursor monomer bearing a secondary amine (2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPM)) is employed. The TMPM is polymerized by ATRP leading to PTMPM homopolymers. The PTMPM is next used as macroinitiator for the ATRP polymerization of the second polymer block, i.e. polystyrene (PS). Once the PTMPM-b-PS block copolymer is obtained, the secondary amines are oxidized to form the electrochemically active PTMA-b-PS block copolymer. Different ATRP polymerization conditions are investigated in order to obtain well defined PTMAb-PS block copolymers with narrow dispersity (D). Finally, the electrochemical behavior of the synthesized block copolymers is characterized by cyclic voltammetry. Cyclic voltammograms are recorded using two different set-ups: a liquid three electrodes set-up with an Aq/Aq^+ non aqueous reference electrode and a Swagelock half-cell configuration employing battery electrolyte and metal lithium as counter and reference electrode.

4.1 Introduction

Self-assembly of block copolymers can be performed either in solution or in bulk, e.g. thin films. This thesis focuses on both aspects. However, before studying the self-assembly processes, the block copolymers need to be synthesized. The targeted application, e.g. thin films or micelles, will determine the relative lengths of the blocks constituting the copolymer. For thin films a block copolymer with around 30 wt% of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) will be synthesized whereas for self-assembly in solution the reverse block copolymers will be preferred. Indeed, a small PS core is usually enough to stabilize micelles. In consequence, the synthesis conditions for the formation of these copolymers will be slightly different depending on the desired PTMA block length.

PTMA can be synthesized either by starting from TMA monomer and its polymerization by nitroxyde friendly polymerization techniques, such as anionic and group transfer polymerizations [1-5] or by starting from a secondary amine precursor of PTMA, i.e. 2,2,6,6-tetramethylpiperidin-4-vl methacrylate (TMPM). This second method is commonly employed for the synthesis of PTMA by free radical polymerizations (FRP).^[6–9] Due to the stringent conditions needed to polymerize PTMA by anionic polymerization and the commercially availability of TMPM precursor, the second strategy was favored, starting from the secondary amine bearing monomer. Since free radical polymerizations do not allow a control of the molar mass neither of the dispersity (D) of the synthesized block copolymers, the focus was made on controlled radical polymerization techniques. The three major ones are NMP, RAFT and ATRP (see introduction for further details). NMP is known to be less suitable for the polymerization of methacrylates and was therefore set aside.^[10] Since the group of Prof. Schubert published a study comparing the three sub-mentioned methods, focusing mainly on RAFT, we decided to focus on ATRP.^[11] Indeed, ATRP is a versatile technique allowing the polymerization of a wide class of monomers and the synthesis of various polymer architectures.^[10,12]

The synthesis of PTMA-*b*-PS block copolymers can be realized by following the three steps shown in Figure 4.1. Starting from a secondary amine precursor of the TMA, i.e. TMPM, the TMPM is polymerized by atom transfer radical polymerization (ATRP) (Scheme 4.1 a). In a second step, the synthesized PTMPM-Cl is used as a macroinitiator for the synthesis of the PS block by ATRP (Figure 4.1 b). Finally the PTMPM-*b*-PS block copolymer is transformed into PTMA-*b*-PS using 3-chloroperoxylbenzoic acid (mCPBA) as oxidizing agent (Figure 4.1 c).



Figure 4.1: Synthetic approach for the formation of PTMA-*b*-PS diblock copolymers: (a) polymerization of TMPM by ATRP, (b) polymerization of styrene from a PTMPM-Cl macroinitiator by ATRP, (c) oxidation of the PTMPM block into PTMA.

4.2 ATRP polymerization of TMPM

4.2.1 Copper bromide based catalyst

In a first approach, the ATRP of TMPM with CuBr was investigated using ethyl α -bromoisobutyrate (EBiB) as initiator and 4,4'-dinonyl-2,2'-dipyridyl (dNbpy) as ligand. The polymerizations were performed in anisole at 80 °C. These conditions were tested with reaction times from 120 to 5 minutes. The resulting polymers demonstrate narrow D ($D = \frac{\bar{M}_w}{M_n}$), below 1.25 (Table 4.1). However initiator efficiencies ($E_i = \frac{\bar{M}_n(th)}{M_n(RMN)}$ 100) were poor and halved when the polymerization time decreased below 10 minutes. At low conversion (below 20 %) the initiator efficiency was about 40 % and increased up to 80 % at higher conversion (43%). This effect is well known in literature and can be explained by a slow initiation with respect to propagation.^[13-16] Additionally, a low E_i may also indicate coupling and termination in the initial stage of the polymerization.^[15]

Table 4.1: Results obtained for the ATRP of TMPM performed with copper(I) bromide in anisole.

$\mathrm{Ent}\mathrm{ry}^{\mathrm{a}}$	${f Time}\ (min)$	$\stackrel{\mathrm{Conv.}^{\mathrm{b}}}{(\%)}$	$\overline{M}_n \ (\mathrm{th})^{\mathrm{c}} \ (\mathrm{g} \ \mathrm{mol}^{-1})$	\overline{M}_n (NMR) (g mol ⁻¹)	$\overline{M}_n \ (\text{SEC})^{d} \ (\text{g mol}^{-1})$	Ðď	E_i^{e} (%)
1	120	97	26,400	$33,\!800$	19,400	1.22	78
2	40	80	21,800	$25,\!900$	15,000	1.21	84
3	20	60	16,400	$20,\!900$	$15,\!000$	1.25	78
4	10	43	11,900	$15,\!100$	10,300	1.21	79
5	5	18	$4,\!950$	$12,\!800$	8,000	$1,\!13$	39

 $^{\rm a}$ Reaction conditions: EBiB/CuBr/dNbipy/TMPM = 1/1/2/120, 50 wt% of anisole, T= 80 $^{\circ}{\rm C}.$

 $^{\rm b}$ Conv. = conversion of the monomer determined by $^{\rm 1}{\rm H}$ NMR (solvent: CDCl₃).

^c Theoretical \overline{M}_n determined via the conversion.

 d Determined by SEC (eluant: $\rm CHCl_3/Et_3N/isopropanol~94:4:2$ in volume; calibrated with PS standards).

^e E_i = initiator efficiency.

In order to slow down the propagation rate of TMPM, the solvent was changed from anisole to toluene and the temperature was decreased to 70 °C. In parallel, different monomer concentrations (50, 60 and 70 wt%) in toluene were also screened (Table 4.2). This resulted in a global decrease of the kinetics of the reaction. At the same time, a decrease of E_i was observed. Even though polymers with narrow D (below 1.19) were obtained, low molar mass PTMPM (below 8000 g mol⁻¹) could not be reached due to the very low E_i at the early stages of the polymerization. As previously mentioned, the low E_i at low conversion can be attributed to a slow initiation with respect to the propagation.

The molar masses of the synthesized PTMPM were calculated either by SEC (calibrated with PS standards) or NMR (integrating the CH_2 from the EBiB chain-end and comparing it to the PTMPM signals, see

Table 4.2: Results obtained for the ATRP of TMPM performed with copper(I) bromide in toluene.

$\operatorname{Entry}^{\mathbf{a}}$	${ m Time}\ ({ m min})$	${f Toluene}\ ({ m wt}\%)$	Conv. ^b (%)	$\bar{M}_n (\mathrm{NMR})$ (g mol ⁻¹)	D^{c}	$E_i{}^{\mathrm{d}}$ (%)
$egin{array}{c} 1 \\ 2 \\ 3 \\ 4 \end{array}$	$45 \\ 15 \\ 45 \\ 15$	50 50 60 60	$46 \\ 26 \\ 46 \\ 15$	20,200 15,500 18,200 18,400	$1.16 \\ 1.19 \\ 1.19 \\ 1.12$	$62 \\ 46 \\ 65 \\ 32$
$5 \\ 6$	$\begin{array}{c} 45 \\ 15 \end{array}$	70 70	$\frac{23}{9}$	$9,900 \\ 9,400$	$\begin{array}{c} 1.18 \\ 1,12 \end{array}$	$\frac{64}{29}$

 a Reaction conditions: EBiB/CuBr/dNbipy/TMPM = 0.5/1/2/120, T= 70 °C.

 $^{\rm b}$ Conv. = conversion of the monomer determined by $^{1}{\rm H}$ NMR (solvent: CDCl_3).

^c Determined by SEC (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^d E_i = initiator efficiency.

below for more details). The molar masses determined by SEC were systematically underestimated indicating that PS and PTMPM chains with the same molar masses are characterized by very different hydrodynamic volumes. Therefore, all further calculations were realized using molar masses calculated by ¹H NMR.

The same reaction conditions were investigated with a higher amount of monomer equivalents, i.e. 450 equivalents. Indeed, the increase in monomer equivalents should decrease the kinetics and allow a better control over the polymerization. As indicated in Table 4.3, a decrease of initiation efficiency was observed after decreasing the catalyst amount. After 2h of reaction at 70 °C, only 10% of conversion were reached. SEC indicates a tailing at small masses, attributed to termination reactions, and a relatively high dispersity (D > 1.2). An increase in temperature accelerates the reaction, 49 % of conversion after 2h30, but no ameliorations of the dispersity neither of the tailing were observed (Figure 4.2).

Conversion determination via ¹H NMR

The conversion was determined via the integration of the region between 5.3-4.9 ppm (H_c) of the ¹H NMR spectrum of the crude mixture. This chemical shift corresponds to the proton next to the ester function of TMPM and PTMPM. The integration of the proton at 6.04 ppm (H_a)

Entry ^a	${ m CuBr}/{ m dNbpy/EBiB}$	Т	Time	Conv. ^b	$ar{M}_n$ (NMR)	D^{c}	$E_i{}^{\mathrm{d}}$
	(equiv.)	(°C)	(h)	(%)	$(g \text{ mol}^{-1})$		(%)
$\begin{array}{c} 1\\ 2\\ 2\end{array}$	$0.5/1/1 \\ 1/2/1 \\ 1/2/1$	70 70 80	$2 \\ 2 \\ 2 5$	9.3 12 48	19,600 18,000 70,000	$1.22 \\ 1.20 \\ 1.22$	$49 \\ 69 \\ 71$

Table 4.3: Results obtained for the ATRP of TMPM using CuBr and 450 monomer equivalents.

^a Reaction conditions: TMPM = 450 equivalents, 50 wt% of anisole.

^b Conv. = conversion of the monomer determined by ¹H NMR (solvent: $CDCl_3$).

 $^{\rm c}$ Determined by SEC (eluant: CHCl_3/Et_3N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^d E_i = initiator efficiency.



Elution time (min)

Figure 4.2: SEC chromatogram of the PTMPM-Br (Table 4.3, entry 3) synthesized by ATRP using CuBr/dNbpy as catalytic system (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

corresponds to one proton of the vinyl function of the TMPM (monomer). Therefore the conversion corresponds to (calculation performed for Table 4.1, Entry 4):

$$Conv. = \frac{H_c - H_a}{H_c} 100 = \frac{1.77 - 1}{1.77} 100 = 43\%$$
(4.1)



Figure 4.3: ¹H NMR of crude PTMPM obtained by ATRP using EBiB/CuBr/dNbipy (Table 4.1, Entry 4) (solvent: CDCl₃).

DP determination via ¹H NMR

The DP was determined by ¹H NMR using the peak corresponding to the polymer chain-end. The initiator employed, i.e. EBib, present a distinct peak at 4.07 ppm (H_a) corresponding to the CH₂ next to the ester function. Therefore, H_a integration was set to two and the resulting integration of H_b at 5.03 ppm, corresponding to the CH next to the ester function of TMPM, gives the DP of the synthesized PTMPM (Figure 4.4).

4.2.2 Copper(I) chloride based catalyst

CuCl/dNbpy catalytic system

Due to the slow initiation with respect to the propagation in the polymerization of TMPM with CuBr, another catalytic system has been tested. CuCl is known to be highly efficient for methacrylate monomers but is less suitable for the synthesis of the second polystyrene block.^[17] Therefore, longer polymerization times are expected for the polystyrene block. Polymerizations were carried out in anisole with CuCl/dNbpy as catalytic system and tosyl chloride (TsCl) as initiator. The effect of


Figure 4.4: ¹H NMR of pure PTMPM obtained by ATRP using EBiB/CuBr/dNbipy (Table 4.1, Entry 4) (solvent: CDCl₃).

monomer equivalents was investigated. The first polymerization tests realized with 120 equivalents of monomer show an E_i around 60 %. Decreasing equivalents of monomer from 120 to 80 decreases E_i from 60 to 45 %. The higher concentration of initiator leads presumably to more coupling and termination during the early stages of the polymerization. Table 4.4 however shows that PTMPM with \bar{M}_n between 5,100 and 10,800 g mol⁻¹ and \bar{D} below 1.08 were obtained.

The low D values give us a clue about a possible controlled behavior of the polymerization. Further kinetic studies were thus conducted (Table 4.5, Figure 4.5). A linear conversion with time was observed after an induction period (~ 3h) (Figure 4.5a) attributed either to the slow formation of the catalyst complex or to the presence of oxygen and impurities.^[18–20] However, the plot of \overline{M}_n versus conversion (Figure 4.5b) shows a linear increase of molar mass with conversion, indicating some controlled character even at high conversion. The previously discussed low E_i can thus be definitely attributed to coupling and termination events during the early stages of polymerization.

Figure 4.6 displays SEC chromatograms measured at different poly-

Entry ^a	TMPM (equiv.)	${f Time}\ (min)$	$\operatorname{Conv.^{b}}_{(\%)}$	$\bar{M}_n (\mathrm{NMR}) $ (g mol ⁻¹)	D^{c}	$\begin{array}{c}E_i{}^{\mathrm{d}}\\(\%)\end{array}$
1 2 3 4 5	120 120 120 80	81 92 305 300	$12 \\ 15 \\ 24 \\ 17 \\ 17$	5,100 6,700 10,800 7,400 6,700	1.08 1.06 1.07 1.07 1.07	$67 \\ 63 \\ 62 \\ 45 \\ 48$

Table 4.4: Results obtained for the ATRP of TMPM performed with copper(I) chloride.

 $^{\rm a}$ Reaction conditions: TsCl/CuCl/dNbipy = 1/1/2, 50 wt% of anisole, T= 80 °C.

^b Conv. = conversion of the monomer determined by ¹H NMR (solvent: CDCl₃).

^c Determined by SEC (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^d E_i = initiator efficiency.

merization times. The SEC traces are generally symmetric except at high conversion where some tailing at high elution times is observed. Such tailing usually results from the termination of low molar mass chains during the polymerization process. However, given the nature of the polymer, i.e. a polymer bearing secondary amines, the tailing could result from interactions between the polymer and the column.

The CuCl/dNbpy catalytic system was also investigated with 450 monomer equivalents. As expected the reaction was slowed down. 38 % of conversion was reached after 24 h of reaction and E_i similar than for 120 monomer equivalents were obtained (Table 4.6, Entry 1).

CuCl/PMDETA catalytic system

Due to the slow kinetic of the reaction using dNpby, N,N,N',N',-N",N"-pentamethyldiethylenetriamine (PMDETA) was investigated as ligand for reactions with 450 monomer equivalents. Indeed, PMDETA is a more activating ligand and faster reaction kinetics is therefore expected.^[17,21,22] By changing the ligand better E_i (higher than 80 %), faster reactions and low \mathcal{D} (< 1.2) were obtained, even at high conversion \mathcal{D} remains below 1.5 (Table 4.6, Entry 2-6). Moreover no tailing at small masses was observed (Figure 4.8). Kinetic study of the system revealed a linear increase of $ln(\frac{[M]_0}{[M]})$ as a function of the polymerization



Figure 4.5: (a) Plot of $\ln([M]_0/[M])$ versus time for the ATRP polymerization of TMPM using CuCl/dNbpy as catalytic system. (b) Plot of $\overline{M}_n(\text{NMR})$ versus conversion (full circles) and $\mathcal{D}(\text{SEC})$ versus conversion (open circle) for the ATRP polymerization of TMPM using CuCl/dNbpy catalytic system.

time as well as a linear increase of the molar masses as a function of the conversion, indicating a controlled behavior of the polymerization (Figure 4.7). However, as for the previous kinetic study, an induction period of a few minutes is observed. Low D below 1.08 were obtained even at high conversion.

DP determination via ¹H NMR

The DP (¹H NMR) determination process for PTMPM synthesized using CuCl differs from syntheses based on CuBr since a different initiator, i.e. a different chain-end, is employed. The initiator employed, i.e. TsCl, presents some distinct peaks at 7.72 (H_b) and 7.31 ppm (H_a)

Table 4.5: Results obtained for the kinetic of TMPM by ATRP using copper(I) chloride.

$\mathrm{Entry}^{\mathbf{a}}$	${f Time}\ (h)$	$\stackrel{\rm Conv.^b}{(\%)}$	\overline{M}_n (th) ^c (g mol ⁻¹)	\overline{M}_n (NMR) (g mol ⁻¹)	$ar{M}_n \ (\mathrm{SEC})^\mathrm{d} \ (\mathrm{g \ mol}^{-1})$	D^{d}	E_i^{e} (%)
1	5	8	-	-	-	-	-
2	7	17	4,800	8,500	5,800	1.06	55
3	9	33	9,200	$14,\!800$	9,800	1.07	61
4	10	28	7,700	15,700	9,800	1.07	49
5	13	46	$12,\!500$	$24,\!300$	13,400	1.07	51
6	24	87	$23,\!900$	45,700	24,600	1.10	52
7	48	97	$26,\!800$	$54,\!000$	26,200	$1,\!18$	49

^a Reaction conditions: TsCl/CuCl/dNbipy/TMPM = 1/1/2/120, 50 wt% of anisole, T= 80 °C.

 $^{\rm b}$ Conv. = conversion of the monomer determined by $^{\rm 1}{\rm H}$ NMR (solvent: CDCl_3).

 $^{\rm c}$ Theoretical \bar{M}_n determined via the conversion.

 d Determined by SEC (eluant: CHCl_3/Et_3N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^e E_i = initiator efficiency.



Figure 4.6: Evolution of the SEC chromatograms with time for the ATRP polymerization of TMPM using CuCl/dNbpy as catalytic system (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

corresponding to its aromatic protons. The integration value of the signal at 7.72 ppm was set to two and the resulting integration of H_b at 5.03 ppm, corresponding to the CH next to the ester function of TMPM,

Table 4.6: Results obtained for the polymerization of TMPM by ATRP using CuCl with 450 monomer equivalents.

Entry ^a	Ligand (equiv.)	$\operatorname{Time}_{(\min)}$	$\operatorname{Conv.^{b}}_{(\%)}$	$\overline{M}_n (\mathrm{NMR})$ (g mol ⁻¹)	D^{c}	E_i^{d} (%)
1	dNbpy (2)	1440	38	55,600	1.25	69
2	PMDETA (1.1)	16	10	14,200	1.18	73
3	PMDETA (1.1)	30	11	15,300	1.17	74
4	PMDETA (1.1)	75	21	31,500	1.13	69
5	PMDETA (1.1)	100	46	57,400	1.11	81
6	PMDETA (1.1)	180	72	91,500	1.15	78

 a Reaction conditions: TsCl/CuCl/TMPM = 1/1/450, 50 wt% of anisole, T= 80 $^\circ\mathrm{C}.$

 $^{\rm b}$ Conv. = conversion of the monomer determined by $^1{\rm H}$ NMR (solvent: CDCl_3).

 $^{\rm c}$ Determined by SEC (eluant: CHCl_3/Et_3N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^d E_i = initiator efficiency.

gives the DP of the synthesized PTMPM (Figure 4.9).

4.2.3 Scale-up

In order to synthesize enough material for the formation of micelles, the reaction conditions were scaled up in order to obtain batches of around three to four grams of the macroinitiator PTMPM-Cl. Therefore the syntheses were performed into a Schlenk flask rather than a Schlenk tube and 25 mg in place of 3 mg of copper were employed. A difference in the kinetics of the reaction was observed. When 46 % of conversion were previously reached in 1h40, 24 % are obtained after 1h15 with the scaled up reactions. Despite the reaction time, no other changes were observed and polymers with controlled molar masses and low D were obtained (Table 4.7).



Figure 4.7: Kinetic study of TMPM polymerization by ATRP using CuCl/PMDETA catalytic system with 450 monomer equivalents: (a) Plot of $\ln([M]_0/[M])$ versus time. (b) Plot of $\overline{M}_n(\text{NMR})$ versus conversion (full circles) and $\overline{M}_w/\overline{M}_n(\text{SEC})$ versus conversion (open circle).



Figure 4.8: Evolution of the SEC chromatograms with time for the ATRP polymerization of TMPM using CuCl/PMDETA as catalytic system and 450 monomer equivalents (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).



Figure 4.9: ¹H NMR of pure PTMPM obtained by ATRP using TsCl initiator (Table 4.5, Entry 4) (solvent: $CDCl_3$).

Table 4.7: ATRP of TMPM using CuCl/PMDETA (scale up).

Entry ^a	CuCl (equiv.)	${f Time}\ (min)$	$\operatorname{Conv.^{b}}_{(\%)}$	DP (NMR)	\bar{M}_n (NMR) (g mol ⁻¹)	D^{c}
$\begin{array}{c}1\\2\\3\\4\end{array}$	$22.5 \\ 22.8 \\ 19.1 \\ 20.9$	$30 \\ 25 \\ 15 \\ 15 \\ 15$	$45 \\ 22 \\ 13 \\ 14$	256 136 82 83	57,900 30,800 18,700 18,900	$1.12 \\ 1.13 \\ 1.18 \\ 1.19$

 a Reaction conditions: TsCl/CuCl/PMDETA/TMPM = 1/1/1.1/450, 50 wt% of anisole, T= 80 °C.

anisole, T = 80 °C. ^b Conv. = conversion of the monomer determined by ¹H NMR (solvent: CDCl₃). ^c Determined by SEC (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; cali-brated with PS standards). ^d E_i = initiator efficiency.

4.3 PTMPM-*b*-PS diblock copolymers by ATRP

This section focuses on the synthesis of well-defined PTMPM-*b*-PS diblock copolymers. Depending on the intended application, block copolymer with different compositions were synthesized. For thin films applications, block copolymers with a minor block of PTMA were synthesized ($\sim 30 \text{ wt\%}$). For micelles applications, the opposite polymers were synthesized, i.e. a minor block of PS representing around 30 wt% of the total molar mass of the polymer. The polymerization of the PS block was carried out using CuCl/PMDETA in toluene (50 wt%), starting from the previously prepared PTMPM-Cl macroinitiator. Because styrene is known to polymerize slower than methacrylates by ATRP, a more activating ligand (PMDETA instead of dNbpy) was selected.^[17,21,22]

Starting from small PTMPM-Cl macroinitiators (7000 < \bar{M}_n < 11,000 g mol⁻¹) for thin film applications, Table 4.8 shows that PTMPMb-PS copolymers with a lower D are obtained at 100 °C than at 80°C (Table 4.8). Well-defined PTMPM-b-PS block copolymers with a PTPM weight fraction varying from 17 to 63 wt% were synthesized without homopolymer contamination and with D below 1.20 (Table 4.8). The increase in dispersity after addition of the second block is commonly observed in ATRP copolymerization and may be attributed to end group loss or other side reactions.^[22] Typical SEC chromatograms of a PTMPMb-PS copolymer and the corresponding PTMPM-Cl macroinitiator are shown in Figure 4.10. Two symmetrical peaks with a narrow molar mass distribution and a shift to higher molar mass for the block copolymer can be observed. The absence of peak corresponding to the macroinitiator, indicates a full reinitiation process of the macroinitiator.

For PTMPM-*b*-PS block coplymers employed in micelles, a longer PTMPM-Cl macroinitiator was selected and a lower amount of styrene equivalents is employed since a shorter PS block was intended (Table 4.8, Entry 4-9). However, reinitiating ATRP from a macroinitiator of 87,900 g mol⁻¹ was unsuccessful and shorter PTMPM-Cl were therefore selected (Table 4.8, Entry 4,5). By using a macroinitiator of 26,600 g mol⁻¹ a conversion of 16 % was reached after 24 h of reaction but SEC analysis revealed that it was essentially due to the formation of homoPS (Table 4.8, Entry 6). Indeed, at 100 °C, 2 wt% per hour of homo PS may be synthesized by self-initiation.^[23] Finally, a good reinitiation without apparition of homoPS neither homoPTMPM was obtained by using a macroinitiator of 18,700 g mol⁻¹.



Figure 4.10: Typical SEC chromatograms of the PTMPM-Cl macroinitiator (dashed curve; Table 4.4, entry 5) and the corresponding PTMPM-*b*-PS diblock copolymer (solid curve; Table 4.8, Entry 2)(eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).



Figure 4.11: Typical SEC chromatograms of the PTMPM-Cl macroinitiator and the corresponding PTMPM-*b*-PS diblock copolymer. (a) PTMPM₁₁₇-*b*-PS₄₀ (Table 4.8, Entry 6), (b) PTMPM₈₃-*b*-PS₃₃ (Table 4.8, Entry 9)(eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

$\mathbf{y}^{\mathbf{a}}$	$\mathrm{PTMPM-Cl}$ $\mathrm{DP}/ar{M_n}^\mathrm{c}/ar{D}^\mathrm{d}$	(0, C)	Styrene (equiv.)	Time (h)	Conv. ^b (%)	DP (PS) ^c	\bar{M}_n (NMR) (g mol ⁻¹)	D^{q}
	47/10,800/1.07	80	800	16	2	62	17,200	1.13
	30/6,700/1.07	100	800	13	10	113	17,000	1.20
	32/7,400/1.07	100	800	48	38	336	42,400	1.17
	256/57,900/1.11	100	500	20	I	1	1	1
	256/57,900/1.11	100	500	48	I	I	I	I
	117/26,600/1.17	100	500	24	16	40	30,700	1.13
	82/18,700/1.19	100	500	24	16	141	33,400	1.17
	82/18,700/1.19	100	500	10	38	59	24,800	1.16
	83/18,900/1.19	100	500	16	6	33	22,300	1.15

Table 4.8: Results obtained for the ATRP of styrene starting from a PTMPM-Cl macroinitiator.

Conversion determination via ¹H NMR

The conversion was determined via the integration of the region between 6.2-7.4 ppm of the crude mixture NMR spectrum, corresponding to the aromatic protons ($H_{aromatics}$). 5 protons of PS (5 H_{PS}), 6 protons of styrene (6 $H_{styrene}$) and 5 protons of the solvent (5 $H_{anisole}$) are present in this integration (Equation 4.3). The contribution of 1 $H_{styrene}$ is set to 1 via the peak at 5.85 ppm. The value of 3 $H_{anisole}$ is obtained by integrating the protons at 3.89 ppm corresponding to the methyl of anisole. Finally, the contribution of 1 H_{PS} can be obtained via Equation 4.4 and the conversion is calculated according to Equation 4.2.

$$Conv. = \frac{1H_{PS}}{1H_{PS} + 1H_{styrene}} \times 100\%$$
(4.2)

$$H_{aromatics} = 5H_{PS} + 6H_{styrene} + 5H_{anisole} \tag{4.3}$$

$$1H_{PS} = \frac{H_{aromatics} - 6H_{styrene} - 5H_{anisole}}{5} \tag{4.4}$$



Figure 4.12: ¹H NMR of crude PTMPM-*b*-PS block copolymer (Table 4.8, Entry 3) (solvent: CDCl₃).

DP determination via ¹H NMR

The DP of the PTMPM block is known and its value is set to the integration of the peak H_a at 5.06 ppm, corresponding to the CH next to the ester function of TMPM. Therefore, the integration of the aromatic region comprised between 6.2 and 7.4 ppm (H_b) corresponds to the five aromatic protons of the PS. The DP of the PS block is obtained by dividing this value by 5, i.e. the number of aromatic protons present onto one unit of styrene (Figure 4.13).



Figure 4.13: ¹H NMR of pure PTMPM-*b*-PS block copolymer (Table 4.8, Entry 3) (solvent: CDCl₃).

4.4 Oxidation of PTMPM into PTMA

Oxidation of the secondary amine group of TMPM allows the formation of TMA, which is a derivative of TEMPO. The reversible redox activity of the nitroxide radical is well-known (Figure 4.14), allowing its utilization as active cathode material for the formation of organic radical batteries.^[8,24,25]

The oxidation was realized in CH_2Cl_2 , using mCPBA as oxidizing agent. The SEC chromatogram clearly indicates a coupling of the poly-



Figure 4.14: Redox process involving the PTMA nitroxide.

mer with 2.3 equiv. of mCPBA (Figure 4.15a) while a clear shift towards shorter elution volumes is observed for the PTMA-*b*-PS SEC trace when 1.5 equiv. of mCPBA were employed (Figure 4.15b). No significant increase in D is observed for the oxidized polymer in this case, indicating an absence of coupling.

 H_2O_2 is another oxidizing agent for the oxidation of secondary amines and has been described in literature as more efficient and allowing full conversion.^[26-28] However, this strategy was not practical in the case of block copolymers containing PS since the PS block was insoluble in the reaction solvent; i.e. in methanol.

4.4.1 Oxidation yield determination

Electron spin resonance spectroscopy (ESR) was employed in order to determine the oxidation rate of PTMA-*b*-PS. ESR is a spectroscopic technique similar to NMR. However, electron spins are excited rather than the spins of atomic nuclei. ESR is a common method to quantify species with unpaired electrons such as stable nitroxyl radicals. Two different ESR spectrometers were employed. The first samples were analyzed in the frame of a collaboration with Dr. Levêque P. and Prof. Gallez B. (UCL) using a Bruker EMX spectrometer (Rheinstetten, Germany) equipped with a high sensitivity ER4119HS resonator and operated in X band at ~9.6 GHz. Since this equipment doesn't allow direct quantification, a calibration was created using 4-hydroxy-TEMPO as standard.

Thanks to a collaboration with Prof. Schubert's group (Jena), a more recent ESR spectrometer that does not require a calibration curve, i.e. an EMXmicro CW-EPR spectrometer (Bruker, Germany), was later employed to perform experiments on powdered samples, using the Spin-



Figure 4.15: SEC chromatograms of PTMPM-*b*-PS (entry 2, Table 4.8, dashed curve) and the corresponding PTMA-*b*-PS (solid curve) for oxidation conditions using 2.3 equiv. (a) or 1.5 equiv. (b) of mCPBA (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

 $Count^{\mathbb{M}}$ software module for quantitative analysis.

The ESR spectrum of TEMPO is dominated by three characteristic lines. However, radical-radical interactions due to close spatial proximity of the nitroxide functions in the PTMA blocks broaden the signal, preventing the observation of hyperfine structures in the PTMA-*b*-PS spectrum (Figure 4.16).

Depending on the samples, oxidation yields from 50 to 95 % were achieved. After a drop-wise addition of mCPBA, the solution was initially stirred at room temperature for 1 hour, leading to oxidation yields between 50 to 65 %. Next experiments were stirred at room temperature over night, leading to oxidation yields between 75 to 95 %. Since no correlation between the DP and the oxidation rate appeared (See Table 5.1 and Table 6.1 for further details), the varying oxidation rate could arise from the purity of the mCPBA employed. Indeed, mCPBA was purified by washing using slightly basic buffer solution. However the purity of the obtained mCPBA was not verified and an impure mCPBA would lead to a lower oxidation yield.



Figure 4.16: ESR spectra (X-band) of PTMA-b-PS and TEMPO with g=2.8310.

4.5 Electrochemical characterization of PTMAb-PS diblock copolymers

Finally, the redox properties of the synthesized PTMA-*b*-PS copolymers were investigated in an half-cell configuration and in solution using a three electrodes set-up.

In order to record a cyclic voltammogram of PTMA-b-PS block copolymers, a three electrodes system composed of an Ag/Ag⁺ non aqueous

reference electrode, a Pt wire counter electrode, a Pt disk working electrode and an electrolyte solution of tetrabutylammonium perchlorate (TBAClO₄) in acetonitrile was employed. Unlike the Ag/AgCl aqueous reference electrode, the value of the redox potential against an Ag/Ag⁺ reference electrode in organic media shifts depending on the solvent, electrolyte and concentration used.^[29] Therefore, ferrocene was employed as an external standard.^[30] Ferrocene presents a potential of 0.11 V vs. the used Ag/Ag⁺ reference electrode (Figure 4.17a).

The cyclic voltammograms of PTMA₇₉-*b*-PS₅₀₂ block copolymers revealed a pair of redox peaks centered at 0.46 V vs. Ag/Ag⁺ and corresponding to the reversible oxidation of the free nitroxide radicals into oxoammonium cations (Figure 4.17a). $I_{pa}/I_{pc} \simeq 1$, indicating a fully reversible redox couple. Since the potential of ferrocene has been reported to be ~ 3.22 V vs. lithium in carbonates-based electrolytes^[31] and is known against the employed Ag/Ag^+ reference electrode, the potential of the PTMA-b-PS vs. Li/Li⁺ can be calculated and is worth 3.57 V (0.46 - 0.11 + 3.22 = 3.57). This value was confirmed by a cyclic voltammetry performed onto $PTMA_{47}$ -b- PS_{62} in an half-cell configuration. To obtain the cathode, PTMA-b-PS was mixed with carbon black as conductive material and PVDF as binder and deposited onto aluminum as current collector. The prepared cathode was assembled into a Swagelock cell (Figure 4.18). Lithium was used as negative and reference electrode and a solution of 1 M lithium trifluoromethanesulfonate (LiTFS) in EC/DEC/DMC (1:1:1 in volume) was employed as liquid electrolyte. The recorded cyclic voltammogram revealed a similar behavior than in the three electrode set-up with a redox wave centered to 3.60 V vs. Li/Li⁺ (Figure 4.17b). This value is in good correlation with the calculated one. As expected, PS has no influence over the electrochemical process.



Figure 4.17: Cyclic voltammograms (scan rate = 0.1 V s^{-1}) of: (a) PTMA₇₉-*b*-PS₅₀₂ and ferrocene using a three electrodes set-up, (b) PTMA₄₇-*b*-PS₆₂ mixed with carbon and binder in an half-cell configuration.



Figure 4.18: Schematic representation of a Swagelock electrochemical cell: 1. current collector, 2. cathode, 3. separator, 4. metal lithium anode, 5. spring, 6. polytetrafluoroethylene (PTFE) insulating container.

4.6 Conclusion

A three step synthesis was developed in order to prepare the PTMAb-PS block copolymers needed for the formation of nanostructured organic radical cathodes. Starting from the ATRP polymerisation of T-MPM, followed by the formation of PTMPM-b-PS block copolymers by ATRP, using the previously synthesized PTMPM as macroinitiators, and finally ending by the oxidation of the block copolymers into the electrochemically active PTMA-b-PS.

Different conditions for the polymerization of TMPM by ATRP were screened. The CuCl/dNbpy catalytic system appeared to be an efficient way to obtain well-defined PTMPM homopolymers with molar masses lower than 15,000 g mol⁻¹. However a kinetic study revealed an unusual induction period at the early stages of polymerization. For the formation of PTMPM macroinitiators with higher molar masses, i.e. > 15,000 g mol⁻¹, reaction kinetics using dNbpy ligand appeared to be too slow and a more activating ligand, i.e. PMDETA was selected. It resulted in a faster polymerization process allowing the synthesis of PTMPM with narrow dispersity. Finally, the synthesis conditions were scaled-up in order to obtain three to four grams of macroinitiator at once.

In a second part, the polymerization of styrene by ATRP, starting from PTMPM-Cl macroinitiators, was demonstrated. Well-defined PTMPM-*b*-PS diblock copolymers without PTMPM homopolymer contamination were synthesized. However, no reinitiation from PTMPM-Cl with molar masses higher than 25,000 g mol⁻¹ was observed.

Thirdly, mCPBA oxidation of the PTMPM block into PTMA was demonstrated. The ESR analysis indicated oxidation yields from 60 to 95 %.

Finally, the electrochemical behavior of PTMA-*b*-PS block copolymers was investigated. Cyclic voltammograms were recorded using two different set-ups. Cyclic voltammetry in a three electrodes system using an Ag/Ag⁺ non aqueous reference electrode demonstrated a redox potential at 0.46 V and an $I_{pa}/I_{pc} \simeq 1$, indicating a fully reversible redox process. Cyclic voltammetry of PTMA-*b*-PS using a Swagelock half-cell with a lithium anode showed an electrochemical activity at 3.6 V, corresponding to the values described in literature,^[25] and confirming the possibility to use such block copolymers as cathodic material in Li-ion batteries. Moreover, the presence of the PS block appeared not to interfere with the electrochemical process and would avoid the dissolution of PTMA in the battery electrolyte.

Experimental part

Materials

Triethylamine was distilled over KOH. Styrene (Aldrich, 99 %) was passed through activated basic alumina $(Al_2O_3, Acros)$ columns before use. Tosyl chloride (TsCl, Fluka, >99 %) was purified by recrystallization into hexane. 3-chloroperoxybenzoic acid (mCPBA, Aldrich, 77 % max) was washed with pH 7 buffer solution (Merck, di-sodium hydrogen phosphate/potassium dihydrogen phosphate). CuBr (Aldrich, 99.999 %), CuCl (Aldrich, 99,999 %), ethyl α -bromoisobutyrate (EBiB, Acros, 98 %), TMPM (TCI), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, Aldrich, 97 %), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98 %), anisole (Acros, 99 %), hexane (Sigma Aldrich), toluene (AnalaR NORMAPUR), dichloromethane (HPCL grade, Fisher Scientific), HCl 36% (Analytical reagent grade Fisher), sodium sulfate anhydrous (Na₂SO₄, VWR), sodium bicarbonate (NaHCO₃, VWR), neutral alumina (Al₂O₃, Acros), polyvinylidene fluoride (PVDF, MTI), N-methyl-2-pyrrolidone (NMP, Fisher Scientific), conductive acetylene black (MTI), electrolyte (1M LiTFS in ethylene carbonate:dimethyl carbonate:diethyl carbonate, 1:1:1 by volume, MTI), lithium foil (Alfa Aesar, 99.9%), acetonitrile (VWR, HyperSolv Chromanorm for HPLC), tetrahydrofuran (Aldrich, Normapur), silver nitrate (Belfolabo), tetrabutylammonium perchlorate (TBAClO₄; Fluka) and all the other chemicals were used as received.

Instrumentation

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired either on a 300 MHz Bruker Avance II or on a 500 MHz Bruker Avance II. Number average molar masses (\overline{M}_n), weight average molar masses (\overline{M}_w), and dispersity (\overline{D}) of the polymers were measured on an Agilent gel permeation chromatography (SEC) system equipped with an Agilent 1100/1200 pump (25 °C; eluant: chloroform/triethylamine/2isopropanol 94:4:2; flow rate: 1 mL/min), an Agilent differential refractometer, a Brookhaven BI- \overline{M}_w A Molecular Weight Analyzer, and two PSS SDV columns (Beads 10 μ m; porosity of column 1: 10,000 Å; porosity of column 2: 1000 Å). The calibration was performed using PS standards. UV-visible spectra were recorded on a Varian spectrophotometer (Cary, 50 Conc). Cyclic voltammetry was performed using an Arbin Instruments Battery Tester, BT-2043 (scan rate: 0.1 mV s⁻¹) or a CH Instruments potentiostat CHI 660B. Pt-disk working electrode (CHI102), Pt wire counter electrode (CHI115) and dry Ag/Ag⁺ nonaqueous reference electrode (CHI112) come from CH Instruments, inc. Swagelock cells come from MTI. Electron spin resonance (ESR) data (UCL) were acquired on a Bruker EMX spectrometer (Rheinstetten, Germany) equipped with a high sensitivity ER4119HS resonator and operated in X band at ~ 9.6 GHz. The parameters of acquisitions were as follows: microwave power 0.5 mW (26dB), gain 2.83104, amplitude modulation 0.03 mT at 100 KHz, center field 350.7 mT, sweep width 30 mT (1024 pts), conversion time 10.24 ms, time constant 20.48 ms. Three scans were acquired for each spectrum. The quantification was performed by double integration of the three-line spectrum of TEMPO as standard. Electron spin resonance (ESR) data (Jena) were acquired on an EMXmicro CW-EPR spectrometer (EMX micro EMM-6/1/9-VT control unit, ER 070 magnet, EMX premium ER04 X-band microwave bridge equipped with EMX standard resonator, EMX080 power unit) by Bruker, Germany. Powdered samples ($\sim 4 \text{ mg}$) were investigated at room temperature and data handling was done on the Bruker Xenon software package, version 1.1b86. For quantitative experiments the SpinCountT software module was used and the SpinCount calculated as the average of three measurements. The degree of oxidation is determined by the ratio between the spin/mg value obtained by ESR and the NO/mg value theoretically calculated for a polymer with a theoretical degree of oxidation of 100%, considering that one nitroxide group corresponds to one electron spin in ESR.

General procedure for the synthesis of PTMPM-Br by ATRP

A solution of EBiB (6.5 μ L, 0.044 mmol, 1 equiv.), TMPM (1190 mg, 5.280 mmol, 120 equiv.), dNbpy (18.0 mg, 0.044 mmol, 1 equiv.), and toluene (1.37 mL, 50 wt%) was degassed three times by freeze-pump-thaw cycling. The degassed solution was introduced into a Schlenk tube containing CuBr (3.2 mg, 0.022 mmol, 0.5 equiv.) and a magnetic bar. The mixture was degassed by two freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 80 °C for 45 min. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al₂O₃ (eluant: CH₂Cl₂). The solvent was removed under reduced pressure. The residue was precipitated twice in hexane, filtered and dried *in vacuo* at 30 °C overnight, affording a white solid (0.42 g, 76%). \overline{M}_n (SEC) = 11,850 g mol⁻¹; \overline{D} (SEC) = 1.16; ¹H NMR (500 MHz, CDCl₃, δ): 5.25-4.90 (a, broad, 1H; CH–O), 4.07 (b, multiplet, 2H; CH₂–O chain-end), 2.05-1.51 (c, broad, 15H; CH₃ + CH₃ backbone),

1.51-0.80 (d, broad, 6H; $CH_2 + CH_2$ backbone).



General procedure for the synthesis of PTMPM-Cl by ATRP

A solution of TsCl (11.6 mg, 0.061 mmol, 1 equiv.), TMPM (1640 mg, 7.273 mmol, 120 equiv.), dNbpy (49.4 mg, 0.121 mmol, 2 equiv.), and anisole (1.65 mL, 50 wt%) was degassed three times by freeze-pumpthaw cycling. The degassed solution was introduced into a Schlenk tube containing CuCl (6 mg, 0.061 mmol, 1 equiv.) and a magnetic bar. The mixture was degassed by two freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 80 °C for 5.08 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al_2O_3 (eluant: CH_2Cl_2). The solvent was removed under reduced pressure. The residue was precipitated twice in hexane, filtered and dried in vacuo at 30 °C overnight, affording a white solid (0.2 g, 49%). \overline{M}_n $(SEC) = 7,800 \text{ g mol}^{-1}; D (SEC) = 1.07; {}^{1}\text{H NMR} (500 \text{ MHz}, \text{CDCl}_{3},$ δ): 7.74 (a, multiplet, 2H; H_{ar} chain-end), 7.43 (b, multiplet, 2H; H_{ar} chain-end), 5.25-4.90 (c, broad, 1H; CH-O), 2.05-1.51 (d, broad, 15H; $CH_3 + CH_3$ backbone), 1.51-0.80 (e, broad, 6H; $CH_2 + CH_2$ backbone).



General procedure for the copolymerisation of PTMPMb-PS by ATRP

A solution of PTMPM-Cl ($M_n = 7,400 \text{ g mol}^{-1}$, D = 1.07; 291 mg, 0.039 mmol, 1 equiv.), styrene (3.61 mL, 31.515 mmol, 800 equiv.),

PMDETA (7.5 mg, 0.043 mmol, 1.1 equiv.), and anisole (3.30 mL, 50 wt%) was degassed three times by freeze-pump-thaw cycling. The degassed solution was introduced into a Schlenk tube containing CuCl (3.9 mg, 0.039 mmol, 1 equiv.) and a magnetic bar. The mixture was degassed by two freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 100 °C for 48 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al_2O_3 (eluant: CH_2Cl_2). The solvent was removed under reduced pressure. The residue was precipitated twice in hexane, filtered and dried in vacuo at 30 °C overnight, affording a white solid (1.160 g, 76%). \bar{M}_n (SEC) $= 29,700 \text{ g mol}^{-1}; D \text{ (SEC)} = 1.17; ^{1}\text{H NMR} \text{ (500 MHz, CDCl}_{3}, \delta):$ 7.74 (a, multiplet, 2H; H_{ar} chain-end), 7.43 (b, multiplet, 2H; H_{ar} chainend), 7.18-6.26 (c, broad, 5H; H_{ar} PS), 5.25-4.90 (d, broad, 1H; CH-O PTMPM), 2.33-1.51 (e, broad, 18H; CH_3 PTMPM + backbone (PS + PTMPM)), 1.51-0.80 (f, broad, 6H; $CH_2 + CH_2$ backbone).



General procedure for the oxydation of PTMPM-b-PS

PTMPM-*b*-PS ($M_n = 17,000 \text{ g mol}^{-1}$, $\bar{D} = 1.20$; 377.3 mg, 0.022 mmol, 1 equiv. of amine functions), CH₂Cl₂ (50.31 mL) and a magnetic bar were introduced into a 250 mL flask under argon.^[32] A solution of mCPBA (393.0 mg, 0.966 mmol, 1.5 equiv.) and CH₂Cl₂ (25.15 mL) was added dropwise at 0 °C during 1 h. The mixture turned to an orange color. The reaction mixture was then stirred for 1 h at 0. The mixture was washed twice with a sodium bicarbonate solution (10%), twice with HCl (0.1 N), and twice with water. The organic phase was dried with sodium sulfate, filtered and the solution was concentrated under reduced pressure. The orange product was precipitated un hexane, filtered and dried *in vacuo* at 30 °C overnight, affording an orange powder (0.283 g, 76%). \bar{M}_n (SEC) = 15,300 g mol⁻¹; \bar{D} (SEC) = 1.21; λ_{max} (ε) = 460 nm, yield = 99% (UV-vis absorption) and 81% (ESR).

Preparation of Ag/Ag^+ non-aqueous reference electrode

A non-aqueous Ag/Ag⁺ reference electrode with porous Teflon tip was filled with a solution composed of 0.01 M AgNO₃ and 0.1 M TBAClO₄ in acetonitrile.

Typical procedure for cyclic voltammetry in solution

The analyzed component (PTMA-*b*-PS or ferrocene) was dissolved into the electrolyte solution (0.1 M TBAClO₄ in acetonitrile) in order to obtain a 0.1 M solution. A three electrodes set-up with a Pt disk working electrode, a Pt wire counter electrode and the previously prepared Ag/Ag^+ reference electrode was used to record the voltammogram.

Typical procedure for preparation of PTMA-*b*-PS Halfcells

The cathode was prepared by mixing PTMA-*b*-PS (\overline{M}_n (GPC) = 15,300 g mol⁻¹; D (GPC) = 1.21; 30 mg) with PVDF binder (10 mg) in NMP (0.6 mL). After complete dissolution of the polymers, acetylene black (60 mg) was added to the solution and stirred for 3 h. The slurry was casted onto an aluminum current collector of a diameter of 17 mm. The electrodes were dried in a vacuum oven at 60 °C overnight. The electrochemical tests on PTMA-*b*-PS were conducted in a half-cell configuration with a Li foil as reference and counter electrode. The cells were assembled in an argon-filled glove box.

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CHAPTER 5

PTMA-*b*-PS micelles as nanostructured organic radical cathodes



Abstract

This chapter focuses on PTMA-b-PS block copolymer self-assembly in solution, i.e. battery electrolyte, to form micelles with an electrochemical active corona of PTMA and a core of PS. The resulting micelles are characterized by dynamic light scattering and atomic force microscopy. Next, the electrochemical performances of the micelles are investigated. Firstly, micelles deposited onto carbon nanotube buckypapers are analyzed. Then, the micelles are employed as catholyte in hybrid-flow batteries with a zinc anode. The self-assembly process and the electrochemical characterization onto carbon nanotube buckypapers have been published in Macromolecule Rapid Communications.^[1] The redox flow batteries with PTMA micelles were analyzed in the frame of a collaboration with Jan Winsberg and Tobias Janoschka from Ulrich S. Schubert's group at the Friedrich Schiller University in Jena and have been published in Polymer Chemistry.^[2]

5.1 Introduction

Self-assembly of block copolymers can be realized either in solid state, i.e. bulk or thin films, or in selective solvents to form micelles. This chapter focuses on the self-assembly of the previously synthesized PTMA-b-PS copolymers in battery electrolyte. In order to achieve the self-assembly process, one block of the diblock copolymer needs to be soluble into the employed solvent while the other block needs to be insoluble in the same solvent. Fortunately, the battery electrolyte composed of EC/DEC/DMC (1:1:1 in volume) with 1 M lithium trifluoromethanesulfonate (LiTFS) electrolyte salt fulfils these requirements. Indeed, the polystyrene block appears to be insoluble in this specific electrolyte whereas the PTMA is soluble, leading to micelles with a corona of PTMA and a core of PS. As previously mentioned, micelles based on block copolymers with stable nitroxide bearing moieties have been studied for medical imaging and drug delivery (See section 2.4.2).^[3–8] However, in all these previously studied systems the nitroxide bearing block was located into the micellar core. To the best of our knowledge this work is the first study on micelles with an electrochemical active corona for the formation or micellar organic radical cathodes. Two different kinds of batteries based on PTMA micelles are investigated in this chapter. Firstly, the electrochemical behavior of micelles deposited onto carbon nanotubes buckypapers via a filtration method is investigated. Secondly, micelles in solution are employed as hybrid-redox flow battery catholyte. Redox flow batteries present the advantage to have electro-active materials dissolved into the battery electrolyte solution. The cathode electrolyte solution, i.e. the catholyte, and the anode electrolyte solution, i.e. the analyte, are stored into two separated tanks and pumped through the electrochemical engine, allowing a fast replacement of the battery materials by simply emptying and refilling the tanks and allowing to easily manage power and capacity separately.^[9–13] The liquid electrodes are generally separated by expensive ion exchange membranes. e.g. Nafion^{TM, [14]} Thanks to the use of polymer materials, such membranes can be replaced by less expensive size exclusion ones like dialysis membranes. A hybrid-flow battery refers to a redox flow battery where at least one active species present one insoluble redox state. In this chapter PTMA micelles are employed as catholyte with a zinc based anode. $Zn^{2+}_{(aq)}$ is reduced to $Zn^0_{(s)}$ during the charge process forming a solid anode. Zinc RFBs are usually combined with halogen cathodes. However I_2 and Br_2 are toxic species and complexing agents are usually added in order to maintain their solubility and increase the safety.^[15] These drawbacks can be overcome by using organic catholyte in place of halogen one.

5.2 Self-assembly of PTMA-*b*-PS block copolymers in solution

The PTMA-b-PS diblock copolymers investigated in the present study were synthesized according to the procedure explained in Chapter 4.1 In order to study the self-assembly of the PTMA-b-PS diblock copolymers in a typical battery electrolyte, block copolymers with different compositions were synthesized, namely PTMA₈₂-b-PS₁₄₁ (57 wt% of PTMA), $\rm PTMA_{82}\mbox{-}b\mbox{-}PS_{59}$ (76 wt% of PTMA) and $\rm PTMA_{63}\mbox{-}b\mbox{-}PS_{35}$ (81 wt% of PTMA),² see Table 5.1 for further details. The aim of this project is to obtain micelles with a core of PS (which is insoluble in the investigated battery electrolyte) and a corona of PTMA (which is soluble in the electrolyte). This design is a prerequisite for a proper operation of the micellar cathodes in a Li-ion battery. Firstly, the amount of the PTMA component in the diblock copolymer should be maximized since it is the electrochemical active moiety affording the possibility to store energy. Furthermore, the PTMA component should be located in the micellar corona to stay in contact with the electrolyte and to allow the diffusion of counteranions (TFS⁻ in our case) required to compensate the oxoammonium cations generated by the electrochemical reaction. Finally, in the case of micelles adsorbed on a carbon nanotube buckypaper, the presence of the PS core is required to avoid migration of PTMA in the bulk electrolyte. In this perspective, spherical micelles with a small PS core and a large PTMA corona are suitable.

Those micelles were prepared by direct dissolution^[16,17] of the PTM- A_{82} -b- PS_{141} and PTMA₈₂-b- PS_{59} samples at 1 and 2 g L⁻¹ in the battery electrolyte composed of 1 M LiTFS into EC/DEC/DMC mixture (1:1:1 in volume). Solubility tests demonstrated that homo-PTMA is totally soluble into the battery electrolyte while homo-PS is insoluble (Figure 5.1). These simple tests give us a clue about the formation of micelles with a PS core and a PTMA corona.

¹The synthesis of block copolymers employed in this chapter were performed by Quentin Maguin in the frame of his master thesis.

 $^{^{2}}$ The numbers in subscript state the average degree of polymerization of the respective blocks.

Table 5.1: PTMA-*b*-PS block copolymers employed for the fabrication of micelles.

Entry	DP^{a}	$ar{M_n} \ ({ m NMR}) \ ({ m g.mol}^{-1})$	D^{b}	PTMA ratio (wt%)	Oxidation yield ^c (%)
$\begin{array}{c}1\\2\\3\end{array}$	$\begin{array}{c} {\rm PTMA}_{82}\text{-}b\text{-}{\rm PS}_{141} \\ {\rm PTMA}_{82}\text{-}b\text{-}{\rm PS}_{59} \\ {\rm PTMA}_{63}\text{-}b\text{-}{\rm PS}_{35} \end{array}$	34,500 26,000 18,900	$1.16 \\ 1.18 \\ 1.17$	57 76 81	$64 \\ 58 \\ 83$

^a Determined by ¹H NMR (solvent: CDCl₃).

^b Determined by SEC (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

^c Determined by ESR.



Figure 5.1: Solubility of homo-PTMA and homo-PS in battery electrolyte (EC/DEC/DMC; 1:1:1 in volume with 1 M LiTFS): (a) homo-PTMA (4 mg mL⁻¹), (b) homo-PS (4 mg mL⁻¹). PTMA is completely soluble giving to the solution its characteristic orange color whereas PS is insoluble and form an aggregate on top of the vial.

5.2.1 Dynamic light scattering

DLS measurements revealed the formation of micellar structures for the investigated copolymers. The CONTIN size distribution histogram for the PTMA₈₂-*b*-PS₁₄₁ sample shows one population of micelles with an average apparent hydrodynamic radius ($R_{h,app}$) of 23 nm and a narrow polydispersity index (PDI) of 0.0539 as calculated by the Cumulant method. The CONTIN size distribution histogram of the PTMA₈₂-*b*-PS₅₉ sample (Figure 5.2a) shows two distinct populations. The first population could correspond to micelles with a $R_{h,app}$ of 17 nm, whereas the second population at 270 nm could correspond to aggregated micelles in the electrolyte. Results obtained for concentrations of 1 and 2 g.L⁻¹ were essentially the same for both investigated copolymers. In order to get more information about the morphology of the micelles, multi-angle analysis (30°, 60°, 90°, 120°and 150°) was performed for the population ascribed to micelles for both samples. Indeed, the first cumulant frequency Γ and the associated scattering vector q^2 allow the calculation of the diffusion coefficient D_s from the slope of the evolution of Γ versus q^2 for different angles (Equation 5.1):

$$\Gamma = D_s * q^2$$
 with $q = \frac{4\pi n}{\lambda} \sin(\frac{\theta}{2})$ (5.1)

Where Γ , q and λ are respectively the first Cumulant frequency, the scattering vector and the wavelength of light.

The plots of q^2 versus Γ (Figure 5.2b for the PTMA₈₂-*b*-PS₅₉ sample) provide a clear linear correlation passing through the origin, indicating that only translational diffusion occurs for both investigated samples.

Knowing the diffusion coefficient (D_s) , the hydrodynamic radius (R_h) can be determined from the Stokes-Einstein relationship:

$$R_h = \frac{k_B T}{6\pi\eta D_s} \tag{5.2}$$

Where T is the absolute temperature, η is the solvent viscosity, k_B is the Boltzmann's constant.

A R_h of 18 nm is obtained for the PTMA₈₂-*b*-PS₅₉ sample and a R_h of 23 nm for the PTMA₈₂-*b*-PS₁₄₁. Those values are in perfect agreement with the $R_{h,app} = 17$ nm and of 23 nm measured at 90 °, respectively. Those results confirm the presence of well-defined spherical micelles for both samples.

5.2.2 Atomic force microscopy

Atomic force microscopy (AFM) provides further evidence for the formation of spherical micelles. Well-defined micelles observed together with some aggregated micelles are obtained for the $PTMA_{82}$ -*b*- PS_{141} sample (Figure 5.3). Those micelles correspond to dried micelles and are characterized by an average height of 30 nm.


Figure 5.2: DLS measurements of micelles prepared from PTMA-*b*-PS block copolymers (2g L⁻¹) in battery electrolyte (1 M LiTFS in EC/DEC/DMC (1:1:1 in volume) mixture). (a) CONTIN size distribution histogram of PTMA₈₂-*b*-PS₁₄₁ (dashed curve) and PTMA₈₂-*b*-PS₅₉ (solid curve), (b) multi-angle analysis (q^2 in function of Γ plot) for PTMA₈₂-*b*-PS₅₉.

Spherical and well-dispersed micelles are obtained for the $PTMA_{82}$ b-PS₅₉ sample (Figure 5.4). These micelles present an average height of 27 nm. Since these micelles are dried and deposed on an AFM substrate, they tend to flatten making difficult a comparison of the two polymer sizes.



Figure 5.3: AFM images $(1.0 \times 1.0 \ \mu m^2)$ of the micelles prepared from PTMA₈₂-*b*-PS₁₄₁ spin-coated onto a silicon wafer ((a) height contrast; (b) phase contrast).



Figure 5.4: AFM images $(1.0 \times 1.0 \ \mu m^2)$ of the micelles prepared from PTMA₈₂-*b*-PS₅₉ spin-coated onto a silicon wafer ((a) height contrast; (b) phase contrast).

5.3 Electrochemical characterizations of micellar cathodes

5.3.1 Buckypaper electrodes

In order to build a Li-ion battery and to perform electrochemical tests, the PTMA-*b*-PS micelles were trapped in a carbon nanotube buckypaper via a filtration approach. Carbon nanotubes in solution were filtered onto a Millipore filtration device leading to a nanotube buckypaper (Figure 5.5). Next, the micellar solution was filtered through the buckypaper, trapping micelles inside the nanotube network. The network of carbon nanotubes should allow not only to minimize the migration of the PTMA-*b*-PS micelles into the bulk electrolyte during battery operation but also to afford a dense conductive network for efficient charge transfer towards the battery current collector. SEM analysis has confirmed the presence of PTMA₈₂-*b*-PS₅₉ micelles onto the entangled network of carbon nanotubes (Figure 5.6). According to Figure 5.6, the PTMA-*b*-PS micelles are rather observed as aggregates on top of the carbon nanotubes buckypaper than inserted in the nanotube network. Therefore, the micelles could be released in the battery electrolyte during battery operation and this could cause a decrease in capacity over cycles (see further results discussed in Figure 5.8)



Figure 5.5: SEM picture of the initial carbon nanotubes buckypaper.

The accordingly obtained micellar cathodes were analyzed by cyclic voltamperometry and galvanostatic cycling in a half-cell configuration. Galvanostatic cycling was performed at $1C^3$ from 3 V to 4 V with a current range of 24 mA g⁻¹. These analyses were performed on the PTMA₈₂-*b*-PS₅₉ micelles since they present the longest block of PTMA, i.e. electrochemical active material. The cyclic voltammogram (Figure 5.7a) reveals a distinct and reversible redox peak centered at 3.6 V (vs Li⁺/Li), corresponding to the reversible oxidation of the free nitroxide radicals into oxoammonium cations. Charge/discharge voltage profiles (Figure 5.7b) reveal the presence of a voltage plateau around 3.7 V (vs. Li⁺/Li) in both charge and discharge. The observed voltage plateau is consistent with the redox behavior of PTMA (3.6 V vs. Li⁺/Li) confirm-

³1C meaning a full charge in one hour



Figure 5.6: SEM picture of $PTMA_{82}$ -*b*- PS_{59} micelles onto the carbon nanotubes buckypaper.

ing that the charge process relies on the oxidation of PTMA to oxoammonium salt and that the discharge process consists in the reverse reaction. Figure 5.7c shows the cycling performances of the micellar cathodes.

The gravimetric capacity of our cathodes was calculated to be 24 mAh g^{-1} (see experimental part for detailed calculations). Although the capacity of the system could be increased by increasing the oxidation level of the investigated micelles, the oxidation level has no influence over the micellisation process since the PTMPM precursor appears to be soluble too in battery electrolyte. With an experimentally measured capacity of 15 mAh g^{-1} , only 65% of the theoretical capacity is retained. This could be explained by a lack of electrical conductivity between the micelles and the carbon nanotube buckypaper. Moreover a loss of capacity is monitored during the process. This loss is attributed to micelles detaching from the carbon nanotube buckypaper and moving towards the bulk electrolyte. Indeed, after the charge process micelles present a positively charged corona. Furthermore, despite their stability in solution, some of the micelles have modified their initial morphology after battery operation and are observed as a polymer film in which the carbon nanotubes are embedded (Figure 5.8).



Figure 5.7: Electrochemical characterization of buckypaper micellar cathodes prepared from $PTMA_{82}$ -*b*- PS_{59} (Current: 0.1 mV s⁻¹; 1M LiTFS in EC:DEC:DMC, 1:1:1 in volume): (a) cyclic voltammogram (scan rate = 0.1 V s⁻¹), (b) typical charge/discharge voltage profiles and (c) capacity retention plot.



Figure 5.8: SEM picture of $PTMA_{82}$ -*b*- PS_{59} micelles onto the carbon nanotubes buckypaper after electrochemical characterizations.

5.3.2 Micellar cathode redox-flow batteries ⁴

In contrast to classic batteries where the electrode active materials are in the solid state, redox-flow batteries (RFBs) present active materials dissolved into the electrolyte. The electrolytes, named catholyte and anolyte, are a mixture comprising the solvent, a supporting electrolyte and a cathode or anode active material. During battery operation, the electrolyte is constantly pumped through the system, circulating from the half-cells and the storage tanks. Our micelles were analyzed in an hybrid-flow battery system. The catholyte was composed of the PTMA micelles whereas the anolyte was composed of zinc. Zinc perchlorate hexahydrate was used as supporting electrolyte and anode active materials. During the charge process, $Zn_{(aq)}^{2+}$ was reduced to $Zn_{(s)}^{0}$, forming a solid anode. The half cells were separated by a size exclusion membrane.

The micellar catholyte was composed of $PTMA_{63}$ - $b-PS_{35}$ at a concentration of 13 mg mL⁻¹ (Table 5.1, Entry 3) (the cathode active material) and 0.5 M Zn(ClO₄)2.(H₂O)6 (the supporting electrolyte) into EC/DEC/DMC (1:1:1 in volume). The anolyte was composed of 0.5 M Zn(ClO₄)2.(H₂O)6 (the anode active material and supporting electrolyte) into EC/DEC/DMC (1:1:1 in volume). The micellar concentration of 13 mg mL⁻¹ corresponds to the maximum of PTMA-b-PS micelles

⁴These results were obtained in collaboration with Jan Winsberg and Tobias Janoschka from Friedrich Schiller University Jena (Germany).



Figure 5.9: Redox-flow electrochemical cell. (Top) Schematic representation of redox-flow electrochemical cell. One half cell comprises: (a) a frame, (b) a PTFE block with hose connections and rubber seal, (c) a graphite/zinc current collector, (d) a rubber sealing, (e) a PTFE flow frame, (f) a rubber sealing and (g) a surface enhancing graphite felt/carbon paper, separated by (h) a size exclusion membrane. (Bottom) Hybrid flow battery set-up comprising: the electrochemical cell, two reservoir tanks (catholyte & anolyte) and a peristaltic pump.

that can be formed in carbonated battery electrolytes. The carbonate mixture was selected due to its good ion conductivity and the possibility

to form micelles. A maximum capacity of 1.17 Ah L^{-1} , corresponding to a theoretical energy density⁵ of 1.5 Wh L^{-1} was achieved and can't be increased due to the limit of solubility of PTMA₆₃-*b*-PS₃₅. The system was investigated using a graphite electrode with graphite felt as current collector, a dialysis membrane with a molecular weight cut-off (MWCO) of 1,000 g mol⁻¹ derived from regenerated cellulose as half-cells separator and a zinc foil as anode.

Charging/discharging experiments were performed at 1 mA cm⁻², using 8 mL electrolyte per half-cell and a flow rate of 20 mL min⁻¹ (Figure 5.10a). A reversible flat plateau at 1.5 V is observed during the charge process. However a potential drop of about 0.3 V appears during the discharge and could be attributed to the internal cell resistance. A long-term stability test was performed by continuous cycling of a static non-pumped battery with a steady current of 1.5 mA cm⁻², revealing a very slow capacity decay. Indeed, 94 % of the initial discharge capacity and up to 99 % of the coulombic efficiency remain after 1000 cycles (Figure 5.10b).

Battery performances at various current densities were investigated, with a capacity of 1.17 Ah L⁻¹ at a flow rate of 20 mL min⁻¹ (Figure 5.10c). The charging/discharging capacity and the potentials of the corresponding plateau were measured at different current densities. A material activity of 93 % for current densities of 0.2 mA cm⁻² was reached. At 1 mA cm⁻² current density the discharge capacity drops to a plateau around 6.11 mAh (65 % of activity). Charging was possible up to 5 mA cm⁻². The coulomb efficiency stayed above 85% with a peak efficiency of 98% at current densities from 1 to 4 mA cm⁻². A linear decline of the voltage efficiency was observed with increasing current densities. The restricted ion conductivity in the applied electrolytes and the consequential increasing potential gap between charging- and discharging plateaus could explain such behaviors.

Concerning the stability of micelles during the electrochemical process, it appeared that micelles are not disrupted during the process. Prior charging, a cloudy catholyte was observed (Figure 5.11) due to a Tyndall effect,^[18] indicating some agglomeration of the uncharged micelles. Next the micelles were charged by chronoamperometry at 1.9 V (Figure 5.12), revealing a clear catholyte solution. The disappearance of aggregates in favor of isolated micelles is most likely due to the positively charged

 $^{^5 \}mathrm{Energy}$ density = capacity times OCV at 50 % SOC (1.3 V for carbonated electrolytes).



Figure 5.10: Electrochemical characterization of PTMA micelles/zinc hybrid-redox flow battery. (a) charging/discharging curves (8 mL electrolyte per half-cell, current = 1 mA cm⁻² and flow rate at 20 mL min⁻¹), (b) static long term stability test (non-pumped hybrid-flow cell, 1.5 mA cm⁻², room temperature), (c) various current density test (8 mL electrolyte per half-cell, flow rate at 20 mL min⁻¹).

corona.



Figure 5.11: Micellar catholyte: (a) prior charging, (b) after charging.



Figure 5.12: Micellar catholyte charging by chronoamperometry at a potential of 1.9 V. Plot of the residual current versus time.

The charged micelles were further characterized by DLS, revealing one population of micelles with an average apparent hydrodynamic radius ($\langle R_h \rangle_{n,app}$) of 40 nm. Moreover, two populations were revealed by intensity weighted distribution ($\langle R_h \rangle_{z,app}$). The main population with a radius of 55 nm is attributed to micelles in solution whereas the second population presenting a radius of 310 nm is attributed to aggregated micelles (Figure 5.13).

Despite good electrochemical performances, the limited solubility of



Figure 5.13: Dynamic light scattering of charged micelles into redox flow battery catholyte: Apparent hydrodynamic radius $\langle R_h \rangle_{n,app}$ (solid curve) and intensity weighted distribution $\langle R_h \rangle_{z,app}$ (dashed curve).

PTMA-*b*-PS micelles in carbonate mixtures restrained the capacity. Indeed, energy densities up to 8.1 Wh L^{-1} were obtained using PTMA-*co*-PEGMA statistical copolymers. Given that organic redox-flow batteries based on small organic molecules rather than polymers can achieve energy densities between 0.3 and 25 Wh L^{-1} , our micellar RFB is in the lower middle of the organic redox-flow batteries in term of energy density.^[19]

5.4 Conclusion

We have demonstrated the possibility to create nanostructured organic radical cathodes by self-assembling diblock copolymers containing an electrochemical active block into micelles. DLS measurements and AFM microscopy revealed the formation of well-defined spherical micelles in the investigated battery electrolyte. Those micelles have been further deposed onto a carbon nanotubes buckypaper, creating a solid organic radical cathode providing at the same time good access to the electrolyte through the solvated PTMA coronal chains for ionic conduction and electrical conductivity for current collectors through the network of carbon nanotubes. The electrochemical behavior of these micellar cathodes was tested, evidencing the characteristic electrochemical activity of PTMA and acceptable electrochemical performances for the accordingly constructed Li-ion battery in a half-cell configuration. Nevertheless, the initial micelles seem to disappear after battery operation at the expense of a polymer film in which the carbon nanotubes are partially embedded. The aromatic rings of the PS blocks could act as anchors on the carbon nanotubes and limit the diffusion of the free PTMA-b-PS chains towards the electrolyte. Apart from being immobilized in a rigid conductive matrix, our micellar organic radical cathodes could also be used for hybrid-flow batteries. Hybrid-flow batteries with zinc anode and a micellar cathode were prepared. Anodic zinc and cathodic micelles dispersed in the electrolyte and stored inside two distinct tanks are pumped through the engine to generate electrical energy. Despite a limited solubility of micelles in battery electrolytes, limiting the maximum capacity of the system, good electrochemical performances were obtained using PTMA-b-PS micelles. In static non pumped experiments, 94 % of discharge capacity and 99 % of coulomb efficiency were obtained after 1000 cycles. In pumped experiments at various current densities, best results were obtained for current density of 0.2 mA cm^{-2} and charging was possible up to 5 mA $\rm cm^{-2}$. Therefore electrochemical active micelles are promising tools as catholyte materials for redox-flow batteries provided that the amount of PS content is minimized in order to obtain a maximum gravimetric capacity and the employed electrolyte is optimized in order to increase the micellar concentration.

Experimental part

Materials

Polyvinylidene fluoride filter (PVDF, Millipore (Durapore Membrane, PVDF, hydrophobic, 0.22 μm , 47 mm, white, plain)), lithium foil (Alfa Aesar, 99.9 %, stored in Ar filled glovebox), carbon nanotubes (NC 7000, Nanocyl), diethyl carbonate (DEC, Sigma Aldrich, anhydrous, 99 %), dimethyl carbonate (DMC, Sigma Aldrich, anhydrous, 99 %), ethylene carbonate (EC, Sigma Aldrich, anhydrous, > 99 %), lithium trifluoromethanesulfonate (LiTFS, Sigma Aldrich, anhydrous, 99,995 % trace metal basis) and all the other chemicals were used as received. Zinc foil $(99.98 \%, \text{thickness } 250 \ \mu\text{m}$ Alfa Aesar) was used to build zinc electrodes. Dialysis membrane derived from regenerated cellulose with a MWCO of 1,000 Da (Spectra/Por[®] 6, Spectrum Laboratories, USA) received as pre-wetted dialysis tubing was cut, rinsed with water/propylene carbonate and stored in the electrolyte solution for at least 24 hours. Graphite felt was cut in appropriate pieces $(2.25 \times 2.25 \times 0.4 \text{ cm}, \text{GFA6}, \text{SGL}, \text{Ger-}$ many). The electrolyte (1M LiTFS into EC/DEC/DMC, 1:1:1 in volume) has been prepared and stored into an argon-filled glovebox.

Instrumentation

Dynamic light scattering (DLS) measurements were performed on a Malvern CGS-3 apparatus equipped with a He–Ne laser with a wavelength of emission at 632.8 nm. The temperature was controlled at 25 °C (viscosity of the electrolyte mixture $\eta = 1.92$ mPas, refractive index n = 1.4004). The results were analyzed via the Cumulants and CONTIN methods. Determination of the refractive index was conducted on a Optilab rEX at 25 °C (Wyatt Technology, USA). Atomic force microscopy (AFM) was performed on a Digital Instruments Nanoscope V scanning force microscope in tapping mode, using NCL cantilevers (Si, 48 N m⁻¹, 330 kHz, Nanosensors). Scanning electron microscopy (SEM) has been performed on a JEOL JSM 7500F. Cyclic voltammetry was performed using an Arbin Instruments Battery Tester, BT-2043 (scan rate: 0.1 mV s⁻¹). Charge/discharge analysis was performed using an Arbin Instrument Battery Tester, BT-2043 (current range of 23 mAh g⁻¹ (1 C), from 3 to 4 V).

Gravimetric capacity determination of micellar cathodes

Gravimetric capacity determination of micellar cathodes = Gravimetric capacity determination of PTMA * wt% of polymer * wt% of PTMA block * oxidation rate =

 $111 * 0.47 * 0.76 * 0.6 = 24 \ mAhg^{-1}$

Where the theoretical capacity of PTMA is 111 mAh g^{-1} , wt% of polymer is the weight fraction of polymer inside the cathode made of PTMA-*b*-PS and carbon nanotubes, wt% of PTMA is the weight fraction of PTMA inside the block copolymer and oxidation rate is the amount of PTMPM oxidized into PTMA.

Typical procedure for the formation of micelles in battery electrolyte

Micelles have been prepared by direct dissolution of the PTMA-b-PS copolymers in the battery electrolyte (concentration of 1 or 2 g L⁻¹) followed by ultrasonic bath treatment during 30 min. The formed micelles have been analyzed by DLS and AFM.

Typical procedure for the deposition of micellar cathodes on carbon nanotubes buckypaper

Carbon nanotubes (10 mg) were dispersed into butanol (250 mL) using an ultrasonic bath for 2h. The solution was filtered onto a PVDF filter with a Millipore filtration hardware leading to the formation of a carbon nanotubes buckypaper. A solution of PTMA-*b*-PS (40 mg; M_n (SEC) = 25300 g mol⁻¹, PDI = 1.18) into the electrolyte (1M LiTFS into EC/DEC/DMC, 1:1:1 in volume; 10 mL) was ultrasonicated during 30 min and filtered onto the previously obtained buckypaper. The accordingly obtained composite cathode consisting of PTMA-*b*-PS micelles embedded in the carbon nanotubes was detached from the PVDF filter and dried overnight in vacuo at 30 °C.

Preparation of PTMA-b-PS half-cells

Electrochemical tests on composite cathodes consisting of PTMA-*b*-PS micelles embedded in carbon nanotubes buckypaper were conducted in a half-cell configuration with a lithium foil as reference and counter electrode. The cells were assembled in an argon-filled glove box.

\mathbf{RFB}

The electrochemical cell was designed and constructed in a flat cell type with a membrane active area of 5 cm² (JenaBatteries GmbH, Germany). Zinc electrodes were cut out of zinc foil (50×65 mm, 5.7 g) and brushed with sandpaper directly before cell assembly. Charging-/discharging tests were conducted on a VMP3 potentiostat/galvanostat (Biologic, France).

For static, non-pumped long-term charging/discharging experiments, both half cells were filled with 3 mL electrolyte solution using a syringe. To study the influence of the current density on the electrical performance of the battery, dynamic measurements were performed, whereat the electrolyte was circulated between the electrochemical cell and the storage tanks with a peristaltic pump (Hei-FLOW Value 01 Multi, Heidolph, Germany). Typically, 8 mL of electrolyte was used with a flow rate of 20 mL min⁻¹. All measurements were carried out at 25 °C under normal atmosphere. The batteries were charged/discharged with constant current and the resulting potential was measured over time. Coulombic efficiencies were calculated by the quotient of discharging current and charging current of the same cycle, voltage efficiencies by the quotient of mean potential of discharging- and charging plateau, energy efficiency by the product of voltage efficiency and coulombic efficiency.

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chapter 6

PTMA-*b*-PS thin films as nanostructured organic radical cathodes



Abstract

This chapter describes the formation of nanostructured thin film organic radical cathodes. First, the self-assembly of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate)-block-polystyrene (PTMA-b-P-S) diblock copolymers in thin films is detailed. In order to improve the nanomorphology obtained via the immiscibility of PTMA and PS domains, the effect of thermal and solvent annealing is investigated. Depending on the processing conditions and the polymer employed, different morphologies such as cylindrical or lamellar are observed. The electrochemical properties of the nanostructured films are further investigated to assess the redox activity of the PTMA domains. Cyclic voltammetry of PTMA-b-PS diblock copolymers, in thin film supported configuration, confirms the reversible redox behavior of the nitroxide radical. Galvanostatic cycling of the thin film nanostructured cathodes reveals good capacity retention with fast charge/discharge response resulting from efficient charge and ion transfer as well as structural integrity. Such nanostructured organic radical cathodes provide opportunities for the fabrication of a new generation of nanostructured organic radical batteries.

The self-assembly study and the electrochemical characterization of PTMA-*b*-PS have been published in Journal of Materials Chemistry A.^[1]

6.1 Introduction

After studying the self-assembly of PTMA-b-PS diblock copolymers into micelles in the previous chapter, this chapter focuses on the self-assembly in thin films.

As previously mentioned in Chapter 2 Section 2.4.3, only a few works have studied the self-assembly of block copolymers with a block containing nitroxide.^[2-4] This work goes further than the aforementioned studies since the self-assembly process and the different morphologies accessible are studied more in-depth. Moreover, electrochemical characterizations are performed on the self-assembled thin films, leading to the first report of nanostructured thin films as organic radical cathode.

Our objective is to obtain self-assembled thin films with cylinders of PTMA embedded in a PS matrix. Indeed, due to the solubility of PTMA into Li-ion battery electrolytes, a matrix of insoluble PS is suitable. Moreover, the PS matrix will add a structural integrity to the cathode thin film. At the same time, continuity between the PTMA domains and the current collector is a prerequisite. According to these criteria, cylindrical domains perpendicular to the current collector are preferred to spherical ones. It is generally admitted for block copolymer self-assembly processes in thin films that the cylindrical morphology is obtained upon using a block copolymer with a volume fraction (f_v) of the minor block comprised between 20 and 30%.^[5,6] Due to the undetermined density of PTMA, f_v has been approximated to the mass ratio. According to this, the mass ratio of the PTMA block in the studied PTMA-b-PS block copolymers has been varied between 18 to 45 wt%.

Two different annealing processes are studied, i.e. thermal annealing or solvent annealing, in order to ameliorate the phase separation. Once the good annealing process determined, the effect of the annealing time, the polymer size and the PTMA ratio are studied. Then the electrochemical properties of the thin films are investigated via a cyclic voltammogram and a charge/discharge analysis.

6.2 PTMA-*b*-PS thin film self-assembly

6.2.1 Spin coating

Thin films of PTMA-b-PS were prepared by spin-coating a solution of polymer onto an ultra flat surface such as a silicon wafer or an indium

tin oxide (ITO) substrate. Spin-coating consists of deposing a drop of polymer in solution onto the substrate. The substrate is then spun at high velocity, generating a centrifugal force that spreads the solution onto the surface from the centre to the edge. At the same time, the solvent evaporates, leaving a polymer thin film onto the surface (Figure 6.1). The thickness of the thin film depends on several parameters such as the rotation speed, the solvent employed and the polymer concentration. Thin films onto ITO substrates with a thickness comprised between 40 nm to 220 nm were prepared using different polymer concentrations in THF and a spin rate of 2000 rpm. As illustrated in Figure 6.2 the films thickness increases linearly with the polymer concentration.



Figure 6.1: Schematic representation of the spin-coating process.^[7]



Figure 6.2: Evolution of the thickness of the PTMA-*b*-PS thin films in function of the polymer concentration. Thin-films were spin-coated on ITO substrate at 2000 rpm using different polymer concentrations in THF.

6.2.2 Thin film self-assembly study

Thin films, with a thickness of approximately 80 nm, were prepared by spin-coating PTMA-*b*-PS solutions (10 mg mL⁻¹) onto 1 cm² silicon substrates. Phase separation is not always observed in the thin film after spin coating (Figure 6.3.a). Indeed, annealing procedures are often required in order to let the polymer chains to reorganize and reach a configuration closer to the thermodynamic equilibrium, increasing the phase separation.^[10-13] The annealing thus allows for getting thin films showing better defined nanodomains in terms of size and shape, regularly distributed in the thin films with well-developed short and long range ordering. Furthermore, a careful control of the annealing conditions can allow the control of the orientation of the nanodomains in the thin films.^[14-16] Two distinct annealing methods are mostly employed to reach these goals. The first one, thermal annealing, consists in increasing the temperature of the thin films in order to overcome the glass transition (T_q) of the polymer blocks and hence to increase their mobility. However, the temperature needs to be kept below the ODT temperature, otherwise the mixing would be favored and a phase separation would not be observed. The second one, solvent annealing, consists of exposing the thin films to vapors of good solvents for the polymer blocks in order to swell them and allow mobility of polymer chains. Table 6.1 summarizes the characteristics of the polymers employed for the self-assembly study.

Entry	DP^{a}	\bar{M}_n (g mol ⁻¹)	D^{b}	PTMA ratio (wt%)	Oxidation yield ^c (%)
		(8 1101)		((70)
1	$PTMA_{32}-b-PS_{336}$	42,900	1.17	18	50
2	$PTMA_{42}$ - b - PS_{323}	$43,\!900$	1.20	23	75
3	$\mathrm{PTMA}_{56}\text{-}b\text{-}\mathrm{PS}_{362}$	$51,\!300$	1.25	27	80
4	$PTMA_{79}$ - b - PS_{502}	71,300	1.31	27	95
4	$PTMA_{42}$ - b - PS_{208}	$32,\!000$	1.15	32	80
5	$PTMA_{42}$ - b - PS_{120}	$22,\!000$	1.19	45	61

Table 6.1: Summary of PTMA-b-PS characteristic features

^a Subscript numbers stand for the degree of polymerization.

^b Determined by SEC (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

^c Determined by ESR.

Thermal annealing

PTMA presents a high glass transition temperature, at ca. 140 °C, and its degradation occurs at around 210 °C making thermal annealing

difficult for this polymer.^[2,17–19] Indeed, thermal annealing of PTMAb-PS at 200 °C for 24 h appears to be unsuccessful to improve phase separation (Figure 6.3b). In order to avoid degradation of PTMA during the annealing process rapid thermal annealing (RTA) was investigated. RTA presents the advantage to be much faster than classical thermal annealing and has led to good results to increase ordering in thin films prepared from PS-*b*-poly(methylmethacrylate) diblock copolymers.^[20] Unfortunately, as for classic thermal annealing, RTA did not succeeded to improve phase separation in PTMA-*b*-PS thin films (Figure 6.3c).

Solvent vapor annealing

Solvent vapor annealing consists in swelling the polymer films under solvent vapors to increase the mobility of the polymer chains, allowing them to reach a more stable thermodynamic equilibrium and therefore increasing the phase separation. Figure 6.4 illustrates the experimental set-up used to perform solvent vapor annealing. The set-up consists in placing the samples onto a glass slide under a glass case with beakers containing the solvents. A weight onto the glass case keeps the system closed, allowing the solvent vapors to fill the system and to swell the polymer films. All beakers independently to the solvent employed were always filled with 5 mL of solvent, ensuring enough solvent during the whole annealing time.

In a first step, different solvent vapors were tested. A wide variety of solvents from polar solvents such as DMF, water, MeOH, CH₃CN, CH_2Cl_2 and DEC to apolar solvents like benzene, hexane, $CHCl_3$ and acetone were empirically screened either alone or with another one in a different beaker. It appeared that the presence of two different solvents, each of them being placed in a distinct beaker, is more efficient than the use of one solvent alone. Best phase separation was obtained for the annealing realized in presence of both dimethylformamide (DMF) and diethylcarbonate (DEC) (Figure 6.5c). Indeed, DMF selectively swells the PS block while DEC is a limited solvent of PS and a good solvent of the PTMA block. Therefore, mobility is imparted to both PS and PTMA chains during the annealing process. Under such conditions, circular domains with an average diameter of 19 nm are visualized by AFM on top of the thin films. These domains could either correspond to spheres or to the apex of cylinders perpendicular to the film surface. However, due to the weight ratio of PTMA (23 wt%) in the starting block copolymer, they most likely correspond to perpendicularly oriented cylin-



Figure 6.3: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA₇₉-*b*-PS₅₀₂ thin films onto silicon wafer with 23 % of PTMA. (a) Without annealing, (b) thermal annealing at 190 °C during 6h, (c) rapid thermal annealing at 220 °C during 60 s. No major morphology change (phase separation) is observed after thermal annealing.

ders. Such configuration is commonly observed in solvent annealed thin films with a cylindrical morphology and results from an alignment of the nanodomains with the solvent front as it evaporates at the end of the annealing process.^[12-14,21] During the screening of solvents, annealing using benzene-H₂O appeared to also permit a good phase separation. We decided to focus onto DMF-DEC since it was giving better results. Cylindrical morphology in thin films can take two different orientations: parallel to the surface or perpendicular to the surface. The orientation



Figure 6.4: Schematic representation of the solvent annealing set-up.

is usually driven by the interfacial interactions between the polymer film and its surrounding, e.g. the film/substrate interface and the film/air (or solvent vapors) interface. The observed perpendicular orientation for annealing with DMF/DEC indicates that both blocks present the same interfacial interactions.^[22] On the other side, solvent annealing with DEC/H₂O shows a cylindrical morphology with cylinders parallel to the surface (Figure 6.5b). Since the film/substrate interface has not changed, the orientation shift can be attributed to the film/solvent vapor interface. Indeed, the PS selective solvent (DMF) has been changed for a non solvent (H₂O), changing orientation of the domains.

The annealing time is also recognized as a key factor.^[16] Indeed, time is required to enable a good swelling of the polymer film, permitting PTMA and PS chains to move and rearrange.^[16] As shown in Figure 6.6 an increase in annealing time results into an increase of the phase separation extent with at least 6 h of annealing needed to reach the optimum structuration.

As expected, the weight ratio of PTMA in the copolymer is also an important parameter that allows tuning the morphology in the thin film. In this respect, different morphologies, from spherical to lamellar, were observed, depending on the weight ratio of PTMA. Higher PTMA weight ratio induced lamellar morphology, as illustrated in Figure 6.7, in which a fingerprint texture typical of a lamellar morphology is observed. Selfassembled morphologies are known to depend on two factors: the volume fraction (f_v) , which has been discussed via the weight ratio structure dependence, and the Flory-Huggins parameter (χN) . In the present



Figure 6.5: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA₄₂-*b*-PS₃₂₃ onto silicon wafers after different solvent annealing conditions during 6 h. (a) Thin film after spin coating without solvent annealing, (b) thin film after annealing with DEC and H₂O, (c) thin film after annealing with DMF and DEC.

study, the varying degree of oxidation, from 50 to 95 % (Table 6.1), is thought to influence the phase separation process and has not been taken into account. Another parameter is N the total degree of polymerization which also varies from one composition to another and has an influence over the phase separation process.

The characteristic domain size is directly related to the total molar mass of the block copolymer. As shown in Figure 6.8, the domains grow larger, the longer the copolymer is at a constant weight ratio. The estimated average size of the domains shifts from 20.9 nm for $\bar{M}_n = 51,300$ to 29.7 nm for $\bar{M}_n = 71,300$ g mol⁻¹, corresponding to an increase of 42 % in domain size.

6.2.3 Do the cylindrical nanodomains crossed the whole polymer film thickness?

In order to determine if the nanodomains of PTMA crossed the whole polymer film thickness, the thin film was crosslinked, detached from the surface and flipped, allowing the observation of the reverse side of the polymer thin film by AFM (Figure 6.9). A phase separation is revealed on the AFM picture of the reverse side of the polymer film, indicating that the phase separation occurs into the whole film thickness. Moreover the phase separation patterns and the domain sizes are similar for the front side and the reverse side, indicating a homogeneous phase separation through the entire film and supporting the hypothesis of cylinders of PTMA spanning over the entire polymer thin films. Indeed, an average domain diameter of 18 nm was measured for the front side and 19 nm for the reverse side. Ideally, an image of the section of the film would be necessary in order to confirm the structure of phase separation inside the film. Unfortunately, despite several tries no image of the film section was obtained.



Figure 6.6: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA₃₂-*b*-PS₃₃₆ thin films spin-coated onto a silicon wafer after annealing with DMF and DEC during different times. From no solvent annealing effect (top-left) to a strong solvent annealing effect after 8h (bottom-right).



Figure 6.7: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA-*b*-PS thin films with different weight ratio of PTMA after annealing with DMF and DEC during 6 h. 18 wt% = PTMA₃₂-*b*-PS₃₃₆; 23 wt% = PTMA₄₂-*b*-PS₃₂₃; 32 wt% = PTMA₄₂-*b*-PS₂₀₈; 45 wt% = PTMA₄₂-*b*-PS₁₂₀.



Figure 6.8: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA-*b*-PS thin films onto silicon wafers with different molar masses for a same PTMA weight ratio of 27 % after annealing with DMF and DEC during 6 h. 51.300 g mol⁻¹ = PTMA₅₆-*b*-PS₃₆₂; 71.300 g mol⁻¹ = PTMA₇₉-*b*-PS₅₀₂.



Figure 6.9: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA₃₂-*b*-PS₃₃₆ thin films annealed 6h in DMF-DEC: (a) front side, (b) reverse side.

6.3 Electrochemical analysis of PTMA-*b*-PS thin films

6.3.1 Selection of a suitable current collector.

In order to perform electrochemical analysis onto PTMA-*b*-PS thin films, the films need to be deposited onto a conductive substrate which will act as a current collector. Indeed, the silicon wafers employed for the self-assembly study are not conductive substrates. Different substrates were considered: n^{++} doped silicon wafers, indium tin oxide substrates and titanium conductive substrates. Four point probe measurement measure the average resistance of a thin layer by passing current through the outside two points of the probe while measuring the voltage across the two inside points (Figure 6.10). When the spacing between the probes is constant and at the condition that the distance between the edges of the film (b) is higher than four time the spacing between the measuring probes (a) and the thickness of the conducting film is less than $0.4 \times a$, therefore the sheet resistance is given by:

$$R_s = 4.532 \times \frac{V}{I} \tag{6.1}$$

Where V is the voltage (V), I the current (A) and R_s the sheet resistance (Ω sq⁻¹).



Figure 6.10: Schematic representation of the four point probes measurement.

According to the sheet resistance values (Table 6.2), the titanium substrate is the most conductive one and therefore in principle the most suitable as current collector. However, the substrate is not as flat as

Substrate	Voltage (V)	Current (A)	Resistivity sheet (R _s) (Ω sq ⁻¹)
Si wafer	20	$0.247 \ 10^{-3}$	367
n++ Si-doped	20	0.597	0.054
ITO	20	$4.75 \ 10^{-3}$	19
Titanium	0.425^{a}	0.247	$1.8 \ 10^{-3}$

Table 6.2: Four point probe measurements of different substrates.

^a The voltage was not set to 20 mV due to the limit of the system.

the other substrates since it presents a roughness around 30 Å, making this substrate less suitable for AFM. Si-doped wafer presents a good conductivity however no cyclic voltammogram was obtained when used. Finally, ITO substrate appeared to be conducting enough to act as current collector and presents a flat surface comparable to silicon wafers employed for AFM spectroscopy, making it a good candidate as current collector for electrochemical analysis of PTMA-*b*-PS thin films.

The influence of the substrate, i.e. silicon wafer or ITO substrates, onto which the thin films have been prepared on the self-assembly process was also investigated. Even if the detailed self-assembly studies presented in the previous section were performed onto silicon substrates, ITO substrates were employed for electrochemical applications. As illustrated in Figure 6.11 the change of substrate from silicon to ITO barely affects the self-assembly morphology.

6.3.2 Electrochemical analysis

The electrochemical tests were performed on ITO substrates using a three electrodes configuration with an Ag/Ag^+ non aqueous reference electrode, a Pt wire counter electrode and a solution of tetrabutylammonium perchlorate (TBAClO₄) in acetonitrile as electrolyte (Figure 6.12).

First, the redox behavior of PTMA-*b*-PS copolymers dissolved in acetonitrile was analyzed by cyclic voltammetry (Figure 6.13). This analysis revealed a pair of redox peaks centered at 0.46 V vs. Ag/Ag^+ , corresponding to the reversible oxidation of the free nitroxide radicals into oxoammonium cations (see Chapter 4 section 4.5 for more details).

Cyclic voltammetry of a PTMA-b-PS thin film supported on ITO



Figure 6.11: AFM images $(1.0 \times 1.0 \ \mu m^2)$ of PTMA₄₂-*b*-PS₃₂₃ thin films annealed 6h in benzene-H₂O onto: (a) silicon wafer, (b) ITO substrate.



Figure 6.12: Three electrode set-up employed for the electrochemical characterisation of PTMA-b-PS thin films.

substrate was further performed. In order to avoid any dissolution of the thin film during electrochemical tests, the PS matrix was cross-linked

by UV light irradiation at 253 nm during 30 min after the solvent annealing. Indeed, under deep UV, PS can be crosslinked without addition of photoinitiator.^[23,24] Deep UV radiations are known to degrade PMMA, a small degradation of PTMA is therefore possible during the UV crosslinking. However, the small amount of radiations employed for the crosslinking should not lead to high amounts of degradation. Typical redox waves of PTMA with a reversible redox peak centered at 0.48 vs Ag/Ag⁺ reference electrode were detected. The intensity of the measured current increases with the number of cycles, before reaching a maximum (Figure 6.13). This behavior can be explained by a progressive swelling of the PS confined PTMA domains by the electrolyte upon cycling, allowing more electrochemical active sites to be reached.



Figure 6.13: Cyclic voltammogram of $PTMA_{79}$ -b- PS_{502} on ITO substrate: scan rate = 0.1 mV s⁻¹, working = ITO substrate, counter = Pt wire, reference = Ag/Ag^+ (0,01 M $AgNO_3 + 0.1$ M $TBACIO_4$) and electrolyte = 0.1 M $TBACIO_4$ in CH_3CN (Potential vs. Li/Li⁺ calculated).

Finally, constant current galvanostatic cycling tests were performed onto PTMA-*b*-PS thin films. A rapid charge/discharge process (I = $23.7 \ \mu A \ cm^{-2}$) was required in order to avoid self-discharge, which was observed at slower rate. Indeed, due to the reduced amount of active material present in a thin film compared to its high surface, self-discharge is a challenging issue. The capacity retention plot shows a good retention of capacity over time (Figure 6.14b). Similar to cyclic voltammetry experiments, an increase in capacity is observed during the first cycles and is attributed to the swelling of the thin film by the electrolyte. Charge/discharge profiles reveal a plateau around 0.48 V vs. Ag/Ag⁺, corresponding to 3.59 V vs Li/Li⁺ (See Chapter 4, section 4.4.1), in both charge and discharge curves which is coherent with the PTMA behavior and a requirement for battery application in order to deliver a constant voltage (Figure 6.14a).



Figure 6.14: Electrochemical characterization of a PTMA₇₉-*b*-PS₅₀₂ thin film deposited onto an ITO substrate and crosslinked by UV for 45 min. Current applied: 23.7 μ A cm⁻². (a) charge/discharge voltage profile; (b) capacity retention plot.

6.4 Conclusion

A nanostructured organic radical cathode was prepared by the selfassembly of PTMA-b-PS diblock copolymers in thin films. In order to control the phase separation morphology, the effect of thermal and solvent annealing was investigated. Thermal annealing appeared to be inefficient. Therefore, solvent annealing was used and resulted in the formation of thin films with different morphologies such as lamellar or cylindrical. PTMA-b-PS thin films with perpendicularly oriented cylinders of PTMA inside a PS matrix were further investigated. Thanks to the UV crosslinked PS matrix, PTMA dissolution into the battery electrolyte was avoided and enhanced mechanical integrity of the cathode is expected. Indeed, after crosslinking, the PTMA-b-PS thin films resist to the spin-coating of organic solvent onto their surface. At the same time, perpendicularly oriented PTMA cylinders allow continuity between the electrochemical active moieties and the ITO current collector. The choice of the solvent used for annealing is a key parameter in order to obtain the desired morphology. The simultaneous use of DMF and DEC gave the best results for our system. Electrochemical activity of PTMA-b-PS using a three electrodes set-up was demonstrated. Cyclic voltammetry of the polymer in thin film was recorded displaying the typical behavior of PTMA. Charge/discharge measurements and capacity retention plot were also performed. This work opens a new field of research for ORBs using block copolymers. Indeed, nanobatteries can find applications for microelectronic devices. Even if the PS is an electrochemical inactive material, this work paves the way towards other block copolymers where the PS moiety can be replaced by another material allowing a synergy with PTMA, such as a conductive polymer.

Experimental part

Materials

N,N-Dimethylformamide (DMF, VWR, HyperSolv Chromanorm for HPLC), diethyl carbonate (DEC, Aldrich, 99 %), acetonitrile (VWR, HyperSolv Chromanorm for HPLC), tetrahydrofuran (Aldrich, Normapur), silver nitrate (Belfolabo) and tetrabutylammonium perchlorate (TBAClO₄; Fluka) were used as received.

Instrumentation

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired on a 300 MHz Bruker Avance II or on a 500 MHz Bruker Avance II. Molar masses (M_n) and dispersity (Đ) were measured on an Agilent size exclusion chromatography (SEC) system equipped with an Agilent 1100/1200 pump (25 °C; eluant: Chloroform : triethylamine : 2isopropanol (94:4:2); flow rate: 1 mL min⁻¹), an Agilent differential refractometer and two PSS SDV columns (Beads 10 μ m; porosity of column 1: 10000 Å; porosity of column 2: 1000 Å). The calibration was performed using polystyrene standards. Electron spin resonance (ESR) spectra were acquired on an EMXmicro CW-EPR spectrometer (Bruker, Germany) from powdered samples. The SpinCount[™] software module was used for quantitative experiments. Rapid thermal annealing (RTA) were performed using a MILA-5000 Lamp Heating Unit from ULVAC. Atomic force microscopies (AFM) were performed on a Digital Instruments Nanoscope V scanning force microscope in tapping mode using NCL cantilevers (Si, 48 N/m, 330kHz, Nanosensors). Cyclic voltammetry were performed using a CH Instruments potentiostat CHI 660B. Charge/discharge tests were performed using an ARBIN Instrument Battery Tester, BT-2043. Pt-disk working electrode (CHI102), Pt wire counter electrode (CHI115) and dry Ag/Ag⁺ non-aqueous reference electrode (CHI112) come from CH Instruments, inc. Four probes electrode measurements were performed onto a Lucas LAB320 coupled with a Keithley 2400 sourcemeter with a potential fixed at 20 mV.

Thin film preparation

Spin coating

Polymer thin films were spin-coated onto silicon chips or ITO substrates of 1 cm^2 for AFM imaging. Silicon wafers were sonicated 15 min in acetone, rinsed with milli-Q water, washed 30 min in piranha solution (3:1 of H₂SO₄ 98%/H₂O₂ 30% solution) and rinsed in milli-Q water.
The substrates were dried by spin-coating at a rotation rate at 2000 rpm during 20 s. ITO substrates of 1 cm2 were washed 15 min in acetone and dried by spin coating at a rotation rate at 2000 rpm during 20 s. Filtered (0.2 μ m PTFE) polymer solutions (10 mg of polymer per 1 mL of THF) were spin-coated at a rate of 2000 rpm during 40 s.

General procedure for thermal annealing process

Samples were placed under a sealed glass case filled with argon. The case was left 24 h into an oven at 200 °C.

General procedure for rapid thermal annealing process

Rapid thermal annealing was performed inside a MILA-5000 heating unit with a nitrogen flux at 8 l/min. A ramp of 10 s was applied in order to reach the target temperature (190 °C). A 60 s plateau was applied at the target temperature. Finally, the heating was stopped and the sample cooled to 40 °C before opening the furnace.

General procedure for solvent annealing process

Samples were placed under a glass case (135 mm diameter, 70 mm height) with two beakers containing 5 mL of solvent each. M beakers are 36 mm wide, L beakers are 45 mm wide. A weight is placed on the glass in order to keep the system hermetic. After the desired time the glass is removed in order to leave the samples to dry.

General procedure for the determination of thin films thickness

The height of thin film was determined by scratching the polymer film and measuring the height by AFM.

General procedure for the determination of the nano-domains sizes

The size of domains were measured using section tool of Nanoscope Analysis software.

General procedure for flipping polymer thin films

After 30 min of UV irradiation at 253 nm, the thin film of polymer deposed onto silicon wafer substrate was submerged 2 h into an aqueous NaOH solution (1.5 M). The floating film onto the surface was caught using a clean silicon wafer substrate and submerged into clean milli-Q water. The film was finally let to dry.

Electrochemical measurements

UV crosslinking

PTMA-b-PS thin films on ITO substrates were placed under three Rayonet photochemical reactor UV lamp emitting at 253 nm during 30 min. The distance to the lamps was of about 3 cm.

Preparation of Ag/Ag^+ non-aqueous reference electrode

A non-aqueous Ag/Ag^+ reference electrode with porous Teflon tip was filled with a solution composed of 0.01 M AgNO₃ and 0.1 M TBAClO₄ in acetonitrile.

Typical procedure for cyclic voltammetry in solution

The analyzed component (PTMA-*b*-PS or ferrocene) was dissolved into the electrolyte solution (0.1 M TBAClO₄ in acetonitrile) in order to obtain a 0.1 M solution. A three electrodes set-up with a Pt disk working electrode, a Pt wire counter electrode and the previously prepared Ag/Ag^+ reference electrode was used to record the voltammogram.

Typical procedure for electrochemical characterisations of PT-MA-*b*-PS thin films onto ITO substrates

Cyclic voltammetry was performed using a three electrodes system with the PTMA-*b*-PS thin film deposited onto an ITO substrate as working electrode, a Pt wire as counter electrode and the previously prepared Ag/Ag^+ reference electrode into 0.1 M TBAClO₄ in acetonitrile solution electrolyte.

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CHAPTER 7

PTMA-*b*-PSNO block copolymers as organic radical cathodes

Abstract

This chapter focuses on the replacement of the PS polymer block in PTMA-b-PS copolymers by an electrochemical active one. To this aim, a styrene derivative monomer bearing a protected nitroxide function, the 4-[(N-tert-butyl-N-tert-butyldimethylsilyloxy)amino]styrene (SSi) is synthesized. The polymerization process of this monomer is then investigated. Free radical polymerization of SSi is firstly studied. Next, controlled radical polymerizations such as ATRP, RAFT and Cu^0 -RDRP are performed. The deprotection of the obtained polymer leads to the formation of poly[4-(N-tert-butyl-N-oxylamino)styrene] (PSNO), an electrochemical active polystyrene derivative bearing nitroxide functions. PT-MPM-b-PSSi block copolymers are finally obtained by Cu^0 -RDRP starting from PTMPM-Br macroinitiators. The deprotection/oxidation of the block copolymer leads to the electrochemically active PTMA-b-PSNO. Both homo PSNO and PTMA-b-PSNO block copolymers are characterized by cyclic voltammetry in a three electrodes set-up with an Aq/Aq^+ non aqueous reference electrode. Finally, phase separation in a PTMAb-PSNO block copolymer thin film is investigated by atomic force mi $croscopy.^{1}$

¹The synthesis of the monomer, its polymerization and deprotection were performed by Guillaume Dolphijn in the frame of his master thesis.

7.1 Introduction

Nanostructured organic radical cathodes based on PTMA-b-PS block copolymers were studied in the previous chapters. PS was used as an insoluble core-forming block for the fabrication of micelles in typical battery electrolytes. In thin films, PS was used as a stable matrix around the PTMA nanodomains, avoiding their dissolution into the battery electrolyte. PS was initially selected as an electrochemical inactive and insoluble block which will not interfere with the electrochemically active PTMA. This chapter goes further into the formation of nanostructured radical cathode thin films by replacing the inactive PS block by an electrochemical active one, increasing the gravimetric capacity of the system. The replacing block needs to play the same role than the PS one. It needs therefore to be insoluble into battery electrolytes. Different nitroxide bearing molecules have already been described in literature.^[1,2] Due to the good results obtained by employing a PS block, we decided to focus onto a styrene derivative bearing a stable nitroxyl radical.^[3] Moreover, the selected nitroxide bearing polystyrene derivative (PSNO) presents the same redox potential than PTMA. A single redox wave is therefore expected for the block copolymer, leading to a material delivering the current at a constant voltage.

Two different styrene derivatives were initially considered to replace the electrochemical inactive PS into the PTMA-*b*-PS block copolymer, i.e. a styrene bearing either one or two nitroxide functions per monomeric unit (Figure 7.1). Indeed, the theoretical capacity increases from 141 mAh g⁻¹ for a monosubstituted monomer to 194 mAh g⁻¹ for the disubstituted one. However, according to literature, the monomer bearing two nitroxide functions presents a non reversible oxidation peak at 1.0 V vs Ag/AgCl. The instability of the redox process was attributed to the lack of a stabilizing *para*-substituent on the nitroxide radicals.^[3] As a consequence, the styrene derivative bearing one nitroxide function per monomeric unit was selected for further investigation.



Figure 7.1: Styrene derivative monomers.

7.2 Monomer synthesis

Since the nitroxyl radicals are not compatible with the controlled radical polymerization employed, a precursor of the nitroxide bearing polymer needs to be synthesized. Two strategies are conceivable: using a secondary amine bearing precursor, in a similar manner than for the synthesis of PTMA, or using a nitroxide protected version of the monomer (Figure 7.2). Since the synthesis of the protected monomer was already reported in literature, this strategy was selected and consists of protecting the nitroxide with a *tert*-butyldimethylsilane function.^[3-5]



Figure 7.2: Possible strategies for the polymerization of nitroxide containing styrene derivatives by CRP. (a) Polymerization of a secondary amine bearing precursor followed by its oxidation; (b) Protection of the nitroxide function before polymerization.

The synthesis of the monomer can be achieved via a three steps synthesis. The first step consists in introducing the nitroxide function onto the aromatic ring. An halogen-lithium exchange using *tert*butyllithium was performed onto *p*-dibromobenzene (1). 2-methyl-2nitrosopropane dimer in solution was then added dropwise and underwent a nucleophilic attack by the previously formed organolithium. After quenching of the remaining *tert*-butyllithium the bromo-4-(*tert*-butyl-*N*hydroxylamino)aniline (2) was obtained with 75 % yield (Figure 7.3).



Figure 7.3: First step of the styrene derivative (SSi) synthesis: introduction of the nitroxide onto the aromatic ring.

The second step consists in protecting the hydroxylamine radical via *tert*-butyldimethylsilane. The reaction was carried out in the presence of imidazole which directed the equilibrium through the formation of bromo-4-[N-tert-butyl-N-(tert-butyldimethylsilyloxy)]aniline (3) (Figure 7.4). Yields up to 95 % were obtained for this reaction.



Figure 7.4: Second step of the styrene derivative (SSi) synthesis: protection of the nitroxyl radical.

Finally, the last step consists in replacing the remaining bromide function by a vinyl one via a Stille coupling. The reaction was performed between an organostannane (tri-n-butyl(vinyl)tin) and (3) via a palladium complex, i.e. tetrakis(triphenylphosphine)palladium(0), as catalyst (Figure 7.5). The final monomer 4-[(*N-tert-butyl-N-tert-butyldimethylsilyloxy*)amino]styrene (SSi) (4) was obtained with a yield of 64 %.



Figure 7.5: Third step of the monomer (SSi) synthesis: Stille coupling.

The three steps synthesis presents an overall yield of 46%. The synthesis was repeated several times in order to have enough materials for the formation of the PTMPM-*b*-PSSi block copolymer.

7.3 Polymerization of the styrene derivative SSi

Different polymerization methods have been tested on the previously synthesized monomer SSi (4). Firstly, its free radical polymerization (FRP) was investigated. Then controlled radical polymerizations such as ATRP, RAFT and Cu⁰-RDRP were studied in order to obtain polymers with lower dispersities and more controlled molecular weight compared to FRP.

7.3.1 Free radical polymerization

The free radical polymerization of the styrene derivative SSi was performed using azobisisobutyronitrile (AIBN) as initiator. The polymerizations were conducted in anisole at 85 °C during 15 h (Figure 7.6).^[3] A light yellow color appeared after a few hours of polymerization, indicating probably some degradation of the polymer or of the monomer. The conversion, measured by ¹H NMR (solvent: CDCl₃), was 80 % after 4h of polymerization without further increase of the conversion with time. Polymers of styrene derivatives bearing protected nitroxide functions (PSSi) with \overline{M}_n varying between 10,400 and 16,900 g mol⁻¹ with dispersities lower than 2.0 were obtained (Table 7.1, Figure 7.7).



Figure 7.6: Free radical polymerization of SSi (4).

Table 7.1: SSi (4) polymerizations by FRP.

Entry	Monomer (equiv.)	Т (°С)	Anisole (wt%)	Time (h)	$\frac{\bar{M}_n{}^{\mathbf{a}}}{(\mathbf{g} \ \mathbf{mol}^{-1})}$	Đ
1	215	80	50	19	$12,\!500$	1.81
2	250	85	50	18	$16,\!900$	1.77
3	200	80	40	19	$13,\!300$	1.99
4	200	85	40	19	$13,\!300$	1.73
5	200	85	40	3.5	10,400	1.73

^a Determined by SEC (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

7.3.2 Atom transfer radical polymerization

Before the formation of PTMPM-*b*-PSSi diblock copolymers, the polymerization of SSi by controlled radical polymerization has been investigated. ATRP was chosen since this method was successfully employed during the previous works on PTMA-*b*-PS block copolymers. The polymerization was firstly studied at 100 °C, using a CuCl/PMDETA catalytic system and TsCl as initiator (Table 7.2). Unexpectedly, no polymer was obtained after the ATRP of SSi. Moreover, an unusual color change in ATRP was observed. Whereas ATRP polymerizations in these conditions usually present a green coloration, a dark brown color was observed after a few hours of polymerization, indicating an unexpected degradation during the polymerization process. In order to avoid



Figure 7.7: SEC chromatogram of a PSSi synthesized by FRP (Table 7.1, Entry 5)(eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

any side reactions, the temperature was decreased to 80 °C but no amelioration was observed. More activating conditions were investigated in order to decrease the reaction time. CuBr/Me₆ TREN catalytic system was thus employed. Indeed, CuBr is known to allow faster polymerizations than CuCl and Me₆ TREN (k_{act} = 0.045) is a more activating ligand than PMDETA (k_{act} = 2.7).^[6,7] However PSSi homopolymers were still not obtained.



Figure 7.8: Atom transfer radical polymerization of SSi (4).

The absence of polymerization was firstly attributed to a slow polymerization rate. However, since the most activating conditions (Table 7.2, Entries 6-7) and a longer polymerization time (Table 7.2, Entry 5) didn't allow the formation of a polymer, the problem has another origin. Another explanation would be the loss of the protecting groups of the nitroxide functions and the subsequent reaction of the freed nitroxides with the polymerization media. The protecting groups could be lost due

Initiator / CuX / Ligand^a Т Time Solvent Entry (°C) (h) (wt%)1 TsCl/CuCl/PMDETA 10015Anisole (50) $\mathbf{2}$ TsCl/CuCl/PMDETA 10020Anisole (40)3 EBiB/CuBr/PMDETA 10048Anisole (40) $\mathbf{4}$ EBiB/CuBr/PMDETA 9024Anisole (50)5EBiB/CuBr/PMDETA 80 Anisole (40)168 $\mathbf{6}$ $EBiB/CuBr/Me_6TREN$ 10048 DMF (40) $EBiB/CuBr/Me_6TREN$ DMF (40) 780 48

Table 7.2: SSi (4) polymerization by atom transfer radical polymerization (ATRP).

a 1/1/1 equivalents.

to the polymerization temperature or side reactions with the copper catalyst. The hypothesis of degradation of the monomer during the reaction is strengthened by the fact that maximum 75 % of the monomer were recovered after the unsuccessful polymerizations.

By FRP the polymerization is probably faster than the degradation/side reactions, allowing the formation of a polymer chain. On the contrary, by ATRP, the degradation/side reactions are faster than the propagation, leading to irreversible termination reactions and the inhibition of the propagation. Therefore, the lower concentration of propagating radicals in ATRP compared to FRP makes it more sensitive to side reactions involving a relatively large amount of nitroxide radicals freed by the unwanted deprotection of the SSi monomer. In consequence, the ATRP polymerization of SSi was not further investigated and other polymerization methods were investigated.

7.3.3 Reversible addition fragmentation chain transfer (R-AFT) polymerization

After the unsuccessful polymerization of SSi (4) by ATRP, RAFT polymerization was investigated. Indeed, RAFT polymerizations are initiated with AIBN in a similar manner than FRP. In RAFT, compared to FRP, a chain transfer agent is added in order to control the polymerization process. The RAFT polymerization of SSi (4) was realized at 100 °C using 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic -

acid (DDMAT) as chain-transfer agent without any success. In order to avoid any degradation the temperature reaction was the PTMPM-*b*-PSSi block copolymer. Unfortunately, conventional CRPs, i.e. ATRP, RAFT, and NMP, are most of the time performed at high temperature (> 70 °C).



Figure 7.9: RAFT polymerization of SSi (4).

Table 7.3: SSi (4) polymerization by reversible addition fragmentation chain transfer (RAFT).

Entry	Monomer (equiv.)	DDMAT ^a (equiv.)	Т (°С)	${f Time}\ (h)$	Anisole (wt%)
$\begin{array}{c}1\\2\\3\\4\end{array}$	$1000\ 1000\ 1000\ 1000\ 1000$	$20 \\ 20 \\ 20 \\ 5$	$100 \\ 80 \\ 65 \\ 70$	48 168 120 96	$50 \\ 50 \\ 40 \\ 40$
5	500	5	70	96	40

^a 1 equivalent of AIBN.

7.3.4 Copper(0) mediated reversible-deactivation radical polymerization (Cu^0 -RDRP)

 Cu^0 -RDRPs are generally performed at temperatures similar to AT-RP. Indeed, the polymerization of styrene has been reported at 90 °C.^[8] However the group of Pr. Zhu has reported the successful polymerization of styrene at ambient temperature by employing copper(0) powder catalyst (Figure 7.10).^[9]

The polymerization of styrene using the above-mentioned method was thus investigated. 25 % of conversion were observed after 20 h of re-



Figure 7.10: Cu⁰-RDRP polymerization of styrene.

action at 25 °C, leading to a PS with a DP of 92, a \mathcal{D} of 1.35 and a molar mass (NMR) of 8,900 g mol⁻¹ (Figure 7.11). Even if the control of the polymerization was not perfect and the initiation efficiency was pretty low ($E_i = 54$ %), a polystyrene was obtained at 25 °C. This method was therefore employed for the polymerization of the styrene derivative SSi (4).



Figure 7.11: SEC chromatogram of the PS synthesized by Cu^0 -RDRP (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

After 20 h of polymerization of SSi (4) at 25 °C, a precipitated polymer was obtained (Figure 7.12). Unlike the SSi monomer and PS, PSSi is not soluble in DMF. In consequence the conversion was not computable. SEC indicated a molar mass of 40,600 g mol⁻¹ with a D of 4.2 (Figure 7.13). Moreover a double population appeared in the chromatogram, certainly due to the inhomogeneity resulting from the precipitation of the polymer during the reaction. Hopefully, the first block of PTMPM will help to keep the PTMPM-*b*-PSSi in solution during the polymerization of the block copolymer.



Figure 7.12: Cu^0 -RDRP polymerization of SSi (4).



Figure 7.13: SEC chromatogram of the PSSi synthesized by Cu^0 -RDRP (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).

7.3.5 PTMPM-b-PSSi diblock copolymer by Cu⁰-RDRP

In order to synthesize the PTMPM-*b*-PSSi block copolymer, a macroinitiator of PTMPM-Br was employed. The PTMPM-Br macroinitiator can either be synthesized by ATRP following the polymerization process described into Chapter 4, Section 4.2.1 or by Cu⁰-RDRP.

PTMPM-Br macroinitiator by Cu⁰-RDRP

 Cu^{0} -RDRP of TMPM was carried out in isopropanol at 40 °and has led to well defined PTMPM-Br with dispersities lower than 1.15 (Table 7.4).^[10] However, the SEC curve showed a fronting through the small molar masses (longer elution times). As previously discussed, the tailing could be due to interactions between the column and the polymer. However, since polymers with similar sizes were obtained by ATRP without observing a tailing in SEC (Chapter 4, Figure 4.6), the tailing observed for this system could indicate a slow initiation rate compared to the propagation (Figure 7.15).



Figure 7.14: Cu⁰-RDRP polymerization of TMPM.

Entry	TMPM (equiv.)	\bar{M}_n^{a} g mol ⁻¹	DP (NMR)	Đ	E_i (%)
$\frac{1}{2}$	$53\\34$	$18,\!800 \\ 8,\!000$	$\frac{80}{48}$	$\begin{array}{c} 1.07 \\ 1.14 \end{array}$	66 70
	1	/	>		

Table 7.4: PTMPM by Cu⁰-RDRP.

^a Determined by ¹H NMR (solvent: $CDCl_3$).

By combining Cu^0 -RDRP and ATRP, macroinitiators of PTMPM terminated with a bromide or a chloride are thus available for the further synthesis of PTMPM-*b*-PSSi block copolymers.

PTMPM-b-PSSi block copolymers by Cu⁰-RDRP

The synthesis of the PTMPM-b-PSSi diblock copolymers was realized by the polymerization of SSi by Cu⁰-RDRP using PTMPM-Br as a macroinitiator (Table 7.4, Entry 2). The same polymerization conditions than for the homoPSSi were used. 90 % of conversion were obtained after



Figure 7.15: SEC chromatogram of the PTMPM-Br macroinitiator synthesized by Cu^0 -RDRP (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

22 h of reaction at 25 °C. The crude polymer was purified by precipitation into MeOH, leading to the PTMPM-*b*-PSSi diblock copolymer (Figure 7.16).



Figure 7.16: PTMPM-*b*-PSSi diblock copolymers by Cu⁰-RDRP.

The obtained polymer presents a very high molar mass ($\bar{M}_n = 86,300$ g mol⁻¹) due to the low initiation efficiency of the process (Figure 7.17). Moreover only a small amount of the polymer was recovered after purification, leading to a low reaction yield (18 %). The SEC chromatogram indicates two different polymer populations. The major one corresponds to the diblock copolymer whereas the small population corresponds to the remaining PTMPM-Br macroinitiator. Given that the low initiation efficiency, a higher amount of remaining PTMPM-Br should be observed. However the polymer purification was realized by precipitation

into MeOH, a good solvent of PTMPM. Therefore most of the PTMPM homopolymer was removed during the purification process.



Figure 7.17: SEC chromatogram of PTMPM-b-PSSi synthesized by Cu⁰-RDRP (eluant: CHCl₃/Et₃N/isopropanol 94:4:2 in volume; calibrated with PS standards).

Additional block copolymer syntheses have demonstrated that the separation of the PTMPM-Br homopolymer from the block copolymer was difficult to achieve. Indeed, when the PSSi block was shorter, the precipitation of the block copolymer was not achievable. In fact, PTMPM is soluble in MeOH and insoluble in hexane whereas PSSi presents the opposite solubilities. In the above-mentioned case, the PSSi block was long enough to drive the solubility and to allow precipitation into MeOH despite the PTMPM block. This was not observed neither achieved for block copolymers with a shorter PSSi block. In consequence, according to the low reaction yield of the purified PTMPM-*b*-PS and the difficult purification, further PTMPM-*b*-PSSi block copolymers were just filtered on aluminum oxide to remove the copper and directly oxidized/deprotected into the electrochemical active copolymers without further purifications.

DP determination via ¹H NMR The DP of the PTMPM block is known and its value is set to the integration of the peak H_a at 5.06 ppm, corresponding to the CH next to the ester function of TMPM. Therefore, the integration of the aromatic region comprised between 5.8 and 7.1 ppm (H_{ar}) corresponds to the four aromatic protons of PSSi. The DP of the PS block is obtained by dividing this value by 4, i.e. the number of aromatic protons present onto one unit of styrene derivative (Figure 7.18). This DP gives us an idea about the size of the PSSi block however an error is done onto the calculated DP since some homoPTMPM remains in the final product.



Figure 7.18: ¹H NMR of the pure PTMPM-*b*-PSSi diblock copolymer (solvent: CDCl₃).

7.4 PSSi deprotection into the electrochemical active PSNO

The deprotection of the PSSi to form poly[4-(N-*tert*-butyl-*N*-oxyl-amino)styrene] (PSNO) was firstly studied with the homopolymer before switching to the PTMPM-*b*-PSSi block copolymer.

7.4.1 HomoPSSi deprotection

The deprotection of homoPSSi was realized by reacting the polymer with *tert-n*-butylammonium fluoride (TBAF) in THF, followed by the addition of silver oxide (Ag₂O) (Figure 7.19). After filtration of Ag₂O, evaporation of the solvent under vacuum and precipitation of the polymer in methanol, an orange powder was obtained. Indeed, after evaporation of the solvent, the remaining solid was totally insoluble. Since the chemical structure around the nitroxide is different in PSNO compared to PTMA, the nitroxide could be less stable and could lead to side reactions. Moreover, as explained for the UV irradiation crosslinking (Chapter 6, Section 6.3.2), PS is prone to self-crosslinking when radicals are generated. The spatial proximity of the nitroxide with the PS structure could therefore lead to crosslinking side reactions. Another drawback of this reaction is the elimination of the silver oxide which is achieved by a filtration of the solution. However it appeared that some Ag_2O remains in solution even after multiple filtrations.



Figure 7.19: Deprotection of PSSi to form the electrochemically active PSNO derivative.

The SEC chromatogram revealed a degradation of the polymer during the deprotection (Figure 7.20). Indeed, a broader dispersity is observed with D = 1.73 for the initial PSSi and D = 6.1 for the final PSNO. Moreover the molar masses distribution broadens in the high molar masses region, confirming the presence of some crosslinking reactions between the polymer chains. Otherwise, the maximum of the peak is shifted to the lower molar masses after deprotection which is due to a change in the random coil of the polymer.

The deprotection yield was next investigated. The IR spectrum of the deprotected PSNO presents pronounced bands at 1247 cm⁻¹ and 1195 cm⁻¹ corresponding respectively to Si-CH₃ and Si-O, indicating remaining protecting groups (Figure 7.22). This was confirmed by ESR direct quantification since, depending on the sample, 30 to 56 % of deprotection yield were achieved. The ESR spectrum of PSNO is similar to the PTMA one (Chapter 4) and, as for PTMA, the hyperfine structure was not observed due to the close spatial proximity of the nitroxide functions (Figure 7.21).

UV-vis spectroscopy with a calibration curve of TEMPO-OH can be employed to quantify the oxidation yield of PTMA. This technique can not be employed for PSNO since the molecule appeared to present



Figure 7.20: SEC chromatograms of PSSi (Table 7.1, Entry 5) and the resulting deprotected PSNO (eluant: $CHCl_3/Et_3N/isopropanol 94:4:2$ in volume; calibrated with PS standards).



Figure 7.21: ESR spectra of PSNO.

a more intense orange color than TEMPO and would therefore require another standard like N-(*tert*-butyl)-N-phenylnitroxide, which is not commercially available (Figure 7.23). The UV spectrum of PSNO revealed a broader and more intense absorbance peak at 460 nm compared to TEMPO-OH for a same radical concentration (Figure 7.24). When diluting the solution, the intensity of the peak at 460 nm decreased and a second peak at 335 nm is revealed (Figure 7.25). This peak is not observed with TEMPO-OH or PTMA and is therefore specific to PSNO.



Figure 7.22: IR spectrum of left: PSSi and right: PSNO.



Figure 7.23: PSNO and the corresponding standard needed for oxidation yield determination by UV-vis spectroscopy.

7.4.2 PTMPM-b-PSSi oxidation/deprotection into PT-MA-b-PSNO

In order to determine if the deprotection of PSSi should be realized before or after the oxidation of PTMPM with mCPBA, a homopolymer of PSSi was reacted with mCPBA and a homopolymer of PTMPM was reacted with Ag₂O. No polymer was isolated after the reaction of PTMPM in the conditions of deprotection of PSSi. An intense orange solid similar to PSNO was obtained after the reaction of PSSi with mCPBA. This change of coloration gives a clue about a possible deprotection of PSSi via mCPBA. Unfortunately the final product was totally insoluble and has not been characterized.



Figure 7.24: UV-vis spectra of PSNO, TEMPO-OH and PSSi with a concentration of 0.06 M of nitroxide functions in CH_2Cl_2 .



Figure 7.25: UV-vis spectra of PSNO, TEMPO-OH and PSSi with a concentration of 0.0075 M of nitroxide functions in CH_2Cl_2 .

Due to the difficulty to isolate a purified PTMPM-*b*-PSSi with a decent reaction yield, the oxidation with mCPBA was realized onto a crude product after its filtration over aluminum oxide to remove the copper. The SEC chromatogram indicates two different populations, one corresponding to homoPTMA remaining in solution ($M_p = 11,500 \text{ g mol}^{-1}$) and the other one to the block copolymer ($M_p = 38,600 \text{ g mol}^{-1}$).

Surprisingly the ESR analysis demonstrated around 20 % of deprotection. This value is really low considering the presence of the PTMA block and the homoPTMA into the final product. However the UV-vis spectrum of the resulting block copolymer revealed the same absorbance behavior than the homoPSNO with a second peak at 335 nm (Figure 7.26 and 7.27), indicating that some SSi units were deprotected into SNO via the oxidation with mCPBA. Given the low deprotection yield, the resulting copolymer is a diblock copolymer where the PSNO block is a statistical block composed of PSSi and PSNO whereas the PTMA block is a statistical block composed of PTMPM and PTMA. The obtained block copolymer could therefore be named P(TMPM-co-TMA)-b-P(S-Si-co-SNO).



Figure 7.26: UV-vis spectra of PTMA-*b*-PSNO, homoPSNO and PTMA-*b*-PS with a concentration of 0.06 M of nitroxide functions in CH₂Cl₂.



Figure 7.27: UV-vis spectra of PTMA-*b*-PSNO, homoPSNO and PTMA*b*-PS with a concentration of 0.0075 M of nitroxide functions in CH₂Cl₂.

7.5 Electrochemical analysis

7.5.1 HomoPSNO

The electrochemical properties of the PSNO were investigated by cyclic voltammetry. Due to a complete insolubility of PSNO into CH_3CN , the polymer was dissolved into CH_2Cl_2 to perform a cyclic voltammogram with a Pt disk working electrode, a Pt wire counter electrode and an Ag/Ag⁺ (0.01 M AgNO₃; 1 M TBAClO₄ in CH_2Cl_2) non aqueous reference electrode. Ferrocene was employed as an external standard and presents a potential of 0.29 vs the Ag/Ag⁺ non aqueous reference electrode. Figure 7.28 represents a cyclic voltammogram of a mixture of ferrocene and hydroxy-TEMPO (TEMPO-OH). The TEMPO displays a potential of 0.29 V vs Fc/Fc⁺. Surprisingly, a passivation of the working electrode occurred during the first cycles leading to a fading of the signal (Figure 7.29). A cleaning of the working electrode allowed a recovery of the signal, confirming that the passivation occurs onto the working electrode.



Figure 7.28: Cyclic voltammogram of ferrocene and TEMPO-OH vs Ag/Ag^+ using 1M TBAClO₄ in CH_2Cl_2 electrolyte solution (scan rate = 0.1 V s⁻¹).

PSNO presents a reversible redox wave centered at 0.29 V vs Fc/Fc⁺, corresponding to the reversible oxidation of the nitroxide into the oxoammonium cation (Figure 7.30). This value is identical to the one observed for TEMPO-OH and PTMA and is coherent with the literature.^[3] Since the objective is to replace the inactive PS by an electrochemical active one, this similarity with PTMA is an interesting property. Indeed, only one potential is expected for the diblock copolymer, allowing a constant



Figure 7.29: Cyclic voltammogram of ferrocene. A passivation of the working electrode leads to a fading of the signal. A cleaning of the working electrode allows to recover the initial signal (scan rate = $0.1 \text{ V} \text{ s}^{-1}$).

potential delivery. Moreover PSNO appears to be insoluble in carbonate based battery electrolytes, i.e. EC/DEC/DMC (1:1:1 in volume) mixture with 1M LiTFS. PSNO can therefore play the same role in the block copolymer than the PS, i.e. to avoid the migration of PTMA into the battery electrolyte. The I_{pa}/I_{pc} ratio is not equal to 1, usually indicating a not fully reversible redox process. However, in this case, the working electrode passivation could be responsible of the phenomenon.



Figure 7.30: Cyclic voltammogram of homoPSNO into 1M TBAClO₄ in CH_2Cl_2 electrolyte solution (scan rate = 0.1 V s⁻¹).

7.5.2 PTMA-b-PSNO diblock copolymer

Cyclic voltammograms were performed onto PTMA-*b*-PSNO polymer thin films supported on ITO substrates in a similar manner than for PTMA-*b*-PS. The polymer was UV-irradiated for 30 min in order to avoid any dissolution of the polymer film during the electrochemical test. The PTMA-*b*-PSNO block copolymer revealed a reversible redox peak centered at 0.31 V vs Fc/Fc⁺, attributed to the reversible oxidation of the nitroxide function into oxoammonium cations (Figure 7.31). Since PSNO and PTMA are oxidized at the same potential the signal can not be attributed to PTMA, PSNO or both. However a second redox peak appeared at 0.1 V vs Fc/Fc⁺. Since this second peak presents the same potential than ferrocene it could correspond to remaining ferrocene or impurities in solution.



Figure 7.31: Cyclic voltammogram of a PTMA-*b*-PSNO thin film deposited onto an ITO substrate and crosslinked 30 min under UV light (electrolyte = 1M TBAClO₄ in CH₂Cl₂; scan rate = 0.1 V s^{-1}).

7.6 Self-assembly study of PTMA-*b*-PSNO thin films

The surface of the PTMA-*b*-PSNO block copolymer thin film was investigated by AFM in order to confirm that both building blocks phase separate. The AFM pictures revealed a mix of small nanodomains (\sim 45 nm) and bigger one (\sim 100 nm), confirming the immiscibility and the phase separation of the polymer blocks (Figure 7.32). The observed domains are much larger than for PTMA-*b*-PS. Indeed, the presence of

homoPTMA into the polymer leads to a swelling of the corresponding PTMA domains. Anyway a good phase separation was observed considering the pictures were taken directly after spin-coating without any annealing process. It can therefore be assumed that a solvent annealing in the good conditions will ameliorate the phase separation and the morphology.



Figure 7.32: AFM images of a PTMA-*b*-PSNO thin film on silicon wafer: (a) 2.0 x 2.0 μ m², (b) 10.0 x 10.0 μ m².

7.7 Conclusion

A styrene derivative monomer bearing a protected nitroxyl function was synthesized via a three steps synthesis with a global yield of 46 %. The first step consisted of an halogen-lithium exchange followed by a nucleophilic attack. Next the nitroxide was protected with a *tert*butyldimethylsilane group. Finally a Stille coupling led to the desired monomer (SSi).

The polymerization of the synthesized monomer (SSi) was firstly studied by free radical polymerization. Polymers with \bar{M}_n up to 16,900 g mol⁻¹ and $\bar{D} < 2$ were synthesized. Next, controlled radical polymerizations were investigated. However ATRP and RAFT appeared to be inefficient due to side reactions occurring at the temperature employed for these reactions. The polymer (PSSi) was obtained by Cu⁰-RDRP at 25 °C in DMF. PSSis with broad dispersities were obtained due to the insolubility of the polymer into the employed solvent. However the successful polymerization of SSi at room temperature by Cu⁰-RDRP opens the possibility to form a block copolymer.

A PTMPM-Br macroinitiator was synthesized either by ATRP or

Cu⁰-RDRP. The PTMPM-Br macroinitiator was next employed for the formation of PTMPM-*b*-PSSi block copolymers by Cu⁰-RDRP at 25 °C in DMF. SEC chromatograms of the polymers revealed a bimodal distribution corresponding to the block copolymers and some remaining macroinitiators. The precipitation of the PTMPM-*b*-PSSi was more challenging than expected since the two block present antagonist solubilities in the used solvents.

The deprotection of the styrene derivative was firstly studied on homoPSSi. The PSNO appeared to present a more intense color compared to PTMA and TEMPO, precluding the quantification of the deprotection by UV-vis spectroscopy. According to ESR measurements a maximum of 56 % of deprotection was achieved. The deprotection conditions would therefore need to be optimized in order to reach higher deprotection yields. The PSNO appeared to be less stable than PTMA and some crosslinking was observed in the final polymer. The PTMPM-*b*-PSSi block copolymer was oxidized via mCPBA. Surprisingly, PSSi seems to be deprotected by mCPBA, leading to the PTMA-*b*-PSNO block copolymer. The ESR analysis indicated around 20 % of oxidation/deprotection yield and the UV-vis analysis confirmed the presence of PSNO. Even if the oxidation conditions need to be optimized, an electrochemical active PTMA-*b*-PSNO was obtained.

The electrochemical properties of the homoPSNO and PTMA-b-P-SNO diblock copolymer were investigated by cyclic voltammetry via a three electrodes set-up with a non aqueous Ag/Ag⁺ reference electrode. The voltammogram revealed a similar redox potential for PTMA and PSNO preventing they distinction in the voltammogram of the block copolymer. However the same potential for both polymer blocks is an advantage since the battery potential will not be disturbed by the presence of the second redox species, i.e. the PSNO.

Finally the formation of PTMA-*b*-PSNO thin films was investigated. A phase separation was observed by AFM without any solvent annealing process. The domains of PTMA were larger than expected due to the presence of homoPTMA swelling the corresponding domains. Even so, the observation of a phase separation without annealing process is a good sign for further self-assembly studies of the PTMA-*b*-PSNO block copolymer. Indeed, with a block copolymer without homoPTMA contamination and by applying the good solvent annealing conditions, a phase separation with a well defined cylindrical morphology could be expected.

Experimental part

Material

2-methyl-2-nitrosopropane dimer (Aldrich) and tert-butyllitium (1.7 M in pentane; Aldrich) were stored at -30 °C before use. tert-Butyldimethylchlorosilane (TCI, > 98.0 %) was stored in a dry desiccator before use. Tetrakis(triphenylphosphine) palladium(0) (Aldrich > 99 %) was recrystallized into cold methanol before use. Tosyl chloride (TsCl, Fluka, 99%) was purified by recrystallization into hexane before use. Copper bromide (I) (CuBr (I), Acros Organics, 98%) and copper chloride (I) (CuCl (I), Acros Organics, 99 %) were kept into a dessicator under reduced pressure. Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %) was distilled before use. 1,4-dibromobenzene (Aldrich, 98 %), imidazole (Acros Organics, 99 %), tributyl(vinyl)tin (Aldrich, 97 %), ethyl-2-bromoisobutyrate (EBiB, Acros Organics, 98 %), 2,2,6,6-tetramethyl-4-piperidyle methacrylate (TMPM, TCI, > 98 %), anisole (Acros Organics, 99 %), hexane (C_6H_{12} , VWR, AnalaR NORMAPUR 99 %), methanol (VWR, AnalaR NORMAPUR 99%), dichloromethane (VWR, AnalaR NORMAPUR 99 %), neutral alumina (Al₂O₃, Acros Organics), copper powder (0) (Acros Organics, 99 %, powder, max. 106 μ m) and all other chemicals were use as received.

Instrumentation

¹H RMN analysis were realized by a 300 MHz (Bruker Avance II) and 500 MHz (Bruker Avance) spectrometer. All NMR analysis were performed in CDCl₃ (Aldrich, 99,8 %). All \bar{M}_n (SEC) and dispersities (D) were measured by size exclusion chromatography Agilent equipped with a Agilent 1100/1200 pump (T = 25 °C; eluant : chloroform / triethylamine / isopropanol (94 : 4 : 2) ; elution rate : 1 mL min⁻¹) a differential refractometer Agilent and two columns PSS SDV (10 μ m beads; column 1 porosity : 10000 Å; column 2 porosity : 1000 Å) and calibrated with polystyrene standards. UV measurements were performed on a spectrophotometer Varian (Cary, 50 Conc). Electron spin resonance (ESR) spectra were acquired on an EMXmicro CW-EPR spectrometer (Bruker, Germany) from powdered samples. The SpinCountTM software module was used for quantitative experiments. CV measurements were performed on an Arbin, BT-2043 (scan rate : 0.1 mV s⁻¹).

Monomer synthesis

Bromo-4-[*tert*-butyl-*N*-hydroxylamino]aniline (2)

Tert-butyl lithium (40 mL, 68.5 mmol, 1.7 M in hexane; 2 equiv.) was added dropwise at -78 °C to a solution of *p*-dibromobenzene (8,034 g, 34 mmol; 1 equiv.) in Et₂O (200 mL). The reaction mixture was stirred for 15 min at low temperature then gradually warmed to room temperature. The solution was again cooled to -78 °C and a solution of 2-methyl-2-nitrosopropane dimer (2.96 g, 17 mmol; 0.5 equiv.) in dry Et₂O (40 mL) was added slowly. The mixture was then stirred for 2 h at room temperature before a saturated aqueous solution of NH₄Cl was added. The organic layer was separated, dried over MgSO₄ and the solvents removed in vacuum. The resulting residue was washed with cold hexane and the resulting solid was purified by chromatography over silica gel by using hexane / Et₂O (5:1) as eluant to obtain (2) (6.2g; 25.5 mmol; 75 % yield) as a white powder. ¹H NMR (300 Mhz, CDCl₃, δ): 7.35 (a, duet, J(H,H) = 6 Hz, 2H, Ph), 7.09 (b, doublet, J(H,H) = 6 Hz, 2H, Ph), 6.51 (c, singlet, 1H, OH) 1.09 (d, singlet, 9H, tBu).



4-[*N-tert*-Butyl-*N*-(*tert*-butyldimethylsilyloxy) amino] bromobenzene (3)

Imidazole (6.1 g, 90 mmol; 3.2 equiv.) and tert-butylchlorodimethylsilane (12.6 g, 83.6 mmol; 3 equiv.) were added to a solution of 1 (6.84 g, 28 mmol) in dry DMF (15 mL), and the reaction mixture was stirred at 60 °C for 24 h. After cooling and addition of H₂O (20 mL) the organic layer was extracted with hexane, dried over MgSO₄ and the solvent removed in vacuo. The residue was purified by chromatography over silica gel by using hexane as eluant to obtain (3) as a colorless oil (9.5g, 95 %). ¹H NMR (300 Mhz, CDCl₃, δ): 7.345 (a, duet, J(H,H)= 6 Hz, 2H, Ph), 7.11 (b, duet, J(H,H) = 6 Hz, 2H, Ph), 1.07 (c, singlet, 9H, tBu), 0.89 (d, singlet, 9H, tBu), -0.13 (e, broad, 6H, CH3).



4-[*N-tert*-Butyl-*N*-(*tert*-butyldimethylsilyloxy) amino] styrene (4)

To a toluene solution (200 mL) of 4-[N-tert-butyl-N-(tert-butyldimethylsilyloxy)amino|bromobenzene (3) (15 g; 41.9 mmol; 1 equiv.) were added tetrakis(triphenylphosphine)palladium(0) (595 mg; 0.51 mmol; 0.012 equiv.), and tributyl(vinyl)tin (15 g, 49 mmol; 1.11 equiv.), and the mixture was stirred at 100 °C for 15 h. The reaction mixture was extracted with ether, washed with water, and dried over $MgSO_4$. The crude product was purified by column chromatography over silica gel with hexane as eluant. The resulting oil was purified by column chromatography over alumina with hexane as eluant to afford a colorless oil (8.17 g, yield 64 %).¹H NMR (300 Mhz, CDCl₃, δ): 7.27 (a, duet, J(H,H)) = 6 Hz 2H, Ph), 7.18 (b, duet, J(H,H) = 6 Hz, 2H, Ph), 6.68 (c, duetduet, J(H,H) = 18-11 Hz, 1H, vinyl), 5.68 (d, duet, J(H,H) = 18 Hz, 1H, vinyl), 5.17 (e, duet, J(H,H) = 11 Hz, 1H, vinyl), 1.09 (f, singlet, 9H, N-t-Bu), 0.90 (g, singlet, 9H, t-Bu), -0.13 (h, broad, 6H, SiCH₃). ¹3C NMR (300 Mhz, $CDCl_3$, δ): 150.9, 136.6, 133.9, 125.19, 125.12, 112.5, 61.0, 26.15, 17.9, -4.7. Mass(ESI): m/z = 306.1 [M + M⁺].

PSSi by ATRP

A solution of EBiB (6.8 mg, 0.0349 mmol, 1 equiv.), SSi (4) (3.189 g, 10.4566 mmol, 300 equiv.), PMDETA (6.0 mg, 0.0349 mmol, 1 equiv.), and anisole (2.950 mL, 50 wt%) was degassed three times by freezepump-thaw cycling. The degassed solution was introduced into a Schlenk tube containing CuBr (5 mg, 0.0349 mmol, 1 equiv.) and a magnetic bar. The mixture was degassed by two freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 90 °C for 20 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al_2O_3 (eluant: CH_2Cl_2). The solvent was removed under reduced pressure. No polymer was obtained.

PSSi by RAFT

In a Schlenk tube containing a solution of anisole (0.15 mL), AIBN (0.54 mg, 0.0033 mmol, 1 equiv.), DDMAT (6.1 mg, 0.0167 mmol, 5 equiv.), SSi (4) (500 mg, 1.64 mmol, 500 equiv.) and a magnetic bar were added. The solution was degassed by three freeze-pump-thaw cycles, filled with argon and stirred for 48 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al_2O_3 (eluant: CH_2Cl_2). The solvent was removed under reduced pressure. No polymer was obtained.

PTMPM by Cu⁰-RDRP

A solution of benzyl 2-bromoisobutyrate (BnBIB) (87.8 μ L, 0.5 mmol, 1 equiv.), TMPM (4 g, 17.7 mmol, 34 equiv.), PMDETA (130 µl, 0.062 mmol, 0.12 equiv.), CuBr₂ (5.5 mg, 0.025 mmol, 0.05 equiv.), isopropanol (9 mL, 65 wt%) and a magnetic bar surrounded with 5 cm of Cu (0) wire was degassed three times by freeze-pump-thaw cycling, filled with argon and stirred in an oil bath at 40 °C for 10 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al_2O_3 (eluant: CH_2Cl_2). The solvent was removed under reduced pressure. The residue was precipitated twice in hexane, filtered and dried in vacuum at 35 °C over night, affording a white solid (3,2 g, 80 % yield, \bar{M}_n (NMR)= 10,800, $\bar{D} = 1.14$). ¹H NMR (300 Mhz, CDCl₃, δ): 7.45 (a, multiplet, 2H, Ph chain-end), 7.34 (b, multiplet, 2H, Ph chain-end), 5.28 (c, singlet, 2 H, CH₂ chain-end), 5.05 (d, broad, 1H, CH-O), 2.05-1.51 (e, broad, 15 H; $CH_3 + CH_3$ backbone), 1.51–0.80 (f, broad, 6H; $CH_2 +$ CH_2 backbone).



PSSi by Cu⁰-RDRP

In a Schlenk tube containing a DMF solution (3.04 mL, 35 wt%), Cu(0) powder (5,56 mg, 0,0875 mmol, 1 equiv.), PMDETA (21,92 μ l,

0,1050 mmol, 1.2 equiv.), methyl 2-bromopropionate (9.8 μ l, 0,0875 mmol, 1 equiv.), styrene derivative (4) (1868,2 mg, 6,1253 mmol, 70 equiv.) and a magnetic bar were added. The solution was degassed by three freeze-pump-thaw cycles, filled with argon and stirred for 22 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al₂O₃ (eluant: CH₂Cl₂). The solvent was removed under reduced pressure. The residue was precipitated twice in methanol, filtered and dried in vacuo at 30 °C over night, affording a white solid ($\bar{M}_n = 40,500 \text{ g mol}^{-1}$; $\bar{D} = 4.2$). ¹H NMR (300 Mhz, CDCl₃, δ): 6.87 (a, broad, 2H, Ph), 6.31 (b, broad, 2H, Ph), 1.79 (c, broad, 1H, CHCH₂), 1.28 (d, broad, 2H, CHCH₂), 1.02 (e, singlet, 9H, N-tBu), 0.9 (f, singlet, 9H, t-Bu), 0.3 to -1 (g, broad, 6H, SiCH₃).



PTMPM-*b*-PSSi by Cu⁰-RDRP

In a Schlenk tube containing a DMF solution (0.521 mL, 35 wt%), Cu(0) powder (1.9 mg, 0,0299 mmol, 1 equiv.), PMDETA (7.49 μ l, 0,0359 mmol, 1.2 equiv.), PTMPM-Br (325 mg, 0,0299 mmol, 1 equiv.), SSi (4) (913.6 mg, 2.9902 mmol, 100 equiv.) and a magnetic bar were added. The solution was degassed by three freeze-pump-thaw cycles, filled with argon and stirred for 22 h. The polymerization was quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over neutral Al₂O₃ (eluant: CH₂Cl₂). The solvent was removed under reduced pressure. The residue was precipitated twice in methanol, filtered and dried in vacuo, affording a white solid (\bar{M}_n (SEC) = 89,300 g mol⁻¹; \bar{D} = 2.32). ¹H NMR (300 Mhz, CDCl₃, δ): 7.7-5.6 (a, broad, 4H, aromatics), 5.2-4.8 (b, broad, 1H, CH-O PTMPM), 2.33-0.3 (c, broad, CH₃ PTMPM + CH₂ PTMPM + backbone (PSSi + PTMPM) + t-Bu PSSi), 0.3-(-1.2) (d, broad, SiCH₃).



Typical procedure for the deprotection of PSSi

To a THF solution (125 mL) of the precursor polymer PSSi (300 mg, 1.64 mmol, 1 equiv.) was added tetrabutylammonium fluoride 1M (2.76 mL, 4.52 mmol, 2.8 equiv.), and the mixture was stirred for 3 h at room temperature. Then, silver oxide (0.378 g, 1.64 mmol, 1 equiv.) was added to the solution, and the mixture was vigorously stirred for 2 h at 0 °C. The oxidizing agent was removed by filtration, and the filtrate was poured into methanol to yield the radical polymer PSNO as an orange powder (Yield: 50 %, \bar{M}_n (SEC) = 13,000 g mol⁻¹; D = 6.1). IR (cm⁻¹) : 2958, 2927 (v Ph-H), 2856 (v methyl C-H), 1357 (v t-Bu C-H), 1247 (Si-CH₃), 1195 (v Si-O).

Electrochemical measurements

UV crosslinking

PTMA-b-PSNO thin films on ITO substrates were placed under three Rayonet photochemical reactor UV lamp emitting at 253 nm during 30 min. The distance to the lamps was of about 3 cm.

Preparation of Ag/Ag^+ non-aqueous reference electrode

A non-aqueous Ag/Ag^+ reference electrode with porous Teflon tip was filled with a solution composed of 0.01 M AgNO₃ and 1 M TBAClO₄ in CH₂Cl₂.

Typical procedure for cyclic voltammetry in solution

The analyzed component was dissolved into the electrolyte solution $(1 \text{ M TBAClO}_4 \text{ in CH}_2\text{Cl}_2)$ in order to obtain a 0.1 M solution. A three electrodes set-up with a Pt disk working electrode, a Pt wire counter electrode and the previously prepared Ag/Ag⁺ reference electrode was used to record the voltammogram.
Typical procedure for electrochemical characterisation of PT-MA-b-PS thin film onto ITO substrates

Cyclic voltammetry was performed using a three electrodes system with the PTMA-*b*-PSNO thin film deposited onto an ITO substrate as working electrode, a Pt wire as counter electrode and the previously prepared Ag/Ag^+ reference electrode into 1 M TBAClO₄ in CH₂Cl₂ solution electrolyte.

Thin film preparation

Spin coating

Polymer thin films were spin-coated onto silicon chips or ITO substrates of 1 cm^2 for AFM imaging. Silicon wafers were sonicated 15 min in acetone, rinsed with milli-Q water, washed 30 min in piranha solution (3:1 of H₂SO₄ 98%/H₂O₂ 30% solution) and rinsed in milli-Q water. The substrates were dried by spin-coating at a rotation rate at 2000 rpm during 20 s. ITO substrates of 1 cm2 were washed 15 min in acetone and dried by spin coating at a rotation rate at 2000 rpm during 20 s. Filtered (0.2 µm PTFE) polymer solutions (10 mg of polymer per 1 mL of THF) were spin-coated at a rate of 2000 rpm during 40 s.

General procedure for the determination of the nano-domains sizes

The size of domains was measured using section tool of Nanoscope Analysis software.

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CHAPTER 8

Conclusions and perspectives



Figure 8.1: Graphical representation of the work performed in this thesis.

This thesis was devoted to the development of nanostructured organic radical polymers. The Chapter 1 was divided into two parts, presenting the general concepts needed for the comprehension of this work. The first part focused on the synthesis of block copolymers and their selfassembly properties in solution and in bulk. The second part presented a short survey about the development of batteries and introduced a new generation of batteries based on organic materials. The Chapter 2 was dedicated to the recent development of organic radical batteries, one of the three major class of organic batteries. The chapter provided an overview of the different stable radical bearing polymers employed for the fabrication of organic electrodes. Indeed, the aim of our work was the development of a new generation of organic radical battery combining the redox properties of selected polymers with the phase separation properties of block copolymers, as explained in Chapter 3.

The attention was firstly focused onto the synthesis of nitroxide containing block copolymers (Chapter 4). The two constituting blocks are PTMA, an electrochemically active polymer, and PS, utilized as an insoluble anchor and as a mechanically reinforced block towards battery electrolyte. The electrochemically active PTMA-b-PS block copolymer was obtained via a three steps synthesis. Starting by the polymerization of a precursor of PTMA, i.e. TMPM, by ATRP. Indeed, controlled radical polymerization cannot be employed to polymerize nitroxide bearing monomers. The obtained PTMPM was next used as macroinitiator for the polymerization of styrene by ATRP. Finally, the PTMPM was oxidized into PTMA using mCPBA as oxidizing agent. The polymerization of TMPM by ATRP was challenging since methacrylates tend to polymerize in a few minutes, preventing any control over the polymerization. However, well defined PTMPM with low dispersities were finally obtained, opening the access to PTMPM-b-PS block copolymers. The length of the constituting blocks needed to be adjusted as a function of the targeted application. For the fabrication of thin films a weight ratio around 30 % of PTMA was desired in order to obtain cylinders of PTMA inside a matrix of polystyrene, whereas for micelles the opposite ratio was wanted in order to maximize the amount of electrochemical active material. The polymerization conditions were therefore optimized as a function of the targeted application. PTMPM-b-PS block copolymers were next oxidized into PTMA-b-PS by mCPBA. Oxidation yields up to 95~% were obtained. However the oxidation yield was sometime as low as 50 % and further investigations over the oxidation procedure should be performed in order to obtain more reproducible results. Finally, cycling voltammetry of the block copolymer was performed and confirmed the reversible redox behavior of PTMA and the electrochemical inertness of the PS block. As a summary, bock copolymers with an active PTMA block and an inert PS were successfully polymerized by ATRP. Copolymers with blocks of different lengths were synthesized in order to provide the materials needed for the subsequent self-assembly studies. This work is the first report on a successful controlled ATRP of TMPM. Future work over the polymerization of TMPM by ATRP should explore the limit of the technique by determining the maximum polymer length obtainable by ATRP. Classic ATRP was employed for this work but other polymerization methods for TMPM are also conceivable. In order to reduce the amount of copper for the polymerization, ARGET ATRP could be investigated. e-ATRP could be employed for the polymerization of TMPM followed by an electrochemical oxidation of the secondary amine into nitroxide radicals, leading to an electrochemically generated polymer. Finally, polymerization conditions could be adapted to an initiator attached to a surface in order to form grafted PTMA onto conductive carbons or other conductive materials.

The behavior of PTMA-*b*-PS block copolymers in battery electrolytes, i.e. carbonate mixtures with lithium salts, was next investigated (Chapter 5). PTMA is soluble in battery electrolytes whereas the PS is insoluble, leading to the formation of micelles with a core of PS and a corona of PTMA. This work was the first report of micelles with a nitroxide polymer block located into the corona rather than into the core. In order to maximize the amount of electrochemical active material, block copolymers with around 75 wt% of PTMA were selected. The micelles were characterized by dynamic light scattering and atomic force microscopy revealing micelles with an average radius of 23 nm. The electrochemical characteristics of the micelles were explored in solid state and in liquid systems. The micelles were firstly filtered onto carbon nanotubes buckypaper, forming a solid cathode. The buckypaper micellar cathode presented a good access to the electrolyte through the solvated PTMA coronal chains and a good electrical conductivity to the current collector through the carbon nanotubes network. A lost of capacity was observed after a few cycles, attributed to micelles detaching from the carbon nanotubes.

The micelles were next employed in a redox flow battery. RFBs are very interesting systems employing liquid cathode and anode, i.e. catholyte and anolyte, stored into two separated tanks and pumped through the electrochemical engine. RFBs allow to manage power and capacity separately. Indeed, the capacity of the system is only related to the size of the tank whereas the power depends of the surface of the membrane, making RFBs really interesting for large-scale energy storage. The redox process of classic RFBs is based on the oxydo/reduction of metals such as vanadium or zinc and needs expensive separation ion exchange membranes like Nafion to keep catholyte and anolyte separated. Indeed, the Nafion membrane can represent up to 40 % of the price of the RFB. The replacement of metals by electrochemically active polymers like PTMA allowed the utilization of cheaper size exclusion membranes such as dialysis ones. PTMA-*b*-PS micelles in carbonate mixture $(EC/DEC/DMC, 1:1:1 \text{ in volume with } 0.5 \text{ M } Zn(ClO_4)_2 \cdot (H_2O))$ were employed as catholyte for an hybrid-RFB with a zinc anode. Good electrochemical performances were obtained for our redox flow micellar batteries. In static non pumped experiments, 94 % of discharged capacity and 99 % of coulombic efficiency remained after 1000 cycles. Future development of micellar cathodes should focus onto increasing the critical micellar concentration of our system. Indeed, the limited solubility of the micelles into the electrolyte limited the maximum capacity of the system. The solubility of the micelles could be increased either by changing the length of the constituting blocks or the carbonate mixture used as electrolyte. Moreover, it is interesting to determine the minimum length of PS block needed to obtain the micelles. The PS is electrochemically inactive and decreasing its size will increase the gravimetric capacity of the micelles. The micelles could also be employed for the formation of PTMA gels. Indeed, the electrochemical active material needs to swell into the electrolyte to optimize the accessibility of the redox functions while the dissolution of the polymer into the electrolyte needs to be avoided. A polymer gel could fulfil these requirements. Other applications of stable nitroxides such as TEMPO and PTMA are catalytic oxidation of primary and secondary alcohols and ESR imaging. The PTMA micelles could be employed for both of these applications. Indeed, for catalysis, the micelles can be easily removed from the reaction medium after reaction by dialysis or filtration.

The fabrication of solid nanostructured organic radical cathodes was investigated in parallel. The objective was to create a thin nanostructured cathode combining the self-assembly properties of block copolymers in thin films and the redox properties of PTMA. Block copolymers with a PTMA block representing between 18 to 45 % of the polymer weight were used for the self-assembly study (Chapter 6). Thin films with a thickness of 80 nm were deposited onto silicon wafers by spincoating. The surface of the films was observed by AFM. Due to a lack of phase separation after spin-coating, annealing of the polymer thin films was investigated. Thermal and rapid thermal annealing revealed to be inefficient to improve the phase separation and were therefore abandoned. Solvent annealing into different solvent vapors was studied. The choice of the solvent appeared to be a crucial parameter in order to ameliorate the phase separation inside the polymer film. Different domain orientation, e.g. domains parallel or perpendicular to the surface, were observed depending on the solvent selected for the annealing. The best

phase separation was obtained with a mixture of DMF and DEC vapors. Another essential parameter was the annealing time and an optimum of 6 h of annealing was found for our system. Different morphologies from spherical to lamellar were observed depending on the PTMA ratio in the block copolymer. The targeted cylindrical morphology with cylinders perpendicular to the surface was obtained for block copolymers with 23 wt% of PTMA, annealed 6h into DMF and DEC vapors. The electrochemical performances of the thin films were investigated revealing a stable capacity over cycling. Further work on PTMA-b-PS thin films should investigate the internal structure of the films by combining thin film sectioning methods, such as microtomy, and microscopy techniques such as SEM or TEM. Moreover, it would be interesting to investigate if the electrochemical performances of the films are dependent of the nanodomain structure or the film thickness.

The formation fo PTMA-*b*-PS thin film cathodes is a first step for the fabrication of thin solid batteries (thinner than 0.5 μ m) created by superposing the different constituents, as illustrated in Figure 8.2. As a first experimentation to reach this goal, a film of PEO-b-PS was deposited onto a PTMA-b-PS thin film (Figure 8.3). The film of PTMA-b-PS was solvent annealed and UV-crosslinked before spin-coating the PEO-b-PS thin film. Finally, a solvent annealing of the superposed films allowed to promote the phase separation of the PEO-b-PS. Indeed, PEO is known to act as solid electrolyte. However, PEO tends to crystallize, decreasing its ionic conductivity.^[1] A PEO-*b*-PS thin film with cylinders of PEO inside the matrix of PS could overcome this limitation by preventing the crystallization via confinement effects. Such layered systems need section imaging in order to check if the PEO domains cross the entire film and align with the PTMA domains. Moreover, electrochemical analysis of such superposed thin films would be a challenging task due to the thickness of the constituents. The phase separation of the PTMA-b-PS could be ameliorated by depositing the film onto a PEO-b-PS thin film which could act as a nanopatterned surface, orientating the phase separation of the PTMA-b-PS. Finally, the PS block could be switched for another block such as an ion conducting block or a doping element, offering a synergy with PTMA. For example the PS could be replaced by a polymer like PEO, increasing the ionic conductivity inside the nanostructured cathode.

As for micelles, block copolymer thin films with nitroxide functions could be employed for the catalytic oxidation of alcohol by swelling the PTMA domains with homoPTMA. After washing of the film, the homoPTMA will be removed, creating an interstitial porosity. The film could be used as catalytic membrane for the oxidation of alcohols by passing the reaction medium through the porous thin film.



Figure 8.2: Schematic representation of a possible nanostructured thin half cell battery made by successive deposition of thin films. The use of block copolymer thin films should allow the creation of a full micro battery, thinner than 0.5 μ m.



Figure 8.3: AFM height images $(1.0 \times 1.0 \ \mu m^2)$ of PS-*b*-PEO (b) annealed 4h into benzene (L), deposited onto PTMA-*b*-PS thin film annealed 6h with DMF (L) and DEC (M) (a). The PTMA-*b*-PS thin film was irradiated 45 min with UV light (253 nm) prior spin-coating of the PS-*b*-PEO thin film.

The last chapter focused onto the replacement of the electrochemical inactive PS block by an active one (Chapter 7). A styrene derivative monomer bearing a protected nitroxide function (SSi) was therefore synthesized and its polymerization was investigated. PSSi was firstly obtained by free radical polymerization. The controlled radical polymerization of this monomer was more challenging than expected. Indeed, ATRP and RAFT appeared to be inefficient to polymerize the monomer due to the presence of side reactions. The protected nitroxide was degraded during the polymerization due to the high temperature employed for the reaction. Therefore, a polymerization method working at room temperature was employed, i.e. Cu⁰-RDRP. PSSi were obtained. However, this reaction didn't allowed a perfect control over the polymerization and needs further investigations. Despite that, Cu⁰-RDRP allowed the formation of PTMPM-b-PSSi block copolymers by initiating the polymerization from a PTMPM-Br macroinitiator. The PTMPM-Br was synthesized either by ATRP or Cu⁰-RDRP. The block copolymer was reacted with mCPBA and PSSi appeared to be deprotected during the reaction. This is the first report of the deprotection of protected nitroxide by mCPBA. Even so, with only 20 % of active nitroxide inside the polymer, the deprotection/oxidation of the block copolymer still needs some optimizations. A thin film with domains of PTMA inside a matrix of PSNO was obtained. Cyclic voltammetry of the film revealed one unique peak at 0.31 V vs Fc/Fc⁺. Indeed, PTMA and PSNO present the same reduction potential allowing the formation of a cathode with an unique working potential. During the experiments, PSNO appeared to undergo self-crosslinking, leading to insoluble materials. This crosslinking reaction was tentatively attributed to the nitroxide reacting with the PS backbone. Further investigations should be performed in order to understand and control this side reaction. Indeed, the self-crosslinking of the PSNO could be exploited to generate auto-crosslinked thin films after spin coating or micelles with a reticulated core. The replacement of PS by another block was a first approach demonstrating the possibility to make a synergy between the constituting blocks.

To conclude, PTMA and in more general stable nitroxide bearing polymers have attracted a great interest over the past decade. Indeed, rare inorganic elements can be replaced by organic ones. Moreover they allow a fast charge/discharge process compared to their inorganic counterpart. PTMA has essentially been studied in mixtures with additives such as conductive carbons. This thesis highlights the first study of nanostructured organic radical cathodes, combining the advantages of PTMA with the typical characteristics of block copolymers. Polymer chemistry offers an infinity of building blocks and therefore a limitless number of possibilities for the fabrication of innovative materials. This work brings the foundations of a new class of organic batteries, named nanostructured organic radical batteries, and is a first approach toward a miniaturization of the batteries for applications such as microbotics or microelectromechanical systems (MEMs).

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