

Linear and Nonlinear Optics Properties of Polyphosphazene/Polynitrile Alternating Copolymers

Denis Jacquemin*

Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, B-5000 Namur, Belgium

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Abstract: The linear and nonlinear optical properties of polyphosphazene/polynitrile alternating copolymers, $-(\text{PH}_2 = \text{N} - \text{CH} = \text{N})_N$, are studied, at the MP2/6-31G(d) level of approximation, by using an oligomeric approach. We report the evolution with the chain length of the geometry, charges, dipole moments, polarizabilities, and first hyperpolarizabilities of two conformers (trans-transoid and trans-cisoid). Comparisons with the polyphosphazene/polyacetylene and poly(thiophosphazene) structures are performed. It turns out that the polyphosphazene/polynitrile copolymers present dipole moment and polarizabilities comparable to polyphosphazene but larger (+50%) first hyperpolarizabilities. The relative response of these copolymers is comparable to the one of standard push–pull systems.

1. Introduction

In the quest for large first hyperpolarizabilities (β), different strategies have been set up to obtain organic materials showing large nonlinear optics (NLO) responses.¹ To reach this goal, one of the difficulties is to combine delocalizable electrons which are necessary in order to get large NLO responses and the asymmetry required because β is an odd term in the dipole moment expansion. Recently, we have been interested in AB oligomers^{2–7} which show asymmetric unit-cells (two different nuclei and two different bonds) and possess mobile electrons. On the contrary to push–pull chains,⁸ a β response may indeed be obtained for any AB chain length, and the β value of the polymer may be nonzero. Two typical examples of AB polymers are polyphosphazene and polynitrile. Polyphosphazene [PP, $-(\text{P}(\text{R}, \text{R}') = \text{N})_N$ where N is the number of unit cells] and its derivatives is an archetype of a successful inorganic polymer. Many applications have been found for PP, from flame retardant materials, to proton-exchange membrane in fuel cells. We refer the reader to ref 9 for a list of applications and references. The β of PP has been measured experimentally¹⁰ and studied theoretically at semiempirical¹¹ and *ab initio*² levels of approximation. In ref 10, it has been found that the response of the PP backbone is negligible, whereas, by adding

chromophore side groups, small nonlinear optics (NLO) responses could be observed. Although the results from semiempirical¹¹ and *ab initio*² studies differ quantitatively, both found that the β of unsubstituted (i.e. $\text{R} = \text{R}' = \text{H}$) PP should be quite small, about one-third of that of classical push–pull systems. Polynitrile [PN, also named polycarbonitrile or polymethineimine, $-(\text{C}(\text{R}) = \text{N})_N$] has been synthesized by Whörle in the 1970s^{12,13} and more recently by Komatsu¹⁴ by ring-opening polymerization (ROP) of triazine. To our knowledge, the NLO properties of PN have not been studied experimentally, but they have been the subject of several theoretical calculations, reviewed in ref 3. It turns out that for PN, β reported to the size of the chain (β/N) can be extremely large; as large as in the best α,ω -nitro,amino-polyacetylene (α,ω -nitro,amino-PA) chains, i.e., much larger than in classical push–pull compounds.^{15,16}

In 1989, Manners, Allcock, Renner and Nuyken¹⁷ presented the first synthesis of PP/PN copolymers, so-called poly(carbophosphazene). Their procedure is based on a ROP of the six-member cycle $-\text{C}(\text{Cl})=\text{N}-\text{P}(\text{Cl}_2)=\text{N}-\text{P}(\text{Cl}_2)=\text{N}-$ which leads after 4 h of heating to a polymer with a CNPNPN backbone sequence. By further reaction with NaOPh (PhNH_2) more stable aryloxy (amino) polymers have been obtained.¹⁷ The aryloxy chains were further characterized by the same group in 1991,¹⁸ and it was found that the poly(carbophosphazene) skeleton is much less flexible than

* Corresponding author e-mail: denis.jacquemin@fundp.ac.be,
URL: <http://www.fundp.ac.be/~jacquemd>.

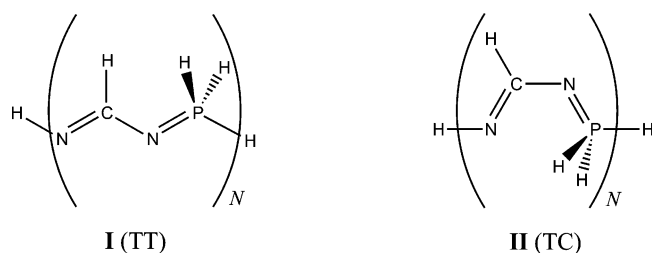


Figure 1. Schematic representation of trans-transoid and trans-cisoid PP/PN alternating copolymers.

PP, probably due to the inherent differences in the π -bonding nature of $C=N$ and $P=N$ double bonds. Following these initial works, additional structures, like various aminocarbo-phosphazenes, have been synthesized.¹⁹ In addition, closely related copolymers, polythiophosphazenes²⁰ and polythionylphosphazene,²¹ both presenting the SNPNPN backbone sequence have been obtained by ROP. We refer the reader to ref 22 for a detailed review of these inorganic polymers. If, six-member CNPNPN cycles are well characterized structures,^{23,24} there are also a few examples of the corresponding eight member cycles showing the CNPNC-NPN sequence.^{25,26} In a recent contribution Rivard²⁶ reports the synthesis of various linear structures including the first component of the alternating PP/PN copolymer, i.e., $P(R_2R')=N-C(R)=N-R''$ which has been characterized by X-ray diffraction. Such CNPN chains would certainly be an opportunity for NLO applications if the large NLO response of PN and the stability of PP could be combined.

In this paper, we investigate the geometry, charges, dipole moment, polarizability and first hyperpolarizability of increasingly long PP/PN alternating copolymers showing the CNPN sequence (Structures **I** and **II** in Figure 1). To our knowledge, no previous *ab initio* investigation has been performed on these systems, though a study of the six member cycles with the CNPNPN and SNPNPN patterns has been performed by Jaeger and co-workers.²⁴ The same group evaluated the structure, conformation and flexibility of polythionylphosphazene.^{27,28} The present study aims to rationalize the impact of copolymerization on β . Such rationalization is particularly welcome as, in this case, the nature of the two “parent” polymers are very different (organic/inorganic, with second/third row atoms, presenting a delocalized electron cloud/island- π bonding, ...).

II. Computational Details

We have selected the MP2/6-31G(d) level for both the geometry optimization and the calculation of electronic properties. With this approach, one takes into account both the indirect (on the ground-state geometry) and direct (on the wave function) dynamic electron correlation (EC) contributions. This choice matches the computational schemes that have been demonstrated to be adequate for both PP and PN. Indeed, for β calculations on PP, it has been found that the MP2/6-31G(d)/HF/6-31G(d) method is sufficient, i.e., direct/indirect EC effects are significant/negligible.² The use of polarization functions being mandatory as expected for compounds presenting third-row atoms. For PN, the impact of EC on the geometry is larger, and the MP2/6-31G//MP2/

6-31G technique provides a semiquantitative estimate of the NLO properties.¹⁶ If the use of polarization (or diffuse) functions modifies the β responses of short PN oligomers,^{16,29} it has a small effect on the corresponding polymeric property. For instance, the MP2/6-31G//MP2/6-31G polymeric first hyperpolarizability per unit cell reaches 13×10^4 au in PN,¹⁶ whereas the MP2/6-31G(d)//MP2/6-31G(d) value is 14×10^4 .³⁰ A similar MP2/6-31G(d) approach has been selected by Jaeger and co-workers for their investigations of the six-membered cycles.²⁴ The calculations have been performed with the Gaussian03 program,³¹ by using the following procedure:

1. The ground-state geometry of each oligomer has been determined by the optimization of its structural parameters. In this first investigation, two conformations have been chosen: planar trans-transoid (TT) and trans-cisoid (TC). The unit cells of the chains are defined according to Figure 1. In addition to planarity, we have also imposed the linearity of the chain, so that the longitudinal axis could be properly defined. To avoid bent chains, all the backbone angles of TT chains have been set equal, whereas in TC chains only two different backbone angles have been used ($X=N-Y$ and $N=X-N$; $X, Y = P$ or C).³² After the geometry optimization, each oligomer has been oriented in the Cartesian frame so that the longitudinal axis runs through the center of the first and the last double bonds.

2. In addition to the dipole component parallel to the longitudinal axis (μ_L), the partial atomic charges have been computed for the optimized geometries using the Merz–Kollman (MK)³³ approaches within the MP2/6-31G(d) approximation.

3. Static electronic polarizabilities (α) and first hyperpolarizabilities (β) have been evaluated for the optimized geometries. In quasilinear chains, the longitudinal components of α and β tensors (α_L and β_L) often dominate the total response for sufficiently long chains. For instance, at the HF/6-31G(d)/MP2/6-31G(d) level, the β_L of the TC octamer ($N=8$; structure **II**) is 5.7 times larger than the next larger component. For this reason, we focus on the longitudinal components in this paper. Because their practical determination at EC levels remains cpu-costly for extended oligomers, the vibrational contributions to α and β (α^v and β^v) have been neglected, although, they could make important contributions to the total static values in conjugated systems.^{34–36} Static α_L and β_L have been evaluated by using the numerical finite-field procedure based on the differentiation of the energies computed under several electric field amplitudes. We refer the reader to ref 4 for a complete description of this procedure. It has been found that the accuracy of the procedure could be slightly improved by performing the finite field (FF) procedure on the MP2 energy corrections (rather than the MP2 total energies) and adding the results to the fully analytic coupled-perturbed Hartree–Fock (CPHF) results computed with the same basis set on the same geometry. By doing so, the final accuracy on the MP2 α_L values is 0.1 au, whereas the accuracy on β_L is estimated to be $\sim 1\%$. In this paper we adopt the usual sign convention for β_L : positive when orientated in the same direction as the dipole moment, negative otherwise.

Table 1. Evolution with Chain Length of the Central Bond Lengths and Bond Angles of Structures **I** and **II**^a

| N | TT, I | | | | | TC, II | | | | | | ΔE |
|---|--------------|-----------|-----------|-----------|-----------------------------------|---------------|-----------|-----------|-----------|------------------|------------------|------------|
| | $d_{N=C}$ | d_{C-N} | $d_{N=P}$ | d_{P-N} | $\alpha_{X=N-Y} = \alpha_{N=X-N}$ | $d_{N=C}$ | d_{C-N} | $d_{N=P}$ | d_{P-N} | $\alpha_{N=X-N}$ | $\alpha_{X=N-Y}$ | |
| 1 | 1.285 | 1.391 | 1.582 | | 120.5 | 1.298 | 1.374 | 1.616 | | 121.7 | 108.6 | +13 |
| 2 | 1.291 | 1.372 | 1.573 | 1.645 | 118.2 | 1.320 | 1.356 | 1.596 | 1.692 | 119.5 | 114.4 | +16 |
| 3 | 1.298 | 1.360 | 1.592 | 1.664 | 117.7 | 1.322 | 1.351 | 1.609 | 1.680 | 119.2 | 115.6 | +17 |
| 4 | 1.305 | 1.351 | 1.598 | 1.655 | 117.5 | 1.328 | 1.344 | 1.612 | 1.672 | 119.1 | 116.2 | +17 |
| 5 | 1.309 | 1.346 | 1.606 | 1.649 | 117.4 | 1.330 | 1.340 | 1.617 | 1.666 | 119.1 | 116.6 | +17 |
| 6 | 1.313 | 1.341 | 1.607 | 1.644 | 117.3 | 1.332 | 1.337 | 1.619 | 1.662 | 119.2 | 116.9 | +17 |
| 7 | 1.316 | 1.338 | 1.614 | 1.640 | 117.3 | 1.333 | 1.336 | 1.622 | 1.660 | 119.2 | 117.1 | +17 |
| 8 | 1.318 | 1.336 | 1.617 | 1.638 | 117.2 | 1.335 | 1.334 | 1.623 | 1.658 | 119.2 | 117.2 | +17 |

^a All results have been obtained at the MP2/6-31G(d) level. Bond lengths are given in Å, angles in degrees. At the extreme right of the table, the energetic difference between TT and TC conformers (ΔE) is reported in kcal/mol per N.

4. The polymeric responses have been obtained by extrapolating the oligomeric values. To carry out the extrapolations, we define the β_L (and μ_L and α_L) per unit cell as $\Delta\beta_L(N) = [\beta_L(N) - \beta_L(N-1)]$. 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 to obtain $\Delta\mu_L(\infty)$, $\Delta\alpha_L(\infty)$ and $\Delta\beta_L(\infty)$ as well as estimates of the corresponding standard deviations. We refer the reader to ref 37 for extra details. To allow direct comparison with previous works, we have also defined the polymeric β per backbone atom: $\Delta\beta_L^{\text{at}}(\infty) = \Delta\beta_L(\infty)/4$ (and similarly for μ and α).

III. Results

A. Geometries and Charges. The backbone geometry and relative stability of the TT and TC conformers are given in Table 1. First, we note that the TT structures are not favored, the TC structures being more stable by 17 kcal/mol per cell, provided $N \geq 2$. This could have been expected because the TC oligomers are the most stable in PP^{2,38} and the TT conformers are also the least stable in PN^{3,39} which favors off-planar structures. For the smallest chain of **II**, the bond lengths are 1.30, 1.37, and 1.62 Å, in reasonable agreement with the experimental values obtained for a similar structure (**5** of ref 26): 1.28, 1.40, and 1.54 Å, with packing effects and side substitutions by large groups (Cl, Ph and *t* Bu). The C=N and P=N bond lengths are also in good agreement with the MP2/6-31G(d) values obtained for the $-C(\text{Cl})=N-P(\text{Cl}_2)=N-P(\text{Cl}_2)=N-$ cycle by Jaeger et al.: 1.33 and 1.60 Å, respectively.²⁴ As TT chain length is increased, the double bonds become longer and the single bonds shorter as expected in conjugated chains. For the longest chains, the bond length alternation, $\Delta r^{\text{TT}} = d_- - d_+$ is 0.018 Å for the PN segment and 0.021 Å for the PP segment. In TC chains, the qualitative behavior is similar, but the two CN bonds are almost equal for medium chains; it even seems that the double/single bond ordering is reversed for $N \geq 8$. For $N = 8$, Δr^{TC} attains -0.001 Å for the PN part and 0.035 Å for the PP part. The negative Δr means that the PN component of long oligomers would favor a cis-transoid (with the double bonds being parallel rather than perpendicular to the longitudinal axis) over a trans-cisoid conformation. These results can be compared to the MP2/6-31G(d) Δr obtained for the 16-unit of TT PN (0.096 Å), TC PN (0.111 Å) and TC PP (0.011 Å) oligomers. Consequently, the copolymer-

Table 2. Evolution with Chain Length of the Charges Borne by the Central Atoms^a

| N | TT, I | | | | TC, II | | | |
|---|------------------|----------------|------------------|----------------|------------------|----------------|------------------|----------------|
| | q^{N^1} | q^{C} | q^{N^2} | q^{P} | q^{N^1} | q^{C} | q^{N^2} | q^{P} |
| 1 | -0.68 | 0.48 | -0.67 | 0.68 | -0.76 | 0.50 | -0.75 | 0.75 |
| 2 | -0.60 | 0.54 | -0.71 | 1.06 | -0.73 | 0.71 | -0.76 | 0.86 |
| 3 | -0.59 | 0.53 | -0.72 | 1.12 | -0.80 | 0.73 | -0.73 | 0.93 |
| 4 | -0.51 | 0.51 | -0.72 | 1.10 | -0.73 | 0.75 | -0.84 | 1.02 |
| 5 | -0.61 | 0.51 | -0.69 | 1.11 | -0.86 | 0.75 | -0.85 | 1.05 |
| 6 | -0.62 | 0.51 | -0.69 | 1.11 | -0.87 | 0.75 | -0.86 | 1.08 |
| 7 | -0.63 | 0.52 | -0.67 | 1.10 | -0.88 | 0.75 | -0.86 | 1.09 |
| 8 | -0.63 | 0.51 | -0.67 | 1.10 | -0.89 | 0.75 | -0.86 | 1.11 |

^a All values are in *e* and have been obtained within the MK approach at the MP2/6-31G(d)/MP2/6-31G(d) level of theory. N¹ (N²) is the nitrogen atom forming the double bond with C (P).

ization clearly results in a Δr decrease for PN (the largest Δr) and an increase of the Δr of PP (the smallest Δr). Therefore, it is difficult to predict, at this stage, if the copolymer is more or less delocalizable than its constituents taken separately.

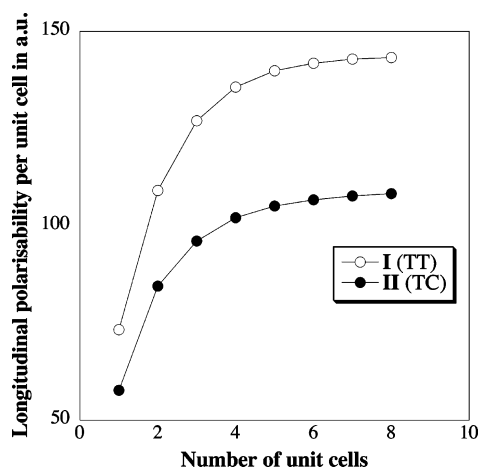
In addition to the geometry of the chains, another parameter is crucial for assessing the delocalization and the asymmetry along the backbone: the charge distribution. Table 2 presents the MP2/6-31G(d) MK charges borne by the central atoms of increasingly long oligomers. For every atoms, the charges are quite constant with chain length. For the most stable conformers (**II**), the charges are $-0.9e$, $0.8e$, and $1.1e$ for N, C and P, respectively. This means that phosphorus and nitrogen on one hand and carbon and nitrogen on the other hand exchange (almost) one electron. In TC PP the same behavior was found,³⁸ whereas in TC PN the exchange attains $1.5 e$ (compared to $0.8 + 0.9 = 1.7 e$ here), leading to the conclusion that the copolymerization has little effect on the partial atomic charges. Note that the C and N charges are smaller in the TT chains, i.e., the exchange of electrons is less pronounced in TT than in TC. Using a Natural Population Analysis rather than the MK approach, Jaeger and co-workers got a similar charge pattern (positive P and C, negative N) for the $-C(\text{Cl})=N-P(\text{Cl}_2)=N-P(\text{Cl}_2)=N-$ cycle, although an even stronger charge exchange was predicted, maybe due to the presence of Cl atoms.²⁴

B. Dipole Moments and (Hyper)polarizabilities. Table 3 gives the μ_L , α_L and β_L of structures **I** and **II**, whereas Figures 2 and 3 depict the evolution with chain length of

Table 3. Longitudinal Dipole Moment, Static Polarizability and Static First Hyperpolarizability (au) of Structures I and II^a

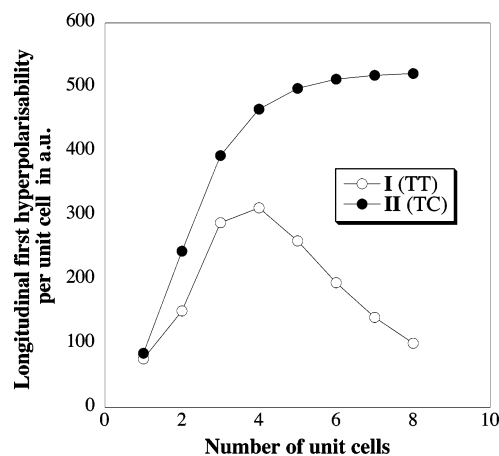
| N | TT, I | | | TC, II | | |
|---------------------|---------|------------|-----------|---------|------------|-----------|
| | μ_L | α_L | β_L | μ_L | α_L | β_L |
| 1 | 1.64 | 73.3 | 76 | 0.39 | 57.7 | 85 |
| 2 | 4.37 | 182.4 | 227 | 2.09 | 142.2 | 329 |
| 3 | 7.86 | 309.4 | 515 | 4.17 | 238.3 | 722 |
| 4 | 11.80 | 445.1 | 827 | 6.53 | 340.4 | 1188 |
| 5 | 16.02 | 585.0 | 1087 | 9.04 | 445.5 | 1686 |
| 6 | 20.43 | 726.8 | 1282 | 11.63 | 552.2 | 2199 |
| 7 | 24.94 | 869.7 | 1423 | 14.29 | 659.9 | 2717 |
| 8 | 29.53 | 1013.0 | 1524 | 16.98 | 768.2 | 3238 |
| ∞^b | 4.9 | 144 | | 2.9 | 110 | 524 |
| Δ_{∞}^b | 0.2 | 1 | | 0.2 | 1 | 2 |

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

**Figure 2.** Evolution with chain length of the MP2/6-31G(d)//MP2/6-31G(d) longitudinal polarizability per unit cell, $\Delta\alpha_L(N)$, of structures I and II.

the static $\Delta\alpha_L$ and $\Delta\beta_L$. The $\Delta\mu_L$ evolution with chain length of both systems presents a standard shape: it increases for small oligomers, then enters a saturation regime where it converges toward the polymeric value. $\Delta\mu_L^{\text{at}(\infty)}$ of I and II are 3.1 and 1.9 D, respectively. The larger longitudinal dipole moment for TT structures was awaited from previous calculations on AB systems.⁵ These values may be compared to their TT/TC PP counterpart 3.3/2.2 D⁴⁰ and to 0.9/0.5 D for TT/TC PN,^{30,41} meaning that it is PP that eventually guides the total dipole moment. As a first approximation, μ_L is mainly connected to the asymmetry rather than to the delocalization,⁴² so we forecast the asymmetry of the copolymers to be closer to that of PP than PN.

As expected for increasingly long compounds,^{42–46} the $\Delta\alpha_L$ rapidly increases with chain length for short oligomers, then enters a saturation regime where it tends toward the asymptotic value characterizing the infinite polymer (Figure 2). The $\Delta\alpha_L^{\text{at}(\infty)}$ is 36 au (28 au) for I (II). The PP(TT/TC)

**Figure 3.** Evolution with chain length of the MP2/6-31G(d)//MP2/6-31G(d) longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(N)$, of structures I and II.

has a MP2/6-31G(d)//HF/6-31G(d) $\Delta\alpha_L^{\text{at}(\infty)}$ of 25/23 au and PN(TT/TC) presents a MP2/6-31G(d)//MP2/6-31G(d) $\Delta\alpha_L^{\text{at}(\infty)}$ of 74/55 au. Therefore it is the less polarizable system (PP) that mainly guides the (quite small) $\Delta\alpha$ amplitude of the copolymer. For comparison, PA⁴⁷ and polysilane⁴⁸ present $\Delta\alpha_L^{\text{at}(\infty)}$ close to 65 au. As α does not depend on the asymmetry but only on the delocalizability, this emphasizes that PP/PN is more delocalizable than PP, although the electron mobility is still limited compared to conjugated compounds. These results are consistent with the island delocalization model proposed for PP.⁴⁹ In this island model, delocalization of valence electrons takes place only for three atoms (PNP). By adding CN segments, one could consider that the electron mobility occurs over five atoms (PNCNP), which explains the limited increase of α_L (+22% for II). On the other hand, in PN, the delocalization takes place over a much larger number of atoms, similarly to PA.

For PP/PN, β_L is always positive for all chain lengths, but the evolution with the chain length of $\Delta\beta_L$ is very different for the two conformers. Indeed, for I, $\Delta\beta_L$ first increases, reaches a maximum for $N = 4$, and then decreases toward a small polymeric limit. This is the typical shape for push–pull systems.^{8,15} In II, the $\Delta\beta_L$ versus N curve is similar to a “polarizability” curve: first an increase due to the delocalization increase, followed by the saturation toward the polymeric limit. As for the dipole moment and polarizability, it seems that PP guides the behavior of the copolymer. Indeed, in PN, both the TT and TC curves are “polarizability”-like, whereas in PP it is only the case for TC and not for TT (push–pull like curve).⁵⁰ To rationalize these shapes, one can split β into chain-ends and unit cells contributions.^{2–6} Indeed, these components are the two parts responsible for the asymmetry. The contribution of each component to β is first increasing with chain length, due to the improvement of electron mobility. For extended oligomers, the chain-end contribution to β becomes constant, while the unit-cell contribution is proportional to the length of the oligomer. For I, the evolution of $\Delta\beta_L$ (depicted in Figure 3) can be interpreted as a consequence of a negligible unit cell contribution and a significant chain-end component: (i) for short oligomers, the chain-end contribution (which is posi-

Table 4. Longitudinal Static First Hyperpolarizability (au) of Structures I and II^a

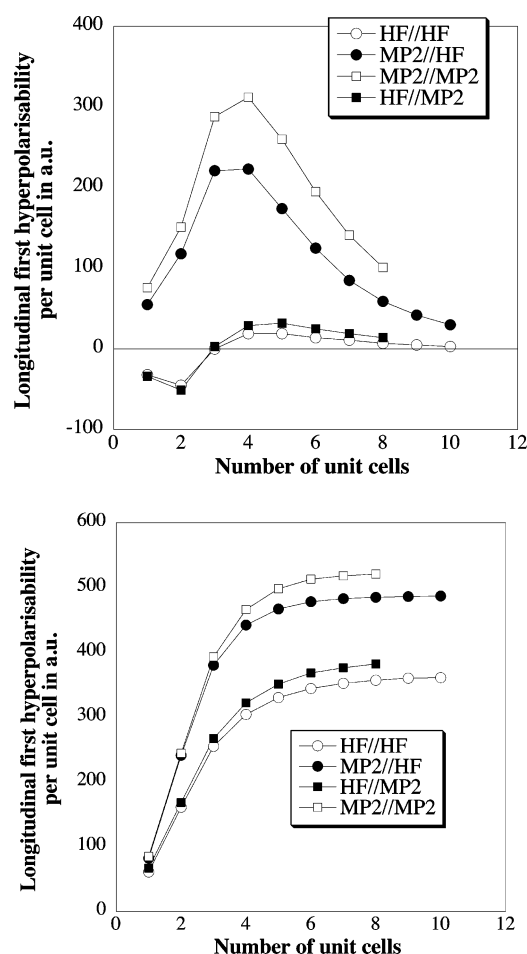
| N | TT, I | | | | TC, II | | | |
|----|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|
| | HF geometry | | MP2 geometry | | HF geometry | | MP2 geometry | |
| | β_L [HF] | β_L [MP2] | β_L [HF] | β_L [MP2] | β_L [HF] | β_L [MP2] | β_L [HF] | β_L [MP2] |
| 1 | -32 | 55 | -34 | 76 | 61 | 82 | 67 | 85 |
| 2 | -77 | 173 | -85 | 227 | 222 | 323 | 235 | 329 |
| 3 | -77 | 394 | -82 | 515 | 477 | 703 | 502 | 722 |
| 4 | -58 | 617 | -53 | 827 | 781 | 1145 | 824 | 1188 |
| 5 | -39 | 791 | -21 | 1087 | 1111 | 1612 | 1175 | 1686 |
| 6 | -25 | 916 | 4 | 1282 | 1455 | 2090 | 1543 | 2199 |
| 7 | -14 | 1001 | 23 | 1423 | 1807 | 2573 | 1919 | 2717 |
| 8 | -7 | 1060 | 37 | 1524 | 2164 | 3058 | 2301 | 3238 |
| 9 | -2 | 1102 | | | 2524 | 3544 | | |
| 10 | 1 | 1132 | | | 2885 | 4031 | | |

^a All results have been obtained with the 6-31G(d) basis set.

tive) dominates the total response, (ii) due to the increase of the electronic delocalization, the amplitude of chain-end contribution increases as the chain lengthens, and (iii) for long chains, the relative impact of the chain-end on $\Delta\beta$ becomes more and more diluted, β becomes constant and $\Delta\beta$ falls down to zero. For **II**, the reverse is true: a large unit-cell contribution combined to a small (and parallel) chain-end contribution. For long chains, each unit cell brings the same contribution to β and $\Delta\beta_L$ becomes constant. For **II**, the $\Delta\beta_L^{\text{at}(\infty)}$ attains 131 au. These results can be compared to the values obtained, using the same conformation for PP (85)² and PN (> 2500)⁵⁰ at the MP2/6-31G(d)//HF/6-31G(d) and MP2/6-31G(d)/MP2/6-31G(d) level of theory, respectively. Similarly to most other properties, the $\Delta\beta_L^{\text{at}(\infty)}$ is mainly guided by PP although there is a significant improvement of the response (+50%). In PP, the $\Delta\beta_L(\infty)$ are limited by delocalization rather than asymmetry,² meaning that if one increases the delocalization (decreases the asymmetry), the $\Delta\beta_L(\infty)$ amplitude is improved. The values obtained for the copolymer are consistent with these findings: smaller $\Delta\mu_L(\infty)$ and larger $\Delta\alpha_L(\infty)$ correspond to larger $\Delta\beta_L(\infty)$. As a consequence, one could expect the TC CNPN chains to have a $\Delta\beta_L^{\text{at}(\infty)}$ response between the PP and the **II** values.

C. Electron Correlation Effects on the First Hyperpolarizability. We have studied the EC effects on the copolymer **I** and **II** because these effects strongly differ in PP and PN. Indeed, the direct and indirect impact of EC are very large in PN(TT). Especially, the direct EC contributions changes the sign of β_L and $\Delta\beta_L$ for short chains, whereas it modifies the amplitude of $\Delta\beta_L(\infty)$ by a factor of 6.4 (the indirect effect leads to an increase of $\Delta\beta_L(\infty)$ by a factor of 1.5).³⁰ For PP(TC), the direct impact is much smaller (1.8), whereas the indirect shift is negligible.² For **I** and **II** the HF/MP2 β_L are given in Table 4, whereas Figure 4a and b depicts the corresponding evolution with N of $\Delta\beta_L(N)$.

Quite surprisingly, the TT copolymers whose NLO responses are dominated by the PP part react more like PN for what concerns EC effects. Indeed, at the HF//HF and HF//MP2 levels, $\Delta\beta_L(N)$ is first negative, reaches a minimum, goes through zero and slowly saturates toward a small asymptotic limit. This means that, at the HF level the chain-end contribution to β_L of **I** is, at least, overshoot and probably

**Figure 4.** Comparisons between the HF/6-31G(d) and MP2/6-31G(d) evolution with chain length of the longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(N)$, of structures **I** (Figure 4a, top) and **II** (Figure 4b, bottom).

pointing in the incorrect direction. The (HF) chain-end contribution is mainly dominated by the PN component of the copolymer. In addition, this means that the incorrect HF behavior in PN is probably due to the N–H terminal bond rather than to the CH₂ end group. The direct EC ratio does not evolve monotonically with N . The indirect EC ratio (MP2//MP2/MP2//HF) presents a smooth shape but is still changing relatively quickly wrt N , from 1.31 ($N = 3$) to 1.44

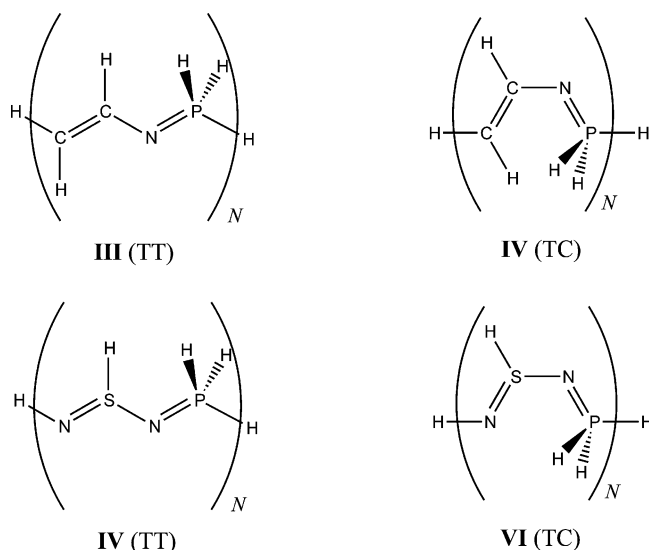


Figure 5. Schematic representation of trans-transoid and trans-cisoid PP/PA and poly(thiophosphazene) alternating copolymers.

Table 5. Longitudinal Dipole Moment, Static Polarizability and Static First Hyperpolarizability (au) of Structures III and IV^a

| <i>N</i> | TT, III | | | TC, IV | | |
|------------------|---------|------------|-----------|---------|------------|-----------|
| | μ_L | α_L | β_L | μ_L | α_L | β_L |
| 1 | 1.24 | 81.1 | 68 | 0.81 | 65.2 | 120 |
| 2 | 3.54 | 198.6 | 262 | 2.64 | 158.8 | 538 |
| 3 | 6.38 | 337.0 | 941 | 4.86 | 266.7 | 1274 |
| 4 | 9.51 | 486.2 | 2053 | 7.32 | 382.0 | 2224 |
| 5 | 12.81 | 641.5 | 3431 | 9.90 | 501.5 | 3305 |
| 6 | 16.21 | 800.5 | 4966 | 12.55 | 623.3 | 4465 |
| 7 | 19.67 | 961.8 | 6599 | 15.25 | 746.6 | 5674 |
| 8 | 23.17 | 1124.4 | 8289 | 17.98 | 870.7 | 6913 |
| ∞^b | 3.6 | 168 | 1869 | 2.8 | 127 | 1440 |
| $\Delta\infty^b$ | 0.1 | 2 | 166 | 0.1 | 2 | 178 |

^a All results have been obtained with the MP2/6-31G(d)//MP2/6-31G(d) approach. At the bottom of the table, the extrapolated polymeric values are given. ^b ∞ gives the extrapolated values whereas $\Delta\infty$ is the estimated extrapolation error; i.e. polymeric values are given by $\infty \pm \Delta\infty$.

($N = 8$). These ratios are slightly smaller than for PN chains of comparable size.³⁰

For TC copolymers, one obtains the classical increase of NLO values when the EC corrections are taken into account, while the qualitative evolution with chain length is conserved. Consequently, the ratio between EC and HF β are much less sensitive to chain length than β itself. Provided $N \geq 6$, the direct EC ratio (MP2//HF/HF//HF) is decreasing with N (from for 1.47 $N = 3$ to 1.40 for $N = 10$), whereas the indirect contribution is almost constant when the chain lengthens (from 1.05 for $N = 3$ to 1.06 for $N = 8$). Actually, if the ground-state geometry of **II** would have been optimized at the HF level, the error on the NLO properties would have been as limited as in PP. The direct EC ratio for the octamer of **II** is 1.41 and can be compared to the ratio obtained for the $N = 16$ TC PP oligomers (1.63)² and TC PN chains (4.1).⁵⁰ The direct EC effects are thus smaller than in the "parent" polymers. The EC contributions seem almost

Table 6. Longitudinal Dipole Moment, Static Polarizability and Static First Hyperpolarizability (au) of Structures V and VI^a

| <i>N</i> | TT, V | | | TC, VI | | |
|------------------|---------|------------|-----------|---------|------------|-----------|
| | μ_L | α_L | β_L | μ_L | α_L | β_L |
| 1 | 2.38 | 76.8 | -284 | 0.48 | 58.5 | -56 |
| 2 | 6.44 | 176.3 | -605 | 2.14 | 138.1 | -67 |
| 3 | 11.09 | 282.6 | -816 | 4.22 | 226.9 | 71 |
| 4 | 15.98 | 391.6 | -934 | 6.49 | 319.4 | 336 |
| 5 | 20.98 | 501.8 | -1004 | 8.87 | 413.8 | 683 |
| 6 | 26.03 | 612.7 | -1048 | 11.29 | 509.1 | 1076 |
| 7 | 31.11 | 724.0 | -1076 | 13.75 | 604.9 | 1498 |
| ∞^b | 5.1 | 112 | | 2.6 | 97 | 557 |
| $\Delta\infty^b$ | 0.1 | 1 | | 0.1 | 1 | 86 |

^a All results have been obtained with the MP2/6-31G(d)//MP2/6-31G(d) approach. At the bottom of the table, the extrapolated polymeric values are given. ^b ∞ gives the extrapolated values whereas $\Delta\infty$ is the estimated extrapolation error; i.e. polymeric values are given by $\infty \pm \Delta\infty$.

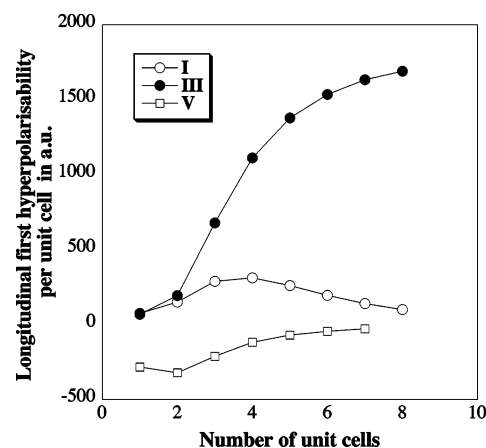


Figure 6. Evolution with chain length of the MP2/6-31G(d)//MP2/6-31G(d) longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(N)$, of structures I, III and V.

independent from each other. Indeed, for $N = 8$, we have (starting with the HF//HF β_L) the following: $2164 \times (3058/2164) \times (2301/2164) = 2164 \times 1.41 \times 1.06 = 3251$ au which is in perfect agreement with the MP2//MP2 amplitude of 3238 au (less than 1% of error).

D. Comparison with Other Polyphosphazene-Based Copolymers. In addition to PP/PN copolymers, we have also investigated two other polyphosphazene-based copolymers. They are displayed in Figure 5. These structures have not yet been synthesized, but polythiophosphazenes with SNP-NPN structures have been reported in the literature.²⁰ The MP2/6-31G(d) μ_L , α_L and β_L of structures **III** and **IV** are given in Table 5. Table 6 provides the corresponding information for compounds **V** and **VI**. The evolution with chain length of $\Delta\beta_L(N)$ is given in Figures 6 and 7, for TT and TC chains, respectively.

There are striking differences between the PP/PA and PP/PN chains. First, for the two conformers, the evolution with chain length of the $\Delta\beta_L(N)$ curves are similar: first a fast increase and then a saturation toward the (nonzero) infinite chain limit(s). These limits are higher than in PP/PN. A possible explanation could be that the replacement of CH=

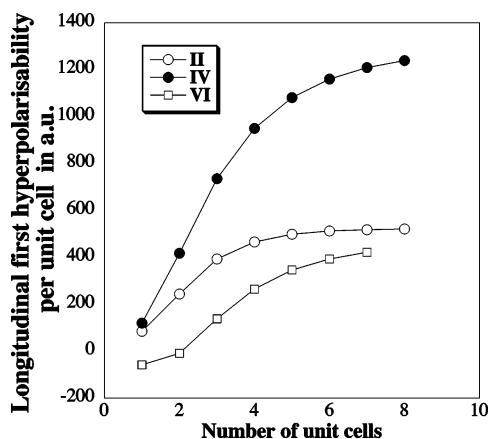


Figure 7. Evolution with chain length of the MP2/6-31G(d)//MP2/6-31G(d) longitudinal first hyperpolarizability per unit cell, $\Delta\beta_L(N)$, of structures II, IV and VI.

N segments by $\text{CH}=\text{CH}$ leads to less asymmetric and more delocalizable copolymers. Consequently, $\Delta\mu_L(\infty)$ decreases while $\Delta\alpha_L(\infty)$ increases. As β is limited by delocalization, one can explain the larger $\Delta\beta_L(\infty)$ for PP/PA than for PP/PN. Nevertheless, the increase (1440 au versus 524 au for TC chains) is larger than what could be expected from the small changes in $\Delta\mu_L(\infty)$ and the 15% improvement of $\Delta\alpha_L(\infty)$. Our hypothesis is that in PP/PN, there is some “destructive” interactions between the two (PP and PN) components that are not observed in PP/PA because PA is perfectly symmetric. The fact that the TT PP/PA polymer presents a nonzero $\Delta\beta_L(\infty)$ is more difficult to rationalize because both PA and PP(TT) chains actually show a zero response! At first, one could simply state that the zero Δr noted in long PP(TT) chains is broken in the PP/PA macromolecule (different bond lengths), explaining the nonzero $\Delta\beta_L(\infty)$. If this appears a valid explanation, it seems therefore difficult to explain the zero $\Delta\beta_L(\infty)$ in the TT PP/PN copolymer. Of course, there is the nonprobable possibility that the TT PP/PA chains present a shape like TT PP/PN, with a maximum occurring for much longer chains lengths ($N \geq 8$).⁵¹

The SNPN oligomers directly parallel the CNPN structures, with a “dromedary-back-type” curve for the TT structure and a “polarizability-like” evolution for the TC structure. However, the response of TT chains is always negative indicating a negative chain-end contribution. The TC SNPN structure, VI, seems less asymmetric ($\Delta\mu_L(\infty)$ reaches 2.6 au instead of 2.9 au) and less polarizable than II ($\Delta\alpha_L(\infty)$ of 97 au versus 110 au). With one favorable factor (the decrease of the asymmetry) against one unfavorable factor (the decrease of the delocalization), the amplitude of $\Delta\beta_L(\infty)$ stays mainly constant (557 au versus 524 au).

IV. Conclusions, Comparisons and Outlook

We have investigated the copolymerization effects upon the geometry, charges, dipole moments, polarizability and first hyperpolarizability of polycarbophosphazene and some of its derivatives. It turned out that the alternating PP/PN copolymer presents dipole moment, polarizability and first

hyperpolarizability that are closer from PP than from PN, indicating that the least delocalizable structure mainly determines the NLO properties of the whole system, although the conformation of the chain has a crucial impact. The EC effects are extremely large for TT but remain limited for TC. However, the TC PP/PN copolymers show a significant improvement over the PP (first hyperpolarizability +50%). These results are consistent with the island- π bonding model in PP: adding $\text{CH}=\text{N}$ groups increases the size the conjugated areas but does not break the island pattern. If one uses PA instead of PN in the structure, the improvement is much larger (+300%). In addition the PP/PA copolymers present a nonzero NLO response for both selected conformations. On the other hand, polythiophosphazene does not constitute an improvement over poly(carbophosphazene) for NLO.

The static $|\beta_L|/W$ (first hyperpolarizability per unit of weight) of the TC copolymers here investigated can easily be estimated from the corresponding $|\Delta\beta_L(\infty)|$: $0.06 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1} \text{ g}^{-1} \text{ mol}$ for II, $0.17 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1} \text{ g}^{-1} \text{ mol}$ for IV and $0.05 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1} \text{ g}^{-1} \text{ mol}$ for VI. One might compare these values to 0.03×10^{-30} for TC PP² and 4.2×10^{-30} for TT PN¹⁶ but also to the 0.02×10^{-30} value reported for polyphosphinoborane (PPB),⁶ 0.78×10^{-30} reported for polysilaacetylene (PSA),⁵ 0.10×10^{-30} for 3-methyl-4-nitroaniline (MNA) monomer,⁵² 0.06×10^{-30} for N-(4-nitrophenyl)-(L)-prolinol (NPP),⁵³ and 0.66 for α,ω -nitro,amino-transhexatriene.⁵⁴ At this point, we can conclude that the copolymers could be interesting for NLO applications if noncentrosymmetric crystal are obtained.

Our research is now focused in determining the origin of the nonzero response for TT PP/PA chains (and nonzero in TT PP/PN), a surprising result as both TT polymers display a zero $\Delta\beta_L(\infty)$. The study of orbital interactions could help in assessing the origin of such differences. In addition, we also investigate the first hyperpolarizability of promising fully inorganic copolymer.

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