Mobility of Side Chains in Poly(diethylphosphazene) As Studied by $^1H/^{13}C/^{14}N$ Triple-Resonance Solid-State NMR

Roberto Simonutti,*,† Wiebren S. Veeman,‡ Frank C. Ruhnau,‡
Maria C. Gallazzi,§ and Piero Sozzani†

Dipartimento di Scienza dei Materiali, Università di Milano, via Emanueli 15,
20126 Milano, Italy; Physikalische Chemie, Gerhard-Mercator-Universität-GH-Duisburg,
Lotharstrasse 1, 47048 Duisburg, Germany; and Dipartimento di Chimica Industriale,
Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

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ABSTRACT: The existence of three polymorphs of poly(diethylphosphazene) has recently been established by MAS NMR and X-ray diffraction characterization. In the present work, the mechanism of motion of the ethyl side groups in the high-temperature modification of poly(diethylphosphazene) is identified and compared to the arrangement of side groups in the low-temperature modification. For this purpose, a rotor-synchronized triple resonance NMR experiment, called TRAPDOR, was applied for the qualitative evaluation of the average distances between carbons and nitrogens in the polymorphs. The agreement between these qualitative average distances and the molecular modeling supports the hypothesis that the ethyl groups undergo a complete rotation about the $P-CH_2$ bond in the high-temperature modification.

Introduction

Poly(organophosphazene)s, macromolecules with a backbone constituted by alternating nitrogen and phosphorus atoms, have been known for about 20 years.[1] Aryloxy- and alkoxy-substituted polyphosphazenes are well-characterized systems. Usually these polymers exhibit a solid-solid transition from a crystalline to a mesomorphic phase, involving a different regime of motion.[2−10] Haw and co-workers[11] showed, for example, by solid-state nuclear magnetic resonance that poly[bis(3-methylphenoxy)phosphazene] in the crystalline phase presents a negligible degree of motion, whereas in the mesogenic phase large-amplitude motions occur; these include unrestricted rotation of the side chain. In the case of poly[bis(4-ethylphenoxy)phosphazene], slow motions were detected also in the crystalline phase.[12,13]

Alkyl-substituted polyphosphazenes have been recently prepared by a polycondensation reaction of suitable monomers.[14,15] The crystal structure and polymorphism of poly(diethylphosphazene) (PDEP) (Figure 1) has been determined by X-ray diffraction and magic angle spinning (MAS) NMR techniques.[16] PDEP presents three polymorphic structures: phases Ia, Ib, and II. Phases Ia and Ib are present in the as-polymerized sample; above 40 °C, only modification Ib survives.[16] It is possible to obtain phase II by recrystallization at 225 °C. ^{13}C MAS NMR spectra showed a surprising multiplicity of signals for phase Ia, which were assigned to different conformations of the ethyl side chains. On the other hand, just one peak is present in phase Ib for, respectively, the methyl and the methylene carbon atom. In this phase, fast motions, as compared to the NMR time scale, can average out the chemical shifts produced by the contributing conformations. The detailed mechanism of this motion is, however, not understood, and questions are still open about the interconversion among conformations and whether long-range interactions can occur among ethyl groups and between ethyl groups and the main chain.

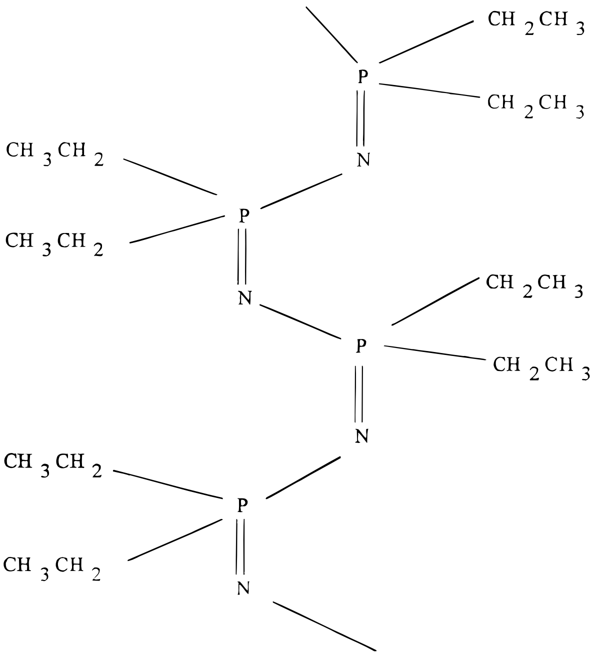

Figure 1. Structural scheme of poly(diethylphosphazene).

A family of experiments, based on double resonance, seem particularly suitable to our study, because they are able to obtain distances between nuclei in the solid state. In particular, we wanted to determine the average distance between the methyl groups of the side chains and nitrogens of the main chain. A comparison between the low- and high-temperature phases could show differences in the CH_3-N distances because of motions in the high-temperature phase. For the determination of carbon (or proton)−nitrogen distances, not many solid-state NMR techniques are available when ^{14}N is considered. The relatively large ^{14}N quadrupolar interaction prevents the use of Overhauser methods or double-resonance techniques based on SEDOR[17] or REDOR.[18,19] Here we employ $^1H/^{13}C/^{14}N$ triple-resonance solid-state NMR (transfer of populations in double resonance: TRAPDOR),[20−22] which is particularly convenient for PDEP.

This method exploits the weak dipolar coupling between ^{13}C and ^{14}N, in a way somewhat similar to the

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[†] Università di Milano.
[‡] Gerhard-Mercator-Universität-GH-Duisburg.
[§] Politecnico di Milano.
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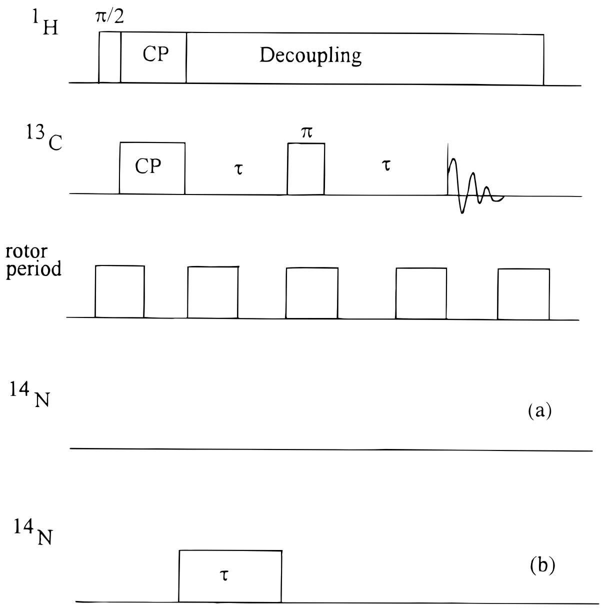

Figure 2. Triple-resonance pulse sequences. Sequence a depicts the reference experiment; in sequence b, the ^{14}N spins are irradiated during the first half of the echo period. CP: cross polarisation. $\pi/2$: 90° pulse. π: 180° pulse.

SEDOR (spin–echo double resonance)[17] and REDOR (rotational echo double resonance)[18,19] experiments. The TRAPDOR technique[20–22] is well suited for cases in which S is a quadrupolar nucleus with integer I, like ^{14}N. For this method, the SEDOR π pulse is substituted by a continuous irradiation at constant frequency of the ^{14}N spins, during the first half of a spin–echo experiment (Figure 2). The ^{14}N irradiation and sample spinning cause transitions among all three ^{14}N energy levels; these transitions induce dephasing of the magnetization of the carbons coupled to nitrogens. This dephasing produces a weakening of the ^{13}C spin–echo and rotor echo. Thus, if a reference experiment is performed under the same conditions but without ^{14}N irradiation (Figure 2a), the triple resonance experiment (Figure 2b) gives an estimate of the strength of the ^{13}C–^{14}N dipolar coupling. In general, the shorter the distance between a given carbon and a given nitrogen, the bigger the intensity loss of the resonance in the triple resonance spectrum.

TRAPDOR was successfully applied to glycine,[20] polyamide-6,[21] *N*-acetyl-DL-valine,[22] and, recently, a template complex formed by poly(methacrylic acid) and poly(*N*-vinylimidazole).[23]

We will show that by using the distance dependence of the TRAPDOR effect, we can characterize the motional behavior of PDEP in the solid state.

Restricted rotation among a few conformational arrangements or complete rotation about the phosphorus–methylene bond, rotating the methyl group, can be thus discriminated on the basis of the averaged TRAPDOR effect.

Experimental Section

Synthesis. PDEP was obtained by heating the monomer $Me_3Si{=}P(OCH_2CF_3)Et_2$ under vacuum at 190 °C for 4 days, according to the procedure already reported.[16]

DSC. A Perkin-Elmer DSC-7 equipped with a CCA-7 liquid-cooling device was used for the calorimetric analysis in the range 10–250 °C. Typical heating and cooling rates were 10 °C/min.

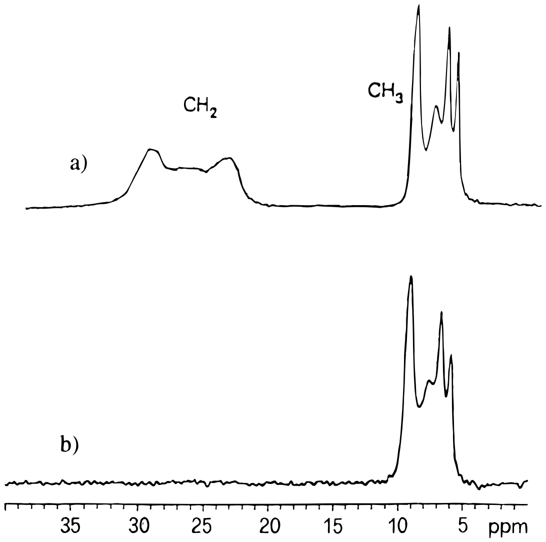

Figure 3. (a) ^{13}C CP MAS spectrum of PDEP at 293 K, using 1 ms of contact time. (b) ^{13}C reference spectrum for triple resonance (no ^{14}N irradiation), using 2000 Hz of spinning speed, τ equal to 10 rotor periods (5 ms), contact time of 1 ms.

X-ray Analysis. X-ray investigations of the polymer were carried out on powder samples with an Italstructures θ/θ diffractometer using Cu Kα radiation.

Solid-State NMR. High-resolution ^{13}C MAS NMR spectra were run at 75.5 MHz on a CXP 300 Bruker instrument operating at a static field of 7.4 T. A Bruker magic angle spinning triple-resonance probe was used with 7-mm ZrO_2 rotors spinning at a standard speed of 2000 Hz. The probe head was tuned to provide a 90° pulse length of 5 μs for ^{1}H (at a frequency of 300.13 MHz) and ^{13}C (at 75.5 MHz). The ^{14}N rf irradiation amplitude corresponds to a 10-μs 90° pulse, as determined with solid ammonium chloride (at a frequency of 21.69 MHz). The third frequency channel was provided by a Bruker CXP 200 console and a Bruker high-power amplifier tuned to 21.69 MHz. The stability of the two combined spectrometers was checked by using ^{13}C-enriched glycine.

All the experiments are performed as follows: the FID's were collected by alternating between the reference experiment and the triple-resonance experiment, 80 scans were added for each experiment before switching to the next. The π pulse on the carbon in all the experiments is synchronized with the rotor spinning, with a spinning speed of 2000 Hz; τ equals 10 rotor cycles. The offset of the ^{14}N irradiation frequency used for PDEP was −15 kHz, relative to the resonance frequency of ammonium chloride.

Results and Discussion

In Figure 3a, the CP-MAS spectrum of the native PDEP at room temperature is reported. It is possible to recognize two main parts: the signals ranging from 5 to 11 ppm are due to the methyl carbons; those from 22 to 32 ppm are due to the methylene carbons. Methyls give rise to four signals, three of them belonging to phase Ia and a fourth at 8.5 ppm, which is broader, belonging to phase Ib. Methylenes show broad signals, probably caused by dipolar coupling to phosphorus; nevertheless, two peripheral peaks due to phase Ia and one central peak due to the phase Ib can be identified. Thus, phase Ia presents two types of methylenes and three types of methyls. The reason of this multiplicity of peaks can be found by considering the side-chain conformations. It is expected that the conformation of the main chain is the usual cis–trans planar arrangement, for both phase Ia and phase Ib, showing an axial periodicity of 4.9 Å. The γ-gauche interaction[24] can easily explain the chemical shifts for methyls and methylenes, considering gauche interaction

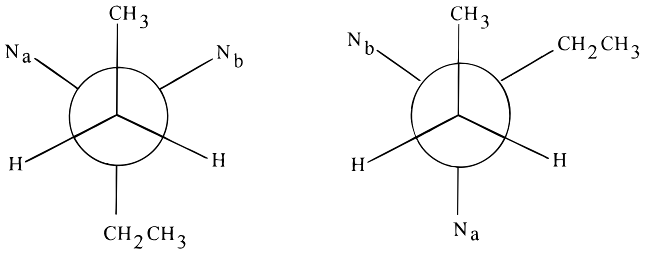

Figure 4. Newman projections, along the P−CH$_2$ bond, of the two basic conformations in PDEP.

Table 1. ^{13}C Chemical Shifts and Conformational Assignments for PDEP at Room Temperature

	chem shift, ppm	phase	γ-gauche interaction[a]
CH$_3$	6.8	Ia	1 CH$_2$ + 1 N s
	7.6	Ia	1 CH$_2$ + 1 N w
	8.5	Ib	conformational dynamical disorder
	10.0	Ia	2 N
	10.2	Ia	1 N w + 1 N
CH$_2$	24.3	Ia	1 CH$_3$
	28.0	Ib	conformational dynamical disorder
	29.9	Ia	no interaction

[a] 1 CH$_2$, 1 CH$_3$, 1 N: one γ-gauche interaction with a methylene, methyl, nitrogen. w: weak (dihedral angle greater than 60°). s: strong (dihedral angle less than 60°).

between methyls and methylenes belonging to different ethyl chains on the same phosphorus and between methyls and nitrogens (Figure 4). Table 1 reports the chemical shifts and assignments to conformations. Therefore, phase Ia is characterized by different conformations fixed on the NMR time scale. In contrast, phase Ib presents only one signal for methyls and one for methylenes. The chemical shift values of phase Ib, which equal the average of the chemical shifts of phase Ia, and the very short carbon spin−lattice relaxation times indicate that these peaks are due to mobile ethyl chains. The side chains interconvert among available conformations, but a complete description of the motions by just the chemical shift and the relaxation data is not possible. These data do not discriminate between fast motions between the two conformations or full rotation around the P−CH$_2$ bond.

In Figure 3b, the spectrum of PDEP, as recorded by the reference experiment (Figure 2a) for the triple resonance, is reported: the echo time (τ) is equal to 10 times the rotor period. With a shorter echo time, the triple resonance effect is too weak and the experimental error too large. With the longer echo time, the spectrum is simpler, the methylenes have completely disappeared, but the methyls present their usual shape. The very short T_2 of CH$_2$ is probably due to the strong dipolar coupling with the directly linked phosphorus atom and/or incomplete ^{13}C−^{1}H decoupling. For this reason, the CH$_2$ signals will not be considered.

It is known that the loss of carbon intensity in the TRAPDOR experiment is very sensitive to the offset of nitrogen frequency;[20] therefore, the offset of the nitrogen from the central carrier frequency of 21.69 MHz was changed within the range from +100 to −100 kHz. The highest loss of intensity was found using an offset of −15 kHz. The triple-resonance spectrum and the reference spectrum of PDEP at room temperature are reported in Figure 5. The intensity ratio between the peaks of phase Ia changes from reference spectrum a to triple-resonance spectrum b; this effect is clearly visible in difference spectrum c. Since the methyl peak of phase Ib becomes narrower and more intense at

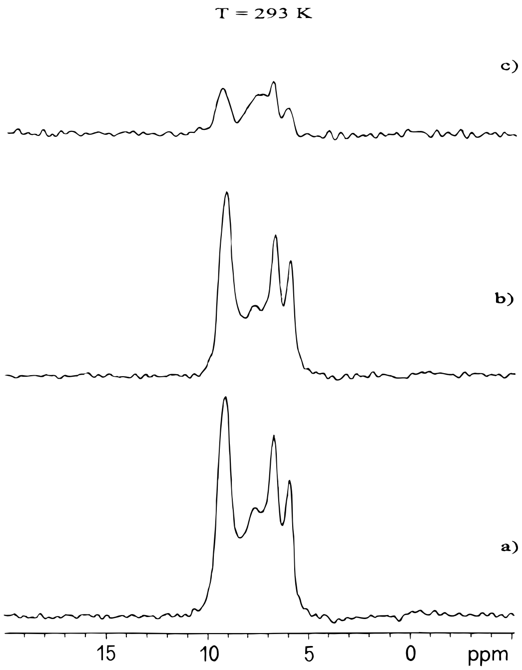

Figure 5. ^{13}C MAS spectra of PDEP at 293 K recorded using the pulse sequences shown in Figure 1. Spectrum a was obtained without ^{14}N irradiation, reference spectrum b with ^{14}N irradiation at a frequency of 21.686 MHz: 2000-Hz spinning speed, spin−echo delay 5 ms (10 rotor times). The difference spectrum c is also shown.

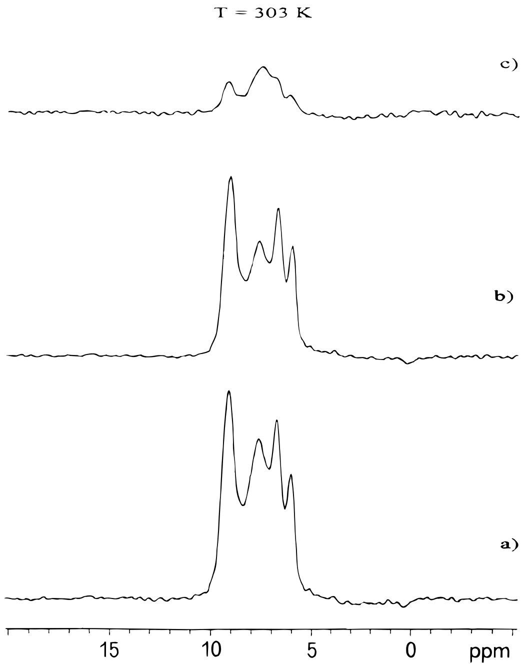

Figure 6. ^{13}C MAS spectra of PDEP at 303 K (a) without ^{14}N irradiation and (b) with ^{14}N irradiation; (c) difference spectrum; same experimental parameters as in Figure 5.

higher temperatures, TRAPDOR experiments were also performed at 303 K (Figure 6), 313 K (Figure 7), and 323 K (not shown). At 303 and 313 K, the behavior is like that at room temperature but more evident, because of the larger content of the mobile phase. At 323 K, only pure phase Ib is present; therefore, it is no longer possible to compare the behavior of phase Ib with that of phase Ia. For a detailed evaluation of the intensity losses, all the spectra were deconvoluted using the Bruker Win−Fit routine. The peaks in the reference spectrum were fitted by varying the amplitude, line

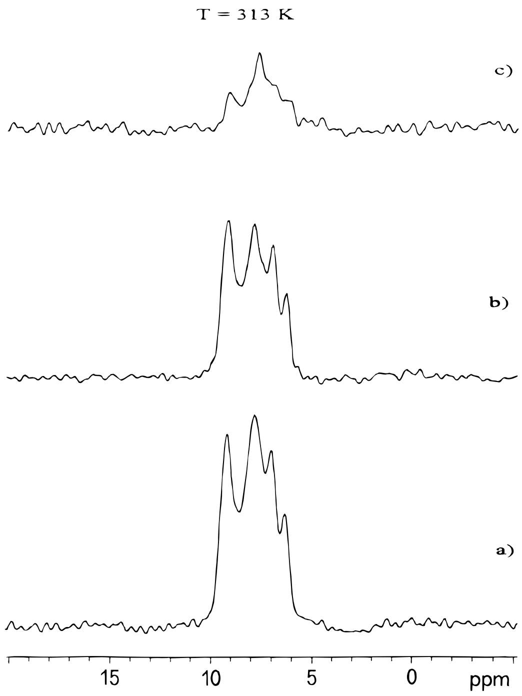

Figure 7. ^{13}C MAS spectra of PDEP at 313 K (a) without ^{14}N irradiation and (b) with ^{14}N irradiation; (c) difference spectrum; same experimental parameters as in Figure 5.

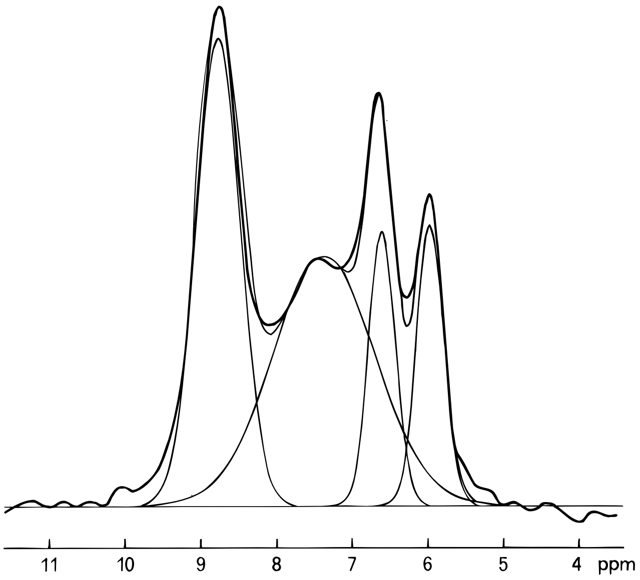

Figure 8. ^{13}C MAS spectrum of PDEP at 293 K without ^{14}N irradiation (Figure 5a), with the deconvoluted signals and the resulting calculated trace.

width, and chemical shift until an optimum was found. The triple-resonance spectrum was deconvoluted using the same optimized parameters. The best peak line shape for all the spectra was found to be 60% Lorenzian and 40% Gaussian. One example of deconvolution is reported in Figure 8 for the reference spectrum at 293 K. The intensities of the peaks obtained by the deconvolution are given in Table 2.

The peak due to the mobile methyl of phase Ib is the most affected by the irradiation of nitrogen nuclei, in fact, the intensity loss for this peak is nearly twice that of the others.

For a quantitative description of the TRAPDOR technique,[21] one needs further information, like the quadrupole coupling tensor of the ^{14}N nuclei in PDEP.

Table 2. Results of the Triple-Resonance Experiment[a]

	chem shift, ppm	phase	intensity loss, % 293 K	303 K	313 K
CH_3	6. 8	Ia	16.7	12.4	31.7
	7.6	Ia	20.6	13.9	30.5
	8.5	Ib	38.0	30.6	41.9
	10.0	Ia	19.5	14.2	22.0

[a] The pulse sequence presented in Figure 1 was used. The intensities are obtained by a deconvolution routine. For the relative intensity loss, $[(I_0 - I)/I_0]100$, where I is the intensity of the defined methyl peak in the triple-resonance experiment and I_0 the intensity of the same methyl peak in the reference experiment. The reported values are the average of two independent experiments.

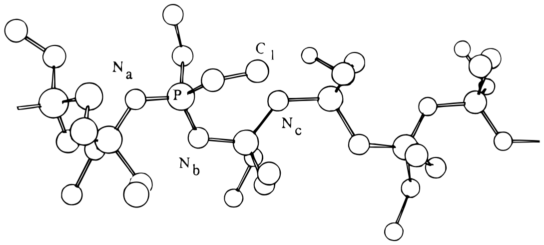

Figure 9. Arbitrary view of PDEP displaying the different ethyl group conformations.

For discussing our results, we will therefore use a qualitative approach. We assume that the TRAPDOR intensity loss is only due to the distance-dependent part of the dipolar interaction;[24] we completely neglect the dependence on the relative geometry of the C−N dipolar tensor and the ^{14}N quadrupolar tensor. Also, we assume that the ^{14}N quadrupolar tensor is not affected by the side-chain motion. If the ^{14}N quadrupolar interaction were affected by the motion, it could modify the evolution of the ^{14}N magnetization during the TRAPDOR effect. For the situation discussed here, it seems extremely unlikely that the side-chain motions affect the quadrupolar interaction on the main-chain nitrogen so much that the adiabaticity of the ^{14}N transitions are influenced. We can then write for the relative intensity decrease in the TRAPDOR experiment

$$(I - I_0)/I_0 = C\gamma_C\gamma_N\hbar^2\sum_n(1/r_{CN_n}{}^3) \qquad (1)$$

where C is a factor which contains the effect due to the instrumental parameters (spinning speed, number of rotor cycles, effective strength of the rf field on ^{14}N channel) and molecule-specific parameters (^{14}N quadrupole interaction), the sum being extended to all the nitrogens that can give an appreciable effect in the experimental conditions used. The intensity loss differences of each peak of the same sample can then be explained considering the distances between the carbons and nitrogens, the value of C being the same. The absolute values of intensity losses are not considered.

The relative loss for methyls in PDEP can thus be explained by taking into account the distances between the methyls and the nitrogens. A conformational arrangement of PDEP is shown in Figure 9; the modeling was done by using the valence angles and bond distances found in the crystal structure of the cyclic trimer of diethylphosphazenes and by using the measurement of the repeat period of poly(diethylphosphazene).[16] In the figure, all dihedral angles are set to those of phase Ia, except the dihedral angle $\angle N_aPCC_1$, which is set arbitrarily. If we consider the complete rotation of methyl C_1 around the $P-CH_2$ bond, we can observe that

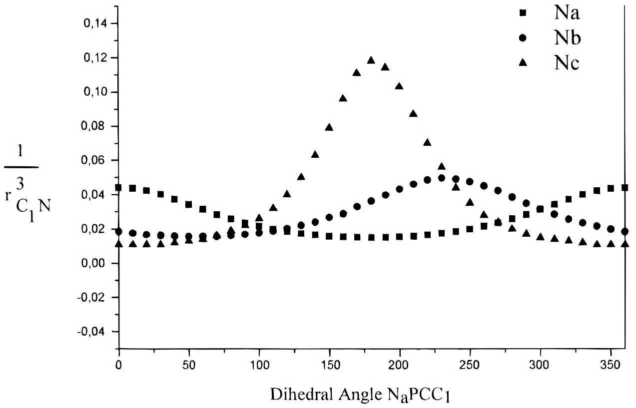

Figure 10. Plot of the inverse third power of the distance between methyl C_1 and nitrogens N_a, N_b, and N_c, as a function of the dihedral angle $\angle N_aPCC_1$.

only three nitrogens can produce effective interactions with carbon C_1: they are labeled as N_a, N_b, and N_c. The other nitrogen atoms are placed too far away in any conformation.

The value of $1/r_{CN_n}{}^3$, which is proportional to the intensity loss, is reported in Figure 10 as a function of the dihedral angle $\angle N_aPCC_1$.

The most striking feature is that the maximum interaction between C_1 and N_c is present at 180°; the value for $1/r^3$ is larger than twice the maximum value for the interaction between C_1 and N_a and between C_1 and N_b. As already established in ref 16, in phase Ia, two conformations are present which are not interconverting within the NMR time scale. In one conformer, methyls are arranged in a gauche position, referring to N_a and N_b atoms (conformation which corresponds to angle $\angle N_aPCC_1$ being nearly equal to 60°). In the other, the methyls are in a gauche position, referring to N_a and to the methylene of the other ethyl chain linked to the same phosphorus (with $\angle N_aPCC_1$ nearly equal to 300°) (see also Figure 4). The dipolar interactions between methyls and nitrogens are quite close for these two conformations, and the calculated intensity losses are comparable and relatively small (see Table 2). On the other hand, in the mobile phase, two types of motion are, in principle, feasible: one mechanism of motion consists only of restricted rotations between the two less-hindered conformations ($\angle N_aPCC_1 = 60°$ and $\angle N_aPCC_1 = 300°$), while the other is a complete rotation about the P−CH_2 bond. The first type of motion, a direct conversion from $\angle N_aPCC_1 = 60°$ to $\angle N_aPCC_1 = 300°$ (and vice versa) without passing through 180°, causes only a limited range of dihedral angles to be transversed; they lie at the outer parts of the *x* axis in Figure 10. The distance *r*, averaged over this range, is nearly the same for the two single conformations at about 60° and 300°. Then, the dipolar interaction between the methyl carbon and the three nitrogens hardly differs for phases Ia and Ib.

When the methyl group is subjected to a complete rotation about the P−CH_2 bond, crossing the maximum at 180°, the differences among the three curves presented in Figure 10 becomes significant. As a matter of fact, the experimental relative intensity loss for phase Ib is nearly twice that of phase Ia (40% against 20%; see Table 2). So large an intensity loss cannot be explained without assuming that a contribution of conformations close to 180° is present. Therefore, we believe that the TRADPOR experiment shows that, in phase Ib, the second type of motion is operative, i.e., a complete rotation about the P−CH_2 bond, causing a strong methyl−N_c interaction during part of the rotation period.

Conclusions

A transfer of population in double-resonance experiment is used for studying the dynamical disorder of the ethyl side chains in the Ib modification of PDEP. The triple-resonance data make it possible to distinguish a full rotation of the CH_3 group around the P−CH_2 axis from a fast jump over a limited angle between the two conformations of phase Ia. The bigger intensity loss of the mobile methyls in the triple-resonance experiment with respect to that of methyls in the fixed conformations can be explained by considering a rotation of methyls around the phosphorus−methylene bond. The rotation brings methyls very near the nitrogen on the next momomeric unit, resulting in a strong dipolar interaction with nitrogen. Thus, we can conclude that, in phase Ib, a wide range of conformations is dynamically explored, including a high-energy conformation not available in the low-temperature modification (phase Ia).

The experiment reported here points out the ability of the TRAPDOR triple-resonance technique not only to describe the miscibility of polymers, as already reported, but also to give great insight into the dynamical behavior of polymers.

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