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Solid-State ^{13}C NMR Study of Poly(3,3-diethyloxetane)

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ABSTRACT: Poly(3,3-diethyloxetane) (PDEO) crystallizes in two different forms depending on the temperature of crystallization. In the higher melting form I crystals the PDEO chains adopt the all-trans T_4 conformation, while the T_2G_2 conformation is found in the lower melting form II crystals. High-resolution ^{13}C NMR spectra of both crystal forms have been obtained by employing cross polarization with high-power proton decoupling and magic angle sample spinning. Chemical shifts observed for both the backbone and side-chain methylene carbon resonances differ by 4–6 ppm between the two crystal forms, while the quaternary and methyl carbon resonances are not as significantly affected. The ^{13}C NMR spectra of PDEO forms I and II are discussed in terms of the differences in their polymer chain conformations (T_4 vs. T_2G_2), with primary emphasis placed upon γ-gauche shielding effects on the ^{13}C resonances. It is concluded that differences in interchain packing and intrachain geometry, rather than γ-gauche effects, are principally responsible for the observed differences in ^{13}C chemical shifts between forms I and II of PDEO. Spin–lattice relaxation times, T_1, measured for each carbon in form I and II crystals indicate that the ethyl side chains in the form II crystals are motionally labile and disordered probably by rapid interconversion between T and G side-chain conformations.

Introduction

The polyoxetanes, $-(CH_2CR_1R_2CH_2O)-$, where R_1 and R_2 are hydrogen atoms or alkyl groups, are an interesting series of polymers because of their abilities to be crystallized in several different polymorphs.[1-6] The C–O bonds in each polymorph are always in the trans (T) conformation, while the C–C bonds can adopt either the T or gauche (G) rotational states. Poly(3,3-diethyloxetane) (PDEO) crystallizes[5,6] in the T_2G_2 and T_4 conformations.

Application of high-power proton decoupling, cross polarization (CP), and magic angle sample spinning (MAS) often results[7-14] in ^{13}C NMR spectra with well-resolved resonances for solid samples. It has been observed[14-19] that the chemical shifts of the carbon resonances in the high-resolution solid-state ^{13}C NMR spectra of polymers are sensitive to the conformations adopted by the polymers in the solid. This sensitivity of solid-state ^{13}C NMR chemical shifts to polymer conformation has been manifested as chemical-shift differences between crystal and amorphous components and between two or more crystalline polymorphs.

X-ray diffraction and calorimetric studies[5,6,20] of PDEO have demonstrated the existence of two distinct crystalline polymorphs produced by altering the conditions for crystal growth. Form I melts at 73 °C and consists of PDEO chains in the all-trans T_4 conformation, while the T_2G_2 conformation is assumed by the PDEO chains in the form II crystals melting at 57 °C. The principal purpose of the present study is the correlation of high-resolution solid-state ^{13}C NMR spectra with the two different crystalline chain conformations adopted by PDEO in the form I and II crystals.

Experimental Section

NMR Measurements. ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer operating at a static field of 4.7 T. Variable-temperature, magic angle sample spinning (MAS) was achieved with a Doty Scientific probe, which utilizes a double air bearing design. Aluminum oxide rotors with poly(chlorotrifluoroethylene) (Kel-F) end caps routinely spun at 3–4 KHz when filled with PDEO. A 45-KHz rf field strength was used for decoupling, with a decoupling period of 200 ms. The optimal cross-polarization (CP) contact time of 2000 μs was employed.

No attempt was made to record the absolute chemical shifts of the observed resonances. Instead the chemical shifts of each carbon type were referenced to the resonances observed for the amorphous carbons.

Spin–lattice relaxation times, T_1, were measured for each carbon in forms I and II PDEO under the CP condition. This was achieved by application of the pulse sequence developed by Torchia.[21]

Sample Preparation and Characterization. The PDEO employed in this work was obtained by cationic ring-opening polymerization of the corresponding monomer as described elsewhere.[5] Two fractions of the bulk polymer with number-average molecular weights ($\bar{M}_n$) 8×10^5 and 5×10^4, as measured by osmometry, were studied.

The samples were melted and crystallized inside the NMR rotors in thermostatic baths set at predetermined temperatures for periods of time sufficient to assure complete crystallization as indicated by previous dilatometric studies.[20] PDEO in form I was obtained by crystallizing from the melt at 60 °C for 2 days and in form II through crystallization at 0 °C for 15 h. Crystallization at 35 °C (for the low molecular weight sample) and at 20 °C (for the high molecular weight sample) yielded comparable amounts of both crystalline forms in the same sample.

Small portions of the PDEO samples were removed before and after performing the NMR experiments, and X-ray diffraction and DSC measurements were conducted to verify the crystalline form obtained. X-ray diffraction diagrams were recorded on a Rigaku diffractometer at 1 deg (2θ)/min. under Ni-filtered Cu Kα irradiation, and the DSC thermograms were obtained at heating rates of 10 deg/min. The degrees of crystallinity developed by the PDEO samples at different crystallization temperatures were also estimated by differential scanning calorimetry with a Perkin-Elmer DSC-4 instrument.

The linear polyoxetane (polytrimethylene oxide) (PTO) and its cyclic tetramer (c-$(TO)_4$) were prepared by the method of Rose[22] using boron trifluoride as catalyst. Our samples of PTO and c-$(TO)_4$ melted at 35 and 70 °C, respectively.

Results

X-ray and DSC Characterization of PDEO Crystalline Forms. The identification of the crystalline modification obtained in each PDEO sample was made by X-ray diffraction and DSC techniques, as described in the Experimental Section. PDEO specimens crystallized at 0 °C correspond to form II. This modification has an orthorhombic unit cell, with a measured fiber period of 6.67 Å.[5] It is characterized by a diffractogram with three strong reflections at 2θ = 9.2°, 17.2°, and 17.6°, as shown in Figure 1a.

Form I was obtained by crystallizing the sample from the melt at 60 °C. In this modification, with a measured fiber period of 4.78 Å and a monoclinic unit cell,[6] the two

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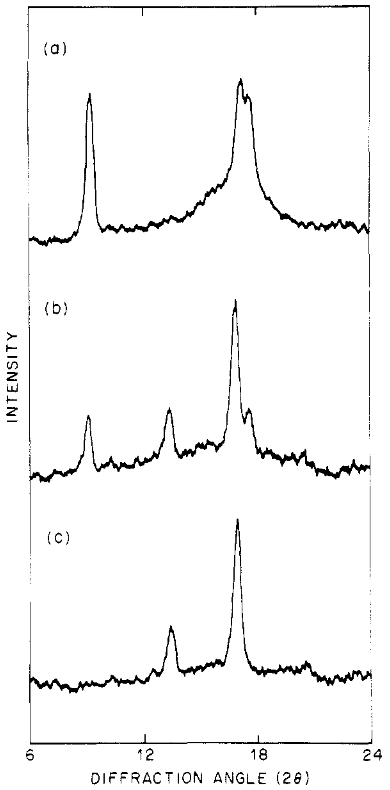


Figure 1. X-ray diffractograms of crystalline PDEO ($\bar{M}_n$ = 50 000) at 25 °C, following various crystallization temperatures: (a) form II from crystallization at 0 °C; (b) forms I and II from crystallization at 35 °C; (c) form I from crystallization at 60 °C.

Table I
Calorimetric Properties of PDEO Crystalline Modifications

form	$\bar{M}_n \times 10^{-3}$	T_m, °C	ΔH_{obsd}, cal/g	ΔH_f,[a] cal/g	% crystal
I	50	69.7	11.8	22.0	54
I	800	78.0	10.3		47
II	50	52.8	6.89	21.0	33
II	800	58.1	6.06		28
I + II	50	72.1, 56.4	5.8, 3.26	22.0, 21.0	26, 16

[a] Reference 20.

strongest diffractometer peaks appear at 2θ = 13.4° and 16.9°, corresponding to 200 and 110 reflections (Figure 1c).

The samples crystallized at 35 °C ($\bar{M}_n$ = 50 000) and at 20 °C ($\bar{M}_n$ = 800 000) contain substantial amounts of both crystalline forms as evidenced in Figure 1b.

The characterization of the crystalline forms was also achieved by measuring the melting temperatures, which differ by ca. 15 °C, with the DSC instrument. These data, together with the melting endotherms and degree of crystallinity also obtained by DSC, are reported in Table I. The differences in crystallinity and melting points between the two molecular weight samples are in agreement with the molecular weight effects observed previously for the PDEO system.[20]

Crystalline modifications were not observed to change as a consequence of the high-speed sample rotation in the MAS NMR experiments.

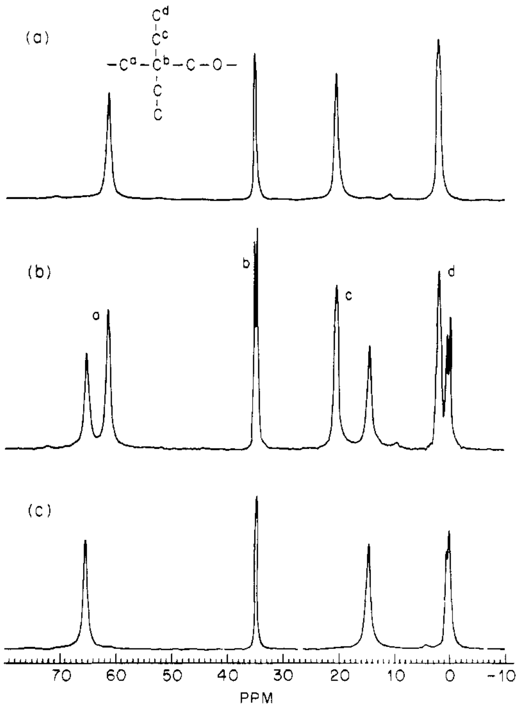
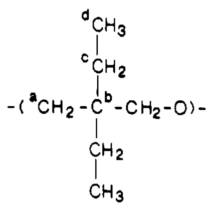


Figure 2. CPMAS spectra of PDEO ($\bar{M}_n$ = 50 000) crystallized at three different temperatures: (a) form I (60 °C); (b) forms I and II (35 °C); (c) form II (0 °C). All three spectra were recorded at room temperature with no reference employed.

Table II
^{13}C NMR Chemical Shifts (ppm)[a] for PDEO in the Solid State



PDEO	a	b	c	d
form I (T_4, T_m = 73 °C)	−5.1	1.1	3.1	1.7
form II (T_2G_2, T_m = 57 °C)	−1.2	0.6	−2.8	−0.3
amorphous	0.0	0.0	0.0	0.0

[a] ^{13}C NMR chemical shifts observed at 25 °C in PDEO ($\bar{M}_n$ = 5 × 10^4) containing both form I and II crystals (see Figure 2) and referenced to the resonances observed for the amorphous PDEO carbons of each type.

Table III
Spin–Lattice Relaxation Times, T_1, for Forms I and II PDEO

	T_1, s			T_1, s	
carbon	form I	form II	carbon	form I	form II
>C<	62	15	CH_2 (side chain)	22	1
α-CH_2	40	14	CH_3	2	1

^{13}C NMR of PDEO in the Solid State. Figure 2 presents the CPMAS spectra of PDEO ($\bar{M}_n$ = 50 000) crystallized at three different temperatures from the melt to produce samples containing form I (Figure 2a), form II (Figure 2c), and form I and II (Figure 2b) crystals. The spectra of PDEO ($\bar{M}_n$ = 800 000) containing form I crystals, obtained with and without cross polarization, are compared in Figure 3, where crystalline and amorphous resonances are seen to be easily discriminated. Table II presents the relative ^{13}C chemical shifts observed for forms I and II PDEO referenced to the corresponding resonances of amorphous PDEO.

Spin–lattice relaxation times, T_1, observed for each carbon in form I and II PDEO crystals are presented in Table III.

CPMAS spectra of PTO and its cyclic tetramer, c-$(TO)_4$, are displayed in Figure 4. The sample of PTO employed

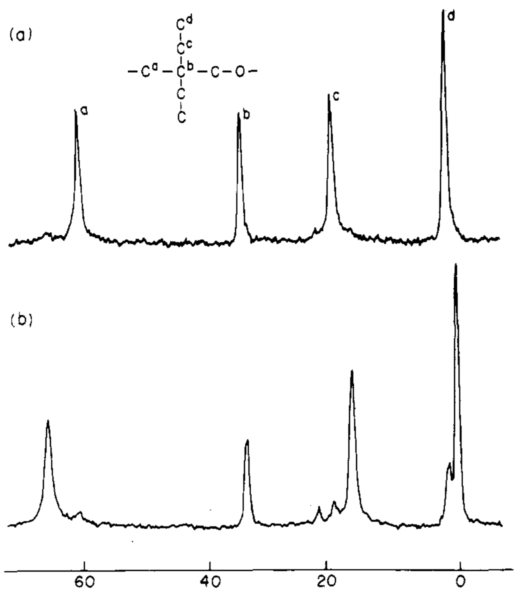


Figure 3. ^{13}C NMR spectra at 60 °C of PDEO ($\bar{M}_n$ = 800 000) containing form I crystals obtained (a) with cross polarization (crystalline resonances) and (b) without cross polarization (amorphous resonances). No reference was employed.

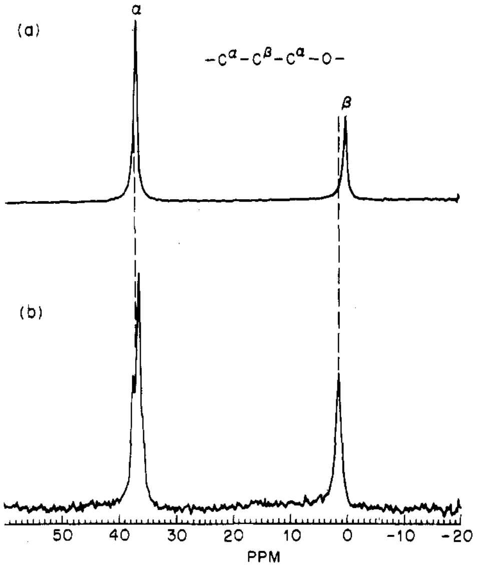


Figure 4. CPMAS spectra of PTO (a) and c-(TO)$_4$ (b) recorded at room temperature, with no reference employed. The β-methylene carbon resonance in PTO is assigned 0 ppm.

in this study contains the T$_2$G$_2$ polymorph, so as to permit comparison of its spectrum with that of c-(TO)$_4$ which crystallizes exclusively in the T$_2$G$_2$ conformation.

Discussion

It has long been established[23] that the ^{13}C chemical shifts of polymers observed in high-resolution ^{13}C NMR spectra of their solutions are sensitive to their microstructures, i.e., stereoregularity, comonomer sequence, and defect structures. More recently[24,25] it has been demonstrated that the microstructural sensitivity of polymer ^{13}C chemical shifts has its origin in the local polymer chain conformation. Microstructural differences produce changes in the average local polymer chain conformation which in turn are manifested as different ^{13}C chemical shifts for the carbon atoms in the vicinity of each unique microstructure.

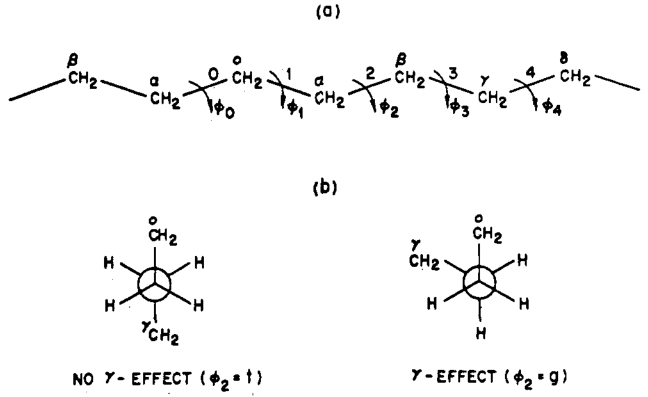


Figure 5. (a) Portion of a paraffinic hydrocarbon chain in the all-T, planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the γ-gauche shielding effect.

The γ-gauche effect,[24] as illustrated in Figure 5, successfully accounts for the microstructurally dependent ^{13}C chemical shifts exhibited by polymers in their high-resolution solution spectra. There are also several examples from the high-resolution spectra recorded on polymers in the solid state[13-19] that indicate the γ-gauche effect also importantly influences the ^{13}C chemical shifts of solid polymers.

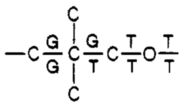
Several authors[15,26,27] have reported that the amorphous carbons in semicrystalline polyethylene (PE) resonate 2–3 ppm upfield from the crystalline carbons. This observation is expected, because the crystalline carbons reside in the all-trans, planar zigzag conformation (no γ-gauche shielding), while the C–C bonds in the amorphous portions of PE possess some gauche character and therefore experience γ-gauche shielding (see Figure 5).

Harris et al.[16] have observed the methylene carbon resonance in crystalline syndiotactic polypropylene (s-PP) to be a doublet split by 8.7 ppm, while for isotactic polypropylene (i-PP) the methylene carbon resonance is a singlet resonating midway between the s-PP methylene doublet. s-PP crystallizes[28] in the –TTGG– conformation where half the methylene carbons experience two γ-gauche effects, while the remaining half experience no γ-gauche interactions. i-PP crystallizes[29] in the –TGTG– conformation, where every methylene carbon experiences one γ-gauche shielding effect. As is observed, we would expect the methylene carbon resonances in crystalline s-PP to be split by 8–10 ppm and the methylene carbons of crystalline i-PP to resonate midway between them.

Poly(1-butene) crystallizes in three distinct helical conformations[30-37] characterized by 3/1, 11/3, and 4/1 monomer units/helical turn, and each backbone approximates the –TGTG– conformation. In passing from the 3/1 to the 4/1 crystal structure the backbone rotation angles open up from perfectly staggered positions (60° dihedral angles) to significantly nonstaggered values (85°). This results in a deshielding of ^{13}C resonances in the 4/1 form relative to the 3/1 form due to the reduction in the magnitude of γ-gauche interactions.

Aside from the three specific examples just discussed, several other reports[14,38,39] on the solid-state ^{13}C chemical shifts observed in crystalline polymers can and have been analyzed in terms of γ-gauche shielding effects. Most pertinent among these is a solid-state ^{13}C NMR study of polyoxetane (PTO) and poly(3,3-dimethyloxetane) (PDMO) by Perez and VanderHart.[39] Both PTO and PDMO can be crystallized in at least two different crystalline forms with different chain conformations in each polymorph. Perez and VanderHart produced and reported spectra of the two crystalline modifications with T$_2$G$_2$ and T$_3$G conformations for each polymer.

While single resonances are observed for all the carbons in the T$_2$G$_2$ crystalline forms of both polymers, in the T$_3$G crystal forms two resonances are observed for the CH_2–O or α-methylene and methyl carbons (PDMO only).



$-\mathrm{C}\frac{\mathrm{G}}{\mathrm{G}}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\mathrm{C}}}\frac{\mathrm{G}}{\mathrm{T}}\mathrm{C}\frac{\mathrm{T}}{\mathrm{T}}\mathrm{O}\frac{\mathrm{T}}{\mathrm{T}}$

PDMO

In the T_3G conformation one α-methylene carbon experiences one γ-gauche interaction while the other α-methylene has no γ-gauche interactions. Both α-methylene carbons in the T_2G_2 crystalline forms experience a single γ-gauche interaction. On the basis of γ-gauche shielding effects we would expect both α-methylene carbons in the T_2G_2 forms to resonate near the most upfield α-methylene carbon in the T_3G forms, while the other T_3G α-methylene carbon should be downfield from these resonances by one γ-gauche interaction with oxygen. While the α-methylene carbons are observed to split by 2.2 (PTO) and 1.3 (PDMO) ppm in the T_3G crystal forms, the two α-methylene carbons in the T_2G_2 forms appear 1.8 (PTO) and 1.9 (PDMO) ppm further upfield from the most shielded T_3G α-methylene carbon resonance.

On the basis of a comparison[40] of the ^{13}C NMR spectra of *n*-alkanes and *n*-alkyl ethers, the shielding produced by an oxygen atom in a γ-gauche arrangement with the α-methylene carbons in PTO and PDMO would be expected to be at least -5 ppm. The fact that the α-methylene carbons are split by only 1.3–2.2 ppm in the T_3G crystal forms, coupled with the observation that both T_2G_2 α-methylenes resonate an additional 1.8–1.9 ppm upfield from the most shielded T_3G α-methylene carbon despite also being in a single γ-gauche arrangement, indicates that γ-gauche shielding interactions do not play the principal role in determining the solid-state ^{13}C NMR chemical shifts observed in PTO and PDMO.

This conclusion is further strengthened by the ^{13}C chemical shifts observed for the methyl carbons in PDMO which all resonate within a 1.1 ppm range in both crystal forms even though all methyls have one γ-gauche interaction with oxygen except one of the T_3G methyls which is γ-gauche to two oxygens. In addition, the β-methylene (PTO) and quaternary (PDMO) carbons, which have no γ-gauche interactions in either crystalline form, are separated by 1.0 (PTO) and 1.8 (PDMO) ppm between the T_2G_2 and T_3G forms. Clearly some source other than γ-gauche interactions, such as crystalline packing effects, must be sought to explain the ^{13}C chemical shifts observed by Perez and VanderHart[39] in crystalline PTO and PDMO samples.

Poly(3,3-diethyloxetane) (PDEO) crystallizes[5,6] into two polymorphs, I and II, with T_4 and T_2G_2 conformations, respectively. In Figure 6 Newman projections about the four bonds attached to the quaternary carbon are presented. The two backbone bonds (1 and 2) are either both T or G in the T_4 and T_2G_2 conformations, respectively. In the form I, T_4 crystals the side-chain bonds are both T, while their conformations are not known in the form II, T_2G_2 crystals. The C–O bonds are T in both crystal forms.

Table IV presents a summary of the number and kinds of γ-gauche interactions occurring in both PDEO crystal forms. Based on these γ-gauche arrangements, we would expect the following behavior for the ^{13}C chemical shifts in PDEO forms I and II: (i) CH_3 should resonate at the same field in I and II, (ii) >C< should resonate at the same field in I and II, (iii) α-CH_2 II should resonate upfield from α-CH_2 I by one γ(O) or by γ(O) – γ(CH_3) depending on whether bonds 3,4 = T or G in form II, and (iiii) CH_2 (side chain) I should resonate upfield from CH_2 (side chain) II by one γ(O) or by γ(O) – γ(CH_3) depending on whether bonds 3,4 = T or G in form II (see Figure 6).

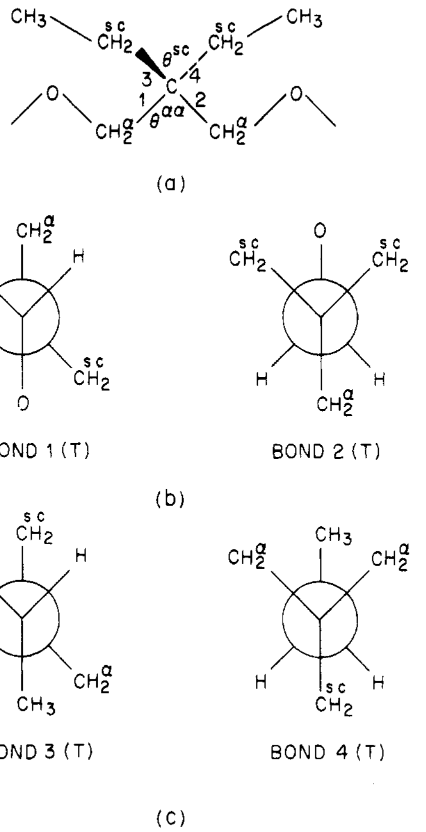


Figure 6. (a) PDEO chain structure. (b) Newman projections along the C–C backbone bonds (1,2) in PDEO. (c) Newman projections along the >C< CH_2 side-chain bonds (3,4) in PDEO.

Table IV
γ-Gauche Interactions in Forms I and II PDEO

	no. of γ-gauche interactions	
carbon	form I (T_4)	form II (T_2G_2)
>C<	0	0
CH_3	2(CH_2)	2(CH_2)
α-CH_2	2(CH_3)	1(O) + if bond 3,4 = T, 2 (CH_3) if bonds, 3,4 = G, 1 (CH_3)
CH_2 (side chn.)	2(O)	1(O) + if bonds 3,4 = T, 0 (CH_3) if bonds 3,4 = G, 1 (CH_3)

A comparison of the three CPMAS spectra of PDEO ($\bar{M}_n$ = 50 000) in Figure 2 makes it readily apparent that the ^{13}C chemical shifts expected for >C< and CH_3 are similar to those observed. However, instead of α-CH_2 II being upfield from α-CH_2 I it resonates 3.9 ppm downfield. Similarly, form II CH_2 (side chain) comes upfield from form I CH_2 (side chain) by 5.9 ppm instead of being downfield as expected. As observed for PDMO by Perez and VanderHart[39] the ^{13}C chemical shifts observed in forms I and II PDEO are not predominantly influenced by γ-gauche shielding effects.

It is natural to consider different packing of the PDEO chains in forms I and II as a possible source of the difference observed in their ^{13}C chemical shifts. The >C< and CH_3 carbons have identical γ-gauche interactions in both PDEO crystal forms, yet there are 0.5 (>C<) and 2.1 (CH_3) ppm chemical shift differences between the two polymorphs. Based on the ^{13}C chemical shift packing effects seen in *n*-alkane,[41] PE,[42] and i-PP[43] crystals, the differences observed between form I and II >C< and CH_3 chemical shifts do not seem atypical.

As another example, we may compare the ^{13}C chemical shifts of PTO in the T_2G_2 crystal form with those observed for its cyclic tetramer, c-$(TO)_4$, which also adopts[44] the T_2G_2 conformation in the crystalline state (see Figure 4). The α-CH_2 ^{13}C chemical shifts differ by 0.3–0.5 ppm and the β-CH_2 shifts by 1.4 ppm between crystalline PTO (T_2G_2) and c-$(TO)_4$. These are not unlike the packing effects observed on the >C< and CH_3 carbons in PDEO. Thus it would appear that packing effects in PTO, PDMO, and PDEO can be as large as 2 ppm.

However, packing effects of this magnitude are not nearly sufficient to explain the observed differences in the ^{13}C chemical shifts of the α-CH_2 and CH_2 (side chain) carbons between forms I and II PDEO which are >4–6 ppm.

In addition to interchain packing effects, there must be some differences in intramolecular chain geometries between forms I and II PDEO. Possibly the valence angles differ significantly between the T_4 conformation in form I crystals and the T_2G_2 conformation in the form II crystals. Such valence angle differences would be expected[46] to produce large ^{13}C chemical shift effects; however, it is a bit more difficult to understand why the >C< and CH_3 carbons would not also be affected.

Let us suppose that the C^{α}–C–C^{α} backbone valence angle ($\theta^{\alpha\alpha}$) is sensitive to the rotational states of the C–C bonds (1 and 2 in Figure 6) and adopts different values for the T and G rotational states. If $\theta^{\alpha\alpha}(G) >$ or $< \theta^{\alpha\alpha}(T)$ then we would expect[47] the valence angle C^{SC}–C–C^{SC} between ethyl side chains (θ^{SC}) to follow $\theta^{SC}(T) >$ or $< \theta^{SC}(G)$. The ^{13}C chemical shift of >C< should be independent of complimentary changes in $\theta^{\alpha\alpha}$ and θ^{SC}, because all four quaternary carbon substituents are methylene carbons. In addition, the methyl carbons are probably sufficiently removed from $\theta^{\alpha\alpha}$ and θ^{SC} to have their ^{13}C chemical shifts unaffected by changes in these valence angles.

Spin–lattice relaxation times, T_1, observed for each carbon in forms I and II PDEO crystals are compared in Table III. The most dramatic differences in T_1's are those observed for the side-chain methylene carbons, i.e., T_1 = 22 s (I) and 1 s (II). Apparently the side chains in the form II crystals possess considerable mobility, most probably as a result of rotations about side-chain bond 3 and 4 (see Figure 6). This implies that the ethyl side chains in form II crystals are conformationally disordered and are likely interconverting rapidly between T and G conformations.

In summary, we believe the large chemical shift differences observed for the methylene carbon resonances in the solid-state ^{13}C NMR spectra of forms I and II PDEO are likely the result of intramolecular geometrical differences between the chains residing in these two polymorphs. Valence angle distortion at the quaternary carbon, which depends on the conformational states of the bonds attached to this carbon, rather than conformationally sensitive γ-gauche effects or differences in interchain packing, seem the most likely source of the large chemical shift differences observed in the solid-state for the forms I and II methylene carbons in PDEO.

In addition, spin–lattice relaxation times observed for both crystalline forms of PDEO indicate that the side chains in the form II crystals are motionally labile and disordered. Rapid interconversion between T and G side-chain conformations seems a likely source of the short T_1's observed for the side-chain methylene carbons in form II PDEO.

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Registry No. PDEO (SRU), 83699-97-2; PDEO (homopolymer), 83699-76-7.

References and Notes

(1) Tadokoro, H.; Takahashi, Y.; Chatani, Y.; Kakida, H. *Makromol. Chem.* **1967**, *109*, 96.
(2) Kakida, H.; Makiro, D.; Chatani, Y.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1970**, *3*, 569.
(3) Takahashi, Y.; Osaki, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1152.
(4) Takahashi, Y.; Osaki, Y.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1863.
(5) Perez, E.; Gomez, M. A.; Bello, A.; Fatou, J. G. *Colloid Polym. Sci.* **1983**, *261*, 571.
(6) Gomez, M. A.; Atkins, E. D. T.; Bello, A.; Fatou, J. G.; Upstill, C. *Polymer*, in press.
(7) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(8) Sarles, L. R.; Cotts, R. M. *Phys. Rev.* **1958**, *111*, 853.
(9) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1972**, *8*, 1.
(10) Lowe, I. J. *Phys. Rev. Lett.* **1959**, *2*, 85.
(11) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1975**, *8*, 291.
(12) Garroway, A. N.; Moniz, W. B.; Ressing, H. A. *Org. Coat. Plast. Chem.* **1976**, *36*, 133.
(13) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1975**, *44*, 361.
(14) Moller, M. *Adv. Polym. Sci.* **1985**, *66*, 59.
(15) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.
(16) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *J. Chem. Soc., Chem. Commun.* **1981**, 15.
(17) Belfiore, L. A.; Schilling, F. C.; Tonelli, A. E.; Lovinger, A. J.; Bovey, F. A. *Macromolecules* **1984**, *17*, 2561.
(18) Sacchi, M. C.; Locatelli, P.; Zetta, L.; Zambelli, A. *Macromolecules* **1984**, *17*, 483.
(19) Terao, T.; Maeda, S.; Saika, A. *Macromolecules* **1983**, *16*, 1535.
(20) Gomez, M. A.; Fatou, J. G.; Bello, A. *Eur. Polym. J.* **1986**, *22*, 43.
(21) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(22) Rose, J. B. *J. Chem. Soc.* **1956**, 542.
(23) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic: New York, 1972.
(24) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.* **1981**, *14*, 233.
(25) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic: New York, 1982.
(26) Kitamaru, R.; Horii, F.; Murayama, M. *Polym. Bull.* **1982**, *7*, 583.
(27) Ando, I.; Yamanobe, T.; Sorita, T.; Komoto, T.; Sato, H.; Deguchi, K.; Imanari, M. *Macromolecules* **1984**, *17*, 1955.
(28) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.
(29) Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. *Makromol. Chem.* **1964**, *75*, 134.
(30) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 52.
(31) Miyashita, T.; Yokouchi, M.; Chatani, Y.; Tadokoro, H. Annual Meeting of the Society of Polymer Science, Japan, Tokyo, 1974, preprint p 453. Quoted in: Tadokoro, H. *Structure of Crystalline Polymers*; Wiley-Interscience: New York, 1979; p 405.
(32) Turner-Jones, A. *J. Polym. Sci., Part B* **1963**, *1*, 455.
(33) Petraccone, V.; Priozzi, B.; Frasci, A.; Corradini, P. *Eur. Polym. J.* **1976**, *12*, 323.
(34) Zannetti, R.; Manaresi, P.; Buzzori, G. C. *Chim. Ind. (Milan)* **1961**, *43*, 735.
(35) Danusso, F.; Gianotti, G. *Makromol. Chem.* **1963**, *61*, 139.
(36) Geacintov, C.; Schottand, R.; Miles, R. B. *J. Polym. Sci., Polym. Lett. Ed.* **1963**, *1*, 587.
(37) Miller, R. C.; Holland, V. F. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 519.
(38) Schilling, F. C.; Bovey, F. A.; Tonelli, A. E.; Tseng, S.; Woodward, A. E. *Macromolecules* **1984**, *17*, 728.
(39) Perez, E.; VanderHart, D. L. *Polymer* **1987**, *28*, 733.
(40) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972; Chapters 3 and 5.
(41) VanderHart, D. L. *J. Magn. Reson.* **1981**, *44*, 117.
(42) VanderHart, D. L.; Khoury, F. *Polymer* **1984**, *25*, 1589.
(43) Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *Polymer* **1982**, *23*, 694.
(44) c-$(TO)_4$ actually adopts the $(T_2G_2T_2\bar{G}_2)_2$ conformation in the crystal[45] due to its cyclic structure. However, both the α- and

β-methylene carbons in PTO (T_2G_2) and crystalline c-$(TO)_4$ experience identical numbers and types of γ-gauche interactions.

(45) Groth, P. *Acta Chem. Scand.* **1971**, *25*, 725.

(46) Reference 39, Chapter 4.

(47) This is a consequence[48] of the conservation of total s and p character of the sp^3 molecular orbitals around $>$C$<$.

(48) Huheey, J. E. *Inorganic Chemistry; Principles of Structure and Reactivity*; Harper and Row: New York, 1972; Chapter 4.

Photochemical Behavior of Poly(organophosphazenes). 5. Photochemistry of Poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, in Solution

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ABSTRACT: In air-equilibrated CH_2Cl_2 or in CH_2Cl_2/CCl_4 solutions, the irradiation of the poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, induces chain scission and degradation of the macromolecule. This process is believed to originate from the breaking of peroxy radicals formed by reaction of oxygen with phosphorus macroradicals derived from unreacted P–Cl groups in the phosphazene polymer. Evidence is given that the benzophenone ketyl radical, the primary photochemical species formed during the photolysis of BzPOP dissolved in hydrogen-donating solvents, is responsible for the formation of phosphorus macroradicals. In the absence of molecular oxygen, bimolecular processes, leading to extensive cross-linking and gel formation, prevail.

Introduction

The photochemical and photophysical behavior of poly(organophosphazenes) (POPs) has attracted considerable attention in recent years[1–4] owing to the substitutive synthetic approach used for the preparation of these polymers. The method, in fact, offers the unique opportunity of obtaining a large variety of different macromolecules just by changing the nucleophiles which substitute the highly reactive chlorine of a polymeric precursor, poly(dichlorophosphazene).[5,6] Due to the characteristics of the phosphorus–nitrogen "double bond" present in these polymers,[7] chromophores appended to the poly(phosphazene) backbone maintain almost unaltered their spectroscopic and photochemical properties, so that the photoreactivity of the resulting POPs appears to be dominated by the photochemical characteristics of the substituents.

In 1979 we started a series of investigations on the photoreactivity of aryloxy- and arylamino-substituted POP, both in solution and in film, with the aim of shedding some light in the photochemistry of these materials.[1,3,4] From these studies it came out that, in all the investigated POPs, the photoreactivity is originated from the first excited singlet state of the chromophore bonded at the phosphazene chain; moreover, it was clear that the presence of molecular oxygen in the irradiated polymer directs the overall photoreaction toward the degradation, while in the absence of oxygen cross-linking prevails. Finally, it was demonstrated that the formation of charge-transfer complexes between side substituent groups on the phosphazene backbone and high electron affinity halogenated solvents introduces in the photochemistry of these polymers alternative pathways for the degradation or cross-linking which enhance significantly the photoreactivity of these materials.

Further investigation on the photophysical behavior of both aryloxy- and arylamino-substituted cyclophosphazenes and poly(phosphazenes) revealed the existence of intramolecular interactions between excited- and ground-state chromophores on the phosphazene backbone, leading to the emission of excimeric species.[8,9]

Parallel studies on the photochemistry and photophysics of POPs performed by Allcock[2] and Webber,[10] respectively, substantially confirmed our results.

Recently,[11] we synthesized and characterized a new polymeric phosphazene material, the poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, BzPOP, in which two benzophenone moieties are attached to the phosphorus atoms of the phosphazene chain.

This polymer proved to be an excellent triplet-state energy donor in heterogeneous phase,[11] able to photosensitize some reactions, occurring in the triplet state, like the trans ⇄ cis isomerization of stilbene and of piperylene, the cycloaddition of indene, and the valence isomerization of norbornadiene to quadricyclene.

During these processes, however, it has been found that BzPOP undergoes a certain degree of insolubilization: the suspicion arose therefore that BzPOP could exhibit a completely different photoreactivity, compared to that of other aryloxy-substituted phosphazene polymers. Owing to the high efficiency by which the triplet state of BzPOP is populated,[11] a photoreactivity of this polymer completely different from that of other aryloxyphosphazenes is not unexpected. This is in agreement also with the fact that substantial differences in chemical reactivity are expected for S_1 and T_1 states of an electronically excited molecule, due to the rather different nuclear structure and electronic distribution of the two states.[12]

Therefore, we believed it was useful to investigate the direct photochemistry of the BzPOP in solution, and in this paper, we discuss research in this field.

Experimental Section

The synthesis, characterization, and spectroscopic properties of the BzPOP have already been reported elsewhere.[11] As previously stressed, the content of unsubstituted chlorine in the BzPOP ranged to 1.1%.

Tetrahydrofuran (THF), CH_2Cl_2, isopropyl alcohol, cumene, benzene, and CCl_4 were Carlo Erba solvents, analytical grade, and

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