3980 *Macromolecules* **2003,** *36,* 3980−3985

Copolymerization Effects upon the Second-Order NLO Responses of Polyacetylene/Polymethineimine

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Received November 8, 2002; Revised Manuscript Received March 30, 2003

ABSTRACT: We have determined the ideal composition of sequenced polyacetylene/polymethineimine copolymers for application as second-order materials. As a result of the interplay between delocalization and asymmetry, there exists for second-order nonlinear optics effects an optimal polyacetylene/polymethineimine composition which is estimated to be between 50% to 66% of polyacetylene. However, the addition of any proportion of polyacetylene between 25% and 75% into polymethineimine already leads to a large increase of the electronic first hyperpolarizability, highlighting the interest of creating such copolymers.

I. Introduction

Numerous developments have been achieved in order to characterize, with theoretical tools, the nonlinear optical (NLO) properties of organic materials.[1−3] From a microscopic point of view, the dipolar first hyperpolarizability (β) is the first term related to macroscopic NLO phenomena (second harmonic generation, dc-Pockels effect and optical rectification). To design efficient materials, i.e., compounds where β scaled to the size (β/N; N is the number of non-hydrogen atoms) or molecular weight (β/W) of the system is large, one has to combine electron delocalizability and asymmetry. This leads to contradictory requirements. Indeed, the most delocalizable compounds, i.e., those which possess efficient π-electrons systems, like polyacetylene (PA) or polycumulene (PC), are often centrosymmetric. To bypass this problem, different strategies have been proposed in the litterature.[2,4−8] The most popular solution is to cap a symmetric delocalizable chain (PA, PC, ...) by an electron-acceptor group, on one end, and an electron-donor group, on the other extremity. This leads to the so-called push−pull conjugated systems. Besides changing the end groups or the nature of the segment, an improvement of β/N of these compounds is only obtained by increasing the number of available π-electrons, i.e., by choosing longer segments. Nevertheless, for large N, the end groups do not interact efficiently anymore, leading to the saturation of β and to a sharp decrease of β/N ($\beta/N \rightarrow 0$ when $N \rightarrow \infty$). This phenomenon was first pointed out by Morley[9,10] and also recently analyzed by considering the vibrational contribution.[11] As a consequence, the graph of β/N vs N presents a maximum that has to be determined in order to optimize the first-order NLO response. The presence of such a maximum perfectly illustrates the interplay between asymmetry and delocalization: small chains are not polarizable enough to provide an optimal β/N, large chains are too symmetric for giving a large β/N. This interplay between delocalization and asymmetry in push−pull systems has been nicely rationalized by Marder and Brédas.[12] A reasonable alternative strategy is to build systems where all components are both asymmetric and possess π-electrons. This is done in the so-called AB (A=B)_x systems. A typical example of such a class of molecule is polyphosphazene (PP),[13,14] PP is based on the alternance of phosphorus and nitrogen atoms. However, first theoretical calculations predict quite small β response for PP oligomers.[15] The same is true for linear boron nitride chains in which the β/N is close to zero for the macromolecule due to a nearly-zero bond length alternation at the center of long chains.[16] A more promising prototype AB compound is polymethineimine (PMI). Indeed, from characterizations carried out at levels including electron correlation (EC), PMI presents a β/N value as large as the best α,ω-nitro,-amino-PA chains, i.e., also larger than most of the compounds synthesized up to now.[11,17] PMI has been synthezised 30 years ago[18,19] and presents a structure similar to PA where half of the C−H groups have been replaced by nitrogen atoms (CH=N)_x. The β response of PMI oligomers has been investigated and analyzed at different levels of theory;[4,17,20−22] the results are summarized in ref 23. It turns out that PMI, and in general AB systems, present a β/N vs N evolution which is often more complex than the corresponding evolution in push−pull systems. Indeed, it may or may not present a maximum, a sign reversal and a nonzero polymeric limit ($N \rightarrow \infty$). To rationalize this complex evolution of β/N, it was found useful to split the response of the system into chain-end and unit cell contributions, both being affected by the increase of delocalizability occurring when chain lengthens.[4,17,21] Additionally, one could state that the unit cell asymmetry is due to the nuclear alternation (A vs B) and to the inherent alternation of single and double bonds (− vs =). In the polymer, where the chain ends do not bring any contribution, both nuclear and bond alternation are required to obtain a nonzero β. At the Hartree−Fock (HF) level, by decreasing the bond length alternation of PMI beyond its optimal value, one increases $[\beta/N]_{N\rightarrow\infty}$, tending to show that the limiting factor of the polymeric response is the delocalization rather than the asym-

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10.1021/ma021665j CCC: $25.00

metry.[21] This is consistent with Hückel results showing that the largest $[\beta/N]_{N\to\infty}$ value would be obtained with both small (but nonzero) nuclear and bond alternations, i.e., large delocalization and small asymmetry rather than the reverse.[20]

To obtain a large β response we study, in this paper, a series of polyacetylene/polymethineimine copolymers. As the limiting factor in PMI is delocalization, we expect that the addition of a small quantity of PA into PMI leads to an increase $[\beta/N]_{N\to\infty}$ even if the asymmetry of the system falls off when PA is added.[30] Nevertheless the optimal proportion of PA to be added in the copolymer cannot be determined beforehand. In addition, this study improves our understanding of the interplay between delocalization and asymmetry at different level of theory.

II. Theory

A. Computational Procedure. To compute the β of stereoregular polymers, one can adopt either the oligomeric approach or the polymeric approach. In the latter, the translational symmetry of the polymer is taken into account and, as a consequence, the macromolecular value is obtained by a single shot calculation.[24] In the oligomeric approach, this value is obtained by extrapolation(s) based on the β values evaluated on increasingly long oligomers. Although the first technique presents many advantages, we have used the second due to the lack of crystal–orbital schemes for obtaining the β of polymers at electron correlated levels.

Our calculations have been performed by using the following procedure:

1. The ground-state geometry of each oligomer has been determined by full optimization of its structural parameters with the Gaussian94 program.[25] These optimizations have been carried out at the HF and second-order Møller–Plesset schemes (MP2) levels, using two basis sets (6-31G and 6-311G*), until the residual forces are smaller than 10^{-5} au. The all-trans conformation has been selected for every copolymer. See Figure 1 for the naming convention used for the sequenced copolymers used in this paper. In this conformation the compounds appear slightly bent because the repulsion of the N lone pair is larger than the repulsion of the C–H bond. The departure from linearity is roughly proportional to the proportion of PMI included in the copolymer but is always modest. After the geometry optimization, each oligomer has been oriented in the Cartesian frame such that the longitudinal axis passes through the first and last double bonds of the CN skeleton.

2. The longitudinal electronic β (β_L) has been calculated on these geometries with various methods (HF, MP2, and MP4) and basis sets (6-31G and 6-311G*). In this work, the vibrational contribution to β (β^v) has been neglected. β^v could make an important contribution to the total static β values in conjugated systems[11,26,27] but its practical determination at electron-correlated (EC) level remains limited to relatively modest systems. At HF level, β_L has been computed by the coupled-perturbed Hartree–Fock (CPHF) method implemented in Gaussian94.[25] However, it is well-known that EC have a significant dual impact on β_L. On 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 an indirect effect on β_L. Both effects could be large and their relative importance depends strongly on the molecular structure considered. In PMI, the direct (indirect) component modifies β_L by 497 (55%).[17] Subsequently, the inclusion of EC effects is necessary to obtain valid structure/β_L relationships of the copolymers treated here. At EC level, the β_L values have been evaluated by using the numerical finite-field procedure. We refer the reader to ref 16 for a more complete description of this procedure.

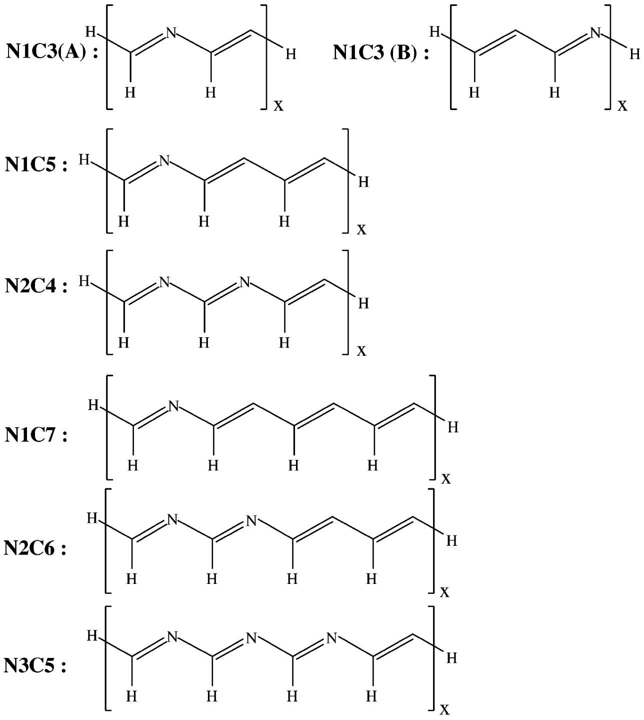

Figure 1. Sketch and naming conventions of the different PA/PMI copolymers used in this study.

3. The polymeric response has been obtained by extrapolating the oligomeric values. To carry out extrapolations, an alternative definition of the β_L per non-hydrogen atom, $\Delta\beta_L = \beta_L(N) - \beta_L(N-1)$, is employed. This definition removes most of the chain end effects: it leads to a faster convergence than β_L/N, though to the same asymptotic limit ($N \to \infty$). Our fitting procedure allows to obtain the average $\Delta\beta_L(\infty)$ and its standard deviation. We refer the reader to ref 21 for more details. In a recent work, Gu and co-workers have shown that for PMI, with a fixed geometry close to the optimal one, the differences between the CPHF β_L extrapolated by this method and the one obtained by the polymeric method are smaller than 3%[28] although the extrapolation method tends to underestimate the error bars.

B. Validity of the MP2/6-31G Approach. In the two following sections, we evaluate the validity of the MP2/6-31G scheme (our reference technique) with respect to the convergence of basis set and EC effects. This study has been performed on the alternating copolymer, poly(methineimine-*co*-acetylene) [sometimes referred to as poly(methineimine-*per*-acetylene)], N1C3(A) (see Figure 1). Together with previous results on PMI, this is sufficient to evaluate the adequacy of the MP2/6-31G approach with regard to semiquantitative (~30%) calculation of β_L of PA/PMI copolymers.

1. Basis Set Effects. In PMI, we have shown that the addition of diffuse functions on C and N atoms does not influence strongly the β_L of medium and long

Table 1. Basis Set Effects on the MP2 β_L of PA/PMI Oligomers (N1C3(A))[a]

N	β_L[MP2/6-311G*//HF/6-311G*]/ β_L[MP2/6-31G//HF/6-31G]	β_L[MP2/6-311G*//MP2/6-311G*]/ β_L[MP2/6-31G//MP2/6-31G]
8	0.45	0.49
12	0.71	0.67
16	0.80	0.74
20	0.85	0.82
24	0.88	
28	0.91	
32	0.92	

[a] The values presented are the ratios with respect to the corresponding 6-31G calculation performed with the same methods. N is the number of non-hydrogen atoms (C and N) in the chain.

Table 2. Impact of the Level of Electron Correlation on the β_L of N1C3(A) Oligomers[a]

	HF/6-31G geometry			MP2/6-31G geometry		
N	HF	MP2	MP4	HF	MP2	MP4
4	−89 (2.78)	−32	−37 (1.16)	−101 (4.2)	−24	−37 (1.54)
8	−392 (−2.18)	180	116 (0.64)	−550 (−1.41)	389	194 (0.50)
12	−793 (−0.55)	1440	1211 (0.84)	−1394 (−0.50)	2808	1958 (0.70)

[a] The values in parentheses are the ratio with respect to to MP2 values obtained at the same geometry. All calculations have been performed with the 6-31G basis set. N is the number of non-hydrogen atoms (C and N) in the chain (1 au of $\beta = 3.2063 \times 10^{-53}$ C^3 m^3 J^{-2} $= 8.641 \times 10^{-33}$ esu).

Table 3. Extrapolated Longitudinal First Hyperpolarizability per Non-Hydrogen Atom of PA/PMI Polymers Obtained at the HF and MP2 Levels

	PMI (%)	$\Delta\beta_L$[HF/6-31G//HF/6-31G]	$\Delta\beta_L$[MP2/6-31G//HF/6-31G]	$\Delta\beta_L$[MP2/6-31G//MP2/6-31G]
N0C2 (PA)	0	0	0	0
N1C7	25	786 ± 69	2142 ± 98	9388 ± 3241
N1C5	33	882 ± 33	2888 ± 221	10108 ± 1638
N1C3(A)	50	1102 ± 78	3504 ± 87	10360 ± 1578
N2C6	50	1126 ± 129	3615 ± 175	10480 ± 2154
N2C4	66	1120 ± 35	4369 ± 276	9524 ± 1348
N3C5	75	1104 ± 79	4315 ± 273	8991 ± 1151
N1C1 (PMI)[a]	100	847 ± 35	4207 ± 102	6520 ± 164

[a] Values taken from ref 17.

oligomers.[17] Indeed, for oligomers with more than eight non-hydrogen atoms, the correction (an increase) is always smaller than 10%. Table 1 lists the ratio (with respect to the MP2/6-31G values) between the MP2 β_L obtained with our two atomic basis sets: 6-31G (double-ζ) and 6-311G* (triple-ζ with polarization functions) on HF and MP2 geometries of N1C3(A) oligomers. Obviously, except for the smallest chains, the differences between β_L obtained with the two basis sets do not exceed 15% though both the geometry and the electronic properties are modified when selecting a larger basis set. In addition, values of Table 1 highlight the decreasing importance of basis set size when oligomer lengthens: for $N = 8$, the MP2/6-311G*//HF/6-311G* [31] β_L is less than half of the corresponding MP2/6-31G//HF/6-31G β_L, for $N = 32$, they differ only by 8%. This is consistent with previous studies (see, for example, ref 29): for long chains, split-valence double-ζ basis sets are sufficient in order to obtain correct longitudinal NLO responses. As our focuses are the long oligomer study and the polymeric limit, the 6-31G basis set is found to be satisfactory.

2. Level of Electron Correlation. In Table 2, we compare the HF, MP2, and MP4 β_L obtained with the 6-31G basis set on the HF and MP2 geometries. As in PMI, the signs of the β_L obtained at the HF and MP2 level are different for $N = 8$ and $N = 12$, stressing the impact of EC. For the longest oligomer investigated in Table 2, the MP4 value is relatively close (15−30%) to the MP2 β_L on both geometries, although the differences are larger on the MP2 geometry. On top of that, the β_L value seems to approach more closely the MP2 response as N increases. Because of practical limitations, it is however difficult to confirm this assertion for longer chains, with larger basis sets or with highly correlated EC scheme such as CCSD(T). Nevertheless, these findings are consistent with the results obtained on PMI: the MP2 scheme overestimates β_L of medium size oligomer roughly by 20%, this overestimation is larger on the MP2/6-31G geometry and decreases as chains becomes longer.[17] It is therefore reasonable to use the MP2 approach which provides the largest part of the total EC correction.

III. Results

A. Polymeric Values. To obtain $\Delta\beta_L(\infty)$ of the copolymers, one has to extrapolate the oligomeric results. Because of the size of the translational unit cell, there is only a limited number of points to carry out extrapolations. As a consequence, extrapolations are difficult, leading to large error bars (∼15−30%). For this reason, we focus on trends rather than on determining the exact value of $\Delta\beta_L(\infty)$ in all the copolymers. Results are shown in Table 3 and plotted in Figure 2. At the MP2/6-31G//MP2/6-31G level, the optimal $\Delta\beta_L(\infty)$ is obtained with proportion of PMI between 33 and 50%:[32] N1C3 and N1C5 give the best compromise between delocalization and asymmetry. Despite the large error bars, it is also clear that, at the full MP2 level,[33] the addition of any proportion of PA into PMI in any proportion between 25% and 75% provides a 40−60% increase of the already large $\Delta\beta_L(\infty)$of PMI. Obviously, the limiting factor of PA is the asymmetry: therefore adding a few nitrogen atoms leads to a large

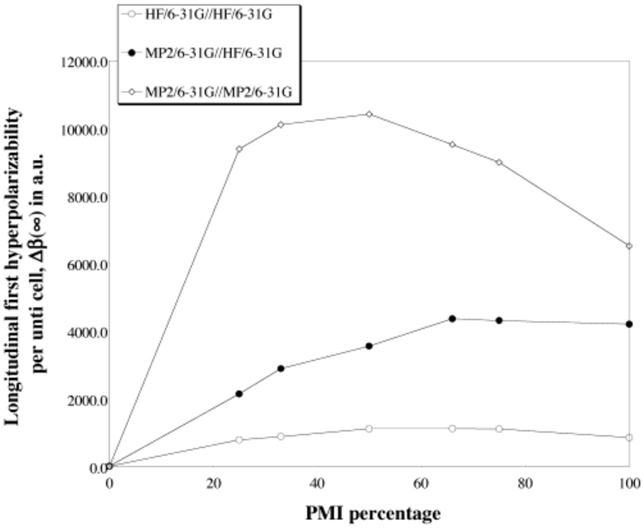

Figure 2. Evolution with the percentage of PMI of the extrapolated $\Delta\beta_L(\infty)$ of PA/PMI copolymers according to the level of approximation used. The values of the 50% copolymer are N1C3(A) and N2C6 $\Delta\beta_L(\infty)$ averaged.

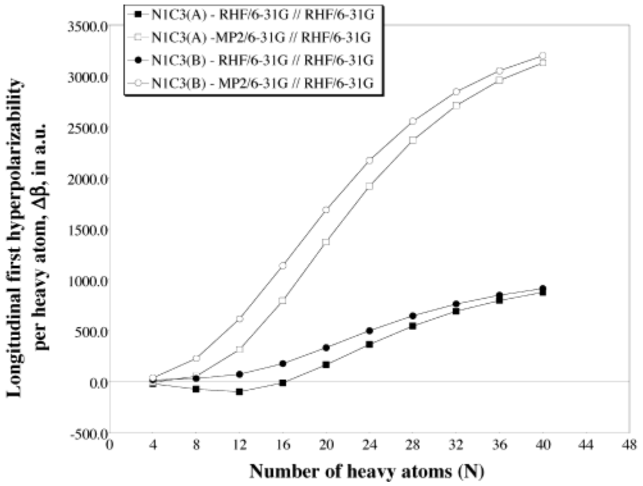

Figure 3. Evolution with chain length of $\Delta\beta_L$ of the N1C3(A) and N1C3(B) chains at the HF and MP2 level (HF/6-31G geometry). All values are in au.

increase of $\Delta\beta_L(\infty)$. The reverse is true for PMI: the limiting factor is delocalization. In addition, PMI $\Delta\beta_L(\infty)$ is relatively far from being limited by asymmetry. On Table 3, the $\Delta\beta_L(\infty)$ of N1C3(A) and N2C6 are extremely close indicating that the influence of the relative position of PA and PMI fragments is limited. It is rather the proportion that dictates the NLO response.

Table 4. HF and MP2 Longitudinal First Hyperpolarizability of PA/PMI Oligomers of Increasing Size Obtained with the 6-31G Basis Set[a]

	geom = HF/6-31G		geom = MP2/6-31G	
N	β_L[HF/6-31G]	β_L[MP2/6-31G]	β_L[HF/6-31G]	β_L[MP2/6-31G]
N1C7				
8	−497	687	604	817
16	−1761	−273	−3228	766
24	−1181	5748	−2772	15 980
32	1790	1709 × 10	5140	4796 × 10
40	6283	3148 × 10	19 607	915 × 100
48	11 583	474 × 100		
N1C5				
6	251	253	−297	−277
12	−1077	−62	−1731	438
18	−1407	3044	−2971	7528
24	−220	10 271	−950	25 490
30	2450	2091 × 10	5684	5421 × 10
36	6174	3378 × 10	16 382	9089 × 10
42	10 564	479 × 100		
48	15 363	630 × 100		
N1C3(A)				
4	−89	−32	−101	−24
8	−392	180	−550	389
12	−793	1440	−1394	2808
16	−845	4613	−1941	9347
20	−187	10 099	−1200	21 460
24	1275	17 777	1447	39 396
28	3457	27 254	6092	62 484
32	6214	3809 × 10	12 495	8968 × 10
36	9403	4992 × 10	20 307	11 995 × 10
40	12 909	6244 × 10	29 192	15 244 × 10
44	16 644	7546 × 10		
48	20 546	888 × 100		
N2C6				
8	−907	−721	−1145	−746
16	−2139	2069	−3739	5293
24	−495	13 987	−1371	31 925
32	4343	3374 × 10	9131	7926 × 10
40	11 171	5800 × 10	25 569	1395 × 100
48	19 062	846 × 100		
N2C4				
6	−342	−35	−416	36
12	−1038	1819	−1674	3419
18	−834	8661	−1999	16 672
24	1213	21 316	1078	4251 × 10
30	4942	3855 × 10	7805	7878 × 10
36	9851	5881 × 10	17 222	1220 × 100
42	15 511	809 × 100		
48	21 633	1042 × 100		
N3C5				
8	−752	130	−981	407
16	−1310	6096	−2409	11 232
24	999	22 604	650	42 654
32	6244	4753 × 10	9300	9090 × 10
40	13 300	7728 × 10	21 427	1486 × 100
48	21 313	1095 × 100		

[a] N is the number of heavy atoms (C and N) in the chain. All values are in au.

B. Evolution with Chain Length. First, we evaluate the impact of chain-end structure on the evolution with N of $\Delta\beta_L$. Two series of the alternating copolymer have been selected: one with both CH ends (N1C3(A)) and one with on CH and one NH terminations (N1C3(B)). Figure 3 displays the HF and MP2 $\Delta\beta_L$ of these two systems obtained on the optimized HF/6-31G geometry. At the HF level, there is no sign reversal in the N1C3(B) case. This illustrates that the chain ends are the main asymmetry contributors for short chains, as it could have been expected from previous calculations.[23] $\Delta\beta_L$ values of N1C3(B) are slightly larger: two different chain ends bring larger chain-end asymmetry, without strongly modifying the delocalizability of the oligomers. As chain lengthens, the chain-end contribution become negligible and the two systems have obviously the same polymeric limit. In addition, the shapes of the MP2 curves are very similar. Subsequently, as our main focus are long compounds limit, we do not continue to investigate the influence of chain ends.

Table 4 gives the β_L of the various oligomers investigated, while Figure 4 is the corresponding plot of $\Delta\beta_L$ vs N obtained at the full MP2/6-31G level. The following observations are made: (1) The different compounds have roughly the same responses though N1C7 presents significantly lower β_L. (2) The larger the PA percentage is, the stronger the increase with respect to N: the N2C6 and N3C5 curves cross. In other words, the curves

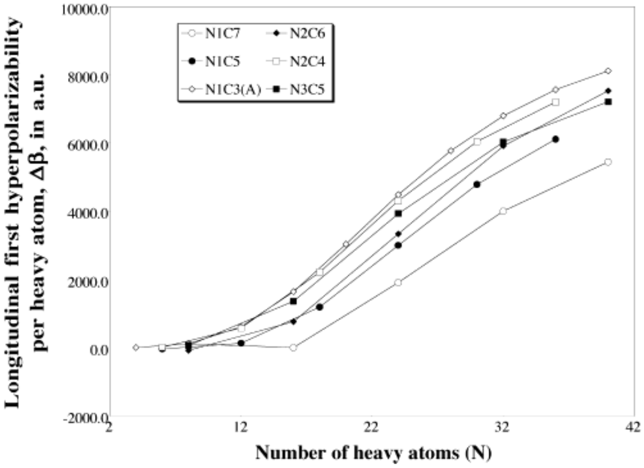

Figure 4. Evolution with chain length of $\Delta\beta_L$ of the different copolymers. These results have been obtained with the MP2/6-31G//MP2/6-31G method.

Table 5. Summary of the Direct and Indirect Effects on the Oligomer and Polymer Chains[a]

	direct contribution		indirect contribution		total contribution
	$N = 48$	$N = \infty$	$N = 24$	$N = \infty$	$N = \infty$
N1C7	4.1	2.7	2.8	4.4	11.9
N1C5	4.1	3.3	2.5	3.5	11.5
N1C3(A)	4.3	3.2	2.2	3.0	9.4
N2C6	4.4	3.2	2.3	2.9	9.3
N2C4	4.8	3.9	2.0	2.2	8.5
N3C5	5.1	3.9	1.9	2.1	8.1
N1C1 (PMI)[b]	?[c]	5.0	1.6	1.6	7.7

[a] The results have been obtained with the 6-31G basis. The direct contribution is estimated on the HF geometry, and the indirect contribution is given by the ratio of the MP2 β_L values on the MP2 and HF geometries. [b] Values taken from ref 17. [c] No chain as large as $N = 48$ was treated in ref 17. However, the value should be between 6.7 ($N = 20$) and 5.0 ($N = \infty$).

corresponding to the largest PMI percentage saturate faster. This is confirmed by noticing that the order of the different curves of Figure 4 at $N = 40$ is a poor indicator of the corresponding macromolecular ordering. Indeed, for $N = 40$, we have N1C3(A) > N2C4 > N2C6 > N3C5 > N1C5 > N1C7; whereas for $N = \infty$, the extrapolations give N2C6 > N1C3(A) > N1C5 > N2C4 > N1C7 > N3C5. (3) For oligomers up to $N = 40$, the change in β_L compared to PMI is, at best, a modest increase even for the most "efficient" chains. Indeed, by adding PA to PMI, one increases the delocalizability but decreases the asymmetry: (a) Having more than 66% of PA segments leads to a too weak asymmetry at this level of theory. (b) The larger the PA ratio, the larger the delocalization, the slower the convergence of $\Delta\beta_L$ with respect to N, the larger the increase of $\Delta\beta_L$ from $N = 40$ to $N = \infty$. As a consequence, although the N1C7 curve is the lowest (up to $N = 40$), it converges very slowly, and N1C7 presents a large polymeric value. (c) $\Delta\beta_L$ of medium-size PMI oligomers is quite large compared to the polymeric value due to the fast saturation of $\Delta\beta_L$ in PMI. The differences between PMI and the PA/PMI copolymers are stronger in the infinite chain length limit (see previous section).

C. Analysis of Electron Correlation Effects. To rationalize the results obtained with the different approximations, we have computed the direct and indirect EC contributions in Table 5. The evolutions are smooth and the trends are clear: the importance of the direct contribution decreases with the size of the chain and increases as a function of the PMI percentage. The indirect contribution follows exactly the opposite trends. As a consequence, while the direct contribution dominates the total EC correction of PMI (5.0 vs 1.6), it is the reverse for N1C7 (2.7 vs 4.4). The overall EC effect increases slightly from PMI (8.0) to N1C7 (11.9). This, in turn, explains that N1C7 which is estimated to lead to a poor response at the HF level (see Table 4) "catches up" at the MP2 level. Again, N1C3(A) and N2C6 provides very similar ratio in Table 4: it is the proportion rather than the relative position of the PMI and PA segments that dictates the physics of these compounds.

Quite interestingly, at the MP2/6-31G//HF/6-31G level, the β_L of PMI oligomers are limited by asymmetry[34] although the corresponding full HF/6-31G and full MP2/6-31G β_L are limited by delocalization. Indeed, for $N = 40$, N3C5 presents smaller MP2/6-31G//HF/6-31G β_L than PMI (77×10^4 vs 86×10^4 au, respectively). From ref 17, we know that the direct contribution of EC acts like an enhancement of the delocalizability of the compounds. Consequently, the maximum β_L requires more asymmetry than at the full HF level.

IV. Conclusions and Outlook

We have investigated the β_L of sequenced PA/PMI copolymers. At the full MP2/6-31G level, it turns out that the addition of a small quantity of PMI into PA or a small quantity of PA into PMI leads to an increase by 50% of the $\Delta\beta_L(\infty)$ of PMI. This indicates that, although its $\Delta\beta_L(\infty)$ is already very large, PMI is too alternating for obtaining an optimal $\Delta\beta_L(\infty)$. We estimate that the proportion of PMI leading to the maximum response is around 33% [poly(methineimine-*co*-acetylene-*co*-acetylene)] to 50% [poly(methineimine-*co*-acetylene)] for the macromolecule. The β/W of N1C3(A) (and N2C6) is of 6.8×10^{-30} cm^5 esu^{-1} g^{-1} mol; 1 order of magnitude larger than most of the experimental structures available. It can be compared to theoretical investigations on two other very efficient compounds: PMI (4.2×10^{-30})[17] and α,ω-nitro,aminopolyacetylene (4.3×10^{-30}).[11] Other conclusions have been drawn: (1) Inclusion of EC for both the geometry optimization and electronic structure calculation is essential in order to assess structure/NLO property relationships in these copolymers. (2) The addition of PA into PMI leads to a slower convergence of $\Delta\beta_L$ with respect to N. (3) It is the proportion rather than the relative ordering of the PMI and PA segments that dictates the polymeric response.

The copolymers considered in the present study have not been synthesized yet. It is our hope that this study would increase the experimental interest in such compounds although their actual stability remains unknown. In addition, the chains considered are isolated and perfectly regular. Further study would be required in order to estimate the impact of disorder as well as medium (solvent or crystal packing) effects.

Acknowledgment. D.J. is indebted to Dr. A. S. Duwez (MPIP, Mainz, Germany) for fruitful discussions. D.J. and B.C. thank the Belgian National Fund for their respective postdoctoral researcher and senior research associate positions. The calculations were performed on the IBM RS6000 cluster of the Namur Scientific Computing Facility (Namur-SCF) as well as on the cluster of PC acquired thanks to a "crédit aux chercheurs" of the FNRS. We acknowledge the support from the Interuniversity Attraction Poles Program on “Supramolecular Chemistry and Supramolecular Catalysis (IUAP No. P5-03)” from the Belgian State (Federal Office for Scientific, Technical, and Cultural Affairs).

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(30) At least at the HF level. At EC level, the limiting factor remains unknown.

(31) In this paper, the usual convention has been chosen to describe the level of calculation electronic structure method//geometry optimization scheme.

(32) The corresponding optimal HF/6-31G//HF/6-31G and MP2/6-31G//HF/6-31G ratio are 50−75% and 66−100%, respectively.

(33) Full MP2 means that the MP2 approximation has been used for both geometry optimization and calculation of β_{L}.

(34) In the macromolecule, the limiting factor of PMI becomes delocalization (see section III.A), although infinitely long PMI is very close to the optimal C/N ratio at this level of theory.

MA021665J