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Ab Initio Assessment of the First Hyperpolarizability of Saturated and Unsaturated Polyaminoborane/Polyphosphinoborane Copolymers

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The linear and nonlinear optical properties of trans-cisoïd saturated and unsaturated polyaminoborane/polyphosphinoborane alternating copolymers are studied at the MP2/6-311G(2d)//PBE0/6-31G(2d) level of approximation, by using the increasingly large oligomer series methodology. We report the evolution with chain length of geometry parameters, partial atomic charges, electric dipole moments, polarizabilities and first hyperpolarizabilities of both phosphorus- and nitrogen-terminated chains. It turns out that for the saturated copolymer, linear and nonlinear optics properties of the saturated copolymer correspond to an average of the response of polyaminoborane and polyphosphinoborane. For the conjugated copolymer, the response is guided by the least delocalizable component.

I. Introduction

The inert white solid polyaminoborane [PAB, $-(NH_2-BH_2)_n-$, n being the number of unit cells] has been synthesized by several groups in the last 30 years,[1−8] using a large panel of physical and chemical reaction pathways. More recently, PAB has been the subject of theoretical investigations aiming at the determation of its structure and properties such as excitation spectra or nonlinear optics (NLO) coefficients.[9−12] Its conjugated counterpart, polyiminoborane, [PIB, $-(NH{=}BH)_n-$] has been successfully obtained experimentally by Paetzold in the 1980s.[13,14] Polyphosphinoborane [PPB, $-(PRH-BH_2)_n-$], the phosphorus PAB analogue, has also been reported with high molecular weights by Dorn, Manners, and co-workers,[15−17] as well as by Denis, Gaumont, and co-workers.[18] We recently investigated unsubstituted (R = H)[19,20] and substituted (R = Ph, Me, and ^{i}Bu)[21] forms. The conjugated form of PPB, [DHPPB, $-(PH{=}BH)_n-$] has not been experimentally observed, though its NLO responses have been theoretically evaluated.[19]

These polymers belong to the AB category. Built on the alternation of two different atoms, they present a nonzero bond length alternation (Δr, the difference between single and double bond lengths),[22] a nonzero dipole moment (μ), and a nonzero first hyperpolarizability (β). Compared to push−pull compounds, the AB chains present many advantages. Indeed, a nonzero response may be obtained for any chain length and the value of β in the polymer often differs from zero, which is not the case in standard push−pull chains.[23] Several AB compounds have been investigated.[11,19,24−31] In regard to the evolution with chain length of β/n of these systems, the compounds may be classified in four categories:

1. β/n is always positive, first increases, and then saturates to the infinite chain limit, as for the polarizability (α/n) in an homologous series of compounds. Polyphosphazene (PP),[28] DHPPB, and PIB follow this behavior.
2. $|\beta/n|$ increases for small chain length, reaches a maximum, and then decreases toward zero, similarly to push−pull systems.[32] Linear boron−nitrogen chains[25] and all-trans polysilaacetylene [PSA, $-(CH{=}SiH)_n-$][29] belong to this category.
3. β/n is first negative, goes down, and reaches a minimum before increasing, changing sign, and eventually saturating toward the polymeric limit. This is typical of PPB.[19]
4. Without changing its sign, β/n first increases, reaches an extremum, then slightly decreases, and finally converges toward a slighlty smaller polymeric value. This is the typical pattern of PAB or cis−transoïd PSA.

It is worth noting that compounds could be incorrectly classified if one uses an inadequate level of theory. For instance, all-trans polymethinimine [PMI, $-(CH{=}N)_n-$] belongs to category 3 if one relies on Hartree−Fock (HF) wavefunction but to category 1 when electron correlation (EC) effects are properly taken care of, i.e., if one uses at least the second-order Møller−Plesset (MP2) level. For a more comprehensive view, these trends can be rationalized by splitting the total β response into a chain-ends (CE) and unit cell (UC) components. In general, as the chain lengthens the contributions from each components increase due to the improvement of the electron mobility. Simultaneously, the relative importance of the CE component in β/n decreases (dilution effect as n increases) and, consequently, for the polymer, only the UC component determines the amplitude of β/n. In these terms, our classification can be explained by:

1. The CE component is negligible with respect to the UC component for all n: only the UC significantly contributes to β (and β/n). The UC contribution to β is first increasing due to the increase of electron mobility but saturates for longer n. In the macromolecule, each UC brings the same contribution to β and β/n becomes constant.
2. The contribution of the UC is practically negligible with respect to the contribution of the CE. This often means that the bond length alternation (Δr) at the center of the AB chains is zero or tends to disappear for the largest systems. There is no

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asymmetry originating from the UC, and only CE is responsible for β. For small n, the CE part to β/n increases due to the fast improvement of electron mobility. For longer oligomer, the CE contribution to β becomes constant due to the saturation of electron mobility. Therefore, the CE component dilutes in β/n and the polymeric ($n \rightarrow \infty$) response tends to zero.

3. The CE and the UC contributions to β and β/n have opposite signs, the former (latter) dominating the total response for short (long) oligomers. For short chains, the CE brings a large negative contribution to β and β/n. This negative contribution to β/n is first increasing with n but becomes smaller for longer oligomers due to the "dilution" effect (see case 2). At some point, the UC and CE contributions to β/n are of equal amplitude but of opposite signs and annihilate: β/n is zero. For extended chains, only the UC contribution plays a role and the system behaves as in case 1.

4. Case 4 is similar to case 3, but with the CE and UC contributions to β having the same direction. The relative weight of the CE component has to be large. Otherwise, case 1 is observed.

In cases 1, 3, and 4, nonzero polymeric values are obtained. To maximize these responses, model calculations show that it is more efficient to have a large delocalization and a small (but nonzero) UC asymmetry than the reverse.[33] This allows a second type of classification of the AB chains, any response being limited either by delocalization or by asymmetry. If delocalization is the limiting factor (this is often the case), increasing the delocalization (and hence decreasing the asymmetry) leads to an increase of β. This is found for PAB and PPB. The reverse, i.e., systems limited by asymmetry, can be illustrated by the 25%-PMI/75%-polyacetylene (PA) copolymer, which are delocalizable but too symmetric.[27]

Recently, Jaska, Lough, and Manners synthesized[34] the first hybrid aminoborane/phosphinoborane linear product, $Me_2NH-BH_2-PPhR-BH_3$ (R= Ph or H), obtained by the reaction of the lithiated phosphine−borane adducts $Li[PPhR-BH_3]$ with Me_2N-BH_2Cl. Chain cleavage reactions were obtained upon thermolysis and gave not only Me_2NHBH_3, $[Me_2N-BH_2]_2$, etc. but also the low molecular weight PPB. The X-ray diffraction study of the R = H linear product gave the structural parameters of this hybrid compound, the first in the oligomeric series of the inorganic PAB/PPB alternating copolymer.[34] To flesh out our understanding of the delocalization/asymmetry interplay, this work aims at rationalizing the copolymerization effects on the NLO properties. The PAB/PPB case (Figure 1) is especially interesting as the two individual series, though similar in nature, possess different NLO responses and, specifically, do not belong to the same AB category (see above). To our knowledge, only two similar studies have been previously performed for the organic PA/PMI[27] and for the organic/inorganic PMI/PP chains.[31]

II. Computational Details

We have selected the PBE0/6-31G(2d) (see below) approach for the geometry optimization and the MP2/6-311G(2d) scheme for the calculation of the electronic properties. This approach has been found accurate for PAB,[11,12] whereas for PPB the less-demanding MP2/6-31G(d)//HF/6-31G(d) has been shown successful.[19] The most accurate and demanding approach has nevertheless to be selected for the copolymer. All the calculations have been performed, with the Gaussian03 program,[35] by using the following procedure:

1. The ground-state geometry of each oligomer has been determined by the optimization of its structural parameters. These optimizations have been performed within the one-parameter Perdew-Burke-Erzenrhof hybrid-DFT functional[36] (PBE0) using the doubly polarized split-valence double-ζ 6-31G(2d) basis set, selecting the ULTRAFINE integration grid and a TIGHT convergence threshold for the residual forces.[37] In this investigation, we use the planar trans-cisoïd (TC) conformation, which is the most stable planar conformer for both PAB and PPB (Figure 1). As chain-end effects have been found to be substantial in PPB, we use two types of chain: a NH_3 terminated series (noted N-end) and a PH_3 terminated series (noted P-end). Similarly, NH_2 and PH_2 terminated PIB/DHPPB chains have been investigated. In addition to planarity, we have also imposed the linearity of the chains, so that a longitudinal axis running through the center of the first and the last backbone bonds could be properly defined. To avoid bent chains, only two different backbone angles have been used (X−B−Y and B−X−B; X, Y = P or N). This linearity constraint is not expected to significantly affect the NLO response.[31]

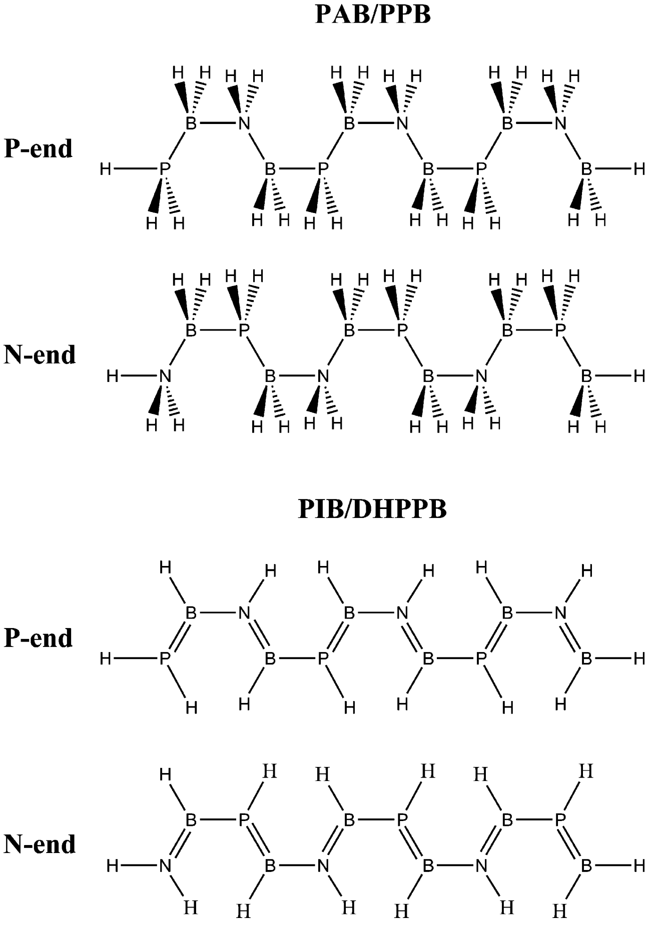

Figure 1. Schematic representation of trans-cisoïd PAB/PPB (top) and PIB/DHPPB (bottom) alternating copolymers. The structures represented correspond to $n = 6$.

2. In addition to the dipole moment component parallel to the longitudinal axis (μ_L), the partial atomic charges have been computed using the Merz−Kollman (MK)[38] approach within the MP2/6-311G(2d) approximation. Static electronic polarizabilities (α) and first hyperpolarizabilities (β) have been evaluated as well. In quasilinear chains, the longitudinal components in α and β tensors (α_L and β_L) tend to dominate the total response for sufficiently long chains. For example, at the HF/6-311G(2d)//PBE0/6-31G(2d) level the β_L for $n = 16$ in N-end PIB/DHPPB, is 6 times larger than the following component. For this reason, we focus on longitudinal components in this paper. Although they could make important contributions to the total static values in conjugated systems,

TABLE 1: Evolution with Chain Length of the Central Bond Lengths and Valence Angles for PH_3 and NH_3 Terminated PAB/PPB Copolymer[a]

	N-end						P-end					
n	$d_{B-N}^{\parallel}$	$d_{B-N}^{\perp}$	$d_{B-P}^{\parallel}$	$d_{B-P}^{\perp}$	$\alpha_{B=X-B}$	α_{X-B-Y}	$d_{B-N}^{\parallel}$	$d_{B-N}^{\perp}$	$d_{B-P}^{\parallel}$	$d_{B-P}^{\perp}$	$\alpha_{B=X-B}$	α_{X-B-Y}
2		1.610	1.969	1.944	110.8	103.4	1.550	1.611		1.970	115.5	110.9
4	1.586	1.586	1.959	1.977	115.9	110.9	1.556	1.591	1.965	1.970	116.1	113.0
6	1.586	1.587	1.975	1.972	116.7	112.1	1.582	1.587	1.967	1.967	116.7	113.4
8	1.592	1.583	1.975	1.969	117.1	112.6	1.585	1.583	1.974	1.966	117.0	113.5
10	1.593	1.581	1.978	1.968	117.3	112.9	1.591	1.581	1.975	1.965	117.2	113.6
12	1.595	1.580	1.978	1.967	117.4	113.0	1.592	1.580	1.977	1.965	117.3	113.6
14	1.596	1.579	1.979	1.966	117.5	113.2	1.594	1.579	1.978	1.965	117.4	113.7
16	1.597	1.578	1.979	1.966	117.5	113.3	1.595	1.578	1.978	1.965	117.5	113.7

[a] All results have been obtained at the PBE0/6-31G(2d) level. Bond lengths are in Å, angles in degrees. n is the number of cells, defined as half of the number of non-hydrogen atoms in the chain.

TABLE 2: Evolution with Chain Length of the Central Bond Lengths and Valence Angles for PH_2 and NH_2 Terminated PIB/DHPPB Copolymer[a]

	N-end						P-end					
n	$d_{B-N}^{\parallel}$	$d_{B-N}^{\perp}$	$d_{B-P}^{\parallel}$	$d_{B-P}^{\perp}$	$\alpha_{B=X-B}$	α_{X-B-Y}	$d_{B-N}^{\parallel}$	$d_{B-N}^{\perp}$	$d_{B-P}^{\parallel}$	$d_{B-P}^{\perp}$	$\alpha_{B=X-B}$	α_{X-B-Y}
2		1.385	1.889	1.805	127.9	121.0	1.433	1.405		1.822	128.7	126.3
4	1.439	1.412	1.875	1.846	128.4	124.3	1.432	1.417	1.859	1.851	128.1	125.8
6	1.435	1.418	1.861	1.853	128.2	124.7	1.429	1.422	1.857	1.855	128.0	125.7
8	1.430	1.421	1.859	1.856	128.0	124.9	1.428	1.423	1.854	1.857	127.9	125.6
10	1.429	1.423	1.855	1.857	128.0	125.0	1.426	1.424	1.854	1.858	127.9	125.5
12	1.427	1.424	1.854	1.858	127.9	125.1	1.426	1.424	1.853	1.859	127.8	125.5
14	1.426	1.424	1.853	1.859	127.9	125.1	1.425	1.425	1.852	1.859	127.8	125.5
16	1.426	1.425	1.853	1.859	127.9	125.1	1.425	1.425	1.852	1.859	127.8	125.4

[a] See Table 1 for more details.

the vibrational contributions to α and β (α^v and β^v) have been neglected, because their practical determination at EC levels remain computationally demanding for extended oligomers. At the MP2 level of approximation, static α_L and β_L have been evaluated by using the finite-field (FF) procedure based on the differentiation of the electric field amplitude-dependent total energies. We refer the reader to ref 25 for a complete description of this procedure. The accuracy of the numerical FF procedure can be slightly improved by performing the FF on the MP2 energy corrections (rather than the total energies) and adding the result to the fully analytic coupled-perturbed Hartree−Fock (CPHF) results. By doing so, the final accuracy on the MP2 α_L value is ~0.1 au whereas the estimated β_L accuracy is 1−2 au. In this paper, we adopt the usual sign convention for β_L, i.e., positive when orientated in the same direction as the dipole moment, negative otherwise.

3. The polymeric responses have been obtained by extrapolating the oligomeric values. To improve the extrapolation procedure, we define the β_L (as well as μ_L and α_L) per unit cell as $\Delta\beta_L(n) = (1/2)[\beta_L(n) - \beta_L(n-2)]$. This definition removes most of the chain end effects and leads to a fast convergence toward the asymptotic limit ($n \rightarrow \infty$). Our fitting procedure allows us to obtain the $\Delta\beta_L(\infty)$ and an estimate of the extrapolation error. We refer the reader to ref 39 for more details.

III. Results

As noted in section II, all the reported data have been obtained with the MP2/6-311G(2d)//PBE0/6-31G(2d) approach. For the PAB and PIB, the corresponding values can be found in ref 11, whereas for PPB and DHPPB, they are provided as Supporting Information. Note that for PPB, the computed μ_L, α_L, and β_L are in good agreement with our previous MP2/6-31G(d)//HF/6-31G(d) results. Indeed, at the MP2/6-311G(2d)//PBE0/6-31G(2d) level, we got for the polymer −2.08, +73, and +110 au for $\Delta\mu_L(\infty)$, $\Delta\alpha_L(\infty)$, and $\Delta\beta_L(\infty)$, respectively, whereas the corresponding values in ref 19 are −2.20, +67, and +109 au. However, for DHPPB, the MP2/6-311G(2d)/PBE0/6-31G(2d) values significantly differ from the MP2/6-31G(d)//HF/6-31G(d) amplitudes. For instance, the MP2/6-311G(2d)/PBE0/6-31G(2d) $\Delta\beta_L(\infty)$ is 31% larger than its MP2/6-31G(d)//HF/6-31G(d) counterpart. Note the typo for the MK Δq in Table 2 of ref 19: they should be negative instead of positive.

A. Geometries and Charges. It is well-known that there is a strong link between NLO properties and the geometry in conjugated compounds.[40] Tables 1 and 2 provide the backbone bond lengths and valence angles at the center of saturated and conjugated copolymers, respectively. For $Me_2NH-BH_2-PPh_2-BH_3$, an experimental X-ray structure is available.[34] Except for the Me and Ph side groups, this corresponds to the N-end PAB/PPB dimer. The experimental bond lengths are 1.598, 1.964 and 1.935 Å for d_{N-B}, d_{B-P}, and d_{P-B}, respectively. Our PBE0/6-31G(2d) values are 1.610, 1.969, and 1.944 Å, respectively, in good qualitative and quantitative (<0.01 Å) with the experiment. In the X-ray structure, the BPB angle (115°) is more obtuse than the NBP angle (110°), and indeed, we qualitatively reproduce this feature, although our angles are ~6° smaller (111 and 103°), probably due to the bulky experimental substituents on phosphorus (Ph instead of H). For short chains (up to $n = 4$), the chain end effects can be significant, and the differences in bond lengths for the N-end and P-end copolymers are sometimes larger than 0.01 Å. As expected, the structure of the central unit cell in longer oligomers is almost insensitive to the nature of CE. Short PAB oligomers favor a cis−transoïd over a trans-cisoïd conformation. Up to $n = 4$, a similar trend is found for the copolymer, at least for the P-end series in which the perpendicular BN bonds are longer than the parallell BN bonds. In long copolymers, one finds two long (phosphorus) and two short (nitrogen) bonds. This allows us to compute two Δr. For the $n = 16$ PAB/PPB oligomer, we found $\Delta r = 0.019$ and 0.013 Å for the PAB and PPB parts, respectively. The corresponding values are 0.014 and 0.017 Å for isolated PAB and PPB, respectively. Although these Δr are similar, the two Δr

TABLE 3: Evolution with Chain Length of the Partial Atomic Charges Borne by the Central Atoms in PAB/PPB[a]

	N-end				P-end			
n	q^{N}	q^{B^1}	q^{P}	q^{B^2}	q^{N}	q^{B^1}	q^{P}	q^{B^2}
2	−0.21	0.11	0.34	−0.16	−0.22	0.09	0.46	0.05
4	0.21	−0.08	0.38	−0.25	0.04	−0.17	0.47	−0.10
6	0.20	−0.19	0.42	−0.35	0.29	−0.16	0.47	−0.31
8	0.34	−0.21	0.45	−0.37	0.29	−0.21	0.45	−0.33
10	0.34	−0.21	0.44	−0.41	0.36	−0.24	0.46	−0.38
12	0.37	−0.21	0.44	−0.40	0.35	−0.21	0.45	−0.39

[a] All values are in $|e|$ and have been obtained within the MK approach at the MP2/6-311G(2d)//PBE0/6-31G(2d) level of theory. B^1 and B^2 are the boron atom forming the shorter bond (in the polymer) with N and P, respectively.

TABLE 4: Evolution with Chain Length of the Partial Atomic Charges Borne by the Central Atoms in Conjugated Chains[a]

	N-end				P-end			
n	q^{N}	q^{B^1}	q^{P}	q^{B^2}	q^{N}	q^{B^1}	q^{P}	q^{B^2}
2	−1.01	0.52	−0.52	0.22	−0.54	0.47	−0.73	0.33
4	−0.79	0.58	−0.71	0.50	−0.73	0.59	−0.77	0.50
6	−0.81	0.58	−0.73	0.50	−0.78	0.55	−0.78	0.60
8	−0.79	0.57	−0.74	0.53	−0.81	0.62	−0.78	0.55
10	−0.79	0.57	−0.73	0.54	−0.81	0.62	−0.79	0.56
12	−0.79	0.57	−0.73	0.54	−0.81	0.62	−0.78	0.57

[a] All values are in $|e|$ and have been obtained within the MK approach at the MP2/6-311G(2d)//PBE0/6-31G(2d) level of theory. B^1 and B^2 are defined according to the 3D structures (see Table 3).

TABLE 5: Longitudinal Dipole Moment, Static Polarizability, and First Hyperpolarizability (au) of PAB/PPB Copolymers[a]

	N-end			P-end		
n	μ_L	α_L	β_L	μ_L	α_L	β_L
2	−1.68	75	−4	−1.40	72	−118
4	−4.87	167	−163	−4.19	163	−374
6	−8.11	265	−272	−7.36	259	−504
8	−11.46	365	−325	−10.69	358	−567
10	−14.86	466	−345	−14.07	459	−592
12	−18.29	567	−348	−17.48	560	−595
14	−21.73	669	−338	−20.92	662	−588
16	−25.17	770	−324	−24.36	764	−574
∞[b]	−1.72	51	30	−1.72	51	16
Δ∞[b]	0.01	1	22	0.01	1	9

[a] All results have been obtained with the MP2/6-311G(2d)//PBE0/6-31G(2d) approach. At the bottom of the table, the extrapolated polymeric values per unit cell are given (see the text for more details on the procedure used to obtain these values). 1 au of $\mu = 2.5418$ D. 1 au of $\alpha = 1.6488 \times 10^{-41}$ C^2 m^2 J^{-1} = 0.14818 Å^3. 1 au of $\beta = 3.2063 \times 10^{-53}$ C^3 m^3 J^{-2} = 8.641×10^{-33} esu. [b] ∞ gives the extrapolated value whereas Δ∞ is the estimated extrapolation error; i.e. polymeric values are given by ∞ ± Δ∞.

TABLE 6: Longitudinal Dipole Moment, Static Polarizability, and First Hyperpolarizability (au) of PIB/DHPPB Copolymers[a]

	N-end			P-end		
n	μ_L	α_L	β_L	μ_L	α_L	β_L
2	−0.91	85	(−)58	−0.11	80	128
4	−0.78	219	(−)622	0.26	211	540
6	−0.36	371	(−)1956	0.77	362	1970
8	0.17	530	3756	1.33	522	3826
10	0.74	693	5811	1.92	685	5911
12	1.33	858	8003	2.52	850	8122
14	1.94	1025	10281	3.13	1016	10406
16	2.55	1191	12603	3.74	1183	12730
∞	0.31	84	1239	0.31	84	1209
Δ∞	0.01	1	55	0.01	1	33

[a] See Table 5 for more details.

reverse their order in the copolymerization process. For PIB/DHPPB, both Δr become negative for sufficiently long chains, meaning that the conjugated copolymer favors a cis−transoïd conformation. This is not surprising as DHPPB and probably PIB behave in a similar fashion. For the phosphorus bonds the Δr reversal takes place around $n = 8-10$, as in DHPPB, the nitrogen bond lengths only becoming equal for $n = 16$, as in PIB.

To assess the delocalizability and the asymmetry of the copolymers, the geometry is not the only parameter: the partial atomic charges pattern is also important. Indeed, even with a zero Δr, a strong charge alternation could impede the electron mobility. The charges borne by the backbone atoms of the saturated and conjugated copolymers are given in Tables 3 and 4, respectively. Provided $n \geq 6$, the charges are almost unaffected by the length of the compound. Likewise (except for the dimer and tetramer) the differences between N and P terminated chains are negligible. The most striking feature is that the charges borne by the atoms reverse sign when going from saturated chains (with negative B, and positive N and P) to conjugated compounds (with positive B, and negative N and P), indicating a likely reversal of asymmetry. This is not surprising as exactly the same phenomena has been found in the pure polymers. If one computes charge alternations for the different components of the copolymer, one obtains 0.6 $|e|$ in PAB, 0.8 $|e|$ in PPB, −1.4 $|e|$ in PIB, and −1.3 $|e|$ in DHPPB. For comparison, the Δq are 0.8 $|e|$ in PAB, 0.9 $|e|$ in PPB, −1.6 $|e|$ in PIB, and −0.8 $|e|$ in DHPPB. Therefore, the charge alternation in PAB/PPB is slightly decreased in the copolymer whereas one finds an averaging effect in PIB/DHPPB. This is well illustrated by the overall charge alternation, $\Delta q = {}^1/_2(q^{N} + q^{P} - q^{B^1} - q^{B^2}) = 0.7\ |e|$ and $-1.4\ |e|$ for PAB/PPB and PIB/DHPPB, respectively, is smaller/lying between the Δq of the pure polymers.

B. Dipole Moments and (Hyper)polarizabilities. Tables 5 and 6 provide the MP2/6-311G(2d)//PBE0/6-31G(2d) μ_L and the static α_L and β_L for the PAB/PPB and PIB/DHPPB copolymers, respectively. The corresponding data for PAB and PIB can be found in ref 11, whereas the NLO coefficients of PPB and DHPPB, computed at the same level of theory are given as Supporting Information. Figures 2 and 3 depict the evolution of $\Delta\alpha_L$ with chain length for saturated and conjugated copolymers, respectively, and provides a comparison with the pure polymers. Figures 4 and 5 depict the corresponding curves for $\Delta\beta_L$.

For PAB/PPB, the dipole moment is almost independent of the CE nature. Indeed, the N-end and P-end $\Delta\mu_L(4)$ only differ only by 13%. The opposite is found in PIB/DHPPB, where the sign of the μ_L of the hexamer depends on the CE. As the chain lengthens, the μ_L of PIB/DHPPB reverses sign, as in the PIB and DHPPB. The dipole moment per UC of PAB/PPB converges to −4.37 D and can be compared to the responses of PAB and PPB: −3.18 D and −5.29 D, respectively. The copolymer $\Delta\mu_L(\infty)$ is the average of the PAB and PPB values: −4.24 D (4% of error). This is consistent with the almost unaffected charges and bond lengths. Nevertheless, for the conjugated copolymer, the dipole moment per UC in the macromolecule (0.79 D) is smaller than the $\Delta\mu_L(\infty)$ in PIB and DHPPB (0.94 D and 0.97 D, respectively), a conclusion that was not possible to draw just from the charges borne by P, N, and B atoms.

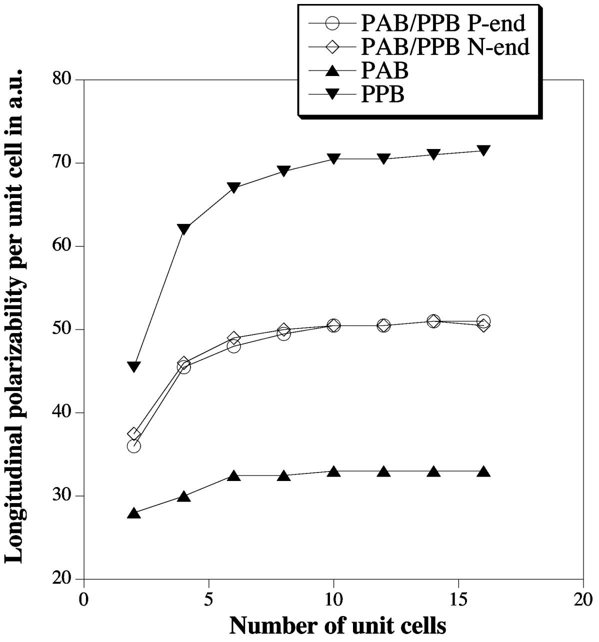

Figure 2. Evolution with chain length of the MP2/6-311G(2d)//PBE0/6-31G(2d) longitudinal polarizability per unit cell, $\Delta\alpha_L(n)$, of PAB, PPB, and PAB/PPB.

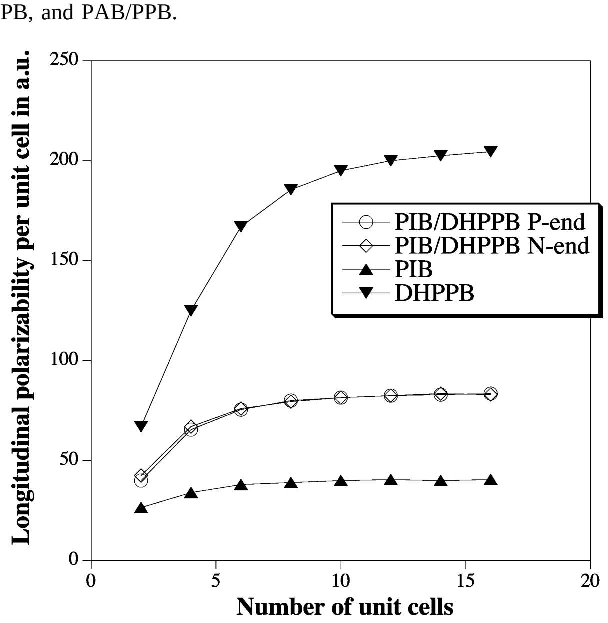

Figure 3. Evolution with chain length of the MP2/6-311G(2d)//PBE0/6-31G(2d) longitudinal polarizability per unit cell, $\Delta\alpha_L(n)$, of PIB, DHPPB, and PIB/DHPPB.

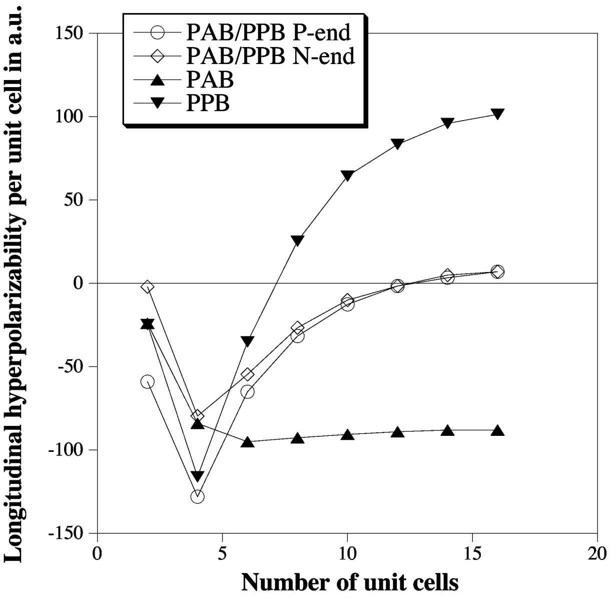

Figure 4. Evolution with chain length of the MP2/6-311G(2d)//PBE0/6-31G(2d) longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(n)$, of PAB, PPB, and PAB/PPB.

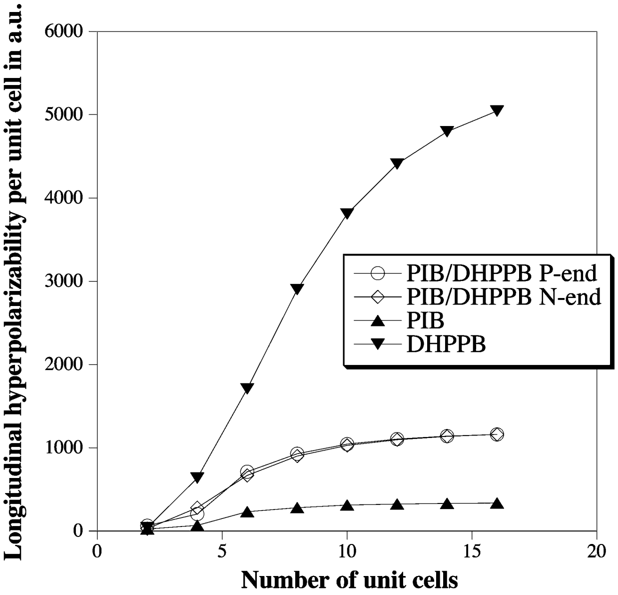

Figure 5. Evolution with chain length of the MP2/6-311G(2d)//PBE0/6-31G(2d) longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(n)$, of PIB, DHPPB, and PIB/DHPPB.

As expected for increasingly long compounds,[41−44] the $\Delta\alpha_L$ of the copolymers increases rapidly with chain length for short oligomers and then enters the saturation regime where it tends toward the asymptotic value characterizing the infinite polymer (Figures 2 and 3). From the data in Table 5, one clearly notes that the CE does not significantly affect the polarizability: the gap between the α_L of the N-end and P-end oligomers does not exceed 4%. The same conclusion comes from Table 6 with maximal discrepancies limited to 6%. The polymeric $\Delta\alpha_L(\infty)$ is 51 au (84 au) for PAB/PPB (PIB/DHPPB). For the saturated chains, one concludes to a simple averaging of the figures of the originating polymers, as in the case of the dipole moment. Indeed, PAB (PPB) has an $\Delta\alpha_L(\infty)$ of 33 (73) au for an average of 53 au (4% of error with respect to the actual value). On the other hand, for the conjugated chains, the polymeric response (84 au) is significantly smaller than the direct averaging of the PIB and DHPPB values, 41 and 207 au, respectively. The resulting 124 au indicates that for delocalized copolymers, the least polarizable component guides the total response because it impedes the electron mobility over numerous UC. On the other hand, in saturated chains, the delocalization is always negligible and the polarizability mainly presents an additive nature.

The statement that μ_L and α_L of PAB/PPB are unaffected by the CE does not hold for β_L. Indeed, for the hexadecamer, the P-end copolymer β_L is still 77% larger than the β_L of the N-end compound. This strong CE influence was expected from the shape of the β/n versus n curves of PAB and PPB (see Introduction). By removing these CE effects, i.e., by computing $\Delta\beta_L(n)$, one gets much more similar responses, provided $n \geq 8$, as illustrated in Figure 4. Accordingly, we can classify PAB/PPB in the third category of AB systems, with a negative response for short oligomers, followed by a sign change and a saturation toward a small but positive polymeric $\Delta\beta_L(\infty)$ limit. In short PAB/PPB, the CE contributions of PAB and PPB have the same sign and responses comparable to the parent polymer are observed. In extended PAB/PPB, for which only the UC plays a role, the contributions originating from the PAB and PPB component almost cancel out and result in a near-zero $\Delta\beta_L(\infty)$. For the tetramer, it is striking to note that the $\Delta\beta_L$ of the P-end (N-end) structure is similar to that of PPB (PAB). This indicates that, for $n = 4$, the largest portion of the CE effects is due to the PH_3 (or NH_3) terminal group rather than to BH_3. Starting from the hexamer, the $\Delta\beta_L(n)$ values for the copolymer are bracketed by the PAB and PPB curves. In the polymer, one predicts a negligible $\Delta\beta_L(\infty)$ (16 ± 9 au) that is completely compatible with an averaging (12 ± 8 au) of the PAB (−86 ± 2 au) and PPB (+110 ± 8 au) values. For the PIB/DHPPB, the $\Delta\beta_L(n)$ versus n curves are following a standard shape, as they all belong to class 1 (Figure 5). The contributions from the CE, which are limited in PIB and DHPPB, are also small in the copolymer. Indeed, except for the dimer, the β_L of the P-end and N-end chains do not differ by more than 15%. For the polymer, the computed $\Delta\beta_L(\infty)$, 1213 ± 29 au, is between the PIB (349 au) and DHPPB (6272 au) results but, being much closer to the PIB response, does not correspond to the average. As for α_L, one could state that the electron mobility of PIB is improved by adding DHPPB units but the delocalization is still impeded by PIB. Similar conclusions were previously drawn for the PP/PMI copolymer.[31]

IV. Conclusion

We have investigated the linear and nonlinear optics properties of the alternating PAB/PPB copolymers and their conjugated counterparts, PIB/DHPPB. It turns out that the effects of copolymerization on the geometries and charges of the chains are relatively small. For the saturated compounds the dipole moments, polarizability and first hyperpolarizability present an additive nature. They are close (∼4% for μ_L and α_L) to the mean values obtained from the pure PAB and PPB polymers. The reverse is found for conjugated compounds: the polarizability and first hyperpolarizability of the copolymer is much closer to the least delocalizable parent, PIB.

The static $|\beta_L|/W$ (first hyperpolarizability per Dalton) of the systems here investigated can easily be estimated from the corresponding $|\Delta\beta_L(\infty)|$: negligible for PAB/PPB and 0.30×10^{-30} cm^5 esu^{-1} g^{-1} mol for PIB/DHPPB. One may compare these values with 0.01×10^{-30} cm^5 esu^{-1} g^{-1} mol for PAB, 0.02×10^{-30} cm^5 esu^{-1} g^{-1} mol for PPB, 0.03×10^{-30} cm^5 esu^{-1} g^{-1} mol for PIB, and 0.95×10^{-30} cm^5 esu^{-1} g^{-1} mol for DHPPB. The response of PIB/DHPPB is similar to that of classical push−pull molecules such as 3-methyl-4-nitroaniline (0.10×10^{-30}),[45] *N*-(4-nitrophenyl)-(L)-prolinol (0.06×10^{-30})[46] or α-nitro-*ω*-amino-*trans*-hexatriene (0.66×10^{-30}).[47] At this point, one can conclude that PIB/DHPPB would indeed present an appealing potential for NLO applications although less than DHPPB. On the other hand, PAB/PPB have negligible NLO responses due to the cancellation of the UC contributions of the PPB and PAB components.

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Supporting Information Available: Bond length alternation, charge alternation, longitudinal dipole moment, static polarizability and static first hyperpolarizability of trans-cisoïd PPB and DHPPB chains. All results have been obtained with the 6-311G(2d) basis set on the PBE0/6-31G(2d) geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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