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# Alkyl Chain Order in a Linear Polymeric Liquid Crystal

**Edward T. Samulski***

*Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268*

**Michelle M. Gauthier, Rita B. Blumstein, and Alexandre Blumstein**

*Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854. Received May 6, 1983*

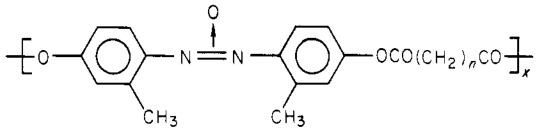
ABSTRACT: The order and mobility of a labeled flexible alkyl chain spacer in the linear thermotropic polymeric nematic liquid crystal poly(2,2′-dimethyl-4,4′-dioxyazoxybenzenedodecanedioyl-$d_{20}$) (poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl-$d_{20}$)]) is explored with deuterium NMR. The quadrupolar splittings of the spacer methylene segments in the nematic melt of the polymer are reported as a function of the temperature and are contrasted with observations on model compounds solubilized in a nematic solvent. The orientational order of the spacer $CD_2$ segments is considerably larger than that of labeled chains appended to low molecular mass liquid crystals. Nonequivalent quadrupolar splittings along the labeled spacer indicate that the spacer does not simply adopt the all-trans conformation. The spacer flexibility does decrease substantially (relative to low molecular mass liquid crystals) as the temperature is lowered in the nematic phase. Speculations are advanced about the source of the large even–odd oscillations reported for thermodynamic properties of linear polymeric liquid crystals as the spacer length is varied.

## Introduction

In the past few years there has been considerable interest in synthesizing thermotropic polymeric liquid crystals (PLCs) in response to a need for new compounds for electrooptic devices and as part of a general goal to develop ultrahigh-strength organic-based materials.[1] Two types of thermotropic PLCs have been considered: side-chain polymers and linear polymers. In both types of polymers prolate mesogenic cores are incorporated into the polymer. In the former type, the mesogenic core is appended to the polymer as a side chain, usually separated from the main chain of the polymer by a flexible alkyl chain spacer. All of the major types of organization in liquid crystals (nematic, smectic, and cholesteric) have been demonstrated by judicious combinations of the mesogen core, the flexibility of the polymer main chain, and the spacer length. The early studies of side-chain PLCs have been reviewed[2] and ref 3 and 4 provide an introduction to the current literature. Linear thermotropic PLCs have been synthesized with mesogenic cores regularly alternating with flexible alkyl chain spacers incorporated into the polymer main chain. Since their introduction in 1975,[5] linear PLCs with smectic, nematic, and cholesteric phases have been reported (see ref 6 for a review).

Generally speaking, the molecular structure of classical thermotropic low molecular mass liquid crystals or mesogens ("monomeric" liquid crystals (MLCs)) can be idealized into two distinct parts: a rigid "core" (usually conjugated aromatic rings) terminated with one or two "flexible chains" (alkyl, alkyloxy, etc.). In the melts of MLCs composed of prolate-shaped mesogens, the basic type of organization (uniaxial nematic (1-D order), stratified smectic (2-D order), etc.) exhibited by thermodynamically distinct phases of these materials is intimately associated with subtle characteristics of the mesogen structure.[7] In particular, the liquid crystal texture and its thermal stability is strongly correlated with lateral substitutions on the core and with the nature of the pendant alkyl chains—their length and presumably, their flexibility.

Linear PLCs also exhibit sensitivity to structural changes both in the core and in the alkyl spacer.[6,8] In particular, lateral chemical substitution on the core yields low-melting PLCs, e.g., the homologous series of polymers prepared by condensation of 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene with the diacid chlorides $ClCO-(CH_2)_n-COCl$:[9-11]



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Extensive studies of this series by X-ray diffraction,[11] magnetic birefringence,[12,13] and differential scanning calorimetry[14] and a proton NMR study of DDA9 (I with $n = 10$)[15,16] suggest that the spacer is not a superfluous part of these polymers; the spacer plays an integral role in determining the degree of organization in the liquid crystalline phases. The results of such studies have been interpreted in terms of an extended alkyl chain spacer in the liquid crystal phase. Herein we report NMR measurements of a deuterium-labeled spacer in the nematic phase of DDA9-$d_{20}$. Direct insights into the structure and dynamics of the spacer group are obtained.

## Deuterium NMR Technique

As a result of an intensive effort devoted to establishing methodologies for probing alkyl chains in liquid crystals, deuterium NMR (DMR) has emerged as a powerful technique because the principal DMR parameters that reflect molecular motion are governed by the coupling between the nuclear quadrupole moment of the deuteron and the local electric field gradient (efg) tensor. Moreover, since in aliphatic molecules the principal element of the efg tensor is directed along the C–D bond vector, DMR enables one to directly monitor the reorientation of this vector in specifically labeled alkyl chain segments.[17]

The DMR spectra of a deuterium-labeled alkyl chain having its mobility constrained by the fluid environment of an oriented uniaxial liquid crystal is dominated by the incompletely averaged quadrupolar interaction and it exhibits a superposition of discrete, well-resolved, quadrupolar doublets. There is one doublet $\Delta\nu_i$ for each motionally inequivalent methylene segment $i$. The magnitude of $\Delta\nu_i$ is a direct measure of the effectiveness of the (anisotropic) molecular motion (intramolecular together with extramolecular reorientation) for averaging the efg at the $i$th segment, thereby giving a uniquely detailed picture of residual order and mobility in the constrained chain.

For labeled alkyl chains appended to an idealized prolate mesogen core, the orientational order of the C–D vectors can be defined in terms of the nematic order parameter $S_Z$ (see introduction in ref 18). $S_Z$ defines the average

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orientation of the mesogen's symmetry axis. The uniaxial symmetry of the nematic fluid, the idealized cylindrical symmetry of the mesogen core, and the uniaxial symmetry (approximate) of the efg tensor about the C–D bond result in a simple expression for the $\Delta\nu_i$. In the rapid-motion limit, i.e., when the correlation time for the motions averaging the efg is $\lesssim 10^{-7}$ s, the quadrupolar splitting exhibited by a labeled segment of the chain is given by

$$\Delta\nu_i = {}^3/_2(e^2qQ/h)\langle P_2(\cos\theta)P_2(\cos\alpha)\rangle P_2(\cos\beta) \quad (1)$$

The angle that the mesogen symmetry axis makes with the nematic director **n** is $\theta$; $\alpha$ is the angle that the C–D bond vector in the $i$th segment makes with the symmetry axis of the mesogen, and $\beta$ is the angle between **n** and the magnetic field ($\beta = 0°$ for nematics with $\Delta\chi > 0$). In eq 1 $\langle ... \rangle$ indicates a time average, and in the idealized limit wherein extra- and intramolecular motion is decoupled, the C–D bond order parameter may be defined as a product of the nematic order parameter and the average over intramolecular isomerization:

$$S_{\mathrm{C-D}} = \langle P_2(\cos\theta)\rangle\langle P_2(\cos\alpha)\rangle = S_Z\langle P_2(\cos\alpha)\rangle \quad (2)$$

Hence, for this limiting case, the experimental determination of the magnitude of $\Delta\nu_i$ together with the value for the quadrupole coupling constant ($e^2qQ/h$ = 168 kHz) yields a direct measure of the average orientation of the C–D bond vector relative to the liquid crystal director. If $S_Z$ can be determined independently, this simple exposition enables one to extract coarse information about the internal mobility of labeled sites in flexible mesogens from experimental values of the quadrupolar splittings.

The analysis is more complex when the relevant motions are slow.[19] Nevertheless, the distribution of C–D bond orientations and details about the nature of the motion can be ascertained. Via such a DMR analysis, the extent of decoupling of the motions of the mesogenic core from that of main chain in side-chain PLCs has been addressed.[20]

## Experimental Section

The synthesis of the 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene mesogen has been described before.[10] It was polymerized in solution with dodecanedioyl-$d_{20}$ chloride (MSD Isotopes; Merck).[21] The number-average degree of polymerization $x$ was determined by end-group analysis using proton NMR.[21] The model diesters, dimethyl dodecanedioate-$d_{20}$ and diphenyl dodecanedioate-$d_{20}$ were prepared by standard techniques.

The DMR measurements were carried out at 38.4 MHz with a high-resolution FT NMR spectrometer (Bruker WM 250). The polymer was equilibrated 20 K above $T_{\mathrm{NI}}$ for 20 min before it was cooled into the nematic range. No substantial changes in the spectrum are noted on leaving the sample for 1 h in the field in the nematic phase (385 K). That is, the orientation of this polymer appears to be rapid and at equilibrium.

The observed line widths are noticeably broader than those reported for similarly labeled MLCs; this probably reflects a superposition of nearly equivalent splittings from oligomers of the DDA9-$d_{20}$ polymer. The large spectral width employed (125 kHz) introduced considerable phasing anomalies (the spectra are reported without base line corrections). However, with the current spectrometer we cannot exclude a solidlike contribution to the base line originating from an unoriented high molecular weight fraction.

The transition temperatures were determined by DSC and polarizing microscopy as described in ref 21 and 22 and are in good agreement with the DMR observations.

## Results and Discussion

The observed difficulty of orienting high molecular weight linear PLCs[16] prompted the preparation of a labeled polymer with a low degree of polymerization ($x$ = 7; $M_n$ = 3200). While the molecular weight is low, systematic thermodynamic measurements using purified oligomers of DDA9 show that the asymptotic behavior of high molecular weight polymers is rapidly reached (i.e., $x$ = 8–10).[22]

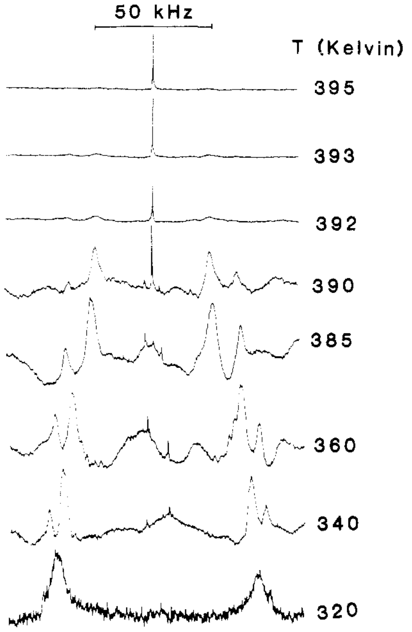

**Figure 1.** DMR spectra of the thermotropic linear polymeric nematogen DDA9-$d_{20}$ with a perdeuterated alkyl spacer (the nematic to isotropic transition $T_{\mathrm{NI}}$ ≡ 392 K; 38.4 MHz, 1000 FID's averaged).

Figure 1 shows the DMR spectra of DDA9-$d_{20}$ as a function of temperature on cooling from the isotropic phase. At the $T_{\mathrm{NI}}$ = 392 K, low-intensity quadrupolar doublets appear centered about the isotropic signal. The doublets increase in intensity but the magnitude of $\Delta\nu_i$ remains constant within the experimental uncertainty until the entire phase is nematic. On further cooling, the $\Delta\nu_i$ increase as the nematic order improves. In the supercooled nematic phase at 320 K, roughly 45 K above $T_g$, the character of the spectrum changes. The pair of quadrupolar splittings is no longer distinguishable, the line width broadens, and the signal-to-noise ratio deteriorates. While the apparent $\Delta\nu_i$ continue to increase below 320 K, the line shapes are less reliable and may not be amenable to straightforward interpretation.[19]

The DMR observations in the viscous polymeric nematic phase are indicative of the rapid-motion limit (see analogous DMR spectra in other viscous liquid crystals, e.g., cholesterics[23]). In Figure 1, the aliphatic quadrupolar splittings *segregate into two groups with the ratio of peak areas roughly 1:4*. The largest splitting is assigned to the $\alpha$-methylenes; we anticipate that internal geometrical constraints at the ester linkage in conjunction with the highly oriented core unit distinguish the proximate $\alpha$-methylenes from the more remote internal segments of the spacer. With such an assignment we conclude that the internal methylenes of the spacer exhibit essentially equivalent quadrupolar splittings. A similar quadrupolar splitting pattern has been observed for a labeled model compound, i.e., a DDA9 precursor mesogen with a core–spacer–core structure.[24]

The effects that chemical modifications of the chain have on the quadrupolar splitting pattern of $n$-alkanes solubilized (~1 mol %) in nematic solvents have been studied. The details of the pattern depend on the internal geometry at the point of substitution and inertial effects.[25,26] From the results of these studies it is reasonable to anticipate that the geometry at the junction of the spacer with the core and the shape and size of the core will

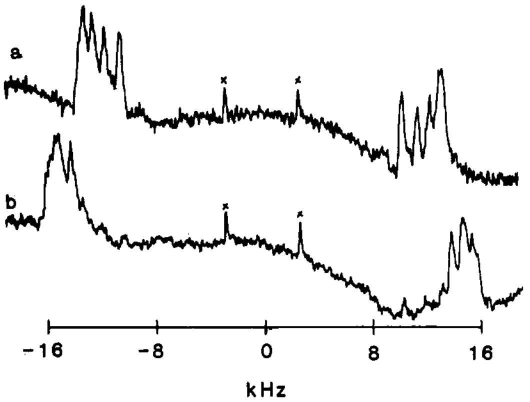

**Figure 2.** DMR spectra of labeled solute chains dissolved (~1 wt %) in the nematic solvent Phase V (Merck) ($T_{NI} - T = 5$ K; 38.4 MHz): (a) dimethyl ester of dodecanedioic-$d_{20}$ acid; (b) diphenyl ester of dodecanedioic-$d_{20}$ acid. The crosses indicate impurity alkyl chain. See text for assignment of the resonances.

impose selective constraints on the spacer as it isomerizes and diffuses in a uniaxial environment. This, in turn, will control the effectiveness of the reorientational motions for averaging the efg tensors at different sites in the spacer and ultimately will be reflected in the appearance of the quadrupolar splitting pattern. One may begin to estimate the magnitude of these effects on the DDA9-$d_{20}$ spacer by examining the DMR spectra of esters of labeled aliphatic diacids oriented in a nematic solvent.

Figure 2 shows the evolution of the quadrupolar splitting pattern of diesters of dodecanedioic-$d_{20}$ acid solubilized (1 wt %) in a "monomeric" nematic solvent, Phase V, a eutectic mixture of low molecular mass liquid crystals (Merck). With increasing size of the terminal substituents, the initially resolved quadrupolar splittings of the individual $CD_2$ units coalesce to essentially a single value, independent of the position of the $CD_2$ units in the chain. Employing observations derived from studies of monosubstituted alkanes,[25,26] we infer that there is a transition from the normal situation wherein the terminal segments of the chain are the most orientationally disordered ($\Delta\nu_\alpha < \Delta\nu_\beta < \Delta\nu_\gamma ...$) to one where this sequence of segmental disorder may be reversed. In the case of the methyl ester in Figure 2a, it appears that the normal situation applies with $\Delta\nu_\delta \cong \Delta\nu_\epsilon$; specific labeling experiments are necessary to make definitive assignments in the cases of the phenyl ester (Figure 2b) and the polymer (Figure 1). Nevertheless, in this context the quadrupolar splitting pattern of DDA9-$d_{20}$ may be viewed as an exaggeration of this phenomenon—the DDA9 spacer may be considered as an alkyl chain with very large terminal substituents. The substituents (mesogen cores) themselves are highly ordered in the nematic molecular field and, in turn, will influence the $\Delta\nu_i$ pattern exhibited by the spacer.

The nematic phase of the *labeled* polymer is readily oriented in a magnetic field of 5.87 T when cooled from the isotropic melt; X-ray diffraction studies of DDA9 and similar polymers magnetically oriented (10–12-T fields) and quenched into a nematic glass confirm that the nematic director aligns parallel to the field.[11] Therefore we can derive the methylene $S_{C\text{-}D}$ from the observed $\Delta\nu_i$ using eq 1 with $\beta = 0$. Figure 3 is a plot of the $\Delta\nu_i$ and $S_{C\text{-}D}$ vs. the temperature; the maxima of the quadrupolar doublets are used to derive the $S_{C\text{-}D}$ of the internal methylenes and that which we have assigned as the $\alpha$-methylenes. The magnitudes of the methylene $\Delta\nu_i$ observed for DDA9-$d_{20}$ polymer indicate that the order of the C–D bond vectors is significantly larger than that in monomeric nematogens. At the same time, however, the nematic order estimated for such polymers is substantially increased over that observed in nematic phases of typical MLCs. The $S_Z$ inferred from proton NMR studies of a DDA9 polymer with $x = 9$ has been estimated to be in the range $S_Z \cong 0.7$–$0.9$ across the nematic (and supercooled nematic) phase of this polymer,[16] in contrast with the value $S_Z \cong 0.4$–$0.6$ observed for MLCs.[17] This increased nematic order relative to MLCs must, of course, be reflected in the $S_{C\text{-}D}$ values of the polymer (see eq 2). High nematic order was in fact necessary to simulate the proton NMR spectra of the DDA9 spacer.[16] However, the marked difference in temperature dependence of the quadrupolar splittings of the internal methylenes and the $\alpha$-methylenes suggests that there is more than a simple increase in the nematic order as the temperature is lowered. This is more striking if one reviews the temperature dependence of the $\Delta\nu_i$ reported for labeled chains appended to the core of MLCs. For such nematogens at reduced temperatures $T_{red} = T/T_{NI} > 0.8$, the $CD_2$ units closest to the core exhibit order parameters of magnitude $S_{C\text{-}D} = 0.15$–$0.2$.[17,25] Concomitantly, the nematic order characteristic of MLCs ($S_Z = 0.4$–$0.5$) with eq 2 yields a crude measure of the internal mobility of the initial chain segments: $\langle P_2(\cos\alpha)\rangle = 0.3$–$0.5$. Moreover, this value for $\langle P_2(\cos\alpha)\rangle$ for MLCs is observed to be essentially independent of temperature, as the $\Delta\nu_i$ scale directly with $S_Z$.

Contrast the segmental mobility of MLCs with that observed for DDA9-$d_{20}$. In Table I we show the values of $\langle P_2(\cos\alpha)\rangle$ estimated from the data in Figure 3 in the nematic range of DDA9-$d_{20}$. In order to determine these estimates we employ values for the temperature dependence of $S_Z$ measured for a higher molecular weight ($M_n = 4000$) DDA9 polymer.[16,21] ($S_Z$ for the DDA9-$d_{20}$ may be somewhat lower but this should not invalidate the trends

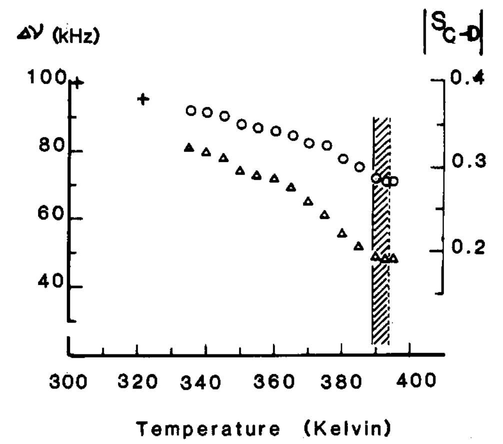

**Figure 3.** Plot of the temperature dependence of the quadrupolar splittings of DDA9-$d_{20}$ and the C–D bond vector order parameter $S_{C\text{-}D}$ for the $\alpha$-methylenes (○) and the internal methylenes of the spacer (△); the shaded region is the two-phase melt (nematic + isotopic) determined by DMR; (+) unresolved solidlike $\Delta\nu_i$.

Table I
Temperature Dependence of Internal Flexibility of DDA9-$d_{20}$

| | | $\langle P_2(\cos\alpha)\rangle$ | |
|---|---|---|---|
| $T_{red}$ | $S_Z$[a] | $\alpha$-$CD_2$ | int $CD_2$ |
| 0.995 | 0.72 | 0.39 | 0.26 |
| 0.984 | 0.76 | 0.40 | 0.29 |
| 0.962 | 0.80 | 0.40 | 0.31 |
| 0.935 | 0.83 | 0.40 | 0.33 |
| 0.920 | 0.83 | 0.41 | 0.34 |
| 0.889 | 0.85[b] | 0.41 | 0.36 |

[a] Values for $S_Z$ from ref 16, Figure 11. [b] Extrapolation.

reported in Table I.) Generally, the magnitudes of $\langle P_2(\cos \alpha)\rangle$ obtained for the spacer are comparable to those reported for $CD_2$ segments close to the core of MLCs. The behavior extracted from the data we have identified with the $\alpha$-methylenes is typical of MLCs in the sense that $\langle P_2(\cos \alpha)\rangle$ remains essentially independent of temperature. However, the behavior of the internal spacer segments is fundamentally different from that of MLCs. There is a conspicuous restriction of the spacer reorientational mobility with decreasing temperature; i.e., $\langle P_2(\cos \alpha)\rangle$ increases by roughly 40% across the nematic range.

Extending the comparison between the behavior of alkyl segments in MLCs and that in PLCs further, it may be of interest at this point to examine the rotational isomeric state (RIS) probabilities[27] calculated from models used to fit DMR observations on MLCs. Recently, Samulski and co-workers succeeded in modeling the $\Delta\nu_i$ of labeled chains in MLCs with a simple equilibrium statistical mechanical average over all conformers of the chain.[25,26,28] In a uniaxial nematic environment certain conformers can be more readily accommodated than others and conformer probabilities were corrected to reflect this preference. In the MLCs, the calculated trans probabilities at a specific bond ($j$), $p_{t;j}$, derived from fitting DMR quadrupolar splittings oscillated in magnitude as a function of distance from the core. Generally, $p_{t;j}$ exhibits a pronounced *even–odd* variation in magnitude; i.e., $p_{t;2} = 0.9$, $p_{t;3} = 0.6$, $p_{t;4} = 0.8$, $p_{t;5} = 0.6$, etc.

It is intriguing to speculate about how such a pattern for the $p_{t;j}$ might influence the properties of the spacer if it persisted in the PLCs. In the MLCs, the oscillations in the $p_{t;j}$ attenuate with increasing distance from the core.[18] In the PLCs, however, two distinct cases may be envisioned. Case I: In spacers with an *even* number of bonds separating two cores, the oscillations in the $p_{t;j}$ propagating into the spacer chain from both ends would destructively interfere, yielding more uniform values of the $p_{t;j}$ in such homologues. Case II: In spacers with an *odd* number of bonds, constructive interference of the oscillations propagating into the spacer chain could enhance the alternating $p_{t;j}$ pattern. This speculative divergence in the behavior of even vs. odd spacer lengths appears to be corroborated by the configurational statistics of disubstituted chains constrained to lie in a repulsive cylindrical field.[29] Furthermore, such behavior may contribute to the dramatic *even–odd* oscillations reported for the temperatures, entropies, and enthalpies of the phase transitions of several homologous series of linear PLCs.[14,30–34]

## Concluding Remarks

The results reported here support the inferences about the spacer obtained in earlier studies of the nematic phase of these polymers: There is significantly increased alkyl segmental orientational order in DDA9-$d_{20}$ relative to the pendent alkyl chains of low molecular mass mesogens. However, both the magnitudes of the observed quadrupolar splittings and the fact that all of the $\Delta\nu_i$ are not identical unequivocally show that the spacer is not restricted to the all-trans conformation. The primary source of the relatively large $S_{C-D}$ observed for DDA9-$d_{20}$ is due to the high nematic order in the polymer liquid crystal. Increased values for $S_Z$ are not unexpected, however, as there is an intrinsic difference between a MLC nematic phase composed of discrete nematogens and the PLC phase with the nematogenic cores embedded in a linear polymer chain. Even in MLCs, the librational reorientation and translational diffusion of mesogens are recognized to be rather cooperative processes in these ordered fluids. Covalently linking mesogens into a linear chain amplifies the dynamical cooperativity and may result in increased nematic order. Additionally, in the polymeric liquid crystal orientational correlations at one point can be propagated intramolecularly along the chain to a remote site, enhancing the local order imposed on a chain segment by extramolecular constraints. However, the efficacy of such enhanced ordering in linear polymeric liquid crystals may be strongly dependent on the number of bonds (*even* or *odd*) in the spacer.

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**Registry No.** (4,4′-Azoxybis(3-methylphenol))·(dodecanedioyl chloride) (copolymer), 79062-62-7; poly[oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl)], 79079-27-9; dimethyl dodecanedioate, 1731-79-9; diphenyl dodecanedioate, 4080-91-5.

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# Solid-State $^{13}C$ NMR Approach to the Structural Investigation of Racemic and Optically Active Isotactic Poly(3-methyl-1-pentene)

**Maria Carmela Sacchi, Paolo Locatelli,* and Lucia Zetta**

*Istituto di Chimica delle Macromolecole del CNR, 20133 Milano, Italy*

**Adolfo Zambelli**

*Istituto Chimico, Università di Napoli, 80134 Napoli, Italy.* *Received March 24, 1983*

ABSTRACT: By $^{13}C$ NMR CP/MAS analysis it is shown that isotactic poly((*S*)-3-methyl-1-pentene) and poly((*RS*)-3-methyl-1-pentene) adopt similar chain conformations in the solid state. The strong tendency of polymer chains to form helices, even in the absence of crystallinity, is confirmed.

A recent $^{13}C$ NMR investigation[1] of the stereochemistry of polymerization of (*RS*)-3-methyl-1-pentene (3M1P) has shown that poly((*RS*)-3M1P) consists of a mixture of copolymer chains containing the *R* and *S* monomers in ca. 2.5:1 and 1:2.5 ratios, respectively, with a Bernoullian distribution. Therefore the optical purity of the enantiomorphic chains is rather low. A similar conclusion may be reached by comparing the broad resonances of the carbon atoms of poly((*RS*)-3M1P) with the sharp resonances of poly((*S*)-3M1P) observed in solution (Figure 1). In addition, previous X-ray studies[1,2] have indicated that poly ((*S*)-3M1P) and poly((*RS*)-3M1P) prepared in the presence of isotactic-specific catalysts have different crystalline structures. The crystal structure of poly((*RS*)-3M1P) has not been determined while poly((*S*)-3M1P) has been described in terms of a helical conformation with four monomer units per turn (i.e., a 4:1 helix)[3] (Figure 2).

The present communication reports preliminary CP (cross-polarization) and MAS (magic angle spinning) $^{13}C$ NMR results on isotactic poly((*S*)-3M1P) and poly((*RS*)-3M1P). The $^{13}C$ NMR solid-state spectra of the two polymers are shown in Figure 3a,b. The chemical shifts of the carbon resonances are summarized in Table I, where they are compared with the chemical shifts in solution for the benzene-soluble fraction of the same polymers. The signal assignment in the solid state was made on the basis of the previous assignment of the solution spectra obtained by using off-resonance decoupling and additivity rules.[4,5] By comparing the solution- and solid-state spectra (Figures 1 and 3, respectively) the most significant differences are observed for the chemical shift of the $C_5$ resonance, which, in the latter, overlaps with the $C_{3'}$ signal and in the line width of the resonances in poly((*RS*)-3M1P), which, in the solution spectrum, are even broader than those in the solid-state spectrum. In light of the results reported in this paper, the line broadening can be reasonably ascribed to the presence, in solution too, of secondary peaks which arise from carbons having different average conformations due to different stereochemical environments.

Table I
$^{13}C$ Chemical Shifts of Isotactic Poly(3-methyl-1-pentene) in Solution and in the Solid State[a]

| C atom[b] | solution poly-((*S*)-3M1P) and poly-((*RS*)-3M1P) | solid | |
|---|---|---|---|
| | | poly-((*S*)-3M1P) | poly-((*RS*)-3M1P)[c] |
| $C_5$ | 12.8 | 14.1 | 13.7 |
| $C_{3'}$ | 13.8 | | (17.9) |
| $C_4$ | 28.6 | 29.0 | 28.9 |
| | | | (22.8) |
| $C_1$ | 32.3 | 32.5 | 32.4 |
| $C_3$ | 36.3 | 36.7 | 36.7 |
| $C_2$ | 36.7 | 38.0 | (40.6) |

[a] Referred to TMS. [b] Carbons of the structural unit are numbered according to Figure 1a. [c] In parentheses are reported the chemical shifts of the smaller resonances, absent in poly((*S*)-3M1P) (see text).

Further work will be devoted to a deeper investigation of the influence that similar local environments can exert, in the solid state, in determining the chemical shifts of the chemically nonequivalent carbons $C_{3'}$ and $C_5$ and to a more detailed line-shape analysis. It must be noted that, despite the presence of two different conformations identified by X-ray diffraction, a single chemical shift was found for both $C_3$ and $C_2$ in poly((*S*)-3M1P). By accounting for the conclusions reached by Petraccone et al.,[3] this could mean that the exchange between the two isoenergetic species is fast on the NMR time scale, so producing a single averaged chemical shift.

Inspection of the solid-state spectra a and b of Figure 3 reveals a strong matching between most of the main resonances of poly((*S*)-3M1P) and poly((*RS*)-3M1P) and at least three substantial differences. (i) The resonance at 38.0 ppm, assigned to $C_2$ in poly((*S*)-3M1P) (Figure 3a), seems to overlap with the signal from $C_3$ at 36.7 ppm in poly((*RS*)-3M1P) (Figure 3b), as the increased intensity of this resonance suggests. The alternative possibility that the $C_2$ signal does not shift but disappears by broadening,

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