Macromolecules 1985, *18*, 2620–2623

NMR Study of Dilute Solutions of Main-Chain Nematic Polyesters in *p*-Azoxyanisole

F. Volino,*[†] M. M. Gauthier,[‡§] and A. M. Giroud-Godquin[‡]

CEN-G, DRF, 85X, 38041 Grenoble Cedex, France

R. B. Blumstein

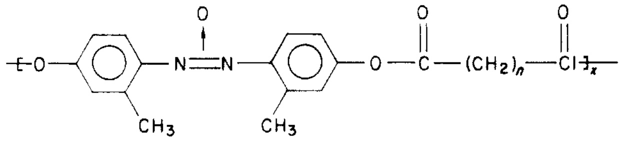
Department of Chemistry, Polymer Science Program, University of Lowell, Lowell, Massachusetts 01854.

Received March 11, 1985

ABSTRACT: Dilute solutions in nematic *p*-azoxyanisole (PAA) of intrinsically flexible nematic DDA9 main-chain polyesters of various average lengths are studied by proton and deuterium magnetic resonance, using protonated, partially deuterated, and perdeuterated molecules. All polymers are found to be in an extended conformation, as in the bulk nematic phase. The order parameters of the solvent PAA molecules and of the solute polymers are deduced by methods previously described. The results are compared with the existing theories of polymer/low molecular mass nematic mixtures. It is found that very long DDA9 polymers tend to form ideal solutions with PAA. A model for such solutions is proposed.

1. Introduction

Thermotropic nematic polymers,[1] in particular polyesters with flexible spacers $(CH_2)_n$ and mesogens in the main chain,[2] have received much attention in the past years. Polymers represented by



formed by condensation of 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene (mesogen "9") with diacid chlorides containing a methylene sequence length n = 2–14, exhibit rather broad nematic ranges at moderate temperatures[3] and a strong and regular even–odd effect.[4] DDA9 polymers corresponding to n = 10 have been extensively studied in bulk. Proton magnetic resonance (^{1}H NMR) line-shape analysis shows that in the nematic phase the chains are stretched with the spacers in a rather extended conformation,[5-7] as expected on general grounds.[8] These results have been confirmed by deuterium magnetic resonance (^{2}H NMR) for DDA9 polymers and model compounds with deuterated spacers.[6,7,9] Mixtures of this polymer with the low molecular mass nematic (LMN) *p*-azoxyanisole (PAA) have been studied[6,7,10] for polymer chain length $\bar{x} \sim 10$ repeating units. Both compounds are found to be miscible in all proportions in the nematic phase. The phase diagram is very similar to that obtained with other nematic polymers under similar conditions.[11,12] The following molecular properties have been found: (i) for all concentrations in the nematic phase, polymer chains are in an extended conformation, as in bulk;[6] (ii) the relative order of the spacer to the mesogen is practically independent of concentration and depends only on reduced temperature;[6] (iii) the structure and conformation of the PAA molecules are very slightly changed in the mixtures, these changes being continuous functions of concentration;[10] (iv) for PAA concentrations smaller than 10% by weight, PAA and mesogen "9" have the same order parameter in the pure nematic phase;[6,7,13] (v) for PAA concentrations larger than 50%, the order parameter of PAA is always larger than that of mesogen "9".[13]

Table I

DDA9	$\bar{x}^a$	R^b	$\bar{M}_w/\bar{M}_n$	ΔT_C,^{c} °C	$s_C{}^d$
H	~44	1.0/1.0		−0.25 ± 0.25	0.99 ± 0.01
L2	~11.3	1.5/1.0	1.24	−1.0 ± 0.25	0.92 ± 0.01
F8	~6.4		1.10	−3.25 ± 0.25	0.86 ± 0.01
Ed20	~7.5	1.0/0.0	~1.1	−3.0 ± 0.25	0.88 ± 0.01

^{a} $\bar{x}$ = average number of repeating units/chain. ^{b} R = ratio of aromatic to aliphatic end groups. ^{c} ΔT_C = depression of the clearing-point temperature of the mixtures relative to pure solvent. ^{d} $s_C = S_C{}^{DDA9}/S_C{}^{PAA}$ (see text for definitions).

In this paper, we present detailed ^{1}H NMR and ^{2}H NMR results concerning dilute solutions (5% (w/w)) of DDA9 polymers in PAA in order to gain insight into the solute–solvent interactions and the statistical properties of such main-chain nematic polymers in a nematic medium.

2. Experimental Section

Four different DDA9 polymers were used. The average number of repeating units ($\bar{x}$), the ratio of aromatic to aliphatic end groups (R), and polydispersities ($\bar{M}_w/\bar{M}_n$) are given in Table I (see ref 14 for details). The H, L2, and F8 polymers are fully protonated and Ed20 has a fully deuterated spacer. Mixtures containing 5% by weight polymers (corresponding to a polymer amount of 5–10 mg) were sealed in standard 5-mm-diameter NMR tubes, evacuated during several hours at room temperature under primary vacuum (~10^{-2} torr). The H, L2, and F8 polymers were mixed with perdeuterated PAAd14, and the Ed20 polymer was mixed with the partially deuterated PAA variety called PAAd6 in ref 15. PAAd6 is fully deuterated on the methyl groups and partially deuterated on the rings near the azoxy moiety for 10% of the molecules. The advantage of the Ed20/PAAd6 mixture is that polymer and solvent can be simultaneously studied in a single ^{2}H NMR experiment, as shown below. For the other mixtures, successive ^{1}H NMR and ^{2}H NMR experiments are required.

Clearing-point temperatures were measured by observing all samples simultaneously (mixtures and pure PAA samples) in heated silicone oil. The samples were equilibrated for several hours at 150–160 °C, well inside the isotropic phase. A very small amount of fine precipitate was observed at the bottom of the tubes, possibly representing some cross-linked degradation products. The clearing points were observed by slowly lowering the temperature. No nematic–isotropic (N + I) biphase was observed that could not be attributed to temperature heterogeneities in the sample (<1 °C). The differences (ΔT_C) between the clearing-point temperatures of the mixtures (T_C) and of the pure solvent ($T_C{}^{(0)}$) measured by this method, and confirmed by the NMR experiments, are given in Table I (these ΔT_C are plotted vs. $\bar{x}$ in Figure 5a). It is seen that the ΔT_C are negative (lowering of the clearing-point temperature) but approach 0 as the polymer chain length increases.

[†] Service de Physique, Groupe Physico-Chimie Moleculaire, member of CNRS.

[‡] Laboratoire de Chimie, Equipe Chimie de Coordination, LA 321.

[§] On leave from the Department of Chemistry, University of Lowell, Lowell, MA 01854.

0024-9297/85/2218-2620$01.50/0

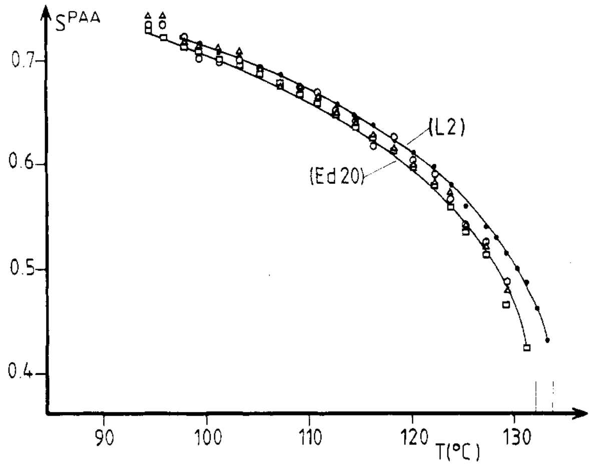


Figure 1. Order parameter vs. temperature of nematic PAA containing 5% (w/w) DDA9 polymers: (●) PAAd14 containing L2 polymer, deduced from the six quadrupolar splittings as in ref 15; (□, ○, △) PAAd6 containing Ed20 polymer (□ deduced from the largest quadrupolar splitting; ○ and △ deduced from H–D dipolar splittings) as in ref 15. The vertical lines indicate the clearing temperature of the corresponding mixture. The full lines were determined by eq 1 with the corresponding values of T_C.

The NMR spectra were obtained with two pulsed NMR Bruker spectrometers: a WM-250 spectrometer working at 38.4 MHz for ^{2}H NMR and a CXP-100 spectrometer working at 75 MHz for ^{1}H NMR. Spectra were taken in the whole nematic range by slowly cooling the samples in steps of 1–2 °C, after equilibrating several hours in the isotropic phase at ~150 °C.

3. NMR Results

Results Concerning the PAA Molecules: Solvent. The ^{2}H NMR of PAAd14 and PAAd6 molecules in 5% (w/w) mixtures are essentially the same as in the pure samples (see, for example, Figures 1 and 3 of ref 15). The nematic order parameter S^{PAA} was extracted from the various splittings of the ^{2}H NMR spectra as explained in ref 15. For mixtures with PAAd14 the six quadrupolar splittings $\Delta\nu_1$–$\Delta\nu_6$ were used in a single fit. It is found that the average structure of the PAA molecules in these mixtures can be considered as unchanged by the presence of 5% DDA9 polymers. For the mixture with PAAd6, the two dipolar splittings $\Delta\nu_{dip}{}^{A,HD}$ and $\Delta\nu_{dip}{}^{B,HD}$ and the single quadrupolar splitting $\Delta\nu_1$[15] were used independently, assuming as previously that the structure of the PAA molecules is the same as in the pure sample. Figure 1 shows typical results for the two mixtures with L2 and Ed20 polymers. We find that the temperature dependence of S^{PAA} for all samples studied can be represented within experimental accuracy by the same empirical law as for the pure samples[15]

$$S^{PAA} = 1.1237(1 - T/T+)^{0.187} \qquad (1)$$

with $T+ = T_C + 1.8 \pm 0.3$ K, where T_C is the actual clearing temperature of the corresponding mixture. In other words, the order parameter of nematic PAA containing up to 5% (w/w) DDA9 polymers is the same universal function of reduced temperature T/T_C (or equivalently of $T - T_C$ since ΔT_C is very small (<4 K) as for the pure material.

Results Concerning the DDA9 Molecules: Solute. Figure 2 shows a typical ^{1}H NMR spectrum of DDA9 polymer in solution in PAAd14. It is very similar to that obtained in a macroscopically aligned bulk polymer[5-7,14] and demonstrates that the molecular conformation is very similar in both cases. Two quantities can be extracted from this spectrum: (i) the nematic order parameter S^{DDA9} of the polymer, more specifically of mesogen "9", which can be deduced from the main doublet $2\delta_N$ as previously described,[5] from the relation

$$2\delta_N/\text{kHz} = 24.06S^{DDA9} \qquad (2)$$

(this is illustrated in Figure 4, where S^{DDA9} computed from eq 2 is plotted vs. $T - T_C$ for samples with different chain lengths); (ii) the relative order of the spacer to the mesogen, which can be pictured by the ratio $\rho_{2/5} = 2\delta_{2/5}/2\delta_N$, where $2\delta_{2/5}$ is the full width at $^2/_5$ of maximum as shown in Figure 2 (see ref 6 for more details).

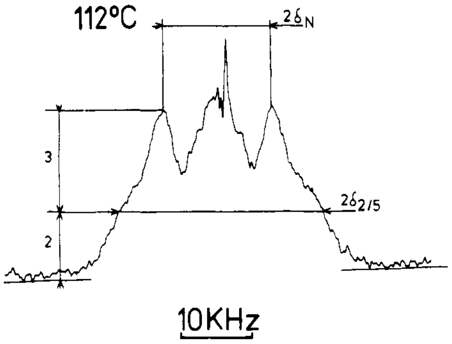


Figure 2. Typical proton NMR spectrum of DDA9 polymer dissolved 5% (w/w) in nematic PAAd14 (DDA9-H polymer at 122 °C). $2\delta_N$ reflects the order of mesogen "9" and $2\delta_{2/5}$ reflects the order of the $(CH_2)_{10}$ spacer. The ratio $\rho_{2/5} = \delta_{2/5}/\delta_N$ can be used to follow the relative order of spacer.

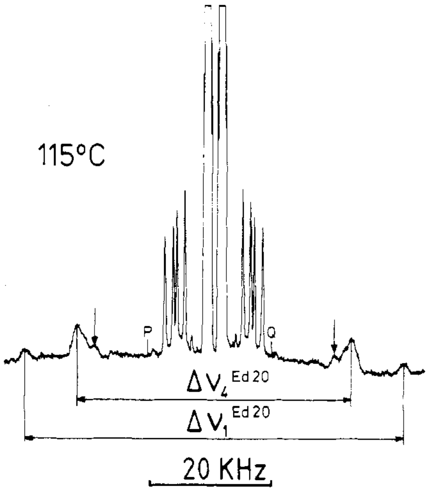


Figure 3. Typical deuterium NMR spectrum of Ed20 polymer dissolved 5% (w/w) in nematic PAAd6. The spectrum between P and Q corresponds to PAAd6 (cf. ref 15). $\Delta\nu_1{}^{Ed20}$ and $\Delta\nu_4{}^{Ed20}$ correspond to the (CD_2) groups of Ed20 polymer. The lines indicated by an arrow may correspond to deuterated monomer molecules. The ratio $\rho_{^2H\ NMR} = \Delta\nu_4{}^{Ed20}/\Delta\nu_1{}^{Ed20}$ can be used to follow the relative order of spacer.

Figure 3 shows a typical ^{2}H NMR spectrum of the Ed20/PAAd6 mixture. This spectrum is easily analyzed by analogy with the spectrum of bulk Ed20 polymer[9] (or 9DDA9-d20, a model compound consisting of a sequence mesogen–spacer–mesogen[6]), and with the spectrum of bulk PAAd6.[15] The central part between P and Q corresponds to PAAd6 (see Figure 3 in ref 15) and was used to extract S^{PAA} as explained in the preceding section. The two doublets $\Delta\nu_1{}^{Ed20}$ and $\Delta\nu_4{}^{Ed20}$ correspond to the methylene groups of the spacers of the Ed20 polymers, the former to the methylene groups attached to the ester groups and the latter to all the other methylene groups. In ref 6 and 9, it was found that in model compound 9DDA9-d20 and in bulk DDA9Ed20, respectively, $\Delta\nu_1{}^{d20}$ was practically proportional to S^{DDA9}. It is possible to estimate rather accurately the corresponding proportionality coefficient by

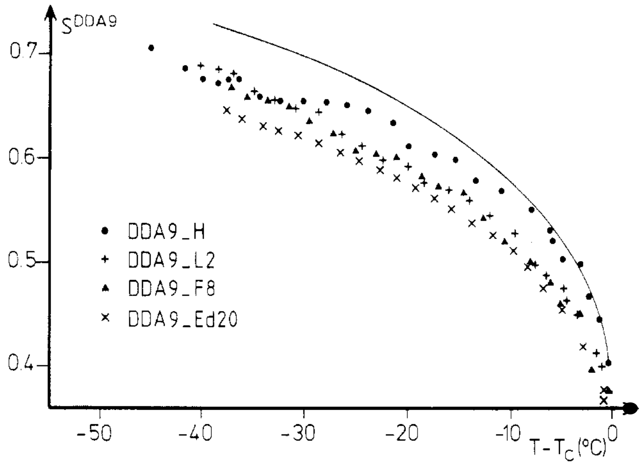


Figure 4. Order parameter vs. $T - T_C$ of DDA9 polymer for mixtures shown. The full line represents the order parameter of the solvent PAA. Note the different temperature dependences.

means of a detailed comparison of experimental and simulated ^{1}H NMR line shapes of DDA9-L polymer[5] with experimental ^{1}H NMR and ^{2}H NMR spectra of polymer DDA9-Ed20[6,9] and of model compound 9DDA9-d20.[6] The result is

$$\Delta\nu_1^{d20}/\text{kHz} = (113.3 \pm 2)S^{DDA9} \qquad (3)$$

This relation is expected to be valid for all DDA9 polymers (or oligomers) deuterated on the spacers. By analogy with $\rho_{2/5}$, the relative order of the spacers to the mesogens, as seen in this ^{2}H NMR experiment, can be characterized by the ratio $\rho_{^2\text{H NMR}} = \Delta\nu_4^{Ed20}/\Delta\nu_1^{Ed20}$.

Figure 4 shows a plot of S^{DDA9} vs. $T - T_C$ for the four mixtures studied, as well as S^{PAA} for comparison. It is observed that near T_C, S^{DDA9} is smaller than S^{PAA} but tends toward S^{PAA} when the polymer chain length increases. This is to be compared with the result concerning the depression of the clearing-point temperature ΔT_C (see section 2). Far from T_C, S^{DDA9} is definitely smaller than S^{PAA} for all samples. Figure 4 shows that the temperature dependence of solute orientational order is influenced by its chain length and that it is different from that of solvent PAA.

The order parameter S_C^{DDA9} of the polymer at the clearing point T_C can be estimated by extrapolation from a plot of S^{DDA9} vs. the corresponding values of S^{PAA}. The results are given in Table I and are shown on Figure 5b, where we have plotted S_C^{DDA9}/S_C^{PAA} vs. $\bar{x}$ ($S_C^{PAA} \approx 0.41$). Comparison with Figure 5a is instructive and indicates that the relative solute–solvent order parameter at the transition and the depression of the clearing-point temperature are closely related phenomena. This result is discussed below.

The relative order of the spacers, as deduced from a plot of $\rho_{2/5}$ vs. $T - T_C$ (see Figure 2 for definition of $\rho_{2/5}$), decreases with increasing temperature, which shows that the spacers disorder faster than the mesogens as the clearing point is approached. At the same reduced temperature the spacers are relatively more ordered in longer solute chains. In contrast, at constant chain length $\rho_{2/5}$ is independent of solute concentration and depends only on reduced temperature, as pointed out previously.[6] This last result can also be inferred from the temperature dependence of $\rho_{^2\text{H NMR}}$ (see Figure 3 for definition of $\rho_{^2\text{H NMR}}$) in the case of polymer Ed20 in bulk and in solution (5% (w/w) in PAAd6).

To summarize, for a given molecular length, the relative order of the spacers and mesogens appears to be a function of reduced temperature only, independent of concentration, i.e., of the nature of the nematic medium in which the polymer is embedded. However, this relative order depends on molecular length: it increases faster with decreasing temperature for longer polymers than for shorter ones.

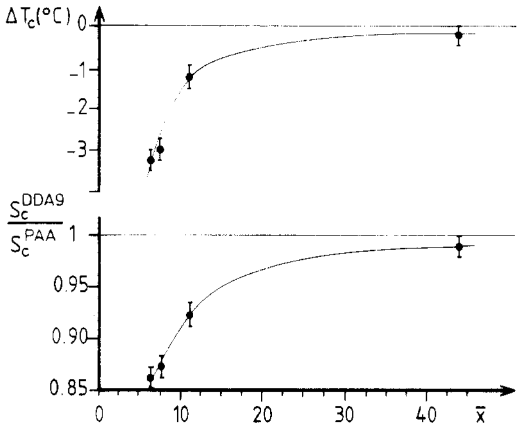


Figure 5. Depression of the clearing-point temperature ΔT_C (a) and ratio of order parameter of mesogen "9" to order parameter of PAA at the N–I transition s_C (b) vs. average degree of polymerization $\bar{x}$ in the 5% (w/w) DDA9/PAA mixtures.

4. Discussion

The main result that emerges from these data is the fact that, as in bulk, the DDA9 main-chain nematic polymers in solution in a nematic medium are in an extended conformation. This is contrary to the behavior of ordinary flexible polymers[16] or side-chain nematic polymers,[17] where the polymer chain is found to deviate only slightly from the isotropic shape. This fundamental difference arises from coupling between the alignment of the various mesogens of the same chain mediated by the nematic medium. Taking this coupling into account, a Landau-type theory of the isotropic–nematic transition shows that the effective persistence length of the polymer may become very large at the transition.[18] In other words, intrinsically flexible polymers such as DDA9[19] may appear to be "rigid" in the nematic phase.

The currently available theories[20,21] of polymer/low molecular mass nematic mixtures cannot be directly applied to analyze the present data since they do not consider this aspect of the problem. In the molecular model of Ten Bosch et al.,[20] the polymers are characterized by an inherent persistence length q. For DDA9, polymers q is similar to the size of the repeating unit, i.e., (much) less than the average polymer length $L \approx \bar{x}q$. For DDA9–L2 polymer $q/L \approx \bar{x} \approx 0.1$. Extrapolation of the theoretical results pictured in Figures 4 and 5 of ref 20 to a concentration of 5% leads to a predicted value $s_C = S_C^{DDA9}/S_C^{PAA}$ of the order of 0.25, to be compared with ~0.92 found in the present study. This discrepancy can be removed if one renormalizes q to a (much) larger value. For DDA9-H polymer where $s_C \sim 1$, we should take $q \sim L$. In short, this model may apply to our system if the inherent persistence length q is replaced by an effective persistence length $q(L)$, which is a function of the polymer length, such that $q(L) \rightarrow L$ for L very large. In other words, this theory applies if very long DDA9 polymers are assumed to be rigid.

The mean field model of nematic mixtures of Brochard et al.[21] cannot be directly applied to our problem since the nematic interaction parameters are taken to be independent of L. For dilute solutions of polymer, this theory predicts that $s_C = S_C^{DDA9}/S_C^{PAA} = u_{AB}/u_{AA}$, where u_{AB} and

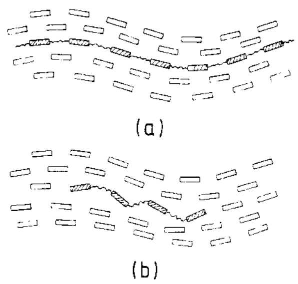


Figure 6. Proposed structure for dilute solutions of DDA9 polymers in nematic PAA: (a) very long polymer, perfect matching; (b) short polymer or oligomer, imperfect matching.

u_{AA} are the PAA/mesogen "9" and PAA/PAA nematic interaction parameters. From this theory, the finding that $s_C \rightarrow 1$ for $\bar{x}$ very large (Figure 5b) means that u_{AB} is a function of L such that $u_{AB}(L) \rightarrow u_{AA}$ for very long polymers. In this limit, the theory also predicts that both the mixtures and pure solvent have the same clearing-point temperature, as observed (Figure 5a). In short, according to the theory developed in ref 21, dilute solutions of very long DDA9 polymers in PAA are nearly ideal solutions.

In fact, the conclusions drawn from the two theories mentioned[20,21] reflect the same physical property: very long DDA9 polymers match the nematic medium almost perfectly (at least at temperatures not too far from the clearing point). The illustration we propose for such dilute solutions is sketched in Figure 6. The nematic phase is pictured as a medium where the local director fluctuates mainly due to hydrodynamic modes,[22] symbolized by the undulation in Figure 6. As a result, the polymer does not behave as a usual rigid rod but simply follows the hydrodynamic modes without perturbing the medium. As the polymer becomes shorter and shorter, the perturbation increases and this is reflected by the decrease of s_C.

At present, we do not know to what extent temperature dependence of S^{DDA9} might also be influenced by differences in polydispersity and aromatic/aliphatic end-group ratio (Table I).

Finally, it is worth noting that the present results depend crucially on the confidence put on the values of the order parameters. Extraction of absolute values of order parameters from spectroscopic data is indeed a delicate question. The methods used here are described in detail in ref 15 and 5 for PAA and DDA9, respectively. The self-consistency of the present results is a further support for these methods.

Acknowledgment. We are indebted to Drs. E. M. Stickles and O. Thomas for assistance with sample preparation and to Drs. F. Brochard, A. J. Dianoux, P. Levinson, C. Noël, P. Sixou, and M. Veyssié for fruitful discussions. This work was supported in part by National Science Foundation Grant DMR-8303989 and by NATO Research Grant No. 475.83.

Registry No. DDA9 (n = 10), 79079-27-9; (2,2′-dimethyl-4,4′-dihydroxyazoxybenzene)·(dodecanedioyl chloride) (copolymer), 79062-62-7; *p*-azoxyanisole, 1562-94-3.

References and Notes

(1) (a) "Liquid Crystalline Order in Polymers"; Blumstein, A., Ed.; Academic Press: New York, 1978. (b) "Mesomorphic Order in Polymers"; Blumstein, A., Ed.; American Chemical Society: Washington, D.C., 1978; ACS Symp. Ser. No. 74. (c) "Polymer Liquid Crystals - Science and Technology"; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1983. (d) Polym. *Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1983**, *24*, (2). (e) "Recent Advances in Liquid Crystal Polymers"; Chapoy, L. L., Ed.; Elsevier Applied Science: Essex, UK, 1984. (f) "Polymeric Liquid Crystals"; Blumstein, A., Ed.; Plenum Press: New York, 1985.
(2) Blumstein, A., Asrar, J., Blumstein, R. B. *Liq. Cryst. Ordered Fluids* 1984, *4*, 311–364.
(3) Blumstein, A.; Vilasagar, S. *Mol. Cryst. Liq. Cryst.* **1981**, *72*, 1.
(4) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.
(5) Martins, A. F.; Ferreira, J. B.; Volino, F.; Blumstein, A.; Blumstein, R. B. *Macromolecules* **1983**, *16*, 279.
(6) Volino, F.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 147.
(7) Martins, A. F.; Volino, F.; Blumstein, R. B. ref 1e, p 279.
(8) de Gennes, P.-G. 1c, p 115.
(9) Samulski, E. T.; Gauthier, M. M.; Blumstein, R. B.; Blumstein, A. *Macromolecules* **1984**, *17*, 479.
(10) Volino, F.; Giroud, A. M.; Dianoux, A. J.; Blumstein, R. B.; Blumstein, A. Proceedings International Conference on Liquid Crystals, York, England, July 1984; *Mol. Cryst. Liq. Cryst.* **1985**, *127*, 103.
(11) Fayolle, B.; Noël, C.; Billard, J. *J. Phys. Coll.*, **1979**, *40*, 3.
(12) Griffin, A. C.; Havens, S. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 259.
(13) Volino, F. Proceedings of the International Symposium on Non-Crystalline Order in Polymers, Napoli, Italy, May, 1985.
(14) Blumstein, R. B.; Stickles, E. M.; Gauthier, M. M.; Blumstein, A.; Volino, F. *Macromolecules* **1984**, *17*, 177.
(15) Dianoux, A. J.; Ferreira, J. B.; Martins, A. F.; Giroud, A. M.; Volino, F. *Mol. Cyrst. Liq. Cryst.* **1985**, *116*, 319.
(16) (a) Dubault, A.; Casagrande, C.; Veyssié, M. *Mol. Cryst. Liq. Cryst.* **1982**, *72*, 189. (b) Dubault, A. Thesis, Paris, 1981. (c) Dubault, A.; Ober, R.; Veyssié, M.; Cabane, B. *J. Phys.* (*Les Ulis, Fr.*) **1985**, *46*, 1227.
(17) (a) Weill, C. Thèse de 3ème cycle, Université Pierre et Marie Curie, Paris VI, 1984. (b) Casagrande, C.; Fabre, P.; Veyssié, M.; Weill, C.; Finkelmann, H. *Mol. Cryst. Liq. Cryst.* **1984**, *113*, 193.
(18) de Gennes, P.-G. *Mol. Cryst. Liq. Cryst.* **1984**, *102*, 95.
(19) Blumstein, A.; Maret, G.; Vilasagar, S. *Macromolecules* **1981**, *14*, 1543.
(20) Ten Bosch, A.; Maissa, P.; Sixou, P. *J. Chem. Phys.* **1983**, *79*, 3462.
(21) Brochard, F.; Jouffroy, J.; Levinson, P. *J. Phys.* (*Les Ulis., Fr.*) **1984**, *45*, 1125.
(22) Warner, M. *Mol. Phys.* **1984**, *52*, 677.