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Blends made from *N*-salicylidene aniline sulfonate derivatives and a polyampholyte matrix: *in situ* synthesis *vs.* solution mixing†

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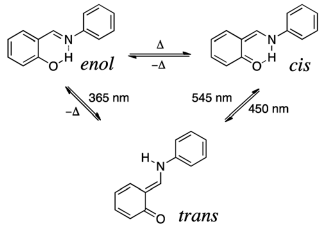
Blend materials were prepared by the insertion of *N*-salicylidene aniline sulfonate derivatives inside an ampholyte polymer matrix. In addition to a classic insertion method based on homogeneous solution mixing, a new methodology was developed. The *in situ* synthesis of guest molecules inside the polymer taking advantages of the ionic nature of the dyes/matrix components is used for the first time for the preparation of blend materials with anionic anils. This method allows a strong electrostatic anchorage of the anion to the host matrix. Insertion occurs without perturbing the lamellar organization of the host polymer matrix. Infrared and diffuse reflectance UV-vis spectroscopies were implemented to investigate the host–guest interactions and an insertion model was drawn.

Introduction

Hybrids resulting from the association of organic/inorganic components at the nano/microscopic level offer numerous opportunities to combine various chemical/physical properties.[1] Various ways of producing hybrid materials exist depending on the selected host matrix,[2] and among these, organic polymers are widely used.[3] The use of molecular switches as guest molecules in hybrid materials is applicable to sensor applications,[4] due to their thermo- and photo-responsive properties.[5] Numerous studies have been carried out on spiropyran derivatives,[6–9] which display a photo-induced colour change due to ring closure or opening. Their photochromism is effective both in solution and in the solid state,[10] and these molecules can be introduced into a host network through insertion[8] or directly by functionalization.[7] However, their low stability and weak fatigue resistance upon cycling represent a major drawback.[11] An alternative to spiropyrans is given by *N*-salicylidene aniline derivatives for which extensive investigations have been undertaken recently.[12,13] Thermochromism is associated with the thermal tautomeric equilibrium occurring between the yellow *cis*-keto form at 298 K and the white enol form at 77 K (Scheme 1). Photoisomerization allows the conversion of *cis*-keto or enol forms into the metastable red *trans*-keto form upon irradiation at 365 nm or 450 nm, respectively (Scheme 1), which leads to photochromism.[14] Several studies have demonstrated the importance of both crystal structure and local surrounding of *N*-salicylidene aniline derivatives in their optical properties.[15] Preparation of hybrid materials with such neutral species allows the modification of the guest environment and thus of its optical properties. Two classes of hybrids can be distinguished according to their preparation method: (i) by insertion of anils into an organised matrix,[16–22] (ii) by mixing anils with a non-ordered polymer.[23,24] Insertion of neutral anil molecules into inorganic networks such as zeolites,[18,21] MCM-41,[19,22] or porous clathrates[16,17] was shown to induce photochromism in non-photochromic guest molecules. This results from both conformational changes of the guest molecules and the modification of the stability of their prototropic forms, leading to the stabilization of the zwitterionic form of *N*-salicylidene aniline derivatives. The photochemical pathway responsible for the *trans*-keto formation is then modified, which is detected in non-photochromic derivatives. In a disorganised neutral polymer such as polyethylene, no changes in energy levels were observed but the modifications of the direct environment provoke a photochromism loss.[24,25] Usually, the *trans*-keto form is metastable and thermal



Scheme 1 Thermo- and photoinduced equilibria of *N*-salicylidene aniline derivatives.

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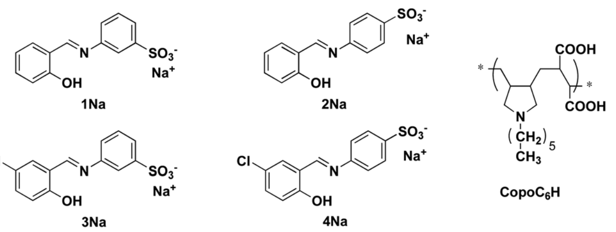


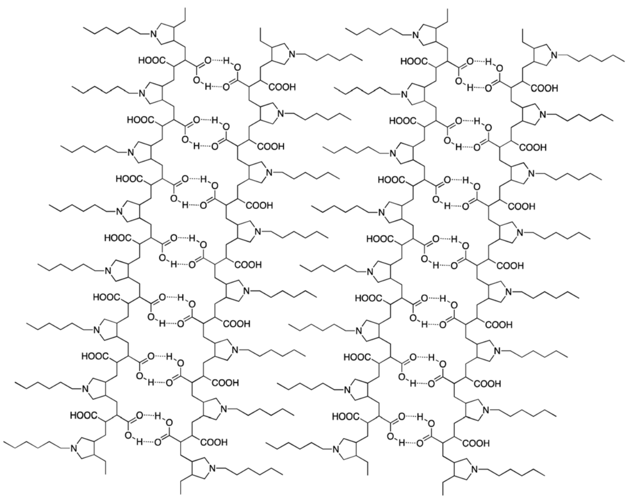
Scheme 2 List of guest molecules (**1Na** to **4Na**) and poly(*N*,*N*-diallylhexylamine-*alt*-maleic acid) matrix (**CopoC$_6$H**).

relaxation to the *cis*-keto form starts directly after its formation.[12b] However, the modification of the local environment reduces the activation energy between *trans*- and *cis*-keto forms and favours the *trans*-keto form instability, cancelling thereby photochromism.[12b]

In this work, an organic polymer, poly(*N*,*N*-diallylhexylamine-*alt*-maleic acid), denoted as **CopoC$_6$H** (Scheme 2), was obtained by a radical copolymerization between a substituted diallylamine and maleic acid,[26] and selected as a host matrix. Because of van der Waals interactions between lateral alkyl chains and hydrogen bonds between carboxylic acids, this polymer is known to feature a lamellar superstructure[26b,27] (Scheme 3), which was used to produce hybrid inorganic–organic materials.[28]

The matrix also behaves as an ampholyte with a global charge dependent on pH conditions: the polymer can be either positively (once or twice) or negatively charged, or be in its zwitterionic state. The polymer charge can thus be tuned in order to favour electrostatic interactions during the insertion of various guest molecules.[4]

Sodium salts of *N*-salicylidene aniline sulfonate derivatives (**1Na** to **4Na** in Scheme 2) were chosen as guest anions for their thermochromic properties, high thermal stability (over 300 °C) and the presence of a permanent charge due to the sulfonate group.[29] These guest molecules were inserted inside the zwitterionic form of the **CopoC$_6$H** matrix either by mixing (m*n*, n = 1–4) or by *in situ* synthesis (i*n*, $n = 1$–4). The *in situ* synthesis represents a novel way to produce blends, taking advantage of the anionic nature of *N*-salicylidene aniline sulfonate derivatives. The origin of the interactions at the interface between the host matrix and the guest molecules, and their impact on the structural and functional properties of both components is discussed, along with an insertion model.



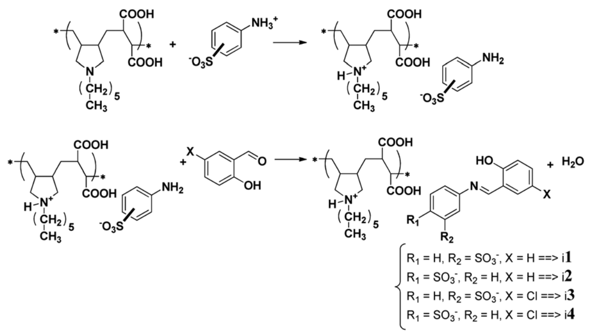
Scheme 3 Lamellar organization model of CopoC$_6$H.

Synthesis

The guest anionic derivatives used in this work are listed in Scheme 2. Two different methodologies were developed to prepare the blends: (i) sodium salts of *N*-salicylidene aniline sulfonate derivatives (**1Na** to **4Na**) were mixed with the amphiphilic matrix (**CopoC$_6$H**) in a methanolic solution; (ii) anions were synthesized within the polymer matrix. The stoichiometry of the insertion is described by the molar ratio between the amounts of anion and the repetitive unit of the copolymer.

For blends of the first series (mixing), methanolic solutions of both the polymer and sodium *N*-salicylidene aniline sulfonate derivatives were prepared and mixed together for 24 h at 25 °C. Afterwards, the solvent was removed under vacuum. All series of blends were prepared by mixing 0.05 up to 2.0 molar equiv. of sodium salicylidene aniline sulfonate salt (**1Na** to **4Na**) per repetitive unit of **CopoC$_6$H.**

In situ synthesis of anions is adapted from the synthesis of sodium salts of *N*-salicylidene aniline sulfonate derivatives[13,29,30] (Scheme 4). In a round bottom flask at room temperature, 1.5 molar equiv. of aminobenzene sulfonic acid are added to a methanolic solution of the polymer under vigorous stirring. Stirring is maintained until most of the suspension cleared (3 h for 4-aminobenzene sulfonic acid and 5 h for 3-aminobenzene sulfonic acid). The solution is then filtered out to remove the excess of sulfonic acid and one equiv. of aldehyde is added to the filtrate. The reaction is followed by ^{1}H-NMR until no more imine is formed; the solvent is then removed under vacuum. The excess of salicylaldehyde is removed by cycles of suspension of the product in dichloromethane using an ultrasonic bath followed by removal of the solvent. The different compounds (**i1** to **i4**) were obtained with good purity. The amount of anion inside the polymer matrix is approximately 0.4 equiv. of anion per repetitive unit of polymer.



Scheme 4 *In situ* synthesis of **i1** to **i4**.

Structural characteristics of blends

Powder X-ray diffractometry (PXRD) allows the study of the structural organization of the blends. On one hand, the polymer matrix presents a lamellar organization deduced from a diffraction peak in the small angle area at 4.8° (Fig. 1).[28]

The corresponding Bragg distance of 1.95 nm reflects the interchain distance of the lamellar organization of the polymer. As stressed above, this organization is due to various H-bonds between carboxylic groups and van der Waals interactions between lateral alkyl chains. On the other hand, salicylidene aniline sulfonate derivatives present significant crystallinity (Fig. 2). The change in structural characteristics of both guest molecules and host matrix is useful to determine the success of the hybridization process, the materials being only considered as true blends when they are homogeneous.

Every material of each family from the first series (mixing) was studied by PXRD in order to check its homogeneity. The insertion limit was defined as the ratio between the amount of anion and the polymer repetitive unit above which crystalline peaks of the guest molecules start to appear. This limit is found to be the same independent of the inserted salt (between 0.45 and 0.55 moles of guest anion inserted per repetitive unit of polymer, Table 1).

In the homogeneous region, a characteristic Bragg distance was calculated from the position of the diffraction peak at small angles corresponding to the host matrix organization. The insertion of guest molecules has, within the precision of the analysis, no influence on the structural properties of the host matrix, in none of the cases studied. Above the insertion limit, the diffractograms correspond to the ones of the guest molecule because the diffraction lines of the blends are masked by the more intense lines of the guest (Fig. 3 and Fig. S1–S3†). For the anions synthesized within the polymer following the *in situ* method, the diffractograms present the same interchain distance as the blends prepared by mixing. There is no significant modification of the polymer organization and no increase of the interchain distance (Table 2).

The planar character of *N*-salicylidene aniline derivatives may explain the absence of modifications of the polymer organization in the blends. On one hand, the guest anion would be inserted between the successive polymer planes. On the other hand, the cation, which has a small dimension should be located near the inserted anion or in the hydrophilic part of the polymer and its presence does not modify the polymer organization. The planarity of the guest molecule in addition to the small volume of the sodium cation would therefore explain the lack of structure modification for homogeneous materials.

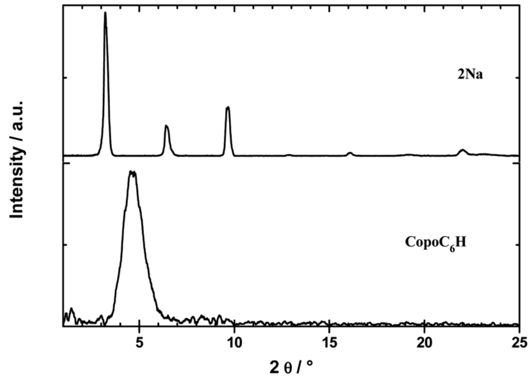


Fig. 1 X-ray powder diffractograms of CopoC$_6$H and 2Na.

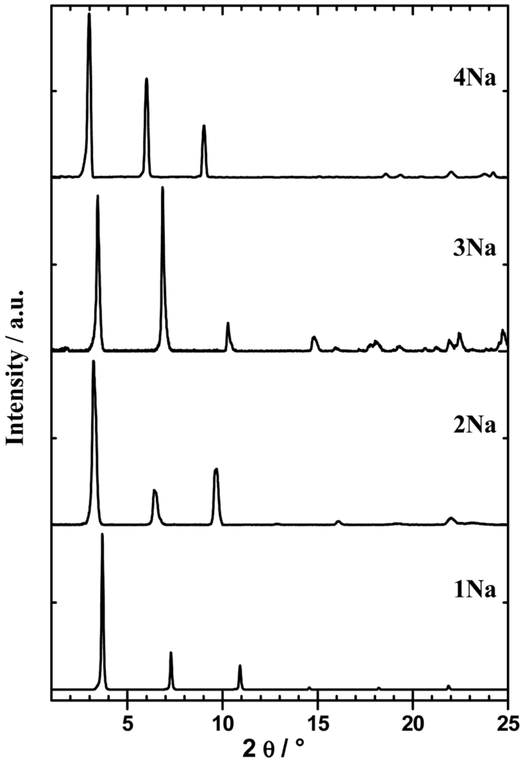


Fig. 2 X-ray powder diffractograms of sodium salts 1Na to 4Na.

Table 1 Insertion limits and selected Bragg distances for blends obtained by the mixing method

Sample	Guest molecule	Insertion limit[a]	d_{Bragg} (nm) below insertion limit	d_{Bragg} (nm) above insertion limit
m1	**1Na**	0.45	1.99 ± 0.16	2.40 ± 0.23[b]
m2	**2Na**	0.45	2.05 ± 0.21	2.77 ± 0.13
m3	**3Na**	0.55	2.04 ± 0.16	2.69 ± 0.12
m4	**4Na**	0.45	1.92 ± 0.13	2.89 ± 0.14

[a] Moles of guest anion per repetitive unit of polymer. [b] Indicative value due to very poor crystallinity.

Infrared spectroscopy

Infrared spectroscopy allows the study of the host–guest interactions through the monitoring of absorption bands related to sulfonate vibrations (from 1200 to 1000 cm^{-1} for the stretching of S=O bonds and from 800 to 600 cm^{-1} for the stretching of S–O$^-$ and C–S bonds).[31] Infrared spectra of sodium salts were

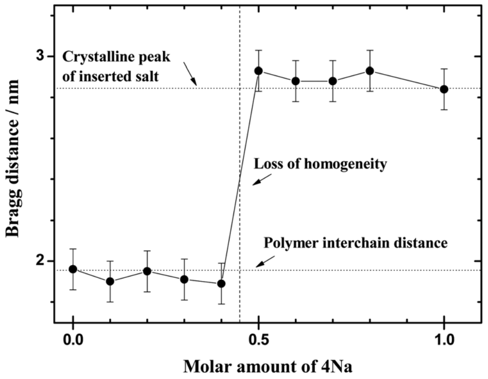


Fig. 3 Evolution of the Bragg distance related to the most intense diffraction peak for **4Na** inserted in **CopoC$_6$H** *vs.* the loading of the host matrix: the loss of homogeneity is defined by the emergence of crystalline peaks of **4Na**.

Table 2 Bragg distances for *in situ* blends and polymer matrix

Sample	Guest anion	d_{Bragg} (nm)
i1	**1**	2.06 ± 0.10
i2	**2**	2.08 ± 0.10
i3	**3**	1.94 ± 0.10
i4	**4**	2.10 ± 0.10
CopoC$_6$H	—	1.98 ± 0.10

compared with those of the anions synthesized inside the polymer matrix through the *in situ* synthesis in order to determine the modifications due to the interactions between the sulfonate and the counter-ion.

The most representative example of modifications of IR spectra is obtained with the blend made by insertion of **2Na** in **CopoC$_6$H**. For **2Na**, the peaks are located at 1134 cm^{-1} (ν_sSO$_2$), 730 cm^{-1} (νS–O$^-$) and 650 cm^{-1} (νC–S) (Fig. 4).

In contrast, the sulfonate function for **i2** is characterized by bands at 1119 cm^{-1} (ν_sSO$_2$), 725 cm^{-1} (νS–O$^-$) and 640 cm^{-1} (νC–S) (Fig. 4). The stretching of S–O$^-$ is located at the same energy for both compounds considering the experimental resolution, but the stretching of O═S═O and C–S are strongly different ($\Delta\bar{\nu}$ = 15 cm^{-1} for ν_sSO$_2$ and 10 cm^{-1} for νC–S); those two vibrations will be used for the comparison between sodium salts, blends obtained by mixing of the guest molecules and the host matrix, as well as by *in situ* synthesis (Table 3).

Between 0.05 and 0.5 equiv. of **2Na** inserted into **CopoC$_6$H**, the sulfonate function presents the same vibrations as **i2** with $\Delta\bar{\nu}$ = 13 cm^{-1} for ν_sSO$_2$ and $\Delta\bar{\nu}$ = 9 cm^{-1} for νC–S. Above the insertion limit and between 0.5 and 1.4 equiv. of anion inserted, the coexistence of two compounds is observed through ν_sSO$_2$ and ν_sCS corresponding to **i2** (at 1120 and 640 cm^{-1}, respectively) and **2Na** (at 1134 and 651 cm^{-1}, respectively), indicating that **2Na** starts to segregate and crystallize independently. After 1.4 equiv., the only molecule detected is **2Na** because the guest molecule is the most abundant in the blend (for 1.4 equiv., 57 wt %) (Fig. 5).

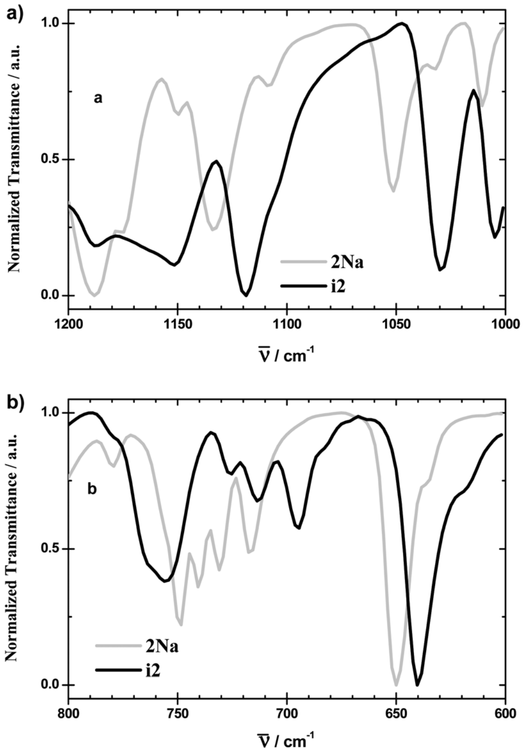


Fig. 4 Comparison between infrared spectra of **2Na** (grey) and **i2** (black) in the area of: (a) SO$_2$ symmetric stretching; (b) SO$^-$ and CS stretching.

Table 3 Comparison of O═S═O symmetric stretching and C–S stretching ($\bar{\nu}$) for sodium salts and stretching differences $\Delta\bar{\nu}$ for the *in situ* method[a]

	ν_sSO$_2$		νCS	
Salt	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	$\bar{\nu}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})
1Na	1120	15	662	7
2Na	1134	15	650	10
3Na	1114	7	628	11
4Na	1134	15	677	8

[a] $\Delta\bar{\nu} = \bar{\nu}_{n\mathrm{Na}} - \bar{\nu}_{in}$.

Similar observations were made for other mixtures (Fig. S4–S6†). In each case (**1Na**, **2Na**, **3Na** and **4Na**) when the anions were inserted inside **CopoC$_6$H**, the interactions between the guest molecule and the host matrix were observed through modifications of ν_sSO$_2$ and ν_sCS.

Optical properties

Diffuse reflectance spectra of *N*-salicylidene aniline derivatives can be divided into three main areas, each one corresponding to one of the three accessible forms. For example, in **4Na**, the enol form gives rise to a band below 400 nm, the *cis*-keto form ranges from 400 to 500 nm, and the *trans*-keto form is located above 500 nm.[12,13]

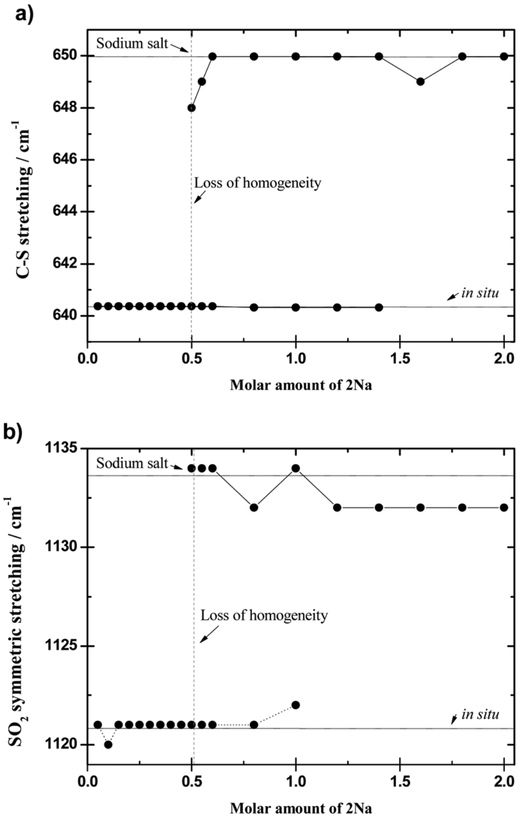


Fig. 5 Evolution of (a) νCS and (b) $\nu_s SO_2$ (right) *vs.* the loading of **2Na** in **CopoC$_6$H**.

Blends obtained *in situ* (from **i1** to **i4**) present similar modifications: the band of the enol form is red-shifted, the *cis*-keto form presents a stronger intensity and a new band is observed above 525 nm, suggesting appearance of the *trans*-keto form (Fig. 6 and Fig. S7–S9†). Interestingly, the *trans*-keto form is stabilized while no photochromic properties of the corresponding blends were observed. Indeed, for *N*-salicylidene aniline derivatives, photochromism leads to a metastable *trans*-keto form which relaxes thermally into the *cis*-keto form. Thus, the change of environment and the subsequent host–guest interactions lead to a modification of the relative stability of the different forms, leading here to the stabilization of a previously metastable form.

Three molecular forms are thus identified in blends obtained by *in situ* synthesis: enol and *cis*–*trans* keto forms, all in equilibrium. The optical properties of blends obtained through mixing of solutions are also modified (Fig. 7, Fig. S10–S11†). Interestingly, these modifications depend on the location of the sulfonate function on the benzene group of the anil (*meta* or *para*). For the insertion of *meta* compounds (**1Na** and **3Na**) inside **CopoC$_6$H**, a blue-shift of the enol band as well as a destabilization of the *cis*-keto form is observed through the intensity decrease of the corresponding band at 450 nm (Fig. 7a). In the case of the insertion of *para* compounds (**2Na** and **4Na**) in **CopoC$_6$H**, a red shift of the band of the enol form is observed as well as the stabilization of the *cis*-keto form (Fig. 7b). All blends display reversible thermochromism on cooling from 293 K to liquid nitrogen temperature.

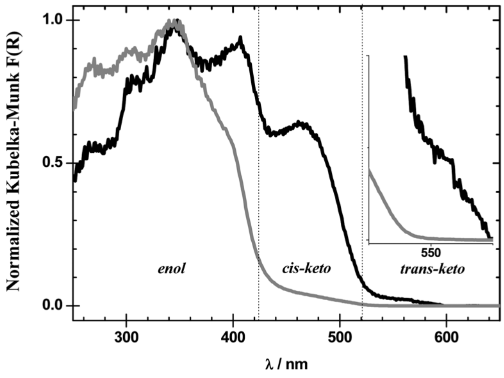


Fig. 6 Diffuse reflectance spectra of **3** (grey) synthesized inside **CopoC$_6$H$_2$$^+$** in comparison to **3Na** (black).

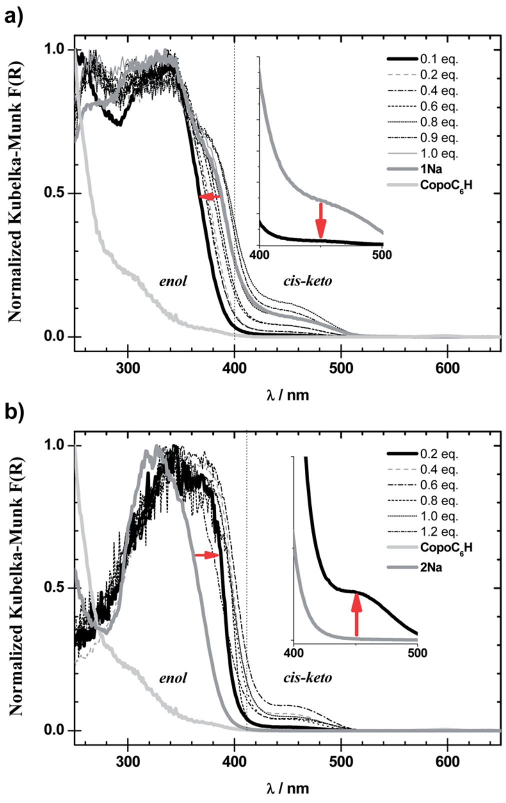
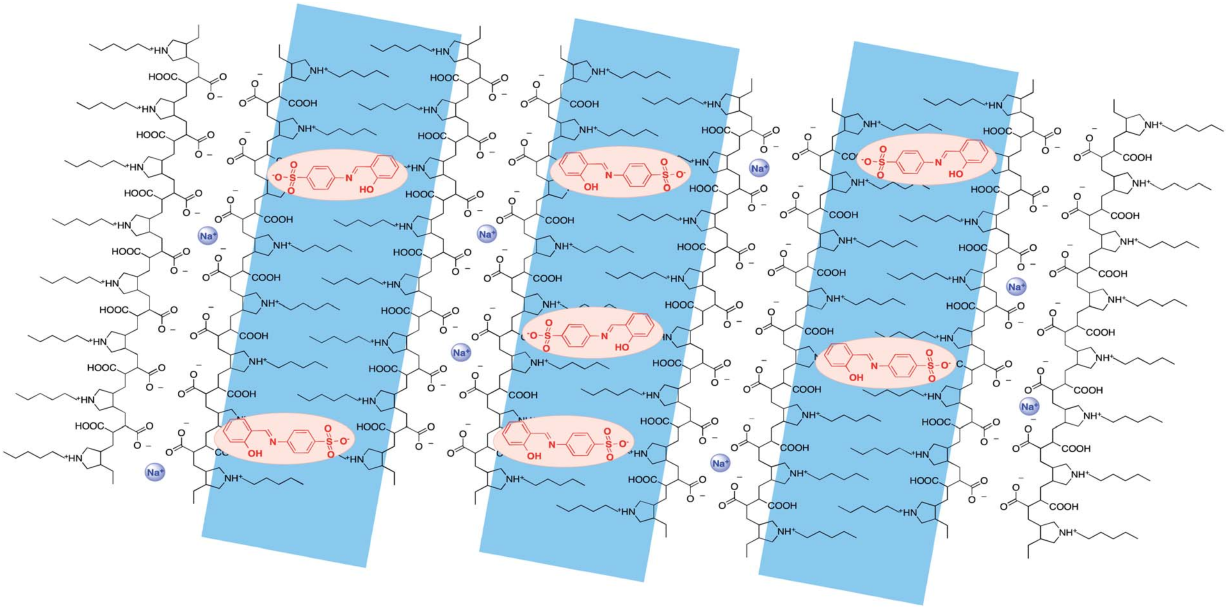


Fig. 7 Evolution of diffuse reflectance spectra of blends obtained by mixing with the loading of (a) **1Na** and (b) **2Na** in **CopoC$_6$H**.

Discussion

In contrast to previous works based on the insertion of neutral *N*-salicylidene derivatives inside a neutral polymer[24,25] or well-defined materials (zeolites, host-crystals,…),[15–22] this study describes a class of blends made of anionic anils inside an organized polymer matrix: sodium salts of anionic salicylidene aniline sulfonate derivatives inside the zwitterionic poly(*N*,*N*-



Scheme 5 Representation model of the insertion of **2Na** inside the **CopoC$_6$H** matrix: the hydrophobic area is highlighted by light blue squares. The planar guest anion **2**, highlighted in red, is inserted between polymer planes and located above the hydrophobic area of the polymer.

diallylhexylamine-*alt*-maleic acid) copolymer. The synthesis of such blends was extended for the first time to the *in situ* synthesis of the guest anions inside the polymer where the ionic interaction was induced by the acid–base reaction occurring during the first step between the aminobenzene sulfonic acid and the polymer (Scheme 4). This method allows a binding of the anil group which differs from previous methods involving covalent bonding.[32] Although the absence or presence of Na ions, according to the solution mixing or *in situ* synthesis, could influence the structural properties, homogeneous materials were successfully obtained up to a certain loading as confirmed by PXRD diffractograms. The interaction was also systematically monitored by infrared spectroscopy. As a result, up to 0.5 molar equiv. of salt could be inserted inside the host matrix by mixing.

Precursor studies dealing with the admixion of charged dyes into polyzwitterions were carried out by Laschewsky *et al.*[33] They report amorphous but homogeneous blends. No obvious correlation between structure and miscibility could however be revealed although the fundamental interaction in such blends is of electrostatic nature, like in our materials.

The anil based materials do not present any photochromism but display modified optical properties as well as thermochromism on cooling. The keto–enol equilibrium was modified for materials prepared by mixing and the *trans*-keto form was stabilized in the *in situ* made materials. Two types of behaviour are observed for blends prepared by the mixing method, the enol/*cis*–keto equilibrium depending on the *para* or *meta* position of the sulfonate function on the aniline part of the guest molecule. When the sulfonate function is in the *para* position (**2Na** and **4Na**), the insertion induces a stabilization of the keto form and the band of the enol form is red-shifted. In contrast, for sulfonate function in the *meta* position (**1Na** and **3Na**), the enol band is blue-shifted and the keto form is destabilized. The same interaction, observed in infrared spectroscopy, is assumed to have a different impact on the stability of the *cis*-keto form because of the sulfonate group position. The sulfonate group has an electron-acceptor behaviour and, depending on its position, its effect on the stability of the *cis*-keto form is different. When the sulfonate is in the *para* position, it destabilizes the keto form in favour of the stabilization of the enol form. The opposite effect is observed when the sulfonate is in the *meta* position, the enol is destabilized and the keto form is promoted. The interaction between the polymer matrix and the guest anion seems to reduce the electron-acceptor behaviour of the sulfonate, which leads to the stabilization of the keto form for *para*-derivatives (**2Na** and **4Na**) with the insertion and the loss of stability of the keto form for *meta*-derivatives.

Changes in optical properties have already been described in other host–guest materials with anils. For instance, the modification of the direct environment of *N*-salicylidene aniline derivatives was reported to lead to a change of the energy levels and relative stability of the different prototropic forms.[15] It was also shown that the insertion of *N*-salicylidene aniline derivatives inside highly structured materials leads to a modification of the geometry of the guest molecule thanks to the structure of the matrix. This insertion allows as well the stabilisation of the zwitterionic form of salicylidene derivatives, which leads to a new photochemical pathway and to photochromism of previously non-photochromic species.[18] For the insertion of non-charged *N*-salicylidene aniline derivatives inside a non-organized polymer, no modification of the structure of the guest molecule was reported (in regard to IR and Raman spectroscopy) but it causes the loss of photochromism.[23,24]

The existence of a stabilized *trans*-keto form without any photochromism may be explained by considering the photochromism of salicylidene aniline derivatives in solution.[34] Three important parameters that regulate photochromism can be considered, namely the viscosity, polarity and protic character of solvents, due to their influence on the stability of the different forms of salicylidene aniline derivatives. Viscosity and polarity influence the lifetime of photochromism in solution: high viscosity and/or high polarity lead to photochromic species with a long lifespan.[35] The protic character of the solvent has however a negative influence on the *trans*-keto stability but is known to improve photochromic occurrence: protic solvents favour intermediates involved in photo-isomerisation.[35] In this work, since blends were prepared using methanol (a polar and protic solvent), photochromic species were expected for blends obtained by *in situ* synthesis. The *trans*-keto form may be obtained in solution and was surprisingly trapped inside the polymer matrix after removal of the solvent. On this basis, the polymer can be considered in a first approximation as a frozen solution in which the *trans*-keto form of guest molecules has been stored.

An insertion model for blends including *N*-salicylidene aniline sulfonate derivatives in interaction with a polyampholytic matrix is proposed (Scheme 5). For blends obtained by mixing below the insertion limit, the salicylidene aniline anion is separated from its sodium counter ion and interacts with the zwitterionic matrix. Above the insertion limit, microcrystals start to form, preventing the homogeneity of the blend. For materials obtained *in situ*, salicylidene sulfonate interacts with the positively charged region of the matrix. The planar and essentially lipophilic guest molecules are inserted between polymer planes, which allows their insertion without any impact on the host matrix organisation.

Conclusions

Two methodologies for the preparation of blends including *N*-salicylidene aniline dyes were described and proved to be successful. The *in situ* synthesis is a promising method for the electrostatic binding of *N*-salicylidene aniline derivatives inside a polymer host matrix. Infrared spectroscopy shows that *N*-salicylidene aniline sulfonate derivatives are electrostatically bounded to the polymer matrix, through the sulfonate group of the guest molecule and the ammonium group of the host matrix. In each material, the polymer organisation is preserved during the insertion and the guest molecules do not interfere with the lamellar organisation. For blends obtained by mixing, the host–guest interactions have a direct impact on the stability of both enol and *cis*-keto forms and thus depend on the position of the sulfonate group in the guest molecule. In *para*-sulfonate compounds (**2Na** and **4Na**), the interaction promotes the *cis*-keto form in contrast to *meta*-sulfonate derivatives where the enol form is stabilized (**1Na** and **3Na**). Moreover, blends obtained *in situ* stabilise the *trans*-keto form in its ground state without featuring photochromic properties. All these considerations lead us to propose an insertion model for this new class of blends.

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