shown by dark-field electron microscopy how the oriented regions are distributed in the sample and how these regions grow. With high-resolution techniques, it has been demonstrated that the smectic layers undulate with a characteristic wavelength and amplitude. The nature of defects that arises during the orientation of the sample has been indicated.

Acknowledgment. We are glad to acknowledge our colleagues, particularly Dr. H. Noether and Dr. G. Schmidt, for many stimulating discussions. To the Deutsche Forschungsgemeinschaft we owe special thanks for financial support within the framework of SFB 262.

Registry No. 1 (copolymer), 97104-71-7; 1 (SRU), 97088-50-1.

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Highly Ordered Main Chain in a Liquid Crystalline Side-Group Polymer

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Received September 28, 1987

ABSTRACT: The molecular order of the polymer chain in a liquid crystalline side-group polymer was studied by solid-state ^2H NMR in the frozen smectic phase. In this system the chain is highly extended perpendicular to the mesogens. The NMR data show that the link between the polymer chain and the mesogens is provided by the conformationally ordered quaternary carbon in the polymer chain. The width of the orientational distribution of the $C-CH_3$ bonds with respect to the director was determined to be ±20°. The ^2H NMR results are in good agreement with small-angle neutron-scattering studies on the same system.

Introduction

In the spacer model[1,2] of polymeric side-group liquid crystals the polymer chain is supposed to retain its random coil conformation. Strictly speaking, this requires the absence of any orientation-dependent inter- and intramolecular interactions between the mesogenic group and the polymer chain. Studies on solutions of linear polymers in a liquid crystalline matrix have indeed shown[3] that the intermolecular contribution to the orientation effect is small; on the other hand, the mesogenic groups have an ordering effect on the polymer chain through intramolecular forces. The anisotropy of the radii of gyration of the polymer chain in liquid crystalline side-group polymers measured by small-angle neutron scattering (SANS)[4,5] showed a strong dependence on the mesophase structure of the systems studied. The first ^2H NMR studies on a polyacrylate and a polymethacrylate have shown a different orientation behavior for these two systems with a polymer chain macroscopically oriented parallel and perpendicular to the mesogenic group, respectively.[6]

In this article, ^2H NMR is used to study the local conformation as well as the molecular order of the polymer chain in a polymethacrylate with a high anisotropy of the radii of gyration,[5] as studied by SANS. A comparison can now be made between the results presented here obtained for systems with the same mesophase structure but with chains of different stiffness and, on the other hand, for systems with different mesophase structures but with chains of the same stiffness.

The mesogenic side group is derived from 4′-butoxyphenyl 4-hydroxybenzoate linked to the polymethacrylate chain via a spacer of six methylene units. ^2H NMR is used as a tool to study the orientation behavior of the polymer chain, which was selectively deuteriated. The spectra are governed by the interaction of the nuclear quadrupole moment with the electric-field gradient of the $C-^2H$ bond, which is intramolecular in nature. Because of the anisotropy of this interaction the information on the local conformation as well as the orientational distribution of the $C-^2H$ bonds can be extracted from the spectra in the glassy state. This supplements the findings of the SANS study, from which only the overall coil dimension could be determined.

Experimental Section

The samples were synthesized as described by Ringsdorf et al.[7] by using deuteriated methacrylic acid. The methacrylic acid was prepared from deuterioacetone and HCN. This synthesis was performed by two companies: Roehm at Darmstadt and BASF at Ludwigshafen.

The polymer was characterized by gel permeation chromatography (GPC), calibrated by similar samples of known molecular weight. The number-averaged molecular weight was found to be 60 000, and the polydispersity was 2.3. The phase behavior was characterized by polarization microscopy and by differential scanning calorimetry (DSC). The glass transition was found at 313 K, the transition from the smectic-A to the nematic phase at 381 K, and the clearing temperature at 386 K. The thickness of the smectic monolayers was found by X-ray diffraction to be 2.8 nm.

The ^2H NMR spectra were recorded on a Bruker CXP-300 spectrometer with a home-built probe fitted with a goniometer and obtained by the solid echo technique with quadrature phase detection, as described elsewhere.[8,9] The sample was macroscopically aligned by the 7-T magnetic field of the NMR spectrometer. To ensure alignment, we heated the sample into the isotropic phase, then tempered it for 1 h at a temperature just below the nematic–isotropic phase transition, and subsequently cooled it slowly below the glass transition temperature over a period of several hours. The angular-dependent measurements were all performed on the glassy state.

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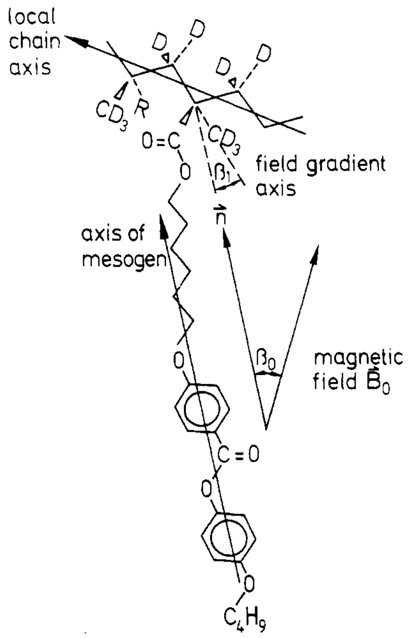

Figure 1. Molecular structure of a liquid crystalline side-group polymer. β_1 denotes the angle between the electric-field gradient and the director. β_0 is the angle between the alignment direction and the magnetic field.

The spectra were analyzed to yield the orientational distribution function on a VAX-750.

Line-Shape Analysis

To help the reader to follow the arguments used later, we briefly review the interrelation between ^{2}H NMR spectra and molecular order.

The ^{2}H NMR spectrum is dominated by the coupling of the electric-field gradient with the nuclear electric quadrupole moment. The frequency, assuming an axially symmetric quadrupole tensor (spin $I = 1$), is given by

$$\omega = \omega_0 \pm \omega_Q \tag{1}$$

$$\omega_Q = \delta(3\cos^2\theta - 1)$$

where δ ($=3e^2qQ/8\hbar^2$) and ω_0 denote the quadrupole coupling constant and the central frequency, respectively.

For isotropic powders, the so-called Pake pattern[10] is obtained corresponding to the isotropic orientational distribution function

$$P(\theta)\,\mathrm{d}\theta = \sin\theta\,\mathrm{d}\theta \tag{2}$$

with θ denoting the angle between the electric-field gradient of the C–^{2}H bond and the magnetic field. In the following, β_1 denotes the angle between the electric-field gradient and the director, whereas β is the angle between the molecular axis and the director of the mesophase (cf. Figure 1), following the notation in ref 11.

If we assume *transverse isotropy*,[12,13] i.e., if (1) the molecules are uniformly distributed around the director and (2) a molecular frame can be chosen such that the principal axes of the field gradient tensor are also uniformly distributed around the unique axis of this frame, the orientational distribution can be expanded in terms of Legendre polynomials:

$$P(\beta) = \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \langle P_l(\cos\beta)\rangle P_l(\cos\beta) = \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \langle P_l\rangle P_l(\cos\beta) \tag{3}$$

where the expansion coefficients $\langle P_l(\cos\beta)\rangle \equiv \langle P_l\rangle$ are the order parameters for a given molecular direction.

The NMR line shape for moderately ordered systems can easily be calculated by using this expansion, because the total spectrum $S(\omega)$ is obtained as a superposition of subspectra weighted by the order parameters $\langle P_l\rangle$ with even l:[11]

$$S(\omega) = S_0(\omega) \sum_{l=0,2,\ldots} (2l+1)\langle P_l\rangle P_l(\chi(\omega)) P_l(\cos\beta_0) \tag{4}$$

Here β_0 is the angle between the director and the magnetic field and $S_0(\omega)$ represents the line shape of an isotropic sample, centered around ω_0:

$$S_0(\omega) = \frac{1}{6\delta}\,\frac{1}{\chi(\omega)} \tag{5}$$

$$\chi(\omega) = \frac{1}{3^{1/2}}\left(\frac{\omega}{\delta} + 1\right)^{1/2} \quad \text{with } -1 \le \frac{\omega}{\delta} \le 2 \tag{6}$$

The ^{2}H NMR experiment is sensitive only to the orientation of the electric-field gradient of the C–^{2}H bonds with respect to the magnetic field. Therefore, the order parameters $\langle P_l\rangle$, obtained in the line-shape analysis, are referred to the unique axis of the field gradient typically along the C–^{2}H bond direction. They can be related to the order parameter of a different molecular direction about which axial symmetry exists, e.g., the chain direction forming an angle Ξ with the C–^{2}H bond by the equation

$$\langle P_l\rangle_{\mathrm{CH}} = \langle P_l\rangle_{\mathrm{mol}} P_l(\cos\Xi) \tag{7}$$

The orientational distribution of the C–^{2}H bonds is obtained as defined in eq 3 for the special case $\beta = \beta_1$ as the angle between the electric-field gradient and the director (cf. Figure 1). The maximum of this function can be interpreted as the most probable angle between the director and the C–^{2}H bond direction. A molecular order parameter of the polymer chain can be derived only if its conformation is known. If an internal motion leads to a time-averaged field gradient tensor, similar arguments hold for its unique axis. In particular, for a rapidly rotating methyl group instead of the three individual C–^{2}H bond directions the C_3 axis of the methyl group is probed in ^{2}H NMR.

This analysis applies only to uniaxial systems of moderate order. For higher ordered systems, as well as for nonuniaxial systems, a more general approach[14,15] should be used.

Results and Discussion

Figure 2 shows experimental and calculated angular-dependent spectra of the polymethacrylate in the frozen smectic-A phase. Each spectrum consists of the superposition of the spectrum of the rigid methylene group and the motional narrowed spectrum determined by the time-averaged field gradient tensor of the methyl group rotating about its C_3 symmetry axis. The following discussion is mainly based on the results for the methyl group. The methylene spectrum lacked sufficient resolution to warrant detailed interpretation. The line-shape analysis outlined above yielded the moments $\langle P_l\rangle_{\mathrm{CH}}$ up to $l = 8$, given in Table I. Note that each moment enters into the analysis with a weighting factor of $2l + 1$. From the determination of order parameters to such a high order, we expect to obtain a meaningful estimate of the orientational distribution function of the C–CH$_3$ bonds $P(\beta_1)$ d cos β_1 given by eq 7 (Figure 3a). This function displays a definite maximum close to half the tetrahedral angle. This suggests that the bisector of the O$_2$C–C–CH$_3$ moiety of the methacrylic chain is largely aligned along the director as indicated in Figure 1. The distribution function has a width

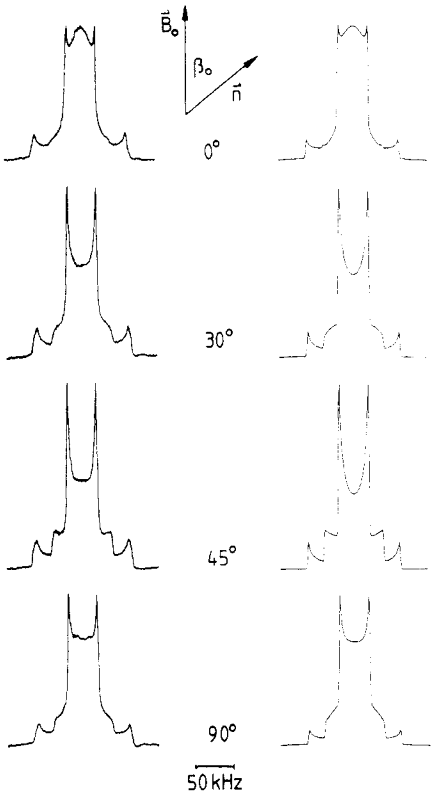

Figure 2. Experimental and calculated spectra in the frozen smectic phase. The angle between the director and the magnetic field is varied.

Table I
Order Parameters $\langle P_l \rangle$ As Determined from the Line-Shape Analysis[a]

l	$\langle P_l \rangle$	$(2l + 1)\langle P_l \rangle$
0	1.0	1.0
2	-0.065	-0.325
4	-0.12	-1.08
6	0.03	0.39
8	0.01	0.17

[a] The third column gives the product of $\langle P_l \rangle$ with the weighting factors $2l + 1$. These factors give the relative contribution of each subspectrum to the total line shape.

at half-height of ±20°, indicating a molecular order parameter for that bisector of $\langle P_2 \rangle_{\text{mol}} = 0.6$ but with the orientation axis of the chain perpendicular to the director. This value was obtained by fitting the orientational distribution function to a spherical Gaussian. Note that this information is obtained *without* assumptions about the conformation of the polymer backbone. The order parameter $\langle P_2 \rangle$, obtained for the mesogenic group, is 0.85. These results indicate that the polymer chain is highly elongated in this system. An all-trans conformation for the polymer chain can be excluded, because in this case the orientational distribution of the C–C^2H_3 bonds and of the C–^2H bonds in the methylene groups should be identical, leading to similar NMR line shapes. A more detailed insight in the chain conformation will be obtained by solid-state ^{13}C magic-angle spinning experiments.[16]

Our ^2H NMR data nicely confirm the conclusions of the SANS study of this system,[5] indicating a high anisotropy (4:1) of the radii of gyration. In addition, our results show that the local conformation at the link between polymer chain and spacer must be well defined. This behavior depends strongly on the type of the mesophase. An analogous system in the frozen nematic phase exhibits a much broader orientational distribution[6] of the C–CH_3 bond directions (Figure 3b) as well as a smaller anisotropy of the radii of gyration.[4] Although the orientational distribution in the frozen nematic system is based only on determination of $\langle P_2 \rangle_{CH}$ and $\langle P_4 \rangle_{CH}$, it also seems to be centered around half the tetrahedral angle. This indicates that the ordering tendency, as well as the conformation at the quarternary carbon in the polymer chain, is already formed in the nematic phase. In both systems the order axis of the polymer chain is perpendicular to the director.

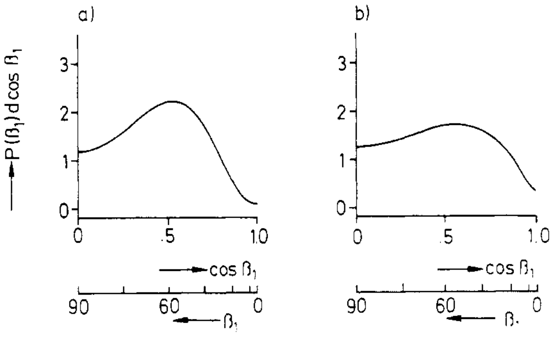

Figure 3. Orientational distribution of the C–C^2H_3 bonds in the frozen smectic (a) and in the frozen nematic (b) polymethacrylate. The maximum of the function in both systems is at half the tetrahedral angle of 54°.

A different behavior was observed for a frozen smectic polyacrylate,[6] where the width of the orientational distribution was higher than in the methacrylate (±50°) and the preferred order axis of the chain was parallel to the director. SANS studies on this system are under way, which should give a more detailed understanding of the ^2H NMR results.

The delicate coupling between polymer chain and mesogenic group is also observed in liquid crystalline elastomers ordered by mechanical forces. In polyacrylates of the same structure, typically, the mesogenic groups tend to align parallel to the axis of stress, whereas they order perpendicular to it in polymethacrylates of the same structure.[17]

These results indicate that the ordering behavior of the mesogenic groups relative to the polymer chain is different in polyacrylates and in polymethacrylates, although the only difference between the chains is the replacement of a hydrogen by a methyl group. This steric factor is probably responsible for the differences between these systems. This hypothesis will have to be proved by investigations of other systems as well as by theoretical considerations.

The theories of Warner et al.[18,19] can model liquid crystalline side-group polymers. The different behavior of the polyacrylates and the polymethacrylates are interpreted on the basis of the interaction between the polymer chain, the spacer, and the mesogenic groups. The results for the polyacrylates are consistent with their n_{III} phase, where mesogenic group and polymer chain have nematic interactions and tend to align parallel. The behavior of the polymethacrylates is consistent with their n_{I} phase, where the repulsive forces between the spacer and the polymer chain are dominant.

Acknowledgment. We thank Dr. Wunderlich (Roehm, Darmstadt) as well as Prof. Schmitt and Dr. Naarmann (BASF) for the preparation of the deuteriated methacrylic acid. Financial support by the Deutsche Forschungsgemeinschaft (SFB 41) is gratefully acknowledged.

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Chain Conformations of Polycarbonate from ab Initio Calculations

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Received August 25, 1987

ABSTRACT: Ab initio calculations with full geometry optimization on diphenyl carbonate (DPC) and diphenylpropane (DPP) are carried out to determine the bond geometries and the conformational energies and then to compute the unperturbed chain dimensions of the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane, or bisphenol A polycarbonate. The bond geometries calculated with the 6-31G* basis sets are in excellent agreement with the experimental values. The conformational energy contours exhibit a rather low energy barrier (ca. 1.9 kcal/mol) in DPP and a nearly flat profile in DPC for the rotations of phenylene groups. Moreover, the trans conformation of the carbonate group is favored by ca. 2.75 kcal/mol over the cis state. Application of these results to the rotational isomeric state model of the polycarbonate chain leads to the prediction of the unperturbed chain dimension of $\langle r^2\rangle_0/M \simeq 1.1$, which supports the previous calculation of Yoon and Flory. This calculated value is in satisfactory agreement with the experimental results of 1.2–1.3, obtained from small-angle neutron scattering from amorphous polycarbonate by Gawrisch et al. and Ballard et al.

Introduction

The chain conformations of the polycarbonate (PC) of 2,2-bis(4-hydroxyphenyl)propane, or bisphenol A polycarbonate, shown schematically in Figure 1a, have been studied by many authors since the first work on this topic was published by Williams and Flory in 1968.[1] The pertinent data are the conformational energies associated with the two torsional angles ϕ_i and ϕ_{i+1} within 2,2-diphenylpropane, the torsional angles ψ_i and ψ_{i+1} within diphenyl carbonate, respectively, and the energy difference between the trans and cis conformations of the carbonate group. Previous works include a number of empirical calculations,[2-6] MNDO-type semiempirical calculations,[7] and STO-3G level ab initio computations with fixed geometry.[8] The calculated conformational energies in conjunction with the geometric parameters determined separately by X-ray structure analyses of the model compounds, for example, were then applied to deduce a number of equilibrium properties.[1,4,9] Some attempts were also made to relate the conformational energetics to the unusual dynamic and mechanical properties of this polymer.[8]

Ab initio quantum mechanical calculations are widely used for the determination of equilibrium geometries, torsional barriers, and electronic excitation energies of small molecules. Recently, improvements in computer hardware and algorithms have permitted the application of these techniques to larger molecules including oligomeric models of polymers with reasonable confidence.[10,11] Ab initio calculations, therefore, have the potential of providing reliable information on bond geometries and conformational energies, when the conventional methodology is not readily applicable due to the difficulty of obtaining X-ray structural data and/or the complicated geometry–conformational energy relationships.

In this paper, we apply ab initio quantum mechanical calculations that allow full geometry optimization to the PC chain to calculate both the geometric parameters and the conformational energies involved. Different levels of basis sets are employed to determine the degree of complexity that is required to match the available experimental results of bond geometries. The bond geometries and conformational energies that are estimated employing the necessary basis sets are then used to compute the unperturbed chain dimensions of PC by the rotational isomeric state method.[1] The usefulness and the potential of the ab initio method is then tested by comparing its predicted value of the unperturbed chain dimension with available experimental results for the PC chain in dilute solutions and in the bulk amorphous state.

Computational Method

The calculations reported herein utilize standard aspects of ab initio quantum chemistry codes. For most closed-shell molecules, molecular geometries can be determined by the solution of the electronic Schroedinger equation at the Hartree–Fock or self-consistent field (SCF) level. The molecular wave function is expanded in a basis of Gaussian functions which represent

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