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Second-order nonlinear optical coefficient of polyphosphazene-based materials: A theoretical study

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The second-order nonlinear optical coefficient of polyphosphazene oligomers of increasing size has been determined by using *ab initio* methods taking into account electron correlation and frequency dispersion effects. The calculated first hyperpolarizability per unit cell converges rapidly with respect to chain length. It attains an amplitude of about one-third of the one of classical push–pull systems. This amplitude can be strongly increased by replacing the nitrogen of the backbone by silicon. The effects of the side groups (H, CH_3, F, Cl, Br, and OH) on the first hyperpolarizability have been investigated as well. The different results have been rationalized in terms of alternations of bond lengths and atomic charges. © *2004 American Institute of Physics.*

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I. INTRODUCTION

Polyphosphazene [PP, $\text{-}(PH_2{=}N)_N^-$ where N is the number of unit cells] and its derivative are becoming one of the most important class of polymers due to their wide range of possible applications. Indeed PP could be used in various fields; for example, to build proton-exchange membrane for fuel cells, to deliver drug in a controlled fashion or to design flame retardant materials. We refer the interested reader to the Ref. 1 for a detailed description of the applications of PP as well as significant references.[2] Our focus in the present paper is the nonlinear optical (NLO) properties exhibited by PP and its derivatives. Allcock and co-workers measured experimentally the polarizability (α)[3] and the first hyperpolarizability (β)[4] of PP. It was found that α of PP is of the same order of magnitude as the one of polyenes.[3] β of PP substituted on its sides by chromophore groups was found to be relatively small in the experimental conditions used in Ref. 4. In Ref. 4, a test has also been performed in order to assess the origin of the NLO response (chromophore groups or backbone). It appeared that the skeleton response is negligible. In the present paper, the β of the PP backbone (substitued or not) is investigated with theoretical tools, in order to rationalize the conclusions of Allcock and explore possible ways to increase β by performing various chemical substitutions. As PP is an AB polymer [$\text{-}(A{=}B)_N^-$], i.e., a polymer where all cells are both asymmetric and possess mobile electrons, it could present large NLO responses. Other prototype AB compounds have been studied previously and, depending on the nature of A and B, very different β values have been obtained. In linear boron nitride chains, the quantity of interest (for measuring its efficiency as a NLO molecule), β reported to the size of the chain (β/N) is close to zero for the macromolecule due to a nearly zero bond length alternation ($\Delta r = d_{B-A} - d_{A=B}$) found in long chains.[5] However, another AB polymer, polymethineimine [PMI,$\text{-}(CH{=}N)_N^-$] is much more promising. Indeed, from characterizations carried out at *ab initio* levels taking into account electron correlation (EC) effects, we concluded that PMI presents a β/N value as large as the best α,ω-nitro, amino-PA chains,[6,7] i.e., much larger than classical push–pull compounds. For example, the β/N of PMI is one order of magnitude larger than the β/N reported for the well-known 3-methyl-4-nitroaniline (MNA) monomer[8] or for N-(4-nitrophenyl)-(L)-prolinol (NPP).[9,10] From our investigations, reviewed in Ref. 11, it turns out that, qualitatively, a maximization of β is reached when a "good" equilibrium between (electron) delocalization and asymmetry is obtained. This could be related with previous works of Marder and Brédas on the NLO properties of push–pull molecules.[12] Such delocalizability–asymmetry equilibrium is difficult to attain. Indeed, delocalizability increases generally when asymmetry decreases and *vice versa* but both are needed in order to obtain substantial β values. To rationalize the β of AB chains, β is generally splitted into chain-end and unit cell contributions, both being affected by the delocalizability of the chain. Additionally, the unit cell contribution can be analyzed in terms of nuclear alternation (A versus B) and bond alternation (single vs double bonds).[13] Obviously large nuclear and bond alternations correspond to large asymmetry and small delocalizability; the opposite relation is also true. In the infinite chain limit the chain-ends do not bring any contribution and both nuclear and bond alternations are required to obtain a nonzero β. From model calculations performed on AB polymers,[14] it has been concluded that these

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two alternations have to be quite small in order to obtain a large macromolecular β, i.e., it is preferable to have small asymmetry and large delocalizability rather than the reverse. Nevertheless, if the bond alternation is large, an optimal β is obtained when the nuclear alternation is large as well. This means that when delocalization is small, the larger the asymmetry, the larger the β; whereas when delocalization is important large β prescribes small (but nonzero) asymmetry. In agreement with these findings, a maximization of the β of PMI (in which A and B are quite similar) could be obtained by a decrease of the asymmetry (and an increase of the delocalizability).[15] As the nuclear alternation in PP is strong (the electronegativity difference between P and N is larger than between C and N) and as the presence of an actual double bond in the molecule is questionable[16] (i.e., electrons of PP are not very mobile), it can be expected that delocalizability is the limiting factor of β in unsubstituted PP as in PMI.

To our knowledge, the only previous theoretical investigation of the β of PP, is due to Chandra Jha *et al.*[17] In Ref. 17, the authors used a semiempirical FCI/PPP (full configuration interaction/Pariser–Parr–Pople) approximation to evaluate the properties of short all-trans PP oligomers [from the trimer ($N=3$) to the hexamer ($N=6$)]. In the present paper, the evolution with N of the β of short- and medium-size (up to $N=16$) PP oligomers is investigated by using EC *ab initio* approaches. This allows efficient extrapolation to the polymeric values.

II. COMPUTATIONAL DETAILS

The calculations have been performed by using the following procedure:

1. The ground-state geometry of each oligomer has been determined by optimization of its structural parameters with the GAUSSIAN 98 program.[18] The optimizations have been carried out up to a point where the residual forces are lower than 10^{-5} a.u. The only constraint was to keep the backbone planar (see Sec. III A). These optimizations have been performed within *ab initio* levels of approximation [Hartree–Fock (HF) and second-order Møller–Plesset schemes (MP2)]. After geometry optimization, each oligomer has been oriented in the Cartesian frame such that the longitudinal axis passes through the center of first and last double (P=N) bonds of the skeleton.

2. In quasilinear chains like PP, the longitudinal component of the β tensor (β_L) dominates the total β (Ref. 19) answer for sufficently long chains. For example, for $N=14$ the β_L evaluated at the HF/6-31G*//HF/6-31G* level [the usual convention for describing the computation method is used: Method for evaluating β//scheme for optimizing the geometry] is three times larger than the next larger component. For this reason, we only focus on this longitudinal component in this paper. β_L has been calculated on the optimized geometries with various *ab initio* methods. The vibrational contribution to β (β^v) has not been calculated. β^v could make an important contribution to the total static β values in conjugated systems[7,20,21] but its practical determination at EC level remains difficult for extended oligomers. Moreover, the relative importance of β^v strongly decreases when dynamic β are considered. Indeed, within the harmonic model, β^v is decreased by a factor of three for the optical rectification (OR) and electro-optic dc-Pockels (EOPE) effects whereas β^v is zero for the second-harmonic generation (SHG) phenomenon. At HF level, static β_L values have been computed by the coupled-perturbed Hartree–Fock (CPHF) method implemented in GAUSSIAN 98.[18] The dynamic β_L have been obtained using a modified time-dependent Hartree–Fock (TDHF) approach—which employs direct inversion in iterative subspace method to speedup the convergence of the iterative procedure—implemented[22] in GAMESS.[23] Density-functional theory (DFT) using conventional XC functionals can not be used to compute β_L because DFT leads to a large overestimation of the NLO properties for extended compounds. For example, SVWN and B3LYP overshoot the β_L of push–pull oligomers by an order of magnitude.[24] Consequently, the dynamic EC effects have been computed within the Møller–Plesset level of approximation. At this level, static β_L has been evaluated by using the numerical finite-field procedure. We refer the reader to Ref. 5 for a complete description of this procedure. Dynamic MP2 β_L have been estimated by using the multiplicative approximation $\beta^{(\text{dynamic,MP2})} \cong \beta^{(\text{dynamic,HF})}\beta^{(\text{static,MP2})}/\beta^{(\text{static,HF})}$. This approximation is known to be efficient when $\beta^{(\text{static,MP2})}$ and $\beta^{(\text{static,HF})}$ are similar[25] which is the case for PP (see Secs. III B and III C). Note that the total EC correction can be splitted into two different contributions. On the one hand, EC modifies the electronic structure and has an direct impact on β_L. On the other hand, the change of equilibrium geometry has indirect effect on β_L. Both effects could be large and their relative importance depends strongly on the molecular structure considered. For example, in paranitroaniline, each effect increases β_L by ~50%.[26]

3. The polymeric response has been obtained by extrapolating the oligomeric values. In order to carry out extrapolations, an alternative definition of the β_L per unit cell, $\Delta\beta_L=\beta_L(N)-\beta_L(N-1)$, is employed. This definition removes most of the chain end effects: It leads to a faster convergence than β_L/N and it converges to the same asymptotic limit ($N\rightarrow\infty$). Our fitting procedure allows to obtain $\Delta\beta_L(\infty)$ and its standard deviation. We refer the reader to Ref. 27 for more details. In a recent work, Gu and co-workers[28] have shown that for PMI, with a fixed geometry close to the optimal one, the differences between the $\Delta\beta_L(\infty)$ obtained by our scheme and the one obtained by the crystal-orbital approach are smaller than 3% and that such extrapolation method tends to underestimate the error bars.

To close this Section, the reader is reminded that the present theoretical calculations face the usual limitations, i.e., the neglect of temperature and pressure effects. Moreover, the chains considered are isolated and perfectly regular. Additional studies would be required for estimating the impact of disorder and/or medium effects.[29]

III. RESULTS

A. Geometry and charges

The geometry of polyphosphazene and of its halogeno derivatives is a well discussed problem in the litterature (see,

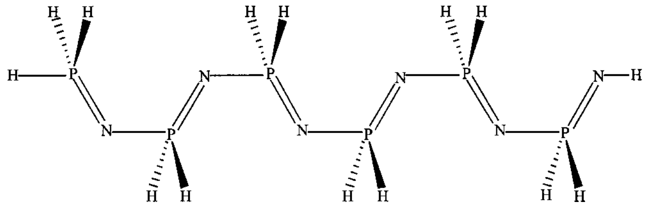

FIG. 1. Sketch of the polyphosphazene oligomers studied in the present work ($N=6$).

for example, Refs. 16 and 30, and references therein). For this reason, the topic was not investigated in details, but tests have been carried out on short chains ($N=2$ and $N=4$) with the MP2/6-311G* scheme to confirm or deny the conclusions of previous works. It is now accepted from both theoretical and experimental investigations that the trans-cisoid conformation (sketched in Fig. 1) is significantly more stable (about 10 kcal/mol[16]) than its all-trans analog. Our findings confirm this statement, the trans-cisoid tetramer is more stable than the corresponding cis-transoid and all-trans forms.[31] Consequently, in the present study, the planar trans-cisoid conformation has been selected. In Ref. 16, Sun raised the issue of the actual planarity of the trans-cisoid chains. Indeed, using density-functional theory (DFT), he found that the backbone of the trans-cisoid conformers slightly (<10 degrees) deviates from planarity. However, at MP2/6-311G* level, trans-cisoid conformers appear to be planar: Starting with a geometry of the conformer distorted with angles chosen from Sun's paper, the tetramer conformation "goes back" to planarity.[32] In addition, there is—to our knowledge—no experimental proof of the nonplanarity of PP. This is consistent with the small energy differences found by Sun (5 kcal/mol per unit cell) and the fact that solid-state effects generally tend to transform helicoidal structures or molecules which slightly deviate from planarity into planar systems.

One of the most important geometrical descriptors for NLO applications is the Δr which is the bond alternation parameter discussed in the Introduction.[12] Table I gives the Δr obtained at the center of PP oligomers investigated at various level of theory. The Δr obtained for PP oligomers are smaller than in polyenes: For $N=8$, the Δr of PP (polyenes) is 0.023 Å (0.070 Å[33]) at the MP2/6-311G* level. Sun,[16] using DFT, found a similar Δr value for $N=8$ (0.024 Å) but assumes that the Δr is converged for this *N*. On the contrary, the Δr is still decreasing at $N=8$. We have carried out extrapolations of the Δr up to the polymeric limit by assuming exponential decrease of Δr. Within this assumption it turns out that HF/6-31G* Δr is predicted to be around 0.004 Å for the polymer. We also note that this Δr value is very different from the one chosen by Chandra Jha *et al.* (0.22 Å for all oligomers) during their NLO calculations.[17] From the methodological point of view, we conclude that (i) 6-31G underestimates the Δr (strongly at HF level), (ii) 6-31G* and 6-311G* provide very close results (always within 2×10^{-3} Å): a double-ζ basis set is sufficient, (iii) the results are almost unaffected by the addition of polarization functions on the hydrogens. For example, the Δr of $N=6$ is 0.033 Å at the MP2/6-311G** level, i.e., the same as at MP2/6-311G* level, (iv) when polarization functions are used, the differences between HF and MP2 geometries are small: HF/6-31G* looks, therefore, like a good compromise (accuracy/cpu-time) for obtaining the ground-state geometry (see also Secs. IV and V.) HF Δr are smaller than MP2 Δr

TABLE I. Bond length alternation (Å) and charge alternation (e) for trans-cisoid polyphosphazene of Fig. 1. All values have been taken at the center of the chains. For the charge alternation, the same methodology is used to compute charges and obtain geometry.

			Bond length alternation, Δr			
N	HF/6-31G	MP2/6-31G	HF/6-31G*	MP2/6-31G*	HF/6-311G*	MP2/6-311G*
2	0.022	0.039	0.061	0.059	0.061	0.058
4	0.018	0.029	0.042	0.044	0.041	0.043
6	0.014	0.024	0.030	0.034	0.029	0.033
8	0.010	0.020	0.021	0.025	0.019	0.023
10	0.008	0.018	0.016			
12	0.006		0.012			
14	0.005		0.009			
16	0.004		0.008			
18	0.004					
20	0.003					
			Charge alternation, Δq			
N	HF/6-31G	MP2/6-31G	HF/6-31G*	MP2/6-31G*	HF/6-311G*	MP2/6-311G*
2	2.295	1.887	1.914	1.549	2.009	1.635
4	2.576	2.094	2.042	1.671	2.171	1.834
6	2.564	2.082	2.018	1.646	2.153	1.767
8	2.565	2.081	2.014	1.646	2.155	1.768
10	2.564	2.080	2.010			
12	2.565		2.008			
14	2.564		2.007			
16	2.565		2.006			
18	2.565					
20	2.565					

TABLE II. Basis set and geometry effects on the longitudinal static first hyperpolarizability of trans-cisoid polyphosphazene chains. 1 a.u. of $\beta = 3.2063\ 10^{-53}\ \mathrm{C}^3\ \mathrm{m}^3\ \mathrm{J}^{-2} = 8.641\ 10^{-33}$ esu.

	Geom=RHF/6-31G			Geom=MP2/6-31G		
N	β[HF/6-31G]	β[MP2/6-31G]	β[MP4/6-31G]	β[HF/6-31G]	β[MP2/6-31G]	β[MP4/6-31G]
2	54	32	35	68	32	38
4	265	231	262	293	188	232
6	584	593		598	415	
8	989	1123		985	775	
	Geom=RHF/6-31G*			Geom=MP2/6-31G*		
N	β[HF/6-31G*]	β[MP2/6-31G*]		β[HF/6-31G*]	β[MP2/6-31G*]	
2	9	1		12	3	
4	64	55		58	39	
6	174	217		157	175	
8	319	455		298	397	
	Geom=RHF/6-31G**			Geom=MP2/6-31G**		
N	β[HF/6-31G**]	β[MP2/6-31G**]		β[HF/6-31G**]	β[MP2/6-31G**]	
2	9	−1		13	4	
4	66	57		59	41	
6	178	225		160	179	
8	328	471				
	Geom=RHF/6-311G*			Geom=MP2/6-311G*		
N	β[HF/6-311G*]	β[MP2/6-311G*]		β[HF/6-311G*]	β[MP2/6-311G*]	
2	−12	−33		−13	−33	
4	60	38		52	25	
6	195	233		181	203	
8	367	508		353	470	
	Geom=RHF/6-311G**			Geom=MP2/6-311G**		
N	β[HF/6-311G**]	β[MP2/6-311G**]		β[HF/6-311G**]	β[MP2/6-311G**]	
2	−11	−31		−9	−26	
4	64	45		59	35	
6	204	248		192	217	
8	383	531				

for all basis sets, although it is the reverse in most conjugated systems, like polyenes[33] or PMI.[6]

If Δr is a good descriptor of the bond alternation parameter (see Introduction), it is difficult to find a property that significantly relates to the nuclear alternation. However, as first approximation, a simple descriptor could be used: The difference of Mulliken charges on adjacent atoms.[34] It is the charge alternation: $\Delta q = q^{\mathrm{P}} - q^{\mathrm{N}}$ measured at the center of the chain. In Table I, we give the Δq of PP oligomers computed with various methods. The Δq obtained are in agreement with the charges calculated by Sun:[16] P and N almost "exchange" one electron. Subsequently, the Δq are very large. Indeed, the Δq of the octamer of PMI (0.750 at the HF/6-31G* level) is less than half of the corresponding Δq in PP. The Δq are converging much faster than Δr: They are almost constant provided $N \geqslant 6$: The nuclear alternation is less affected by the variation of chain length than the bond alternation. In what concerns the importance of the level of theory to be used, it appears that: (i) HF overestimates Δq by 25%; (ii) the differences between HF and MP2 Δq are mostly due to the methodology, not to the geometry. Indeed, the MP2/6-31G* Δq computed on the HF/6-31G* geometry (1.540, 1.579, 1.625, and 1.621 for $N = 2-8$) are within 1% to 6% of the full MP2 values; and (iii) 6-31G overestimates Δq by 20% whereas 6-31G* and 6-311G* values agree quite well (~7% for $N = 6$ and 8).

B. Choice of a computation method for β_L

In order to draw correct chemical conclusions about the structure–property relationships in PP and its derivatives, it is necessary to determine a suitable level of theory. Table II compares the β_L of small and medium-size oligomers obtained with various methods and geometries.

The indirect (due to the geometry shift) impact of EC is relatively small. Indeed, for $N \geqslant 6$, the variation of β_L resulting from a HF-to-MP2 geometry shift ranges from 4% to 21% when polarization functions are included in the basis set. Moreover, this percentage tends to decrease with N. The direct impact of MP2 is larger (from 11% to 43% when polarization functions are used) and, more importantly, it increases with N. This direct EC contribution should therefore be accounted for. From MP4/6-31G results, it seems that the MP2 correction to β_L could be slightly overestimated, i.e., that "correct" β_L value are between HF and MP2 results, but probably closer to MP2. This was already noticed on PMI[6] but, due to practical limitations, it is impossible to confirm–

TABLE III. Bond length alternation (Å), charge alternation (e) and longitudinal static and dynamic first hyperpolarizability of trans-cisoid polyphosphazene chains. All results have been obtained on the HF/6-31G* geometry with the 6-31G* basis set. Δq have been obtained with the MP2 approach. At the bottom of the Table, the β values per unit cell of the polymer are given (see the text for more details on the procedure used to obtain these values).

			$\omega=0.0$	$\omega=0.65$ eV		$\omega=1.165$ eV		$\omega=0.0$
N	Δr	Δq	β[HF](0;0,0)	β[HF]($-\omega;\omega$,0)	β[HF]($-2\omega;\omega,\omega$)	β[HF]($-\omega;\omega$,0)	β[HF]($-2\omega;\omega,\omega$)	β[MP2](0;0,0)
2	0.061	1.540	9	9	9	9	8.3	1
4	0.042	1.579	64	64	64	64	66	55
6	0.030	1.625	174	174	176	176	182	217
8	0.021	1.621	319	321	325	325	338	455
10	0.016	1.617	483	486	493	493	514	734
12	0.012	1.615	657	662	670	671	701	103×10
14	0.009		837	842	854	855	894	134×10
16	0.008		1020	1027	1041	1042	1091	166×10
$\Delta\beta(\infty)$			94±2	95±3	96±3	96±3	101±3	170±10

deny it for larger basis sets, on longer oligomers or with higher-order EC methods.

The 6-31G basis set overestimates strongly (roughly a factor between two and three) the β_L of PP. Subsequently, this basis set can only be used for qualitative purposes (nevertheless, see Sec. IV). This deficiency of 6-31G does not originate only from the incorrect geometry. Indeed, the HF/6-31G (MP2/6-31G) β_L obtained from the HF/6-31G* geometry of the octamer is 773.1 a.u. (1115 a.u.), which is quite different from the corresponding 6-31G* β_L of 319 a.u. (455 a.u.). As for the geometry, the addition of a set of polarization functions on hydrogens has a very little effect. This prooves that β_L is mainly determined by the PP backbone not by the hydrogens, as could be expected. Finally, we note that the addition of a third valence shell in the basis (6-311G* vs 6-31G*) has also a relatively small effect, provided $N>4$: It increases β_L by about 15%.

As a consequence, the MP2/6-31G*//HF/6-31G* method is found adequate to obtain a semiquantitative (~30%) accuracy on the β_L of medium-size and longer PP oligomers. As this method also provides reasonable approximation to the geometry and charges (see Sec. II), this technique is mainly used in the following.

C. Amplitude of β_L of the oligomers and polymer

Table III gives the results of our calculations on increasingly long PP oligomers. During TDHF calculations, the same two energies (0.65 and 1.17 eV) as in Ref. 17 have been selected, they correspond to two traditional laser frequencies. Figure 2 shows the evolution of dynamic (SHG) MP2 β_L per unit cell $[\Delta\beta_L(N)=\beta_L(N)-\beta_L(N-1)]$ obtained within the multiplicative approximation. For all N, β_L is parallel to dipole moment of the chain. The different curves of Fig. 2 present a standard shape: A fast increase followed by a saturation to the polymeric limit. For short chains, the power low exponent ($\beta\propto N^y$) has been estimated to be $y=3.1$ (MP2 value obtained for $N=4$ to $N=8$). The fact that there is neither fall-off of $\Delta\beta_L(N)$ or change of its sign indicates that the chain-end contributions to β_L are relatively small and probably parallel to the unit cell contribution. This contrasts with PMI[11] and linear boron-nitride chains.[5] The curves in Fig. 2 saturate quickly. Indeed for $N=14$, the MP2 $\Delta\beta_L(N)$ is already more than 90% of the polymeric value for PP, whereas such a percentage is only reached for $N=18$ in PMI.[6] This rapid saturation illustrates the lack of mobility of the electrons of PP. As the Δr of PP is small, this small delocalizability is principally due to the large charge alternation. The fast saturation of $\Delta\beta_L(N)$ makes it possible to obtain accurate polymeric values: 170±10 a.u. (static MP2).

Frequency dispersion effects are weak for all chain lengths, even the SHG values computed with an incoming light of 1.17 eV energy are within 3% ($N=4$) and 7% ($N=12$ to ∞) of the static values. To rationalize this, random phase approximation (RPA) calculations have been performed to determine the excitation energies of PP. For the first four oligomers ($N=2-8$), it turns out that the first excited state is 7.2~7.3 eV above the ground state and that the excitation energy is stable with N (variations are smaller than 1%). This explains the small dispersion effects with 0.65 and 1.17 eV frequencies.

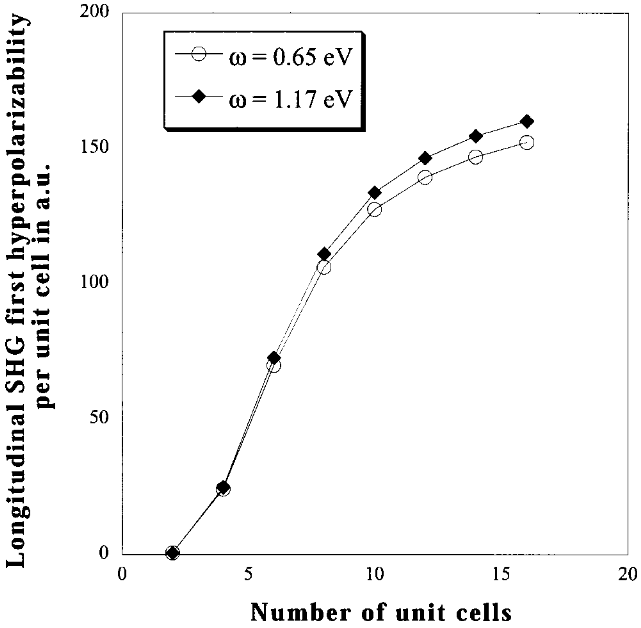

FIG. 2. Evolution with chain length of the longitudinal first hyperpolarizability (SHG) per unit cell $[\Delta\beta_L(N)]$ of PP oligomers. These results have been obtained at the MP2/6-31G*//HF/6-31G* level of approximation by using the multiplicative procedure.

It is interesting to see that the static β_L curves computed at the HF/6-31G*//HF/6-31G* and HF/6-31G//HF/6-31G levels are becoming parallel for medium-size N. By extrapolation to $N \rightarrow \infty$, a ratio between the two methods could be obtained for the macromolecule: 0.348 ± 0.002.[35] As a consequence, one can use extrapolations of the 6-31G values and this ratio in order to obtain the 6-31G* $\Delta\beta_L$ of the polymer. Since 6-31G values are much cheaper to calculate, one can take advantage of longer chains (up to $N=20$ in this case) to perform the extrapolations. The HF/6-31G* value obtained in this way is $(267\pm2)\times(0.348\pm0.002)=93\pm1$ which is consistent with the value obtained by direct extrapolation (94 ± 2). The same can be done for the MP2/6-31G*//HF/6-31G* β_L: $403\pm8\times0.421\pm0.002=170\pm3$ in perfect agreement with 170 ± 10 but with better accuracy.

Finally, the agreement between the values obtained in the present study and the semiempirical results of Ref. 17 is good for the 0.65 eV β_L. Indeed, for $N=4$ $(N=6)$, Chandra Jha and co-workers obtained a dominant component to $\beta(-2\omega;\omega,\omega)$ of 30 (190) a.u. whereas we have 55 (220) at the MP2/6-31G*//HF/6-31G* level.[36] However, the 1.17 eV values differ substantially: They obtained -1 (-210) a.u. for $N=4$ $(N=6)$ whereas we have 56 (228) a.u. They found that depending on N and ω, chains could be on either side of resonance, whereas, $\hbar\omega=1.17$ eV is still far from resonance in the case of our calculations. This is explained by the differences in excitation energies (3.7 eV for infinitely long PP in Ref. 17) that could possibly be related to the geometry or the parametrization of the Hamiltonian selected in Ref. 17.

TABLE IV. Bond length alternation (Å, HF/6-31G*), charge alternation (*e*, MP2/6-31G*) and static longitudinal first hyperpolarizability (a.u.) of trans-cisoid $X\text{-}(PX_2{=}N)_N\text{-}X$ chains. These results have been obtained on the optimized (HF/6-31G*) geometries.

N	Δr	Δq	β[HF/6-31G*]	β[MP2/6-31G*]
		X=H		
2	0.061	1.540	9	1
4	0.042	1.579	64	55
6	0.030		174	217
8	0.021		319	
		X=F		
2	0.099	1.933	−25	−8
4	0.059	2.003	15	56
6	0.038		100	194
8	0.027		210	
		X=Cl		
2	0.053	1.441	84	61
4	0.049	1.511	219	275
6	0.035		385	562
8	0.026		577	
		X=Br		
2	0.077	1.626	120	70
4	0.040	1.704	297	353
6	0.031		484	691
8	0.022		712	
		X=OH		
2	0.042	1.925	−2	−7
4	−0.014	2.078	−134	−189
6	−0.016		−288	−412
8	−0.017		−460	
		X=CH_3		
2	0.053	1.739	133	141
4	0.032	1.858	322	375
6	0.023		558	686
8	0.016		826	

D. Addition of side groups

A way to increase the small β_L of PP could be to use side groups which tune Δr and Δq of the chain in a such a way that electron mobility is increased. As PP presents small Δr but large Δq, side groups that would decrease the latter would be welcome. We have used different side groups (H, CH_3, F, Cl, Br, and OH) in order to assess their influence on β_L (Table IV). These side groups have been selected because they constitute models of experimentally used substituents (especially Cl). Each oligomer has been optimized with only one constraint: The conformation of the P–N backbone (planar trans-cisoid as previously). For the nonatomic side groups (OH and CH_3), the geometries obtained correspond at least to one of the local minima but are not guaranteed to be the global minima as different geometries would be reasonable for the side groups.

From Table IV, one can see that, for $N=6$ and 8, the ordering of Δr is

$$F > Cl > Br > H > CH_3 > OH,$$

with the most striking feature being the change of sign of Δr when OH groups are used. Aside from this exception, most groups have a relatively small effect on Δr (the magnitude of the variations w.r.t. H is within ~30% for $N=8$). The Δr of the halogeno derivatives agree with Sun's results:[16] The same ordering is obtained (for $N=4$) and the Δr of Table IV are within 0.01 Å of Sun's DFT values. Nevertheless, for $N=8$, the halogeno compounds have similar Δr indicating that this order may change for longer chains. A different ordering is found for Δq

$$OH > F > CH_3 > Br > H > Cl.$$

Only Cl is able to lower Δq while the variations between the different groups are relatively small (the magnitude of the variations w.r.t. are within ~30% for $N=4$).

The ordering of β_L strongly depends on the criterion selected: Stand-alone β_L $(Br > CH_3 > Cl > OH > H > F)$, β_L reported to the molecular weight of the molecule $(CH_3 > OH > H > Cl > Br > F)$, y, i.e., the power low exponent of $\beta \propto N^y$ $(H > F > OH > Cl > Br > CH_3)$.[37] This illustrates the relatively small overall impact of side groups on β_L. For $N=6$, the stronger variations are of the order of a factor of 3, less than one order of magnitude. Consequently, the chains treated in Table IV are too short for determining the most efficient side groups for NLO applications on the polymer. The only clear case is fluorine: It leads to less efficient NLO materials than unsubstitued PP. This can be related to larger Δr and Δq obtained with F compared to H: Fluorinated chains present smaller delocalization and, therefore, smaller β_L.

Interestingly the three groups that are most representative of actually synthesized macromolecules (Cl, OH, and CH_3) lead to quite large β_L, although one cannot assess

TABLE V. Bond length alternation (Å), charge alternation (e) and static longitudinal first hyper-polarizability (a.u.) of trans-cisoid H-$(PH_2{=}CH)_N^-$H and H-$(PH_2{=}SiH)_N^-$H chains. All Δq have been calculated at the MP2/6-31G* level of approximation.

	-$(PH_2{=}CH)_N^-$							
	Geom=RHF/6-31G*				Geom=MP2/6-31G*			
N	Δr	Δq	β[HF/6-31G*]	β[MP2/6-31G*]	Δr	Δq	β[HF/6-31G*]	β[MP2/6-31G*]
2	0.081	1.333	15	12	0.082	1.327	20	18
4	0.046	1.402	133	130	0.050	1.393	140	138
6	0.032	1.397	391	473	0.035	1.387	404	486
8	0.023	1.397	738	966	0.026	1.386	764	997
10	0.018	1.397	1135	1547				
12	0.014		1560	218×10				
14	0.012		2001					

	-$(PH_2{=}SiH)_N^-$							
	Geom=RHF/6-31G*				Geom=MP2/6-31G*			
N	Δr	Δq	β[HF/6-31G*]	β[MP2/6-31G*]	Δr	Δq	β[HF/6-31G*]	β[MP2/6-31G*]
2	0.046	0.127	95	113	0.051	0.121	126	145
4	0.029	0.170	662	574	0.034	0.148	729	604
6	0.023	0.160	2033	2101	0.027	0.135	2171	2124
8	0.019	0.158	4012	4555	0.022	0.133	4295	4674
10	0.017	0.156	6374	7615				
12	0.015		8968	1106×10				
14	0.014		11705					

correctly the convergence of β_L w.r.t. N. However, we expect that Cl substituents which diminish Δq will lead to a $\Delta\beta_L(\infty)$ value at least as large as the $\Delta\beta_L(\infty)$ of the unsubstituted PP.

E. Effect of nuclear substitution within the backbone

Besides changing side groups, another way to increase the β_L of PP is to change the nature of the AB alternance. For this reason, we have investigated two model polymers where the nitrogen have been replaced by either C–H[PC,-$(PH_2{=}CH)_N^-$] or Si–H[PSi,-$(PH_2{=}SiH)_N^-$] (see Table V for their β_L values). We have kept the same conformation (planar trans-cisoid, Fig. 3) as for PP in order to ensure valid comparisons. Test calculations reveal that trans-cisoid PC and PSi conformers are indeed more stable than the planar trans-transoid and cis-transoid analogs. The PC and PSi oligomers have a tendency to become nonplanar helical structures (favored from the energetical point of view), but a study of these conformers is beyond the scope of the present paper.

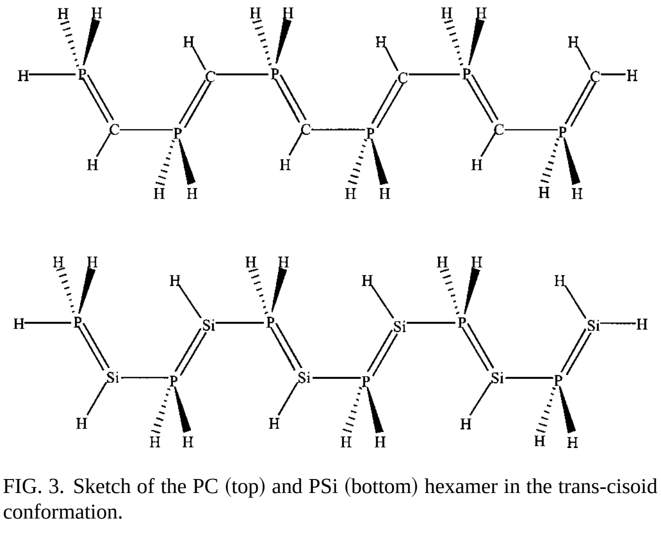

FIG. 3. Sketch of the PC (top) and PSi (bottom) hexamer in the trans-cisoid conformation.

We have optimized the ground-state geometry of PC and PSi oligomers. As for PP, the Δr of PSi and PC chains is estimated to be larger at the MP2 level than at HF level. Compared to PP, PC chains have larger Δr for all N, whereas, for PSi, it is only true provided $N>8$: The Δr of PSi decreases relatively slowly with N. The Δq of PC are slightly smaller than in PP, whereas the one of PSi are one order of magnitude smaller, indicating a serious decrease of the nuclear asymmetry and an associated increase of the electron mobility. These differences of Δq follow the same trends (PP>PC$\gg$PSi) as the differences of electronegativity between P and N, P, and C, P, and Si, as one could have be expected.

As for PP, it appears that 6-31G* is a satisfactory basis set. Indeed, the use of triple-ζ basis set does not lead to large modifications.[38] The addition of a set of polarization functions on the hydrogens has a negligible effect as well. As for PP, the 6-31G basis set strongly overestimates β_L for PC whereas, for PSi, it provides reasonable β_L at the MP2 level.[39] From Table V, one can also see that (i) As for PP the HF/6-31G* is sufficient to characterize the geometry: The variations of β_L when using MP2/6-31G* optimized structures are very small. Indeed, the change of geometry (from HF to MP2) provokes an increase of Δr but a decrease of Δq, leading to a small total impact on β_L amplitudes; (ii) the MP2 direct contribution is quite small compared to PP: It is only 30% (12%) for the octamer of PC (PSi) but it increases with N. For the polymer we roughly estimate this direct MP2 correction to β_L to be around 60% and 45% for PC and PSi, respectively—this can be compared to the PP value: 81%.

Figure 4 depicts the evolution of the static $\Delta\beta_L$ of PP, PC, and PSi as a function of N. Obviously, the $\Delta\beta_L$ of PSi is

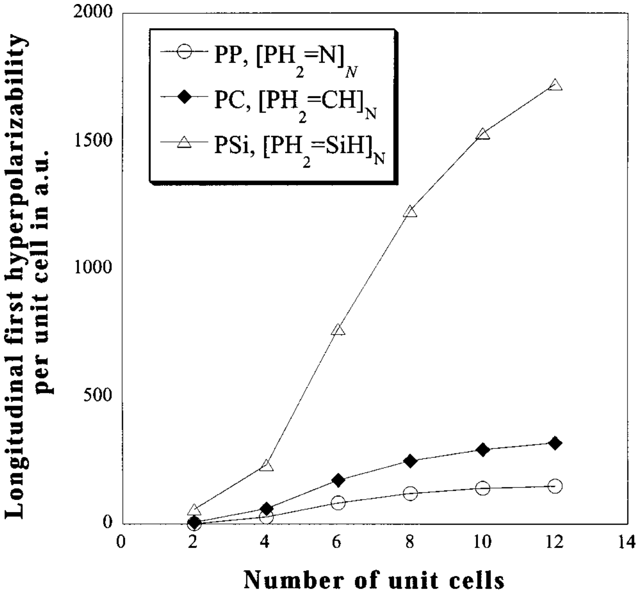

FIG. 4. Evolution with chain length of the static (ω=0.0) longitudinal first hyperpolarizability per unit cell $[\Delta\beta_L(N)]$ of PP, PC, and PSi oligomers. These results have been obtained at the MP2/6-31G*//HF/6-31G* level of approximation.

much larger and converges more slowly with N than the $\Delta\beta_L$ of PC and PP, indicating the potential interest of such polymer for NLO applications. The extrapolated polymeric HF/6-31G*//HF/6-31G* (MP2/6-31G*//HF/6-31G*) $\Delta\beta_L$ are 245±15 (396±45) for PC and 1650±180 (2426±370) for PSi. For the long oligomers and the polymer we, therefore, predict that: $\beta_L[\mathrm{PSi}]\sim 6\beta_L[\mathrm{PC}]$ and $\beta_L[\mathrm{PC}]\sim 2.5\beta_L[\mathrm{PP}]$. This ordering can be related to the first excitation energies of PC (5.3 eV) and PSi (2.8 eV): Both are significantly smaller than the PP value. This also suggests that the dynamic β_L of the three systems differ even more strongly than their static values. Taking into account the fact that Δr are quite close for the three systems, one can see that the ordering of β_L qualitatively follows the inverse of Δq. As smaller Δq are related to smaller nuclear asymmetry and larger delocalization, this phenomenom confirms that the β_L of PP is limited by delocalization, not by asymmetry. The larger delocalization in PSi also explains the slower convergence of $\Delta\beta_L$ with respect to N. In addition, this highlights that Δr is not a sufficient parameter for determining β_L: The largest β_L amongst the three systems (PP, PC, and PSi) corresponds to the largest Δr, which is the reverse of the expected trend for compounds with relatively small electron mobility.

IV. CONCLUSION

We have investigated the efficiency of PP as second-order NLO polymer. It appears that β_L/N converges quickly with chain length and that the static polymeric value is predicted to be 170 a.u. per unit cell. This corresponds to a β_L per unit of weight (per atom) of $0.03\times10^{-30}\,\mathrm{cm}^5\,\mathrm{esu}^{-1}\,\mathrm{g}^{-1}\,\mathrm{mol}\,(0.4\times10^{-30}\,\mathrm{cm}^5\,\mathrm{esu}^{-1})$, about one-third (one-half) of the value reported for MNA, $0.10\times10^{-30}\,\mathrm{cm}^5\,\mathrm{esu}^{-1}\,\mathrm{g}^{-1}\,\mathrm{mol}\,(0.8\times10^{-30}\,\mathrm{cm}^5\,\mathrm{esu}^{-1})$,[8] but more than one (two) order(s) of magnitude smaller than the value reported for PMI,[6] $4.2(38)\times10^{-30}$. This relatively small value of PP is explained by the large charge alternation between phosphorus and nitrogen atoms that impedes electron delocalization. As the addition of side groups does not modify deeply this separation, there is relatively little influence of the side groups on the NLO response of long PP oligomers. A better strategy in order to increase β is to replace nitrogen by silicon in which case one diminishes strongly the charge alternation without modifying deeply the bond alternation, leading to a polymeric NLO response of $0.33\times10^{-30}\,\mathrm{cm}^5\,\mathrm{esu}^{-1}\,\mathrm{g}^{-1}$ mol, i.e., in the range of the synthesized push–pull molecules.

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[32] However, other conformations (glide plane, coil,...) could possibly be more stable than planar TC chains.

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[35] See EPAPS Document No. E-JCPSA6-120-307417 for the 6-31G values. A direct link to this document may be found in the online articles HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

[36] Nevertheless, this agreement between *ab initio* and semi-emperical results is probably originating from a fortuitous cancellation of different errors.

[37] These ordering are based on MP2/6-31G* results.

[38] For example, for the octamer of PC (hexamer of PSi), the MP2/6-311G(d)//HF/6-311G(d) β_L is within 13% (4%) of the corresponding MP2/6-31G(d)//HF/6-31G(d) values.

[39] At this level 6-31G β_L are roughly 30% smaller than 6-31G(d) β_L .