JOURNAL OF MATERIALS SCIENCE 30 (1995) 2023–2028

Nematic–smectic biphase of a main-chain liquid crystalline polyether

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Shear alignment studies of a semirigid, main-chain liquid crystalline polymer found very different behaviour within a low temperature, birefringent phase than within the higher temperature, nematic phase. Using X-ray scattering techniques and thermal analysis, the low temperature "intermediate" phase was identified as a nematic phase with approximately 5–10 vol % smectic cophase. Unique thermal characteristics of the intermediate phase are described.

1. Introduction

Recent studies on model semirigid, main-chain liquid crystalline (LC) polymers have shown that nematic ordering within the mesophase exerts strong influence on physical properties, such as viscosity and selfdiffusion [1–3]. For example, in the nematic systems investigated, data on melt viscosity, η, the tracer diffusion coefficient, D^*, and the selfdiffusion coefficient, D_s, showed that activation energies changed dramatically at phase transitions [1, 4]. Values of activation energies for diffusion within the nematic melt for these polyethers were on the same order of magnitude as nematic low molar mass (LMM) liquid crystals and less than the values that would be expected for non-LC polymers far above their glass transition temperatures [1]. Studies of the mechanism of melt diffusion within the nematic phase suggested the presence of both cooperative motion between LC polymer chains and a high degree of diffusional anisotropy [1, 2]. These intriguing results led to an interest in similar studies in a smectic mesophase, since molecular motion within the smectic mesophase will be more constrained due to positional ordering of the chains, in addition to the orientational ordering of the chains found in the nematic mesophase.

One of the model systems studied, a dihydroxy-α-methylstilbene (DHMS) based polyether, with mixed aliphatic spacer groups (DHMS-7,9), appeared to be a candidate smectic material. It had a finely textured, birefringent phase within a 30 °C temperature range below the nematic region. At the time the phase was first observed, similar DHMS containing polymers had been tentatively reported to have a smectic phase [5], although this identification was later called into question [6].

Physical property measurements on DHMS-7,9 indicated that the low temperature, intermediate phase was quite distinct from the nematic phase, and was thus potentially a smectic phase or two phases coexisting. For example, D^* and D_s had apparent activation energies with large absolute values, in contrast to values within the nematic phase which were much closer to zero. The data listed in Table I provides examples. Diffusion coefficients appeared to be far more process-dependent in the intermediate region, compared with behaviour in the nematic region. Orientation parameter measurements and thermal data within this region also showed unusual behaviour, as will be discussed in the results section.

Polarizing optical microscopy and filament tube X-ray scattering techniques did not describe the ordering within the intermediate liquid crystalline phase. After additional study with (i) electron spin resonance and (ii) X-ray diffraction using a rotating anode source, it was concluded that the intermediate phase was primarily a nematic phase with a small amount (5–10 vol %) of a more highly ordered component. By studying the thermal transition characteristics, the secondary component was determined to be a smectic phase.

This work has been contributed because such nematic–smectic biphases may be more prevalent than has been apparent in the literature until recently [7]. In the solid phase, LC and crystalline states can coexist [8]. Yet in the LC state, different isomorphic structures, i.e. order within the same mesomorphic subclass, have been understood to be immiscible [9–11]. Hence easily discernible phase separation would be expected between nematic and smectic components. In addition to apparently contradicting this miscibility rule, a nematic–smectic biphase can be easily mistaken for a pure phase, particularly if one relies solely on thermal data and optical microscopy. Concurrently, Hanna *et al.* have identified a nematic–smectic biphase in a liquid crystalline polyester

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TABLE I Apparent activation energies for melt diffusion in the intermediate and nematic phases[a]

Molecular weight (weight average)[b]	Phase	D^* (kJ mol^{-1})	D_s (kJ mol^{-1})
15 500	Biphase	84	–
	Nematic	18	–
29 000	Biphase	–	40
	Nematic	–	12
33 500	Biphase	39	–
	Nematic	1	–

[a] Diffusion data in the nematic phase, previously published in [1], is included here for comparison purposes

[b] Weight average molecular weight, M_W, of the matrix material for diffusion measurements. Tracer molecular weight, $M_W = 29\,000$

[7]. In that system, transesterification is thought to contribute to sequence segregation, which then gives rise to smectic order within an otherwise nematic melt. This paper shows that the only identification of the biphasic composition of this model LC polyether (in which no chemical mechanism exists for sequence segregation) which is consistent with the experimental data is that of a smectic–nematic biphase.

2. Experimental procedure

2.1. Materials

Monomer and polymer synthesis and molecular weight characterization for dihydroxy-α-methylstilbene based polyethers have been covered in previous publications [1, 6]. Thermal transition temperatures were obtained using a DuPont differential scanning calorimeter and a Perkin–Elmer DSC-2C differential scanning calorimeter. Heating and cooling rates varied from 5 to 20 °C min^{-1}. Mesophases and transition temperatures were first studied optically using a Leitz polarizing microscope equipped with a Mettler FP-82HT hot stage. Molecular modelling was performed using Alchemy II® 2.0 software package produced by Tripos Associates Inc.

2.2. X-ray scattering experiments

Rotating anode X-ray scattering experiments were designed to detect a volume fraction of the secondary component down to 5%, assuming a statistical profile of scatterers. To examine the intermediate phase, the sample was heated into the nematic phase (150 °C), allowed to equilibrate, cooled at 20 °C min^{-1} to 125 °C, and then cooled further at 0.5 °C min^{-1} to 105 °C, where it was held for 20 h in the X-ray beam. To examine the nematic phase, the sample was heated to 150 °C at 10 °C min^{-1} and held for 7 h. The crystalline phase was examined by cooling to 30 °C at 10 °C min^{-1}, equilibrating, and then heating to 60 °C at 10 °C min^{-1} and holding for 16 h.

The primary X-ray beam from the rotating anode source provided a flux of 10^6 counts s^{-1}. A germanium monochromator was chosen for its high resolution of 0.06 °. An aluminium cradle was designed to hold a Mettler FP-82HT hot stage, which contained the sample holder in the path of the incident X-ray beam. The sample holder consisted of a 1 mm thick piece of aluminium with a 1.5 mm diameter hole into which the sample was packed. The diffracted X-rays were monitored using a one-dimensional detector, which swept through a range of 2θ during each scan. For large diffraction angle scans, the sample was also rotated through θ to keep the primary X-ray beam passing through the centre of the sample. For the smaller diffraction angle scans $\theta = 0$ °. Monitor counts of approximately 7.5×10^6 were collected at each 2θ setting. Several scans were acquired and compiled for each set of experimental conditions for a good signal-to-noise ratio. Data were collected and analysed with Unix-based X-ray diffraction software, release 2.13, and the "C-plot" software package, both from Certified Scientific Software.

The Cornell high energy synchrotron source (CHESS) was used for real time X-ray scattering experiments, high resolution flat film experiments and X-ray rheometry. The X-ray beam had a flux of 10^{11} photons s^{-1} with 0.5 mm collimation. Kodak DEF-5, 12.5 × 12.5 cm, flat film was used at a camera length of 80 mm to record the diffracted beam. For dynamic experiments, a one-dimensional Oma III detector modified for use with X-rays was used in place of the flat film to observe the changes in microstructure at rates of up to 15 μs per scan.

To probe the change in the microstructure of the material under the influence of a shear field, an X-ray shear cell developed by the Dow Chemical Company was used at CHESS. The cell consisted of two parallel plates of boron nitride that were independently heated to control the temperature of the sample from room temperature up to at least 350 °C. A shroud surrounding both the fixed plate and the rotating plate served to maintain a stable temperature and to allow for a degree of environmental control. The plates were mounted perpendicular to the incoming X-ray beam. The shear field for a given sample thickness was determined by the rate of rotation of the spinning plate and by the position of the X-ray beam from the centre of the plate. A more complete description of the device is detailed elsewhere [12].

3. Results and discussion

An illustration of the semirigid liquid crystalline model system, DHMS-7,9 is shown in Fig. 1. Upon melting, at T_m, but below the transition to the nematic mesophase, T_{xn}, shown in Fig. 2, DHMS-7,9 forms a finely textured, birefringent phase as seen with polarizing optical microscopy. The micrographs in Fig. 3 illustrate the textural differences between the intermediate and nematic phases. Fig. 2 illustrates the thermal transitions of the low molecular weight DHMS-7,9 sample (number average molecular weight, $M_n = 6000$) chosen for the rotating anode experiments, because it is characteristic of samples with $M_n = 5000$ and higher. The high viscosity of the intermediate phase prevents the development of an optically identifiable texture. The phase is not present within oligomers studied, but does appear in samples with M_n above 5000. The intermediate to nematic transition temperature increases to 130 °C as molecular

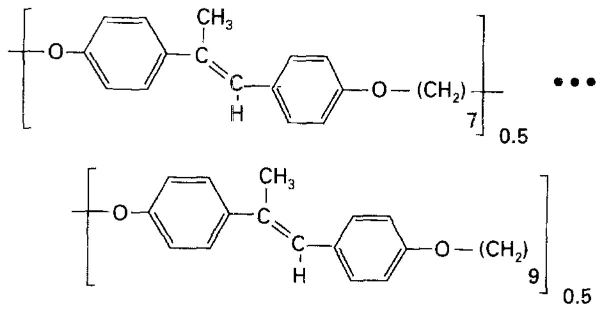

Figure 1 Chemical structure DHMS-7,9 model LC polymer.

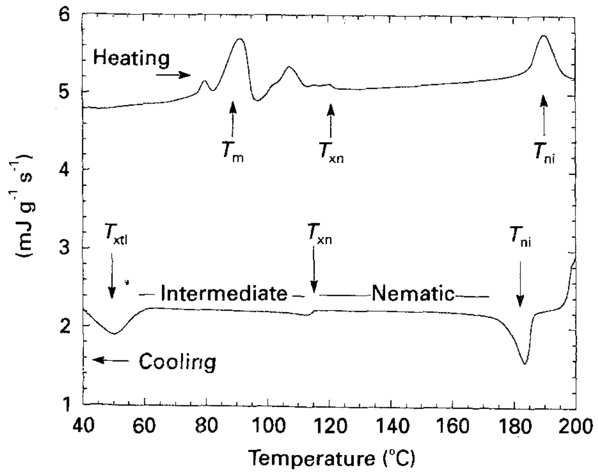

Figure 2 Differential scanning calorimetry data for DHMS-7,9 (M_n = 6000). Temperatures for melting, T_m, the intermediate (biphase) to nematic transition, T_{xn}, clearing, T_{ni}, and crystallization, T_{xtl}, are indicated with arrows. On the cooling curve, the nematic and intermediate phases are designated.

weight increases to 20 000. Fig. 4 shows the trend in the transition at T_{xn} and the clearing transition, T_{ni}, with increasing molecular weight.

Shear alignment behaviour of the intermediate phase contrasts sharply with alignment behaviour of the nematic phase. X-ray rheometry was used to measure the orientation parameter of DHMS-7,9 during steady state shear at 1 s^{-1}, as shown in Fig. 5. The orientation parameter, S, can be defined to measure deviation from the nematic director as

$$S = 0.5[3 < (\cos\theta_n)^2 > -1]$$

where θ_n is the angle between the backbone of the polymer and the nematic director. For an isotropic melt, convention defines $S = 0$, while $S = 1$ denotes perfect alignment. For the points attainable*, DHMS-7,9 appeared to exhibit an increase in the value of the orientation parameter with temperature within the intermediate phase, followed by a decrease within the nematic phase, and little change within the isotropic phase.

This shear alignment behaviour along with the rheological observations [4], magnetic alignment observations†, and diffusion behaviour [1] could be caused by either

1. a nematic–crystalline biphase,
2. nematic–smectic biphase, or
3. a pure smectic phase.

X-ray diffraction studies, however, rule out the possibility of a pure smectic phase. Flat film synchrotron diffractograms in static mode and dynamic mode experiments using a one-dimensional detector showed no evidence for a smectic or crystalline component between T_m and T_{xn} for samples with various molecular weights.

Rotating anode experiments were therefore designed to identify a fraction between 5 and 10 vol % [13]. A low molecular weight sample was chosen for its lower viscosity and, presumably, more rapid growth of the secondary phase. The solid–mesophase transition was not a concern during the cooling cycle, since the sample was not undercooled. Optical observations and dynamic X-ray diffraction analysis of this

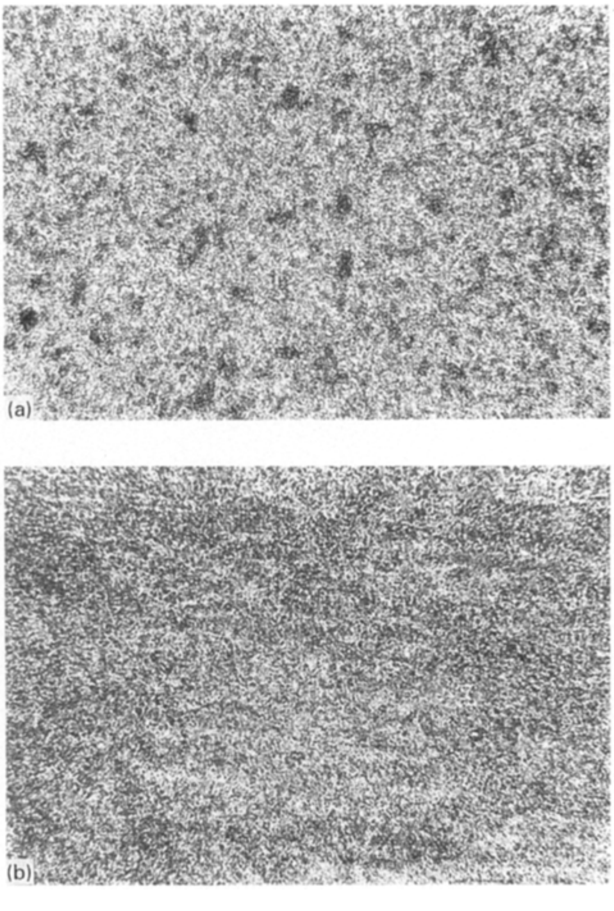

Figure 3 Polarizing optical microscopy of (a) the intermediate phase at 115 °C and (b) the nematic phase at 150 °C.

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*Attempts to shear align with the X-ray rheometer at temperatures slightly below the nematic regime were successful for only two points. At very low shear rates, DHMS-7,9 within its intermediate phase could be sheared uniformly, but as shear rates increased to 1 s^{-1}, the sample began to break up. Upon cooling, the solid sample pealed into concentric rings.

†X-ray rheometry results are supported by measurements of orientation in bulk samples aligned in a 13.5 Tesla magnetic field at the Bitter National Magnet Laboratory. Samples aligned at temperatures slightly below T_{xn} showed a lower degree of orientation after 2 h than did samples aligned at temperatures above T_{xn}. The sluggish response to the same applied field implied that the intermediate phase has a lower degree of freedom.

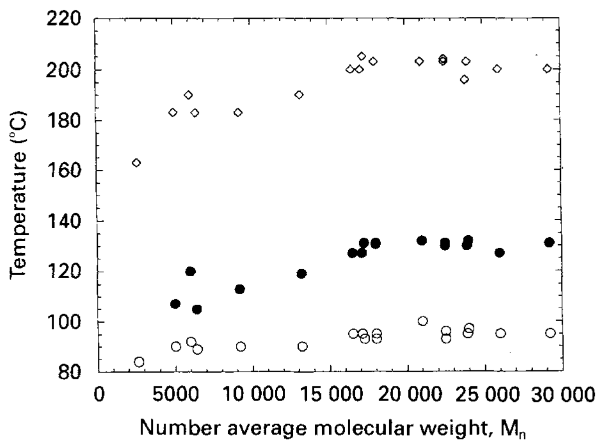

Figure 4 Transition temperatures as a function of molecular weight. The melt transition (○), the biphase–nematic transition (●) and the nematic–isotropic transition (◇) are shown. The sample at $M_n = 6000$ had a very narrow molecular weight distribution and hence somewhat higher transition temperatures than the other samples in the low range.

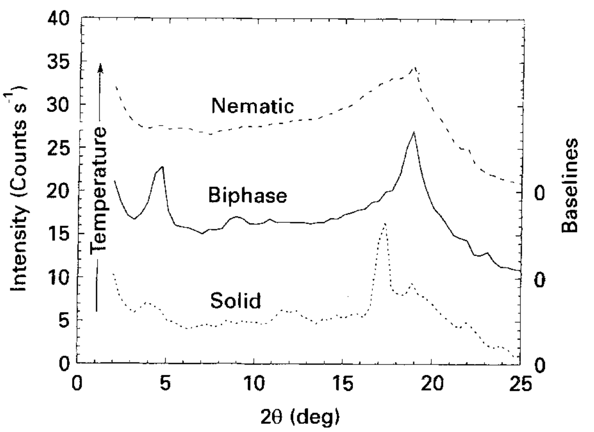

Figure 6 Rotating anode X-ray diffraction results for DHMS-7,9 ($M_n = 6000$) annealed in the nematic (150 °C, – – – –), biphase (105 °C, ———) and semicrystalline solid regions (60 °C, ...). All data is plotted on the same scale (shown for solid on left axis); baselines are shifted. $\theta = 1$–$12.5°$ and $2\theta = 2$–$25°$.

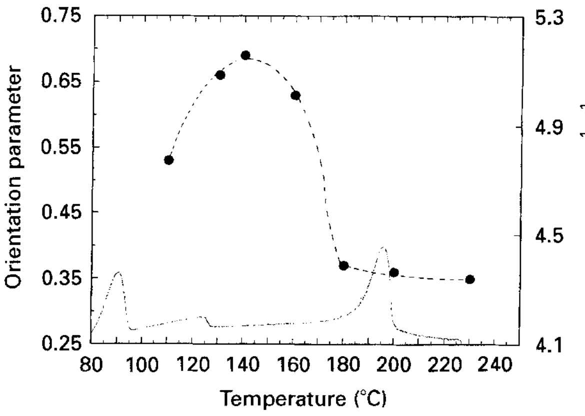

Figure 5 Orientation parameter during steady state shear (●) is plotted with differential scanning calorimetry data for DHMS-7,9 ($M_n = 14500$).

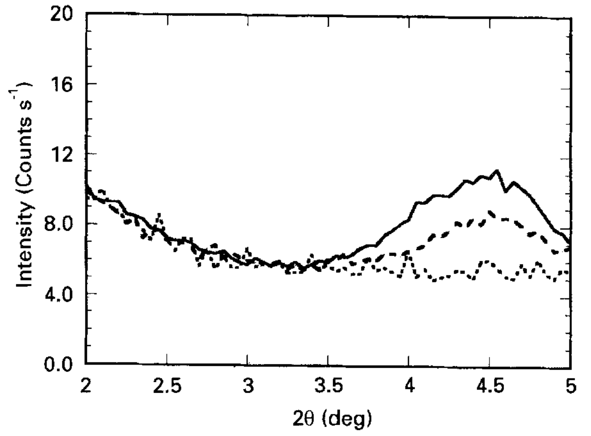

Figure 7 Rotating anode X-ray diffraction results at $\theta = 0$. Scan 1 (...) is at time 0, scan 2 (– – – –) is at time ≈ 4 h, scan 3 (———) is at time ≈ 15 h. Temperature is 105 °C, within the biphasic region.

sample show no change in texture over very long annealing times (> 6 h) between T_m and T_{xn}. The intermediate phase was observed at 105 °C, the nematic phase at 150 °C and the solid phase at 60 °C.

X-ray data collection focused on the smectic spacing region, 2–5 nm, at high resolution. Results (shown in Fig. 6) indicated that the ordered component within the intermediate phase was distinct from the crystalline phase. The intermediate phase showed two intense reflections: the wide angle reflection corresponding to nematic order, and the low angle reflection corresponding to a correlation length typical of smectic order. In between the θ–2θ scans, the small angle region was observed with a 2θ scan at fixed θ. These data, taken at three different times and plotted in Fig. 7, show none of the sharpness seen in Fig. 6. While the possibility that the peak sharpness seen in the wide-angle region of Fig. 6 is due to some crystalline order evolving over time cannot be ruled out, as has been observed in LC polyesters [14, 15], the apparent sharpness is also consistent with statistical fluctuation. Better count statistics would be required to prove the existence of crystalline order.

The *d*-spacings of the peaks in Fig. 6 are listed in Table II. Comparing the measured *d*-spacings with dimensions of the average monomer length calculated with molecular modelling software*, it was determined that the component could be either smectic A or smectic C. Given the "kink" that the ether linkage may be expected to impart upon the chain, the smectic C may be the more probable choice. Yet the absence of identifiable texture makes it difficult to distinguish clearly between smectic A and C order, or to refute the idea that it could be a cybotactic nematic phase.

Electron spin resonance (ESR) data provide supporting evidence of a two component phase, as opposed to a single cybotactic nematic mesophase. DHMS-7,9 was labelled with a free radical-containing moiety [16] and studied using high field and X-band techniques. Preliminary results indicate that two phases are present in the intermediate temperature

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*After energy minimization using Alchemy™, the dimension of DHMS from oxygen to oxygen is 1.2 nm, the width across the phenyl ring is 20.5 nm. The average length of the spacer group, assuming full extension, is 1.37 nm. Thus the monomer length is approximately 2.6 nm.

TABLE II *D*-spacings for DHMS-7,9 in three phases

Solid (nm)	Biphase (nm)	Nematic (nm)
0.401	0.401	0.401
0.467	0.467[a]	0.467[a]
0.512[a]		
	0.980	
1.040		
	1.860[a]	
2.210		

[a] Indicates intense peaks in Fig. 6

region, while one phase is present in the nematic region [17]. Since previous low field experiments using an unattached probe did not distinguish between the intermediate phase and the nematic phase, one can estimate that the secondary component has a concentration below 10%.

Confirmation that the secondary component in the intermediate phase has smectic order comes from the thermal analysis data in Fig. 1. The transition at T_{xn} is reproducible on heating and cooling, and as can be seen in Fig. 1, little undercooling is observed. Various annealing cycles have been shown by X-ray diffraction analysis to produce different crystalline forms of the polymer that vary in T_m by 20 ° [1]. In each thermal treatment studied, however, the position of T_{xn} is not affected. Both of these observations are characteristic of mesophase behaviour [18]. The observation that the transition temperature, T_{xn}, is affected by increasing molecular weight to a greater degree than is T_m fits in with this argument as well [18], since end-groups will have a greater effect on LC transitions than on a melt transition [19]. Hence the ordered secondary phase must be a smectic cophase.

The intermediate–nematic transition has a unique thermal response that has made it difficult to identify the secondary component purely from thermal data. In Fig. 5, one can see that in higher molecular weight samples for which secondary melting peaks are absent, there is a slow rise on the left-hand side of the transition and a sharp fall on the right-hand side of the transition. The shape of this transition on the DSC plot is both characteristic and reproducible at all heating rates. The effect of polydispersity on the shape of the transition is slight. Lower polydispersity fractions will show a sharper peak with better definition. Yet, in all cases, the shape of the peak prevents a simple computation of the heat of transition. It does appear that the enthalpy of the intermediate–nematic transition is less than that of either the melt or clearing transitions, again implying that the transition is a mesophase–mesophase transition.

Analogous polyesters based on the DHMS mesogen and an equimolar ratio of spacer groups, seven and ten carbons in length, did not show this intermediate transition. Number average molecular weights up to 25 000 by gel permeation chromatography were examined and found to be nematic over the LC region [20]. DHMS based polycarbonates do not show an intermediate transition either. They are monotropic, demonstrating only a nematic phase prior to crystallization during cooling from the isotropic melt [21]. However, an intermediate phase similar in nature to the one identified in DHMS-7,9 was observed in polyethers using a single spacer, nine carbons in length, and mixed mesogens (80% DHMS and 20% 2,2′-dimethyl-4,4′-dihydroxyazoxybenzene) [3].

The smectic component may arise from a particular sequence of monomers that yield a block-copolymer-like segment within the otherwise random copolymer chains. The sequences must be formed during synthesis, as no chemical mechanisms exist to allow sequence segregation within the melt. If these blocky segments tend to form smectic order, it might be expected that the regions would phase separate, since nematic and smectic phases are immiscible [9]. If the minor component forms from a blocky segment rather than from a free polymer chain, with this particular sequence distribution that would explain why every fraction above $M_n = 5000$ demonstrates an intermediate phase, and no amount of "purification" removes the transition. Thus, the effect is not caused by a chemical impurity, or by molecular weight heterogeneity. The blocky segment hypothesis also explains why a change in the texture of the intermediate phase with time cannot be observed visually. The microphase separation of the blocky segment would be held in place by the rest of the random copolymer chain, similar to the segregation of entanglements observed in polymeric smectics [22]. The increase in orientation parameter with temperature within the intermediate phase may be due to an increase in the equilibration time associated with the changes within the smectic component as temperature increases.

This study supports recent work on random LC polyesters comprised of 1-hydroxy-4-benzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), which were studied to answer the question of how solid phase crystallinity could evolve even when quenching was rapid [7]. Discovery of a minor smectic component (which could serve as nucleation sites for crystal growth) within an otherwise nematic mesophase explained the fast crystallization kinetics. These studies showed the smectic phase had important consequences on the solid structure formation [14, 15].

An integral part of the conclusions about the biphase in the HBA–HNA system was the large role of transesterification in the formation of the smectic component [7], as opposed to diffusion of the rigid chains. In DHMS-7,9, diffusion is the only mechanism available for segregation of blocky sequences and the formation of more highly ordered phases. Furthermore, a previous study on LC polyesters has shown that chemical heterogeneity can be quite prevalent in "random" copolymer systems [23]. Hence, this work suggests that the explanation of transesterification to induce sequence segregation is most likely not required for the formation of smectic–nematic biphases in polyester systems.

In summary, the intermediate phase of DHMS-7,9 polyether has been identified as a smectic–nematic biphase, with the amount of smectic component estimated to 5–10%. This very small amount of secondary component has been shown to have a large effect on the physical properties of an LC polymer. The characteristics of the thermal transition to the nematic phase are thought to be unique to this class of polyethers, although the presence of the low temperature biphase is perhaps more common.

Acknowledgements

Support for this study came from the National Science Foundation. The authors wish to acknowledge J. Brock (Cornell) for access to his rotating anode source and W. Podulka (Cornell) for his help with the data analysis; R. Bubeck (Dow) for use of the X-ray rheometer; R. Colby and J. Gillmor (Kodak) for advice on the rheological experiments; D. Xu, J. Moscicki and J. Freed (Cornell) for ESR studies; and O. Thomas (Dow) and A. Windle (Cambridge) for helpful discussion. V. Tsukruk (West Michigan) is particularly thanked for his advice on the design of the rotating anode experiments.

References

1. E. HALL, C. K. OBER, E. J. KRAMER, R. H. COLBY and J. R. GILLMOR, *Macromol.* **26** (1993) 3764.
2. E. HALL, C. K. OBER and G. GALLI, *Liquid Cryst.* **14** (1993) 1351.
3. E. HALL, C. K. OBER, E. J. KRAMER, R. H. COLBY, J. R. GILLMOR and G. GALLI, *Mater. Res. Soc. Symp. Proc.* **248** (1992) 113.
4. J. R. GILLMOR, R. H. COLBY, E. HALL and C. K. OBER, *J. Rheol.* **38** (1994) 1623.
5. V. PERCEC, T. D. SHAFFER and H. NAVA, *J. Polym. Sci., Lett. Ed.* **22** (1984) 637.
6. V. PERCEC, H. NAVA and H. JONSSON, *J. Polym. Sci. A., Polym. Chem.* **25** (1987) 1943.
7. S. HANNA, A. ROMO-VRIBE and A. H. WINDLE, *Nature* **366** (1993) 546.
8. J. CAMPOY, C. MARCO, M. A. GOMEZ and J. G. FATOU, *Polym. Bull.* **27** (1991) 81.
9. H. SACKMANN and D. DEMUS, *Mol. Cryst. Liq. Cryst.* **21** (1973) 239.
10. C. NOEL, in "Polymeric Liquid Crystals", edited by A. Blumstein (Plenum, New York, 1985) p. 2.
11. G. HARDY, F. CSER, K. NYITRAI and K. KISS, in "Liquid Crystals and Ordered Fluids", Vol. 4, edited by A. Griffin and J. F. Johnson (Plenum, New York, 1984) p. 1061.
12. S. MCNAMEE, PhD thesis, Cornell University (1994).
13. V. TSUKRUK, University of West Michigan, Private communication.
14. D. J. WILSON, C. G. VONK and A. H. WINDLE, *Polymer* **24** (1993) 227.
15. S. HANNA and A. H. WINDLE, *ibid.* **33** (1992) 2825.
16. D. XU, J. K. MOSCICKI, J. H. FREED, E. HALL and C. K. OBER, *Liq. Cryst.* in preparation.
17. D. XU, J. K. MOSCICKI, D. BUDIL and J. H. FREED, Unpublished data.
18. C. NOEL and P. NAVARD, *Prog. Polym. Sci.* **16** (1991) 55.
19. Y. S. FREIDZON, N. I. BOIKO, V. P. SHIBAEV and N. A. PLATE, *Dokl. Akad. Nauk SSSR* **304** (1989) 1419.
20. E. HALL, PhD thesis, Cornell University (1994).
21. Y. Y. CHEN, P. CEBE, H. SCHREUDER-GIBSON, A. BLUM and W. YOEMANS, *Macromol.* **27** (1994) 5440.
22. S. D. HUDSON, A. J. LOVINGER, M. A. GOMEZ, J. LORENTE, C. MARCO and J. G. FATOU, *ibid.*, **27** (1994) 3357
23. C. K. OBER, S. McNAMEE, A. DELVIN and R. COLBY, in "Liquid-Crystalline Polymers", edited by R. A. Weiss and C. K. Ober, ACS Symposium Series 435, American Chemical Society (Washington, DC, 1990) p. 220.

Received 3 March
and accepted 11 August 1994