Macromolecules 1992, 25, 5991–5999

Solid-State ^{13}C NMR Studies of Molecular Motion in MBPE-9 and MBPE-5

Jinlong Cheng, Yimin Jin, and Bernhard Wunderlich*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, and Chemistry Division of Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6197

Stephen Z. D. Cheng, Michael A. Yandrasits, and Anqiu Zhang

Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325–3909

Virgil Percec

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106–2699

Received November 18, 1991; Revised Manuscript Received June 30, 1992

ABSTRACT: The molecular motion in the polymers poly[oxy(3-methyl-1,4-phenylene)ethylene-1,4-phenyleneoxynonamethylene], MBPE-9, and poly[oxy(3-methylene-1,4-phenylene)ethylene-1,4-phenyleneoxypentamethylene], MBPE-5, was studied at various temperatures on cooling with solid-state ^{13}C NMR. The techniques used were (1) cross-polarization and magic-angle spinning (CP-MAS), (2) dipolar dephasing, and (3) conventional one-pulse NMR with two-level broad-band proton decoupling (BILEV) under MAS conditions. The observed changes in chemical shift are interpreted in terms of the γ-gauche effect. The mobility in the flexible spacer in MBPE-9 decreases on cooling from the melt at a mesophase transition (345.6 K at 10 K/min), which indicates that ordering in this spacer is the driving force in this transition, while the phenylene groups remain mobile. A second transition at 331.0 K is linked with the phenylene groups becoming restricted in their motion. Both states reached on cooling from the melt are conformationally disordered (condis phase). The similarity of the high-temperature phase with a liquid crystalline phase is discussed. In MBPE-5 the cooling rate in the NMR experiments is limited and only the low-temperature condis phase could be identified.

Introduction

The repeating units of poly[oxy(3-methyl-1,4-phenylene)ethylene-1,4-phenyleneoxynonamethylene], MBPE-9, and poly[oxy(3-methyl-1,4-phenylene)ethylene-1,4-phenyleneoxypentamethylene], MBPE-5, consist of an aromatic part, ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$), and a flexible alkoxy spacer represented by $O-(CH_2-)_nO-$, where $n = 9$ and 5 for MBPE-9 and MBPE-5, respectively.

These polymers have been studied previously by various techniques, including thermal analysis, X-ray diffraction, and polarized light microscopy.[1] The pertinent observations to the present research are as follows. (1) On cooling at a sufficiently fast rate from the melt, *two* exothermic transitions occur. At a cooling rate of 10 K/min the following peak temperatures are observed: 345.6 and 331.0 K for MBPE-9, and 329.3 and 318.0 K for MBPE-5. On subsequent heating only single transitions were observed (for MBPE-9, a peak at 355.5 K and for MBPE-5 a broad transition starting from 307.0 K and ending at 365.0 K). This led to the conclusion that these polymers show a monotropic, metastable mesophase.[1] (2) The onset temperature and the heat of the transition from the melt to the metastable mesophase is independent of cooling rate, while that of the second exotherm, (i.e. the transition from the mesophase to the room-temperature phase) is strongly dependent on the chosen cooling rate (331 K at 10 K/min, and 338.5 K at 2.5 K/min, for the example of MBPE-9). It was suggested on the basis of these and other observations that these polymers, along with others in the MBPE-*n* series, may possess a monotropic liquid crystalline phase.

A thermodynamic analysis[1a,d] of the transition from the isotropic melt to the mesophase showed a close-to-zero entropy contribution of the aromatic group ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) to ΔS_i, the entropy of isotropization (i.e. the transition to the isotropic melt). This is at variance to observations made for typical liquid crystal forming systems.[2-6] On the other hand, the total transition entropy changes from the room-temperature phase to the melt (81.4 and 106.3 J K^{-1} mol^{-1} for MBPE-5 and MBPE-9, respectively,[1a] both computed for 100% presence of the ordered phase) do not suffice to account for the expected entropies fusion from the empirical rules, valid for large numbers of large and small molecules[6,7] (about 100 and 140 J K^{-1} mol^{-1} for MBPE-5 and MBPE-9, respectively). A similar deficiency in heats of fusion was recently studied for a liquid crystalline forming small molecule (OOBPD)[8] and could be linked to remaining conformational disorder that ultimately and gradually freezes to a glassy condis phase.

The questions that need to be clarified for the MBPE-*n* are concerned with the changes in order and motion in the mesophase and in the room-temperature phase. Their answers should make it possible to characterize the mesophases better.[6,9]

Direct observation of the mobility of the individual carbons is possible through high-resolution solid-state ^{13}C NMR. In this paper, qualitative information on the conformations of carbon–carbon bonds in MBPE-9 and MBPE-5 has been obtained at five selected temperatures, covering the range of the transitions. It is shown that at phase transitions the amount of entropy change measured by DSC can be linked to the number of C–C bonds that have changed their conformations by using the empirical rules of fusion.[6,9] This number of carbon–carbon bonds can also be independently measured by solid-state NMR via the γ-gauche effect of the ^{13}C chemical shift. Good agreement exists between the results of the two independent techniques. The applied techniques were high-

0024-9297/92/2225-5991$03.00/0

resolution ^{13}C CP-MAS, dipolar dephasing, and conventional one-phase NMR with two-level proton decoupling (BILEV) under MAS conditions.

Liquid Crystals, Plastic Crystals, and Condis Crystals

In recent years increasing arguments have arisen about the distinction between the various mesophases. In order to help with the discussion a short review of the mesophase classes is given in this section. The special mesophases of polyethylene, polytetrafluoroethylene, polypropylene, *trans*-1,4-polybutadiene, polyoxybenzoate, and polypara-xylylene, for example, have in the past been called smectic liquid crystals (for a discussion see refs 6 and 9). To account for the special behavior of mesophase polymers, terms such as viscous liquid crystals,[10] one-dimensional plastic crystals,[11] and columnar liquid crystalline phases[12] have been suggested. All these namings were often overlapping and did not always consider the earlier established definitions fully.

One should note that the definitions of liquid and plastic crystals were made before the recognition of macromolecules as a class of molecules, and were based on the recognition of translational and orientational disorder and motion of the molecule *as a whole*. In order to achieve disorder in a thermotropic mesophase, it was generally assumed that the liquid crystalline material must possess a rigid rod- or disklike mesogen and the plastic crystalline material, a close-to-spherical mesogen.[13]

Macromolecules show on fusion a negligible amount of translational (positional) and orientational disordering.[7] Almost all their entropy of fusion can be linked to conformational disordering. In a thermotropic liquid crystal the conformational motion of a flexible spacer gives the mesogen a possibility of "translation-like" disorder and motion. With a proper mesogen and sufficiently long flexible spacer, the mesogens in a macromolecule can have orientational order while being positionally disordered.[6] Close-to-spherical mesogens, as required for plastic crystals, are more difficult to incorporate in macromolecules if their motion involves rotation about more than one axis. A globular macromolecule might itself become a mesogen, but its almost macroscopic size would prevent mobility in the mesophase. One-dimensional plastic crystalline phases and columnar phases, as seen in some liquid crystals for small, rigid molecules are only superficially similar to the macromolecular mesophases. The difference is that the motion in the small molecules involves rotation or translation of the molecule as a whole, while in a macromolecule the motion is conformational; i.e. in macromolecules, rotation is based on segmental motion. Thermodynamically, segmental disorder leads to considerably larger increases in entropy than disorder of the whole molecule.

It was pointed out in 1984[6] that for macromolecules a different mesophase may exist, that of the conformationally disordered crystal, or short, the condis crystal. In a major review more than 100 condis crystals of small and large molecular size were analyzed.[9] It has become clear that liquid crystals and plastic crystals that have conformational isomers always show almost as much conformational disorder in the mesophase as is seen in the melt.[14] Condis crystals, in contrast, do not show the characteristic translational or orientational disorder and motion of the molecule as a whole seen in liquid and plastic crystals, respectively. Only the flexible parts of the molecules remain fully or partially disordered and mobile. These condis crystals lose their large-amplitude conformational motion at lower temperature either at a further ordering transition, by gradual ordering, or without complete ordering in a glass transition.

Using the model of wormlike molecules, it was predicted by Ronca and Yoon[15] that the shortest possible rigid mesogen, that of C–C in a sequence of CH_2 groups could cause a liquid crystal phase only at temperatures less than 75 K. At such a low temperature both the crystallization/melting and the glass transition have intervened on cooling so that liquid crystalline polyethylene and *n*-alkanes cannot be realized. Closer to the melting temperature of polyethylene (414.6 K) and long-chain *n*-alkanes, conformational disorder becomes possible, however, and leads sometimes even to a crystallographically different condis phase.[9] The occurrence of a liquid crystal phase at a given temperature is thus critically dependent on the size and geometry of the rigid mesogen and the ranges of existence of a glass or of more ordered crystals. The condis phase, in contrast, can occur independent of the existence of a mesogen. It can arise gradually by the introduction of relatively uncorrelated conformational motion and the corresponding disorder, or it can arise at a sharp transition temperature to a more symmetrical, lower density crystal structure with more cooperative conformational motion.[9]

When it was shown by Cheng et al.[1a] that in the mesophase of the present polymers the aromatic sequence does not contribute to the entropy of ordering, the question was raised whether a "flexible" alkyl sequence can cause the whole molecule to become a liquid crystal or if the polymer molecule as a whole, or over long segments, attains sufficient translational *and* orientational order so that the mesophase is better described as being a condis crystal.

In this paper, analysis of the order and the molecular motion of the carbon atoms in MBPE-9 is studied and it will be documented that, indeed, on cooling, the flexible sequence orders first, but retains conformational disorder; i.e. it does not become a rigid mesogen. At the second stage of ordering, it will be shown that mainly the aromatic sequence is involved, while the flexible sequence has not changed much. The low-temperature phase is, thus, still a condis crystal, with conformational motion left in the CH_2 groups via kinks and jogs, and in the aromatic sequence via 180° ring flips.

Experimental Section

Samples and Prior Characterization. The preparation of the polymers involved coupling 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and α,ω-dibromoalkanes.[16,17] The molecular weights were reported to be 19 000 ($M_w/M_n = 1.9$) and 20 600 ($M_w/M_n = 1.4$) for MBPE-5 and MBPE-9, respectively.[16] The melting peak at 10 K/min heating rate ranged from 307.0 to 365.0 K for MBPE-5 and had a peak at 355.5 K for MPPE-9. The glass transitions were at 288.5 and 272.0 K, and the first mesophase transitions (on cooling at 10 K/min) at 329.3 and 345.6 K for the respective polymers. Typical crystallinities, measured by comparison of the X-ray intensity in diffraction peaks and in the diffuse halo and of heats of fusion, were 0.44 for MBPE-5 and 0.54 for MBPE-9 on cooling at 10 K/min.[1a,c,d]

Instruments and Experiments. All solid-state ^{13}C NMR measurements were made with a Nicolet NT 200 spectrometer operating at 200.07 and 50.31 MHz for ^1H and ^{13}C, respectively. The solid-state probe was purchased from Doty Scientific, Inc., and has a design similar to that described in the literature.[18] The probe has variable-temperature capability over the range 150–430 K. For chemical shift thermometry it is necessary to calibrate the sample temperatures above 300 K. This was done by measuring the proton resonances of liquid ethylene glycol[19] through the decoupler at various temperatures under the same spinning rate as for the solid-state experiments. The cylindrical sample container (rotor) was made from a single crystal of Al_2O_3 (sapphire) and has a diameter of 5 mm. The end cap pairs used for the rotor were made from brown plastic Vespel (Registered trademark for a DuPont polyimide). The sample was spun with nitrogen gas at 4.5 kHz at the magic angle for all measurements. After stabilizing temperature and sample spinning rate, prior to each measurement, the probe was tuned and matched with a 2382 spectrum analyzer (100 Hz to 400 MHz) made by Marconi Instruments.

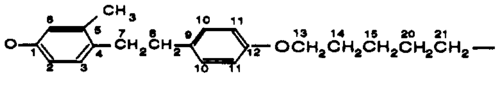
The conventional one pulse of ^{13}C with two-level decoupling of protons (BILEV) was used to obtain the spectra of the mobile molecules, such as the isotropic melt and the amorphous fraction below the melting temperature but above the glass transition temperature. The pulse width used for ^{13}C was 3 μs, corresponding to a 55° pulse angle, and the recycle delay between two successive pulse sequences was 3 s.

The ^{13}C spectra of the rigid materials were obtained using the methods of cross-polarization, high-power proton decoupling, and magic-angle sample spinning (CP-MAS).[20] The spin contact/lock time was 1 ms and the 90° pulse width for protons was 5 μs. The recycle delay was 5 s. The dephasing experiments were carried out by inserting a dephasing delay, τ, following C–H cross-polarization and prior to signal acquisition (when $\tau = 0$ μs, the dephasing experiment is identical to the standard CP-MAS).[21]

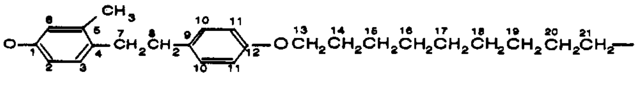
Unless specified otherwise, all spectra were acquired with 200 accumulations. Phase cycling was used in both the ^{13}C and the ^{1}H channels. The data size was 8 or 16 kilowords (16 bits per word) for a spectral width of 10 000 Hz (200 ppm). The ^{13}C chemical shift values were referenced indirectly relative to TMS (tetramethylsilane) via hexamethylbenzene (the CH_3 resonance is 17.37 ppm). The spectrometer field drifting was estimated to be less than 0.05 ppm during a variable-temperature run. In order to relate to the DSC work, the variable-temperature ^{13}C NMR spectra were taken by decreasing the temperature stepwise.

Results

Chemical Shift (δ) of the Melts. The repeating units of the polymers MBPE-5 and MBPE-9 are shown below with the numbering of the distinguishable carbon atoms used in this paper. For MBPE-5 there are only five methylene groups in the flexible spacer, therefore, the central carbon is numbered C-15, and the numbers of C-16 through C-19 are not used.



MBPE-5



MBPE-9

MBPE-9. The proton-decoupled ^{13}C spectra of the melts at 373 K for MBPE-9 and 410 K for MBPE-5 obtained with BILEV, can be found in Figures 1 and 2, and the chemical shifts, δ, in Tables I and II, respectively.

The assignment of the methylene ^{13}C's in the alkoxy chain of MBPE-9 was made by starting with the spectrum of *n*-nonane whose ^{13}C δ values are known to be, from the end (methyl) to the center, 14.2, 23.3, 32.6, 30.0, and 30.3 ppm.[22] In MBPE-*n* the methylene carbons of the alkoxy chain are, however, subject to the influence of *substituent effects* from the oxygen. The available data on the alkyl carbons of aralkyl ethers[23] (with the group of phenylene–oxygen–alkyl) show that when the alkyl chain consists of more than five carbons, the oxygen has positive substituent effects (deshielding) of +55 and +5.8 ppm on the α- and β-carbons, i.e., C-13/C-21 and C-14/C-20, respectively. Thus the measured values of 68.66 and 30.06 ppm, listed in Table I, are assigned for C-13/C-21 and C-14/C-20, respectively. The oxygen, however, has a negative substituent effect (shielding) of about −6.4 ppm on the γ-carbon,[23] i.e. C-15 and C-19, which causes them to resonate at 26.72 ppm. The rest of the carbons are not influenced by the oxygen, therefore, their δ values agree well with the respective carbons in *n*-nonane. The signals of C-16 through C-18 show one single, intense peak at 30.06 ppm, overlapping with C-14/C-20.

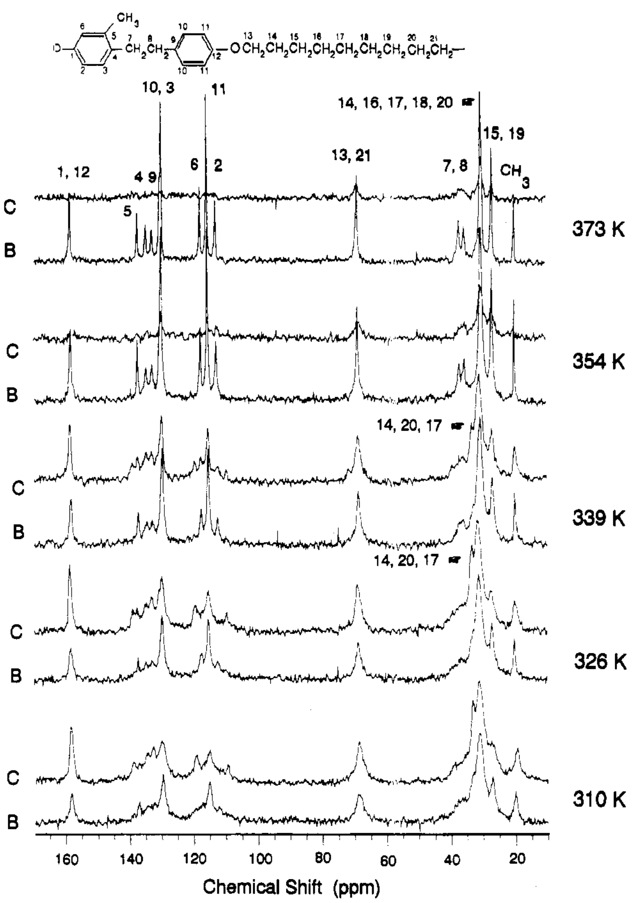


Figure 1. Variable-temperature ^{13}C NMR spectra of MBPE-9. The temperatures are listed. The labels B and C stand for BILEV and CP-MAS, respectively.

The ^{13}C's in the ethylene linkage between the two phenylene rings (C-7 and C-8) show a pair of sharp signals at 36.8 and 35.3 ppm, respectively.

For the aromatic carbons, the assignments can also be made on the basis of the consideration of substituent effects. Detailed values of the substituent effects on the aromatic ^{13}C's can be found in the literature.[22,24] The predicted values are in good agreement with the measured ones. The δ values for all the aromatic carbons are also listed in Table I.

MBPE-5. Similar considerations as for MBPE-9 apply for MBPE-5 with the exception of C-15. The position of C-15 in MBPE-5 is special because it has two oxygens as γ-substituents from the ends of the aliphatic spacer. In this case two γ-substituent effects, 2(−6.4) ppm, should be added to the base value of 34.7 ppm of *n*-pentane, to give 21.9 ppm, being closest to the observed signal at 23.31 ppm. The chemical shifts for MBPE-5 are listed in Table II.

Differences between the predicted and measured δ values are due to the fact that the predictions are based on *solution* spectra of *small molecules*; therefore, they may not be fully applicable to the molten state of polymers. Nevertheless, the predictions are still sufficiently close to the measurements to permit an unambiguous assignment.

Chemical Shifts of the Solid State. The ^{13}C chemical shifts of the increasingly solid samples are also listed in Tables I and II for MBPE-9 and MBPE-5, respectively (see also Figures 1 and 2). Two sets of values are given for each temperature. One was obtained with the CP-MAS mode of measurement; the other with BILEV. These values can only be rationalized with a knowledge of the molecular motion and conformation, therefore, the dis-

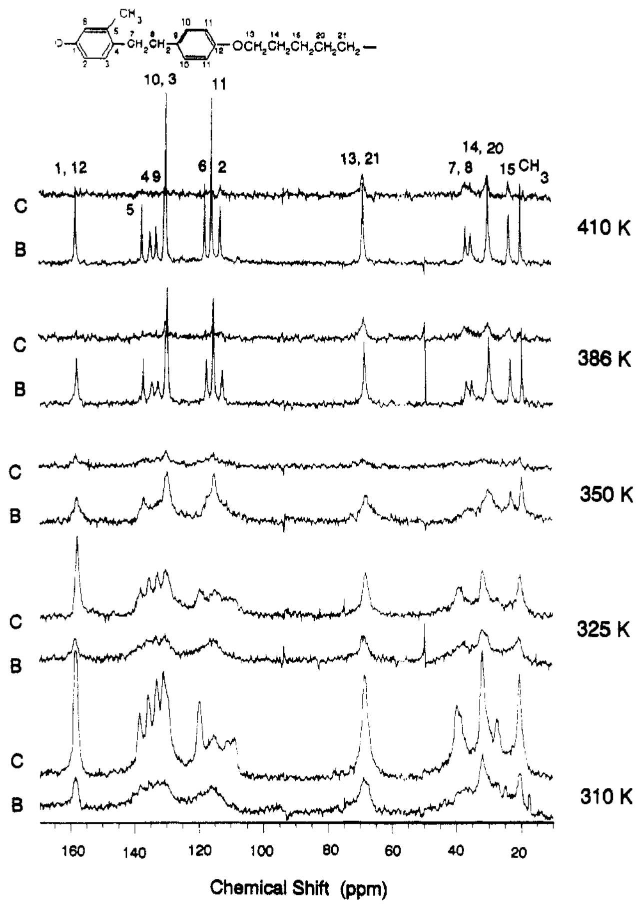


Figure 2. Variable-temperature ^{13}C NMR spectra of MBPE-5. The temperatures are listed. The labels B and C stand for BILEV and CP-MAS, respectively.

Table I
^{13}C δ Values (in ppm Relative to TMS) for MBPE-9[a]

	310 K	326 K	339 K	354 K	373 K
C1, C12	158.9/158.1	158.5/158.1	158.4/158.1	NA[b]/158.1	NA/158.2
C2	109.9/112.1	109.4/112.2	109.5/111.3	NA/112.5	NA/112.7
C3, C10	130.5/129.5	129.6/129.5	129.5/129.6	129.6/129.5	NA/129.6
C4	135.0/134.4	134.4/124.6	134.5/134.4	NA/134.4	NA/134.5
C5	139.6/137.0	138.9/137.1	138.8/137.1	NA/137.1	NA/137.1
C6	119.6/NA	119.4/117.1	119.4/117.4	NA/117.4	NA/117.5
C7	38.8–35.0[c]	38.6–35.0	38.4–35.0	NA/36.9	NA/36.8
C8	38.8–35.0	38.6–35.0	38.4–35.0	NA/35.3	NA/35.3
C9	133.2/132.4	132.8/132.8	132.9/132.7	NA/132.5	NA/132.6
C11	115.4/115.0	115.0/115.1	115.2/115.2	NA/115.2	NA/115.4
C13, C21	69.1/68.3	68.8/68.5	68.6/68.6	68.6/68.6	68.63/68.7
C14, C17, C20	33.8/32.8	33.1/31.0	33.3/30.6	30.1/30.2	30.2/30.1
C15, C19	27.5/27.1	27.3/27.1	27.0/27.0	26.8/26.8	26.8/26.7
C16, C18	31.7/31.1	31.5/31.0	30.9/30.6	30.1/30.2	30.2/30.1
CH_3	20.0/20.0	20.1/20.1	20.0/20.1	20.0/19.9	NA/19.8

[a] The first value is measured with the CP-MAS pulse sequence, and the second value is from BILEV. [b] "NA" stands for not available, because either no signal is detected or the signal is too broad. [c] Because of broadening, two values separated by a – sign indicates the approximate range.

cussions of the assignments of chemical shifts below the melting temperature are postponed to the discussion where a full description of the conformations about the various C–C bonds is presented.

Dipolar Dephasing Spectra. For each polymer, the dipolar dephasing experiments were carried out at two typical temperatures: (1) between the two transitions and (2) below the second transition on cooling. The spectra are shown in Figures 3–5.

Discussion

Table II
^{13}C δ Values (in ppm Relative to TMS) for MBPE-5[a]

	310 K	325 K	350 K	386 K	410 K
C1, C12	158.1/158.2	157.9/158.4	158.1/158.3	NA/158.0	NA/158.1
C2	111.0/108.7	110.2/NA	NA/NA	NA/112.6	112.7/112.8
C3, C10	130.7/130.7	130.2/130.2	129.8/129.6	129.6/129.7	129.6/129.6
C4	135.5/NA	135.4/135.8	NA/NA	NA/134.5	NA/134.6
C5	138.1/138.1	138.1/138.6	NA/137.1	NA/137.2	NA/137.2
C6	119.4/NA	119.6/NA	NA/117.2	NA/117.4	NA/117.6
C7	40.2–38.2	40.1–38.1	NA/36.4	37.0/36.7	36.7/36.6
C8	40.2–38.2	40.1–38.1	NA/36.6	37.0/35.0	35.1/35.0
C9	132.9/NA	132.7/133.1	NA/NA	NA/132.6	NA/132.7
C11	115.0/115.0	115.0/115.1	114.9/115.0	115.1/115.3	115.4/115.5
C13, C21	68.3/68.2	68.1/68.4	68.4/68.2	68.5/68.4	68.6/68.6
C14, C20	31.7/31.7	31.8/31.9	NA/30.1	29.8/29.8	29.8/29.8
C15	27.3/27.3	27.3/NA	23.2/23.1	23.4/23.3	23.4/23.3
CH_3	20.4/20.4	20.3/20.4	20.0/19.8	19.8/19.7	19.7/19.7

[a] Table notes are the same as for Table I.

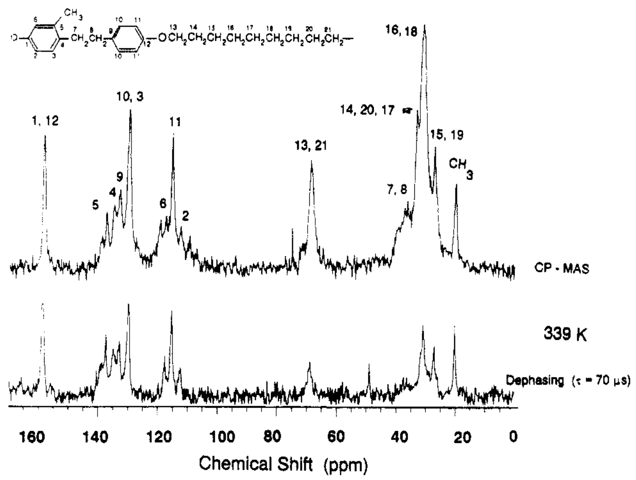


Figure 3. ^{13}C NMR spectra of MBPE-9 at 339 K: (top) measured with CP-MAS; (bottom) measured with dipolar dephasing, with a delay of 70 μs.

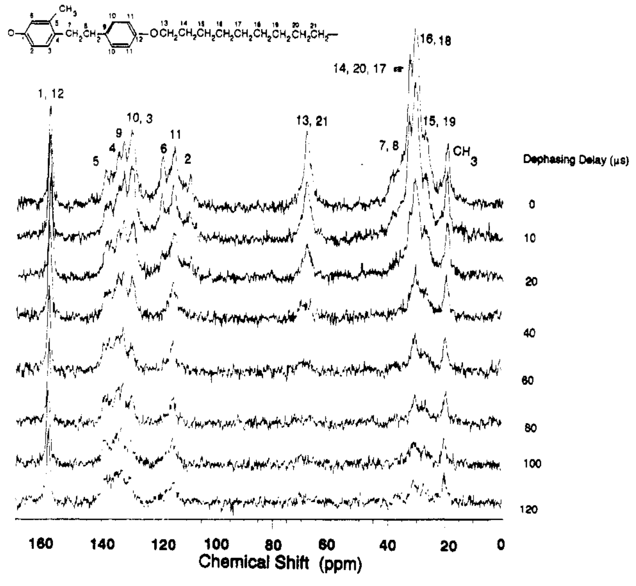


Figure 4. Dipolar-dephasing ^{13}C NMR spectra of MBPE-9 at 310 K. From bottom to top the dephasing delays are 120, 100, 80, 60, 40, 20, 10, and 0 μs.

Basic Principles of the Interpretation of the Variable-Temperature ^{13}C NMR Data. Three pulse sequences were used, namely the CP-MAS, the dipolar dephasing, and the BILEV, as described in the Experimental Section. The first two were used for the observation of rigid carbons.[21] The BILEV experiment is designed to detect signals from mobile carbons only, i.e. those of short ^{13}C T_1 values. The mobile carbons should be in the melt or any remaining liquidlike sequences in the partially crystallized samples. Even in liquid crystalline samples one expects largely only BILEV signals from all carbon

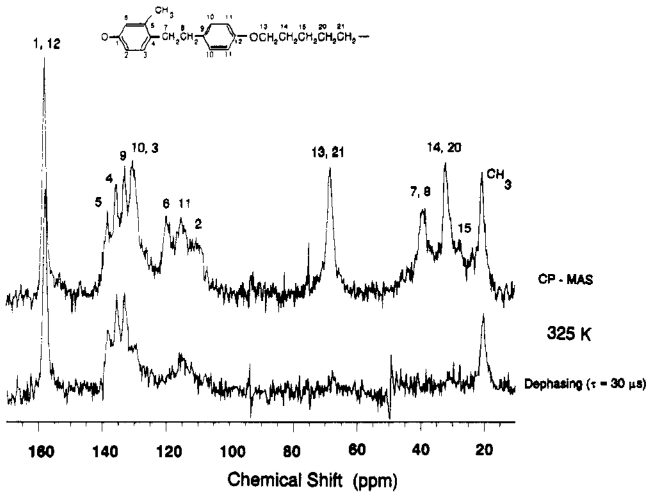


Figure 5. ^{13}C NMR spectra of MBPE-5 at 325 K: (top) measured with CP-MAS; (bottom) measured with dipolar dephasing, with a delay of 30 μs.

atoms. It is, therefore, possible to detect signals separately from a system that is heterogeneous (one phase is more-ordered and rigid; and the other less-ordered, mobile) by using different pulse sequences.

For rigid carbons which show signals in CP-MAS, the connection between the molecular mobility and the dephasing behaviors of the nuclear spins can be understood on the basis of the following considerations. In a dipolar dephasing experiment, the signal decreases with an increase of the dephasing delay τ. When $\tau = 0$, the spectrum is identical to that of a CP-MAS, and maximum signal intensities are observed. The decrease of the ^{13}C magnetization during the dephasing delay, characterized by the effective spin–spin relaxation time T^*_2, depends on the strength of the dipolar interaction between the ^{13}C and ^{1}H. The ^{13}C–^{1}H dipolar interaction is, in turn (1) proportional to the number of interacting protons, (2) dependent on $(r_{CH})^{-3}$, where r_{CH} is the internuclear distance, and (3) inversely related to the rate of motion; i.e. a rapidly rotating group could appear as if its protons were farther away from the ^{13}C. It is thus possible to separate the carbon atoms into three categories according to their number of attached protons and their mobility: (1) *Signals of rigid, protonated ^{13}C* will be suppressed by virtue of dephasing because of a short spin–spin relaxation time (T^*_2) arising from strong and dispersed dipolar local fields. (2) *Signals of mobile, protonated ^{13}C* will be less suppressed because of the relatively long spin–spin relaxation time arising from partially averaged, therefore, weaker dipolar local fields. The methyl carbon resonances thus still remain, because of the rapid methyl group rotations that reduce the ^{13}C–^{1}H dipolar couplings. (3) *Signals of nonprotonated ^{13}C* will be least affected because of even longer spin–spin relaxation time resulting from the fact that the carbon atoms are far away from any protons (>0.2 nm compared to 0.109 nm for a direct C–H bond). This method has been used for T^*_2 measurement of ^{13}C in some plastic crystals for studying molecular motion.[25,26]

Information on the alkyl chain conformation and motion can be obtained from the temperature dependence of the chemical shift of ^{13}C. In the solid state, especially in the nonionic polymeric systems, even though the molecules are packed in close proximity and their δ reflects these packing effects, one finds that the intramolecular conformations are the most important influence on the ^{13}C chemical shifts.[27,28] The δ of a given ^{13}C is influenced by substituents in the α-, β-, and γ-positions relative to the observed carbon, giving α-, β- and γ-substituent effects. The α- and β-substituents have fixed contributions to the δ value of the observed carbon as long as the chemical structure of the molecule is fixed. The γ-substituent effect has a conformational origin,[27,28] because the observed carbon, $^{\circ}$C, and its γ-substituent, $^{\gamma}$X, are separated by three intervening bonds, $^{\circ}CH_2$–CH_2–CH_2–$^{\gamma}$X, and their mutual distance and orientation are variable, depending on the conformation of the central bond. Therefore, the change of the ^{13}C δ is due to change in the conformation (or rotational state) of the central bond between $^{\circ}$C and $^{\gamma}$X. For a ^{13}C to be more shielded by a γ-substituent, $^{\gamma}$X, it has been suggested that the $^{\circ}$C and $^{\gamma}$X must be in a gauche arrangement. The effects of such γ-gauche shielding can be evaluated to be $\gamma_{C\text{-}C} = -5.2$ ppm and $\gamma_{C\text{-}O} = -7.2$ ppm.[28] In the melt or in solution, the rotating C–C bonds are expected to have a population of about 40% gauche conformation, a value based on an energy difference of about 2.8 kJ/mol between gauche and trans conformation and an approximate temperature of 400 K.[29] Accordingly, one expects after a transition from a fully ordered, all-trans conformation to the one with 40% of gauche that the δ of the ^{13}C decreases (becomes more shielded) by $\Delta\delta = 2(0.4)(-5.2)$ ppm $= -4.16$ ppm. The factor of 2 accounts for the situation that two γ-substituents exist, one on each side of the carbon atom in question. If only one of the two γ-substituents has changed, while the other remains the same, the $\Delta\delta$ is expected to be only $0.4(-5.2)$ ppm $-$ 2.08 ppm. Similarly, if neither of the γ-substituents changes its spatial relationship with respect to $^{\circ}$C, $\Delta\delta$ is zero. Overall, as temperature is increased, the δ of a ^{13}C in linear paraffin chains may change by amounts close to -2.08 or -4.16 ppm.

MBPE-9. In Figure 1, the CP-MAS spectrum of the melt (373 K) still shows some signals from the CH_2 sequence, although they are much weaker than in the BILEV spectrum. This indicates that even in the melt there are some alkoxy chains that are still rigid enough to cross-polarize. The aromatic ^{13}C's in the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) group, in contrast, show no signal with CP-MAS, indicating that rotational motion of the phenyl groups is rather fast.

As temperature is decreased to 354 K, the intensities of the ^{13}C CP-MAS signals increase as a result of decreased mobility. For the first time the phenylene carbons also show weak signals. The intensity of the BILEV spectrum is, however, still much higher, indicating that the sample is still quite mobile.

On cooling to 339 K, calorimetry shows an exothermic transition with an entropy loss of 16.7 J K^{-1} mol^{-1}. This transition was interpreted as a change from liquid to liquid crystal, but it was also shown at the same time that practically all of the entropy of transition originates in the flexible CH_2 sequence.[1c] This can be supported by a comparison of the NMR spectra between 354 and 339 K, to be explained in the following.

In the methylene sequence, the CP-MAS signals of C-15 and C-19 remain approximately the same before and after the transition, indicating that the bonds C-13–C-14, C-16–C-17 (for C-15), C-17–C-18, and C-20–C-21 (for C-19) remain mobile to give the same trans-to-gauche ratio as in the melt and thus do not contribute to the entropy change. Similarly, the unchanged chemical shifts of C-13 and C-21 indicate that the bonds C-14–C-15 and C-19–C-20 also remain at a comparable gauche content. Thus, in the methylene sequence there are six bonds (as specified here) that do not change their gauche concentrations on cooling from the isotropic melt to the mesophase. Because the motion about C-14–C-15 and C-17–C-18 and about C-16–C-17 and C-19–C-20 is not changed by the phase transition, one can predict that the signals for C-16 and

C-18, respectively, should be relatively constant at 30.1 ppm (only 0.7 ppm shifting is observed).

On the other hand, there appears a new signal at 33.3 ppm in the CP-MAS spectrum on cooling from 354 to 339 K (Figure 1). This new peak grows in intensity as the temperature is decreased to 326 K. The downfield shift is 3.2 ppm and could be attributed to the loss of two γ-gauche effects. Excluding the six C–C bonds which do not change their gauche characters, as shown above, the following bonds may be involved in a conformational change: O–C-13, C-15–C-16, C-18–C-19, and C-21–O. The change from 40% gauche to all-trans in these four bonds should cause C-14, C-17, and C-20 to resonate downfield by an amount of roughly two γ-gauche effects, i.e., 4 ppm, being close to the observed value of 3.2 ppm. Thus, the new peak at 339 K can be assigned to C-14, C-17, and C-20. The relatively weak intensity of the new peak at 33.3 ppm that contains the signal of three carbon atoms as compared to that at 30.9 ppm that contains signals of only two carbon atoms may be explained by the CP pulse sequence which discriminates resonances of carbon atoms of different mobilities. In this case, the chosen CP pulse sequence favors the two more mobile atoms, C-16 and C-18.

In the dephasing spectrum in Figure 3, the greatest signal suppressions occur for C-14, C-17, and C-20, while the signals for C-16, C-18, C-13, C-21, C-15, and C-19 remain clearly visible. This is to be interpreted that the motion of these carbons is reduced most after going through the transition, supporting the assignments that the resonance of 33.3 ppm is due to C-14, C-17, and C-20. This conclusion is also consistent with the observation made by BILEV experiment at 339 K shown in Figure 1. The signals of rigid carbons C-14, C-17, and C-20 can hardly be seen in the BILEV spectra of Figure 1, while the fairly good BILEV signal-to-noise ratio of the other carbons suggests that the other carbons are more mobile.

Based on the observations that only C-14, C-17, and C-20 have changed their chemical shifts (downfield) and become more rigid, it is possible to draw a picture on the overall conformation of the methylene spacer, as shown in the following diagram:

$$-O\overset{t}{-}C\underset{13}{-}C\underset{14}{-}C\underset{15}{\overset{t}{-}}C\underset{16}{-}C\underset{17}{-}C\underset{18}{\overset{t}{-}}C\underset{19}{-}C\underset{20}{-}C\underset{21}{\overset{t}{-}}O-$$

From this diagram, one can see that the first phase transition on cooling from the isotropic melt leads to four bonds becoming fixed in trans conformations (those marked with t), while the rest still undergo trans–gauche conversions (i.e., are disordered). This picture is basically in agreement with ordering found for the methylene spacers in some main-chain polymeric liquid crystal systems,[30-35] in which the spacers adopt an extended (i.e., trans-rich) conformation. The prediction that trans states are alternatively placed along the methylene sequence[34,35] is, however, not fulfilled for MBPE-9.

The change of conformations in these four bonds (O–C-13, C-15–C-16, C-18–C-19, and C-21–O) on transition to trans could cause an entropy change of up to 4 × 9.5 J K^{-1} mol^{-1} = 38 J K^{-1} mol^{-1}, calculated according to an empirical rule for the entropy of fusion.[7] This value is then multiplied by the fraction of crystallinity of 0.54, to give a value of 20.5 J K^{-1} mol^{-1}, being close to the observed value of 16.7 J K^{-1} mol^{-1}. The crystallinity was determined before by calorimetry,[1a,d] and is supported by an estimate of the mole fraction of cross-polarizable ^{13}C's (seen by the peak area of the C-14/C-20 resonances in CP-MAS at 339 K) versus the total number of carbons (seen by the area of peaks in CP-MAS plus that in BILEV at 339 K). This observation on the alkoxy chain carbons leads to the conclusion that the entropy change of 16.7 J K^{-1} mol^{-1} at the first transition on cooling is due to a partial ordering of the alkoxy chain and not of the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) group, which is in agreement with a close-to-zero entropy contribution from the aromatic part which was inferred before by Yandrasits et al. by extrapolating the transition entropy to zero methylenes in the flexible chain.[1c]

As the temperature is decreased from 354 to 339 K, the signals from the ethylene linkage, i.e., C-7 and C-8, also undergo some noticeable changes. Their line width becomes broader and the average resonance position shifts downfield (chemical shift becomes larger). The increase in the line width reflects a detectable distribution of environments, resulting from a slowing-down of the motion. While the increase of the average chemical shift cannot be interpreted by the conformational-dependent γ-gauche effect, as described above, since the alkyl chain (ethylene in this case) is not sufficiently long. For short chains the intermolecular packing effect on the change of ^{13}C chemical shift becomes important. Therefore, the change in the resonances of C-7 and C-8 cannot be simply interpreted.

To further support the surprising result of partial ordering in the flexible chain, one needs also examine the mobility of the aromatic group ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) itself. The experimental evidences on the mobility (to be discussed below) indicate that the motional behavior of the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) group deviates rather remarkably from that of a mesogen in the classical liquid crystal systems (supposed to be a linear rigid group).

At 339 K, a comparison between the CP-MAS and the dephasing spectra of MBPE-9, shown in Figure 3, indicates that (1) the signal intensities of nonprotonated carbons C-1, C-4, C-5, C-9, and C-12 are, as expected, the least affected when compared to those of protonated carbons. This observation can also be used as further confirmation that the chemical shift assignments for the nonprotonated carbons were correct and (2) the signals from the protonated aromatic carbons C-2, C-3, C-6, C-10, and C-11 as well as that of C-7 and C-8 have been somewhat suppressed. The suppression of the signals from these carbons is, however, only slight, even with a long dephasing delay of 70 μs. This indicates considerable motion is left in the rings. A detailed description of the motion in the phenylene groups can, however, not be derived from the results of the present NMR experiments because of their rather qualitative nature. The degree of disorder in the high-temperature mesophase must be similar to that found in the melt, otherwise, if there would have been a change to 180° flips (jumps between two identical symmetry sites), there should have been an entropy decrease noticeable by calorimetry when going to the high-temperature mesophase. The ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) groups produce thus little or no orientational order, in contrast to the behavior in liquid crystals with a rigid mesogen.

The spectrum of ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) obtained with CP-MAS at 339 K in Figures 1 and 3 can be decomposed into two sets of resonance lines. One resembles the higher temperature (354 or 373 K) BILEV spectrum, and the other is that found at lower temperature (326 or 310 K) in the CP-MAS spectrum.

The discussion of the motion and entropy gives a better understanding of the nature of the mesophase of MBPE-9 formed after the first transitions on cooling. The BILEV (mobile part) and CP-MAS (rigid part) spectra show an approximately equal intensity. Since the fraction of the rigid component does not change significantly on going beyond the second transition (see Figure 1) and the calorimetic crystallinity of similarly cooled samples at room temperature is about 50%,[1] one can identify this rigid fraction with the part that will ultimately end up as the room-temperature crystallinity. An important conclusion of this observation is that the high-temperature mesophase is only involving about 50% of the sample. Assuming from the calorimetric extrapolation with CH_2-spacer chain length and the present discussion of motion that little or no entropy change occurs in the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) sequence on going through the high-temperature exotherm, one can calculate that the measured entropy of transition of 16.7 J K^{-1} mol^{-1} matches the estimated entropy of transition of 50% of the nine CH_2 groups to an atmospheric pressure condis phase which was shown in ref 9 to have an entropy of transition of about 3.5 J/(K mol of CH_2). The γ-gauche effect lets one, furthermore, derive that bonds O–C-13, C-15–C-16, C-18–C-19, and C-21–O are practically always in the trans conformation after cooling through the high-temperature exotherm. The loss of conformational disorder of these four bonds of the 50% of the sample that becomes ordered, accounts also for about $0.5 \times 4 \times 9 = 18$ J K^{-1} mol^{-1}, close to the measured amount. The specific conformational restrictions derived from the NMR data permit the suggestion of the predominant existence of 2g1, 2g2, 2g3, and 3g3 kinks and jogs out of the class of conformations which leave the bundles of CH_2 sequences in a largely extended, parallel, low-energy conformation,[36] as was proposed by Pechhold.[37] The nomenclature 2g or 3g indicates the number of gauche bonds in the kink or jog. The final number (1, 2, or 3) indicates the shortening of the chain in multiples of half the unit cell length of the crystallographic orthorhombic chain. In addition to the shortening in the chain direction, there are displacements in the *a*- and *b*-directions. The 2g defects introduce 33% of gauche conformations, the 3g defects, 50%. It is thus easy to make up the above assigned equilibrium concentration of gauche conformations in the sequence restricted by the experimentally determined trans bonds. The mechanisms of alternating between the various possible defects was shown in the recent molecular dynamics simulations of Sumpter et al.[38] to be frequent and based on the thermal, random generation of gauche defects at times in the picosecond range.

The ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) sequence shows in this high-temperature mesophase only the beginnings of the restriction of motion, insufficient to increase the entropy significantly. It is interesting to note that the analogous polyparaxylylene [PPX, $(-C_6H_4-CH_2-CH_2-)_x$] shows also high-temperature condis phases. These have been studied by thermal analysis[39,40] and by molecular mechanics computation.[41] In the high-temperature mesophase of MBPE-9 the aromatic sequence must be much more disordered than in the β_2-phase of PPX, which shows an entropy of 14.3 J K^{-1} mol^{-1} on crystallization.

On further cooling of MBPE-9 from the high-temperature mesophase at 339 K to 326 and 310 K, the chemical shift values of the alkoxy chain carbons do not change significantly ($\leq$0.7 ppm), as can be seen in Table I and Figure 1. The dephasing experiment at 310 K, Figure 4, shows that even with the a dephasing delay of 120 μs, the signals of C-15 and C-19 (at 27.5 ppm) as well as C-16 and C-18 (31.65 ppm) can still be observed, indicating a residual mobility which keeps the chain conformationally disordered. The observed entropy at the second transition (36.3 J K^{-1} mol^{-1}, with a cooling rate of 10 K/min)[1a,c] is thus not likely to be due to major amounts of ordering in the alkoxy chain.

On the other hand, a large change can be observed in the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) sequence after the second transition to the room-temperature phase. The coexistence of the different conformations seen at 339 K in the CP-MAS spectrum becomes no longer observable, as indicated by the resonances of C-2 and C-6 in Figure 1. Each distinguishable carbon atom in the rings produces only a single "rigid" line. In the dipolar dephasing experiment, shown in Figure 4, the CP-MAS signals from C-2 (109.9 ppm), C-6 (119.6 ppm), and C-3 (130.5 ppm) can be suppressed with a shorter dephasing delay (40 μs), indicating that the methyl-substituted phenylene ring has become much less mobile. The slowing-down of motion in this ring may introduce sufficient order to be linked to the observed entropy change of 36.3 J K^{-1} mol^{-1}. The signals of the unsubstituted phenylene ring carbons, on the other hand, cannot be suppressed, even with a τ of 120 μs, as can be seen from the signals of C-11 (115.4 ppm) and C-10 (130.5 ppm) in Figure 4. Thus, this ring remains quite mobile at 310 K. Judging from the mesophase transitions in PPX [$\Delta S_i = 14.3$, $\Delta S_{d2} = 2.7$, $\Delta S_{d1} = 9.9$ J K^{-1} mol^{-1}],[39,40] one could expect an entropy change of about 54 J K^{-1} mol^{-1} for complete, or 29.2 J K^{-1} mol^{-1} for 54%, crystallization of the ($O-C_6H_3CH_3-CH_2-CH_2-C_6H_4-O-$) group. Additional perfection in the packing of the $(CH_2-)_9$ sequence (i.e., change in intermolecular interactions which is usually small compared to the change in intramolecular interaction, i.e., conformational change, for long alkyl chains), which can be shown by the gradual increases of their δ values with a decrease the temperature from 339 to 310 K, can easily make up the remaining entropy loss of (36.3 − 29.2) = 7.1 J K^{-1} mol^{-1}.

The reason that the methyl-substituted phenylene ring becomes immobile at 310 K may be related to the inter- and intramolecular interactions. The latter causes a strong steric interaction between the CH_3 and the methylene group of C-7. This type of interaction has been discussed for the two adjacent methyl groups in hexamethylbenzene.[42] The unsubstituted phenylene ring is, in contrast, relatively free to rotate about its 1,4-axis. The former can be deduced from the thermal behavior of PPX.

The low-temperature phase of MBPE-9 (310 K) is still conformationally disordered to some degree, as is indicated by the observations that (1) the unsubstituted phenylene ring is still mobile and (2) there are still six bonds in the CH_2 spacer which possess a high gauche character. From these six disordered bonds one expects a further entropy of disordering of about 57 J K^{-1} mol^{-1} (or 31 J K^{-1} mol^{-1} for the 54% crystalline sample). On further cooling this excess entropy can be reduced by continued ordering as in a normal liquid, ending in a glass transition which could be proven by an analysis of the heat capacity. Another possibility would be the existence of further transitions at lower temperature, a less likely alternative since qualitative DSC down to 150 K showed no evidence for such a transition. Again, detailed heat capacity measurements, in progress, should be able to resolve this remaining problem. A similar behavior was recently observed in our laboratory in the ^{13}C NMR and thermal analysis of the condis phases of *N,N'*-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD),[8] a small molecule that forms liquid crystals at high temperatures.

MBPE-5. The same analysis can be made on the sample of MBPE-5. The variable-temperature NMR spectra are shown in Figure 2. At 410 K, in the isotropic melt, the CP-MAS spectrum shows residual resonances of the CH_2 sequence and C-7 and C-8, but not of the aromatic ^{13}C atoms, indicating again rigidity of the flexible spacer even in the melt, similar to that of MBPE-9. The resonances not observable in the CP-MAS spectrum at 410 K are traceable to weak $^{13}C-^{1}H$ dipolar interactions resulting from phenyl rotation.

As the sample is cooled to 401 K (spectra not shown) and 386 K, still above the reported first transition temperature, the spectra are essentially the same as that of the isotropic melt, as can be seen in Figure 2 and also the chemical shift values in Table II. This indicates that on cooling the sample remains liquid at 386 K or even lower.

At 350 K, the CP-MAS spectrum shows increased intensities from aromatic ^{13}C's in the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) group as a result of reduced mobility. On the other hand, the spectrum shows decreased signal intensities of the $-CH_2$ sequence. This is probably due to a motion having correlation time of 10^{-5}–10^{-6} s^{-1} which are more effective to reduce the proton spin–lattice relaxation time in the rotating frame to such a small value that the cross polarization can no longer occur.[43] A CP-MAS experiment with variable spin lock/contact time would be necessary to prove this point. Such an experiment at 350 K is for MBPE-5, however, not possible because the sample is continuously perfecting its order. In the BILEV spectrum, although the chemical shift values are still that of the melt, the line widths are broadened significantly when compared to those at higher temperatures (e.g. 386, 401, and 410 K). The broadening arises when the motion of the groups under consideration give rise to strongly fluctuating dipolar fields. The broadening caused by the motion of 10^{-5}–10^{-6} s^{-1} generally cannot be removed by the high-power proton decoupling because it is of the same order of magnitude as the intensity (50 kHz) of the rf field applied through the decoupler. Thus, both the CP-MAS and BILEV spectra indicate that the CH_2 sequence undergoes a large-amplitude motion of 10^{-5}–10^{-6} s^{-1}. This motion is considered to be a slow motion on the NMR time scale and is most probably due to chain diffusion. The diffusion also exists at higher temperatures, but with a somewhat higher rate such that the dipole–dipole interaction can be averaged and results in line narrowing. These observations can be interpreted with the beginning of a crystallization process, in which the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) groups are gaining order, which is made possible (or helped) by the decreased motion of the alkyl chains. The spectra of 350 K are thus an intermediate between the melt and the room-temperature phases. The appearance of the spectra are expected to be dependent on the length of isothermal observation time.

At 325 K, a single phase transition was observed in DSC (onset temperature is 329.3 K) when the sample is cooled at a rate of slower than 2.5 K/min, which is the average cooling rate used in the NMR measurements. The NMR spectra of both BILEV and CP-MAS in Figure 2 are almost identical to that of 310 K, except that the intensity of the CP-MAS spectrum is slightly lower than that of 310 K. In the dephasing experiment, Figure 5, except for the $-CH_3$ carbon, signals from all other protonated carbons were suppressed even with a shorter delay (30 μs compared to 70 μs for MBPE-9). The chemical shift values also indicate stiffening of the molecule. For C-15, the δ changes from 23.2 ppm at 350 K to 27.30 ppm at 325 or 310 K. This large difference must be attributed to two γ-gauche effects and corresponds to the change of the conformation in the bonds of C-13–C-14 and C-20–C-21 from a high gauche concentration in the liquid phase (386 K and above), to an all-trans on stiffening, while for the indistinguishable carbons C-14 and C-20, the δ changes by about 2 ppm, due to one γ-gauche effect in the bonds of C-13–O and C-21–O, respectively. On the other hand, δ values of C-13 and C-21 remain constant when temperature is decreased, indicating that the conformations in the bonds C-14–C-19 and C-15–C-20 at 310 K have gauche character comparable to that in the melt.

From the analysis of γ-gauche effect, above, one can easily derive the entropy loss for the transition. Except two bonds, namely C-14–C-15 and C-15–C-20, all other bonds in the CH_2 sequence have changed their conformation and should each contribute 9.5 J K^{-1} mol^{-1}, which amounts to 4×9.5 J K^{-1} mol^{-1} = 38 J K^{-1} mol^{-1}. The ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) group contributes an additional 54 J K^{-1} mol^{-1} (see analysis on PPX and MBPE-9 in this paper). Therefore, for a sample of 100% crystallinity at 310 K, one expects to observe an entropy of fusion of 38 + 54 = 92 J K^{-1} mol^{-1}. This value is in sufficient agreement with the value of 81.4 J K^{-1} mol^{-1} observed by DSC.[1]

The similarity between the spectra at room temperature and at 325 K can be attributed to the fact that a rather slow cooling rate ($\leq$3 K/min) had to be used for decreasing the sample temperature in the NMR experiment. It was shown before by DSC that the existence of the mesophase is largely dependent on the cooling rate. The mesophase of MBPE-5 is hardly observable if the cooling rate is slower than 2.5 K/min.[1]

Conclusions

(1) The mobility of the ($-C_6H_3CH_3-CH_2-CH_2-C_6H_4-$) and the alkoxy chain have been described for MBPE-9 and MBPE-5. The results suggest that conformational disorder exists in all phases of both polymers. An analysis of heat capacity to low temperature is in progress and may resolve the question of freezing of the remaining conformational motion at temperatures below room temperature.

(2) The order of the higher-temperature phase of MBPE-9, observed on cooling between two exotherms, is realized by partial ordering of CH_2 sequences (with four C–C bonds being largely fixed in the trans conformation), while in the room-temperature phase, the methyl-substituted phenylene ring also participates in creating increased order without a much further increase in the order of the CH_2 sequence. The observed transition entropies could be linked to the transition of polyethylene from the melt to its condis phase and of polyparaxylylene from the melt to its crystal phase.

(3) For MBPE-5, the high-temperature mesophase, observed by DSC on cooling, cannot be traced by NMR, because it undergoes fast transformation to the room-temperature phase. Since the low-temperature CP-MAS spectrum shows a larger downfield movement in the chemical shifts compared to that of the melt, and a very short effective T^*_2, MBPE-5 seems to be able to form more perfect crystals than MBPE-9. Still, the room-temperature phase has two disordered bonds, making the crystals conformationally disordered.

(4) The facts that speak for identifying the high-temperature mesophase as liquid crystalline are mainly the broad X-ray diffraction peak and the transition that occurs on cooling almost without supercooling.[1] The facts that speak against it are the partial crystallinity shown by the present NMR experiments, the absence of a rigid mesogen,[1] and the transition being driven by the ordering caused by partial gauche–trans changes in the flexible spacer, similar to the changes in the well-known hexagonal (condis) phase of polyethylene.[9] This flexible spacer seems according to the model calculations of Ronca and Yoon unable to form a liquid crystalline phase in the observed temperature range.[15]

(5) A possible resolution of the contradiction in (4) is to suggest that all observed properties can be exhibited in polymorphs of conformationally disordered macromolecular crystals (condis crystals) without the need to invoke a liquid crystalline, mesogen-caused structure. While the

typical properties in thermotropic liquid crystals can be linked to the partial orientational ordering of rigid mesogens that maintain positional diffusive motion, condis crystals are basically orientationally ordered and show at sufficiently high-temperature translational (positional) diffusion, not based, however, on mesogen motion, but rather on segmental diffusion along the chain. This segmental diffusion is documented by the fact that chain extension occurs on crystallization of several polymers into a condis phase.[9]

The fast crystallization, though surprising, is not without precedence in condis crystals. Polypropylene crystallizes on sufficient quenching almost instantaneously to a metastable, conformationally disordered phase;[9] poly(oxybenzoate-*co*-naphthoate) similarly forms on cooling a metastable condis crystal phase.[44,45]

Finally, it is of interest to draw attention to the lyophilic liquid crystals that have been classified as liquid crystals, despite the fact that the function of the mesogen is taken over by a completely differently functioning phase boundary. Most characteristic properties are linked to the conformational disorder and motion of the mobile part of the molecules. Similarly, block copolymer morphologies can superficially be similar to liquid crystalline morphologies so that initially these compounds were linked to liquid crystalline morphologies despite thermodynamic dissimilarities. By inclusion of newly discovered phases[1] into the classification "liquid crystal", a similar disservice would be done to the understanding of this class of polymers, which may become as important as the "truly liquid crystalline macromolecules".

Summary

To summarize the results of this study, we would suggest that in this new class of polymers with flexible segments of aromatic and aliphatic segments, properties can be reached that combine the different natures of conformational disorder of these segments. In their homopolymers, as represented by polyparaxylylene and polyethylene, both polymers display stepwise transitions to mesophases that have been identified as condis crystals. In the "alternating copolymer" the larger volume requirement of the aromatic sequence seems to stabilize the paraffin condis crystal. The paraffin segment, in turn, acts as an in-chain solvent for the otherwise much higher melting aromatic sequences.

Acknowledgment. This work was supported by the Division of Materials Research, National Science Foundation, Polymers Program, Grant No. DMR 8818412, and the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References and Notes

(1) (a) Cheng, S. Z. D.; Yandrasits, M. A.; Percec, V. *Polymer* **1991**, *32*, 1284. (b) Ungar, G.; Feijoo, J. L.; Keller, A.; Yourd, R.; Percec, V. *Macromolecules* **1990**, *23*, 3411. (c) Yandrasits, M. A.; Cheng, S. Z. D.; Zhang, A.; Cheng, J.; Wunderlich, B.; Percec, V. *Macromolecules* **1992**, *25*, 2112. (d) Yandrasits, M. A. Ph.D. Dissertation, Department of Polymer Science, The University of Akron, Akron, OH 44325-3909.

(2) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.

(3) Lenz, R. W.; Jin, J. I. *Macromolecules* **1981**, *14*, 1405.

(4) Ober, C. K.; Jin, J. I.; Lenz, R. W. *Polym. J.* **1982**, *14*, 9.

(5) Lenz, R. W. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 21.

(6) Wunderlich, B.; Grebowicz, J. In *Liquid Crystalline Polymers II/III*; Gordon, M., Plate, N. A., Eds.; Advances in Polymer Science; Springer Verlag: Berlin, Heidelberg, 1984; Vols. 60/61, p 1. Xenopoulos, A.; Cheng, J.; Yasuniwa, M.; Wunderlich, B. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 63.

(7) Wunderlich, B. *Crystal Melting*; Macromolecular Physics; Academic Press: New York, 1980; Vol. 3.

(8) Cheng, J.; Jin, Y.; Liang, G.; Wunderlich, B. *Mol. Cryst. Liq. Cryst.* **1991**, *213*, 237.

(9) Wunderlich, B.; Möller, M.; Grebowicz, J.; Baur, H. *Conformational Motion and Disorder in Low and High Molecular Mass Crystals*; Advances in Polymer Science; Springer Verlag, Berlin, 1988; Vol. 87.

(10) Schneider, N. S.; Desper, C. R.; Beres, J. J. In *Liquid Crystalline Order in Polymers*; Blumstein, A., Ed.; Academic Press: New York, 1978.

(11) Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Karis, T. *Macromolecules* **1988**, *21*, 2777.

(12) Ungar, G.; Feijoo, J. L.; Percec, V.; Yourd, R. *Macromolecules* **1991**, *24*, 953.

(13) Smith, G. W. In *Plastic Crystals, Liquid Crystals, and the Melting Phenomenon. The Importance of Order.* Brown, G. H., Ed.; Advances in Liquid Crystallography; Academic Press: New York, 1975; Vol. 1.

(14) Wiedemann, H. G.; Grebowicz, J.; Wunderlich, B. *Mol. Cryst. Liq. Cryst.* **1986**, *140*, 219.

(15) Ronca, G.; Yoon, D. Y. *J. Chem. Phys.* **1982**, *76*, 3295.

(16) Percec, V.; Yourd, R. *Macromolecules* **1988**, *21*, 3379.

(17) Percec, V.; Yourd, R. *Macromolecules* **1989**, *22*, 524.

(18) Doty, F. D.; Ellis, P. D. *Rev. Sci. Instrum.* **1981**, *52*, 1868.

(19) van Geat, A. L. *Abstracts of the 10th Experimental NMR Conferences*; Mellon Institute: Pittsburgh, PA, March 1969.

(20) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.

(21) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

(22) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981.

(23) Sadtler Research Laboratories, Division of Bio-Rad Laboratories, Inc. *Carbon-13 NMR*; Bio-Rad: Philadelphia, 1986.

(24) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

(25) Alla, M.; Lippmaa, E. *Chem. Phys. Lett.* **1976**, *37*, 260.

(26) Komoroski, R. A., Ed. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Marchand, A. P., Eds.; Methods in Stereochemical Analysis; VCH Publishers, Inc.: Deerfield Beach, FL, 1968; Vol. 7.

(27) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982.

(28) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publishers, Inc.: New York, 1989.

(29) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley-Interscience: New York, 1969.

(30) Abe, A. *Macromolecules* **1984**, *17*, 2280.

(31) Abe, A.; Furuya, H. *Macromolecules* **1989**, *22*, 2982.

(32) Furuya, H.; Dries, T.; Fulaus, K.; Abe, A.; Ballauff, M.; Fischer, E. W. *Macromolecules* **1990**, *23*, 4122.

(33) Furuya, H.; Abe, A. *Macromolecules* **1991**, *24*, 2999.

(34) Yoon, D. Y.; Bruckner, S. *Macromolecules* **1985**, *18*, 651.

(35) Bruckner, S.; Scott, J. C.; Yoon, D. Y.; Griffin, A. C. *Macromolecules* **1985**, *18*, 2709.

(36) Wunderlich, B. *Crystal Structure, Morphology, Defects*; Macromolecular Physics; Academic Press: New York, 1973; Vol. 1.

(37) Pechhold, W. *Kolloid Z. Z. Polym.* **1968**, *228*, 1.

(38) Sumpter, B. G.; Noid, D. W.; Wunderlich, B. *J. Chem. Phys.* **1990**, *93*, 6875.

(39) Kirkpatrick, D. E.; Wunderlich, B. *Makromol. Chem.* **1985**, *186*, 2595.

(40) Kirkpatrick, D. E.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 931.

(41) Miller, K. J.; Hollinger, H. B.; Grebowicz, J.; Wunderlich, B. *Macromolecules* **1990**, *23*, 3855.

(42) Takeda, S.; Fujiwara, T.; Chihara, H. *J. Phys. Soc. Jpn.* **1989**, *58*, 1793.

(43) Jelinski, L. W.; Melchior, M. T. In *High-Resolution NMR of Solids* Dybowski, D., Lichter, R. L., Eds.; NMR Spectroscopy techniques; Marcel Dekker, Inc.: New York, 1987.

(44) Cheng, S. Z. D. *Macromolecules* **1988**, *21*, 2475.

(45) Cheng, S. Z. D.; Janimak, J. J.; Zhang, A. *Macromolecules* **1989**, *22*, 4240.

Registry No. MBPE-5 (copolymer), 143495-39-0; MBPE-5 (SRU), 143495-41-4; MBPE-9 (copolymer), 143495-40-3; MBPE-9 (SRU), 143495-42-5.