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Synthesis and characterization of spin-labelled and spin-probed side-chain liquid crystal polymers

David Stewart and Corrie T. Imrie*
Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, UK
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A synthetic methodology is reported for the preparation of spin-labelled side-chain liquid crystal polymers in which the label is covalently attached to the polymer backbone. Thus, a mesogenic methacrylate, 6-(4-methoxy-4′-oxy-azobenzene) hexyl methacrylate, was copolymerized with methacryloyl chloride and the resulting copolymer esterified using 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-hydroxy TEMPO). Unreacted acid chloride groups were subsequently esterified using methanol. The analogous 6-(4-methoxy-4′-oxy-azobenzene) hexyl methacrylate/methyl methacrylate copolymer not containing the spin-label was also prepared and doped with a nitroxide radical, 4-oxo-2,2,6,6-tetramethylpiperidinyloxy (4-oxo-TEMPO). The thermal behaviour of the labelled and unlabelled polymers was identical, both exhibiting nematic behaviour. The electron spin resonance (e.s.r.) spectra of the labelled and probed systems have been recorded as a function of temperature. The temperature at which the extrema separation in the e.s.r. spectrum is 50G (T_{50G}) for the spin-probed polymer was estimated to be approximately equal to the onset temperature of the glass transition as determined by differential scanning calorimetry. This unusual result is rationalized by proposing that the spin probe is preferentially dissolved in the side-chains. Thus T_{50G} correlates with a relaxation process of the side-chains. By comparison, T_{50G} for the labelled polymer is equal to the onset temperature of the nematic–isotropic transition suggesting that T_{50G} may correlate with a confinement of the polymer backbone by the nematic field. Copyright © 1996 Elsevier Science Ltd.

(Keywords: side-chain liquid crystal polymers; e.s.r. spectroscopy; free radicals)

INTRODUCTION

Side-chain liquid crystal polymers (SCLCPs) continue to be the focus of considerable research interest. Much of this activity can be attributed to the application potential of SCLCPs in a wide range of advanced electro-optic technologies including, for example, information storage[1], holographic imaging[2], and non-linear optics[3]. It should not be overlooked, however, that SCLCPs are also of fundamental interest as they provide a demanding challenge to our understanding of the factors that promote self-organization in condensed matter[4–6].

A SCLCP consists of three structural units; a polymer backbone, a mesogenic unit and a flexible spacer which attaches the mesogen to the polymer. The chemical structures of each of these components have been varied in a systematic fashion which in turn has allowed for the development of empirical rules relating molecular structure to the macroscopic transitional properties[4–6]. These permit the rational design of new materials having targeted properties. By comparison the dynamics and ordering of these structural units within the mesophases and glass phases have received much less attention although we should note that important studies have employed ^{2}H nuclear magnetic resonance (n.m.r.) spectroscopy[7] and dielectric relaxation spectroscopy[8]. This is a somewhat surprising situation as the microscopic behaviour will, to a large extent, determine the performance of the polymer in many of the proposed applications. A technique which has been used with considerable success in the characterization of low molar mass liquid crystals is electron spin resonance spectroscopy (e.s.r.)[9,10]. This has also been used extensively in the characterization of polymer systems[11].

Surprisingly, however, e.s.r. has been used rarely in the characterization of SCLCPs[12–15] although it offers much potential for the determination of dynamic and structure parameters in such materials. The e.s.r. experiment requires the sample either to be spin-labelled (i.e. a free radical is attached covalently to the SCLCP) or spin-probed (i.e. a free radical is physically dispersed in the sample). The latter experiment is the more straightforward, although the results may be ambiguous because of the uncertainty in the location of the probe molecule within the system as compared to a chemically attached label at a well-defined site. It is worth noting, however, that the two experiments, if performed on the same sample, often provide useful complementary information[11]. To our knowledge only the spin-probe experiment has been performed using SCLCPs[12–15]. Spin-labelled SCLCPs have attracted attention recently as potential organic magnets and the label has either been attached to the terminal chain of the mesogenic group[16] or incorporated directly into the mesogen[17].

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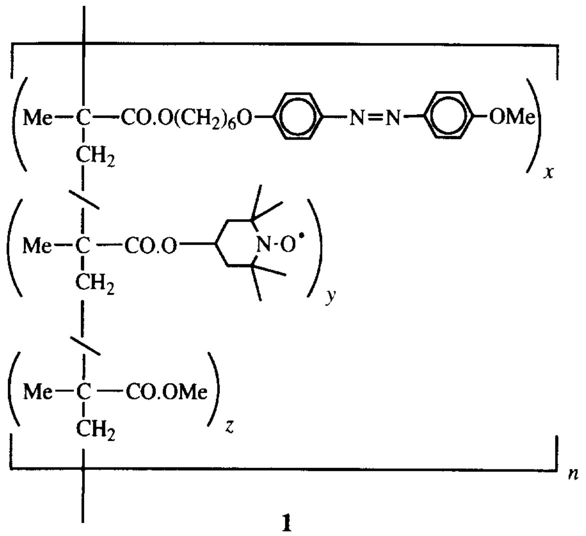
* To whom correspondence should be addressed



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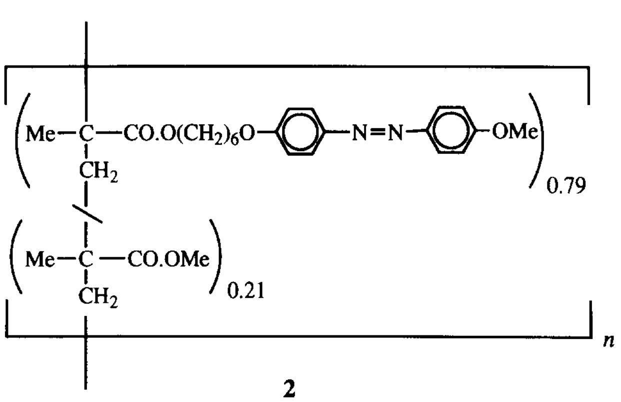

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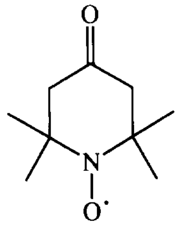

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Unfortunately, these materials have not been characterized using e.s.r. spectroscopy.

In this paper we report a synthetic methodology for the preparation of spin-labelled SCLCPs in which the label is covalently attached to the macromolecular backbone. Using this route we prepared the spin-labelled polymer, **1**, and also measured its e.s.r. spectrum as a function of temperature. In order to compare the behaviour of **1** with a spin-probed system, we prepared polymer **2** and doped it with 4-oxo-2,2,6,6-tetramethylpiperidinlyloxy (4-oxo-TEMPO), **3**.

EXPERIMENTAL

The synthetic route used for the preparation of polymers **1** and **2** is shown in *Scheme 1*.

Materials

Benzene was distilled over calcium hydride. 1,6-Dibromohexane, methyl methacrylate (from calcium hydride) and methacryloyl chloride were purified by vacuum distillation. AIBN was recrystallized from toluene, washed with petroleum spirits (80–100°C) and dried under vacuum. All other reagents were used as received.

4-Hydroxy-4′-methoxy-azobenzene (**4**) was prepared according to the method described by Steinstrasser and Pohl[18]. Thus, a solution of sodium nitrite (28.9 g, 419 mmol) in distilled water (150 ml) was added slowly with vigorous stirring to a solution of *p*-anisidine (50.4 g, 409 mmol) in 3 M hydrochloric acid (500 ml) at 0°C. The resulting diazonium salt solution was then slowly added to a stirred solution of phenol (39.4 g, 419 mmol) in 10% aqueous sodium hydroxide (400 ml) at 0°C. The dark brown suspension was acidified and the precipitate collected. The crude product was washed with copious amounts of water and dried under vacuum.

Yield: 79.6 g, 85%; m.p.: 139–141°C. Infra-red (i.r.) (KBr): 3412 cm^{-1} (OH). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 7.0, 7.9 (m, aromatic, 8H), 3.9 (s, ArO$\underline{CH_3}$, 3H).

1-Bromo-6-(4-methoxy-azobenzene-4′oxy)hexane (**5**) was prepared using the procedure described by Attard *et al.*[19]. Thus, a mixture of **4** (14.5 g, 63.6 mmol), 1,6-dibromohexane (119.5 g, 490 mmol), potassium carbonate (70.0 g, 507 mmol) and acetone was refluxed, with stirring, for 24 h. The reaction mixture was filtered hot and the residue washed with acetone. The acetone was removed under reduced pressure and petroleum ether (40–60°C) added to the concentrated organic extracts. The resulting precipitate was collected and dried. The crude product was recrystallized with hot filtration from ethanol.

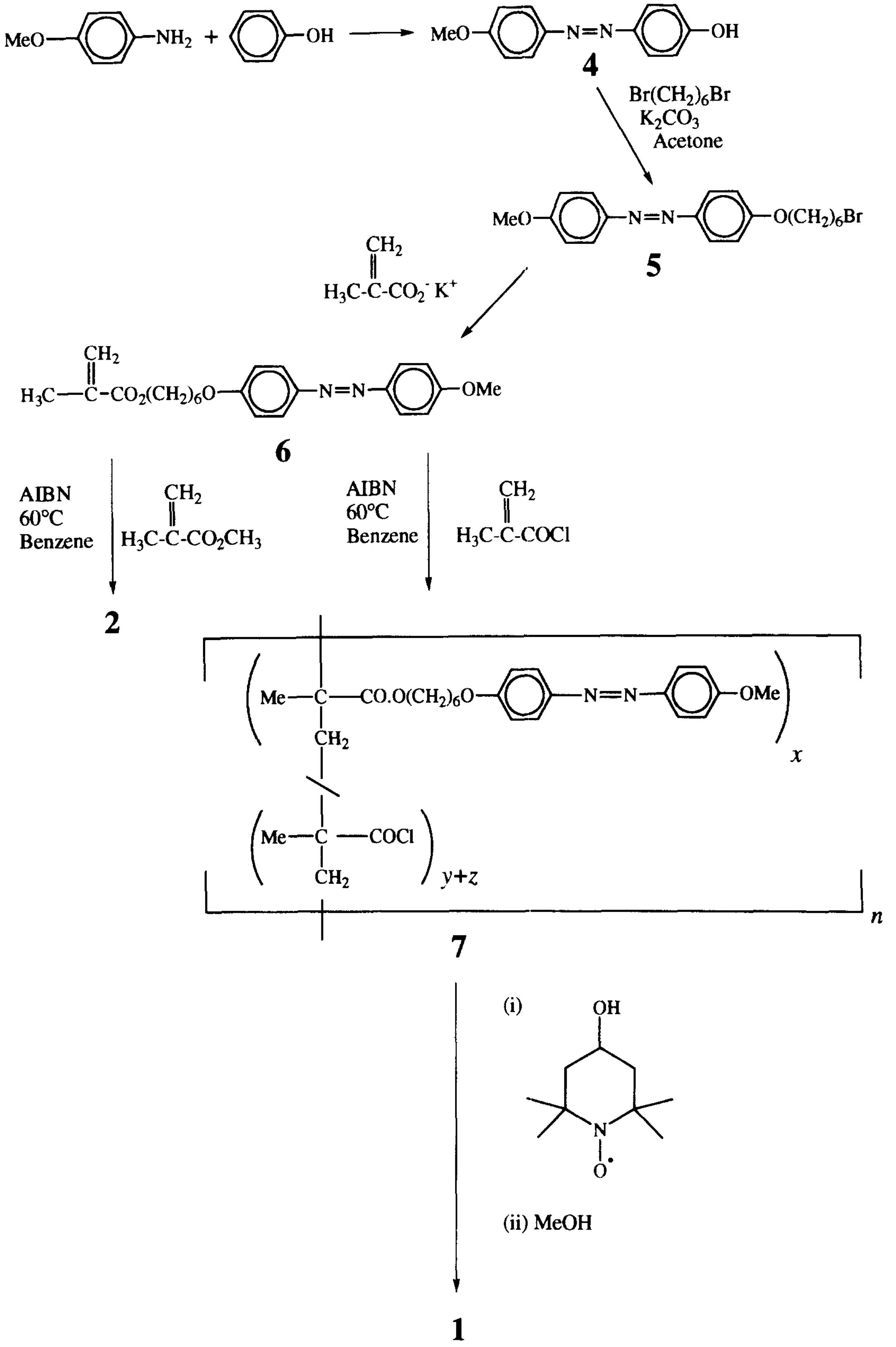
Yield: 11.5 g, 46%; m.p.: 102–104°C. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 7.0, 7.9 (m, aromatic, 8H), 4.0 (t, O$\underline{CH_2}$, 2H, $J = 6.4$ Hz), 3.9 (s, ArO$\underline{CH_3}$, 3H), 3.4 (t, $\underline{CH_2}$Br, 2H, $J = 6.7$ Hz), 1.5–1.9 (m, $CH_2(\underline{CH_2})_4CH_2$, 8H).

6-(4-Methoxy-4′-oxy-azobenzene) hexyl methacrylate (**6**) was prepared using the procedure described by Craig and Imrie[20]. Methacrylic acid (5.6 g, 65 mmol) was added dropwise to potassium hydrogen carbonate (6.3 g, 63 mmol) and stirred at room temperature for 5 min to form potassium methacrylate. A solution of 1-bromo-6-(4-methoxy-azobenzene-4′-oxy) hexane (11.4 g, 29.1 mmol) and hydroquinone (0.02 g, 0.18 mmol) in *N*,*N*′-dimethylformamide (500 ml) was added to the potassium methacrylate and the resulting mixture stirred at 100°C for 24 h. The reaction mixture was allowed to cool and added to distilled water (500 ml). The resulting precipitate was collected and redissolved in dichloromethane. The organic solution was washed twice with 5% aqueous sodium hydroxide solution and twice with water, dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was recrystallized with hot filtration from ethanol.

Yield: 6.2 g, 54%; m.p.: 88–89°C. I.r. (KBr): 1707 cm^{-1} (vs C=O). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 7.0, 7.9 (m, aromatic, 8H), 5.5, 6.1 (s, $\underline{CH_2}$=C-, 2H), 4.2 (t, $\underline{CH_2}$-O.OC-, 2H, $J = 6.6$ Hz), 4.0 (t, ArO$\underline{CH_2}$, 2H, $J = 6.4$ Hz), 3.9 (s, ArO$\underline{CH_3}$, 3H), 1.2–2.0 (m, $CH_2(\underline{CH_2})_4CH_2$, $\underline{CH_3}$C(CO.O), 11H).

Polymerization

Appropriate amounts of the two comonomers, i.e. **6** and either methyl methacrylate or methacryloyl chloride, were dissolved in benzene and 1 mol% AIBN added as



Scheme 1

initiator. The reaction mixture was degassed under vacuum using the freeze–pump–thaw method and flushed with argon for 10 min. The reaction mixture was heated in a water bath at 60°C to initiate the copolymerization. For copolymer **2** the copolymerization was terminated after 48 h by precipitation into methanol. The copolymer was purified by repeated dissolution in chloroform and precipitation into petroleum spirit (40–60°C). For copolymer **3**, after 48 h, the reaction mixture was diluted using benzene (30 ml) and a solution of 4-hydroxy-2,2,6,6-tetramethylpiperdinyloxy (4-hydroxy TEMPO) (0.3 g, 1.75×10^{-3} mol) in pyridine (5 ml) added. The reaction mixture was allowed to stir at 60°C overnight under a positive pressure of argon. The nitroxide-labelled polymer was then collected and purified in an identical manner to that

Table 1 Molecular weights and thermal properties of the copolymers

Polymer	Conversion (%)	M_n (g mol^{-1})	Polydispersity	DP	T_g (°C)	T_{NI} (°C)	ΔH_{NI} (J g^{-1})
1	78	6100	2.42	18	69	118	2.93
2	82	5420	2.96	16	68	114	3.22
2 + **3**^{a}		–			71	114	3.22

^{a} Copolymer **2** doped with nitroxide radical **3**

described for **2**. The i.r. spectra of **1** did not contain peaks associated with the carboxylic acid group. It is assumed, therefore, that any acyl chloride groups which did not react with 4-hydroxy TEMPO instead reacted with methanol yielding the methyl ester.

Copolymer **2**: ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 6.9, 7.8 (m, aromatic, 1.00 H), 3.9–4.1 (m, $\underline{CH_2}$-O.OC-, ArO$\underline{CH_2}$, 0.50 H), 3.8 (s, ArO$\underline{CH_3}$, 0.37 H), 3.6 (s, $\underline{CH_3}$-O.OC-, 0.10 H), 1.1–2.2 (m, $CH_2(\underline{CH_2})_4CH_2$, 1.40 H), 0.7–1.1 ($\underline{CH_3}$C(CO.O), 0.50 H).

Spin-probing

1.5 ml of a solution of 4-oxo TEMPO (5×10^{-3} g, 2.94×10^{-5} mol) in dichloromethane (100 ml) was added to a solution of **2** (0.5 g) in dichloromethane (20 ml). This solution was allowed to stir at room temperature overnight and then evaporated under reduced pressure. The spin-probed sample was dried under vacuum overnight.

CHARACTERIZATION

The proposed structures of all the products, except the spin-labelled polymer, were verified by ^{1}H n.m.r. spectroscopy using a Bruker AC-F 250 MHz n.m.r. spectrometer and by Fourier transform infra-red (*FT* i.r.) spectroscopy using a Nicolet 205 *FT* i.r. spectrometer. The molecular weights of the copolymers, **2** and **3**, were determined by gel permeation chromatography (g.p.c.) using a Knauer Instruments chromatograph equipped with two PL gel 10 μ mixed columns and controlled by PL GPC SEC V5.1 software. Chloroform was used as the eluent and the chromatograph was calibrated against polystyrene standards.

The thermal behaviour of the materials was characterized by differential scanning calorimetry (d.s.c.) using a Polymer Laboratories PL-DSC equipped with an autocool accessory and calibrated using an indium standard. The time–temperature profile was identical in each case. Thus, each sample was heated from −20 to 200°C, isothermed at 200°C for 3 min, cooled from 200 to −50°C, isothermed at −50°C for 3 min, and finally reheated from −50 to 200°C. The heating and cooling rates in all cases was 10°C min^{-1}. Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit.

The e.s.r. spectra were recorded using a Bruker ECS 106 ESR spectrometer equipped with a Eurotherm variable temperature controller. Each sample was heated from 263 K to 408 K, cooled from 408 K to 263 K and reheated. Spectra were recorded at 5 K intervals and the sample was allowed to isotherm at the temperature for 5 min prior to recording the spectrum.

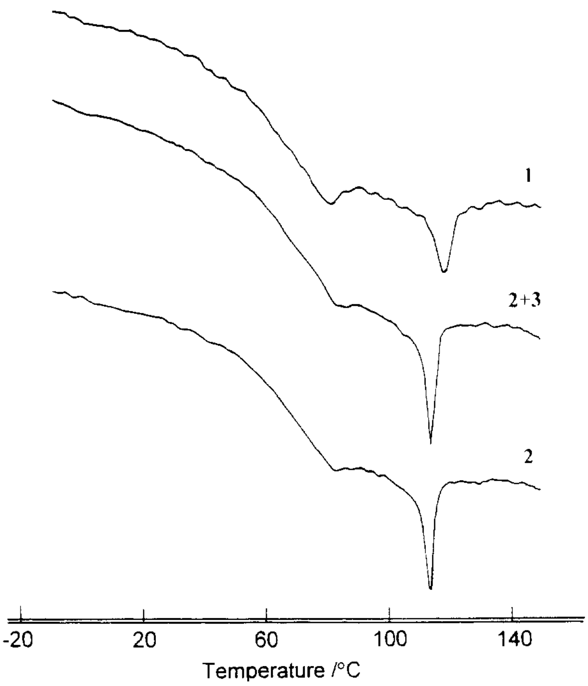


Figure 1 D.s.c. second heating traces for copolymers **1** and **2**, and for **2** doped with the nitroxide spin-probe **3**

RESULTS AND DISCUSSION

The composition of copolymer **2** was established using ^{1}H n.m.r. spectroscopy. This was not possible for the spin-labelled polymer **1** but, as we will see, the thermal behaviour of **1** and **2** is identical implying the chemical composition is similar. This view is supported by e.s.r. spectroscopy which suggests that the mole fraction of nitroxide label incorporated in **1** is low. Indeed, using the reaction methodology shown in *Scheme 1*, we were unable to introduce significant amounts of the label into the copolymer **7** containing up to 0.2 mol fraction methacryloyl chloride. This strongly suggests that steric factors involving the bulky mesogenic side-chains inhibit the reaction of the label and acid chloride. It is not possible to comment directly on the microstructures of **1** and **2** but we have shown recently that a structurally similar mesogenic methacrylate and methyl methacrylate undergo azeotropic copolymerization[21]. Thus we assume that copolymer **2** possesses a random distribution sequence of the two monomers.

Table 1 lists the molecular weights and thermal properties of the polymers **1** and **2** and also the transition

Figure 2 E.s.r. spectra of **2** doped with **3** recorded on reheating the sample

temperatures for the spin probed sample. The molecular weights of the polymers are relatively low and the thermal properties of these materials probably lie just within the molecular weight dependent regime[22]. However, the polymers exhibit similar degrees of polymerization and thus a comparison of their properties is valid; the degree of polymerization listed for **1** was calculated assuming the mole fraction of mesogenic units was the same as in **2** and that half of the available acyl chloride groups were labelled while the remainder reacted with methanol. The d.s.c. traces obtained on reheating samples of **1** and **2** are shown in *Figure 1*; each polymer exhibits a second order transition at lower temperatures and a weak first order transition at higher temperatures. These were assigned using the polarizing microscope as the glass and clearing transitions respectively. In order to obtain clear, characteristic optical textures, using which phase identification was possible, the polymers were heated to approximately 10°C above their clearing temperature and cooled at 0.1°C min^{-1}. Thus, on cooling schlieren textures developed which contained both types of point singularity and the phase is therefore assigned as a nematic. On cooling to room temperature this texture was unchanged and thus the second order transition is assigned as the glass transition. The enthalpies associated with the clearing transition (see *Table 1*) support the assignment of the nematic phase; the entropy change associated with the clearing transition for **1**, expressed as the dimensionless quantity $\Delta S/R$, is 0.31 and for **2** is 0.34. It is important to note that the transition temperatures and associated enthalpies for **1** and **2** are equal within experimental error, and thus the spin-label does not appear to significantly influence the thermal behaviour. *Figure 1* shows also the d.s.c. trace obtained during the second heating of the copolymer **2** doped with the spin-probe **3** and the data extracted from this is equal to that obtained for undoped **2**, see *Table 1*. In addition, the spin probed sample also exhibited a characteristic nematic schlieren texture. Thus, as expected, doping **2** with **3** has not changed the thermal behaviour of the polymer.

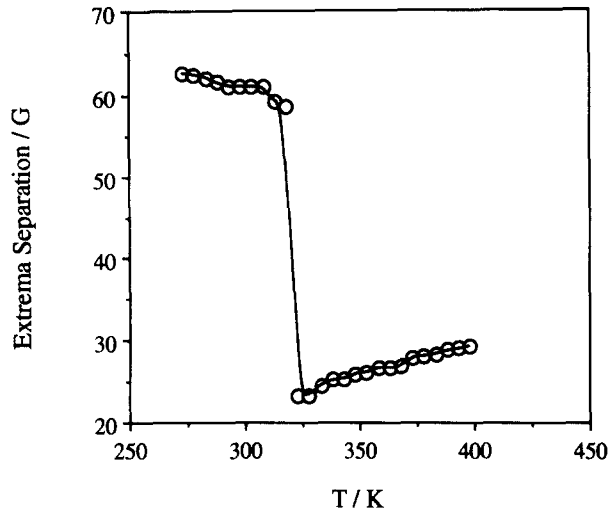


Figure 3 Dependence of extrema separation on temperature for **2** doped with **3**

Figure 2 shows the dependence of the e.s.r. spectra recorded for polymer **2** probed with the nitroxide **3** as a function of temperature. At lower temperatures, characteristic broad-line slow motion spectra are obtained in which the extrema separation is approximately 62G. On heating, the outer extrema in the spectrum move inwards and at the higher temperatures the spectra have collapsed to the motionally narrowed form, in which the extrema separation is approximately 25–30G. The motionally narrowed spectra do not exhibit three equally spaced lines of equal intensity and this indicates that the motion of the probe is anisotropic. At temperatures just below the spectral collapse, a characteristic double peak feature is observed which derives from a distribution of correlation times spanning the slow and fast motion regimes[23].

Figure 3 shows the dependence of the extrema separation on temperature for the spectra collected for **2** doped with **3**. The temperature at which the extrema separation is 50G[24,25] (T_{50G}) is approximately 45°C. T_{50G} is used to characterize the narrow temperature region over which the mobility of the probe, expressed as a correlation time (τ), increases from the slow (10^{-9} s $< \tau <$ 10^{-7} s) into the fast regime ($\tau < 10^{-9}$ s). T_{50G} is often considered as simply a high frequency ($\approx 10^7$ Hz) glass transition temperature[26,27] (T_g) and is

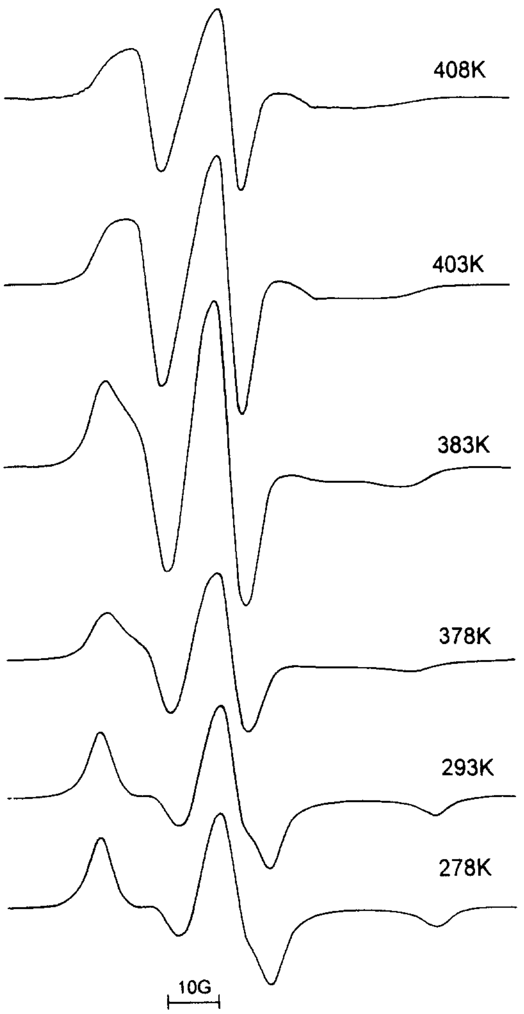


Figure 4 E.s.r. spectra of **1** recorded on reheating the sample

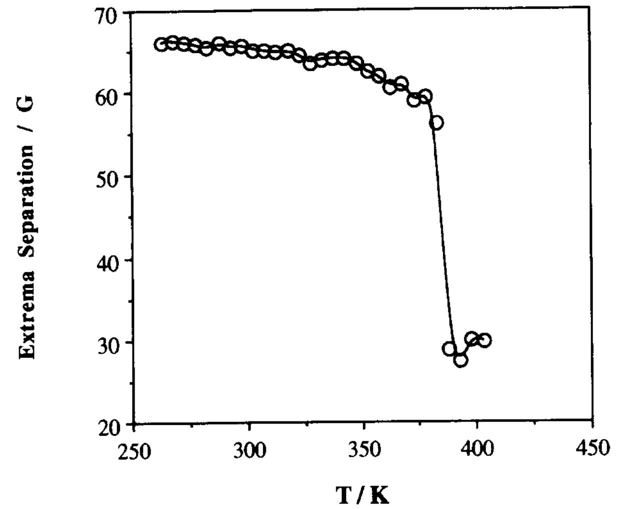


Figure 5 Dependence of extrema separation on temperature for **1**

therefore normally greater than T_g. It is important to note, however, that T_{50G} need not be associated with a particular relaxation of the polymer matrix and it is possible for the probe to tumble with the frequency associated with T_{50G} at $T < T_g$[28]. Indeed, it must be remembered that the spin-probe method is a reporter technique, and thus T_{50G} is a direct reflection of the mobility of the nitroxide probe and not of the host in which it is dissolved. The motion of the probe, however, is normally sensitive to the dynamic state of the polymer matrix and T_{50G} for the majority of the nitroxide probe/polymer systems falls into the temperature range in which probe mobility is determined by segmental reorientation of the polymer[28]. As we have seen, the value of T_{50G} estimated for **2** doped with **3** is 45°C and is comparable with the onset of the glass transition, 54°C, measured using d.s.c. (The values of T_g listed in *Table 1* correspond to the mid-point of the baseline step.) T_{50G} is normally found to be greater than T_g although examples have been reported for which $T_{50G} < T_g$[26,29]. The physical significance of $T_{50G} < T_g$ is unclear but it has been suggested that the mobility of the probe may be determined by local segmental relaxations (β, γ, δ transitions) provided that the volume of the polymer segment involved in the relaxation is greater than the volume of the probe and the frequency of the relaxation is $\approx 10^7$ Hz[30]. An alternative explanation for $T_{50G} < T_g$ considers a specific interaction between the nitroxide probe and a backbone segment resulting in a localized plasticization of the backbone[28]. For SCLCPs it is generally considered that microphase separation occurs in which the side-chains constitute one domain while the polymer backbones form another. A more realistic interpretation of the observation that $T_{50G} \leq T_g$ for polymer **2** probed with **3** proposes that the nitroxide radical is preferentially located in a side-chain region and not in a backbone domain. Thus the mobility of the probe reflects the dynamic state of the side-chains and T_{50G} correlates with a relaxation of the side-chains. Indeed, the interpretation of the dielectric relaxation spectra obtained for SCLCPs has invoked such processes occurring below T_g[8].

We now turn our attention to the spin-labelled polymer **1**. *Figure 4* shows the dependence of the e.s.r. spectra recorded for **1** as a function of temperature; decomposition of the spin-label prevented the acquisition of spectra above 403 K. At low temperatures the spectra are qualitatively identical to those obtained for **2** probed with **3**, see *Figure 2*. The motionally narrowed spectra of the labelled polymer indicate that the rotation of the nitroxide is strongly anisotropic. *Figure 5* shows the dependence of the extrema separation on temperature for the e.s.r. spectra of **1** and using this the estimated value of T_{50G} is 109°C, an increase of 64°C over that estimated for the spin-probed system. T_{50G} for the spin-labelled polymer is equal to the onset of the nematic–isotropic transition, 112°C; (the values of the nematic–isotropic transition temperatures listed in *Table 1* correspond to peak maxima temperatures). The nematic–isotropic transition is a first-order transition and hence not expected to exhibit a strong frequency dependence. T_{50G} may, therefore, correlate with either a frequency-shifted T_g or with the nematic–isotropic transition temperature. Small angle neutron scattering studies have established that for exclusively nematogenic SCLCPs, the backbone adopts a weakly prolate shape in the nematic phase and that the backbone on average lies along the director[31]. As we have seen, the degree of polymerization of **1** is relatively low and in consequence the length to breadth ratio of the macromolecule is small. Therefore, in order to adopt an anisotropic shape for the formation of the liquid crystal phase the backbone must be strongly confined by the nematic field. It is possible that T_{50G} reflects this confinement of the polymer backbone. Further speculation concerning the physical significance of T_{50G} in these systems and its value in characterizing SCLCPs must now await the characterization of a wide range of labelled/probed systems.

CONCLUSIONS

To our knowledge this is the first report of the characterization of spin-labelled SCLCPs by e.s.r. spectroscopy and also the first attempt to use the concept of T_{50G} in order to identify relaxation processes and transitions in SCLCPs. We have shown that spin-probe and spin-label experiments yield complementary information; specifically, the probe appears to dissolve preferentially in side-chain regions and reflects their dynamic state while the label yields information on the dynamic state of the polymer backbone. In consequence, T_{50G} for the probe and label correlate with differing processes. It is now necessary to test the generalization of these observations using a range of differing SCLCPs, and such studies are in progress.

ACKNOWLEDGEMENT

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REFERENCES

1 Bowry, C. and Bonnett, P. *Opt. Comput. Proc.* 1991, **1**, 13

2 Ikeda, T. and Tsutsumi, O. *Science* 1995, **268**, 1873

3 Möhlmann, G. R. and van der Vorst, C. P. J. M. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie and Sons, Glasgow, 1989, Chapter 12

4 Percec, V. and Pugh, C. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie and Sons, Glasgow, 1989, Chapter 3

5 Percec, V. and Tomazos, D. in 'Comprehensive Polymer Science, First Supplement' (Eds S. L. Aggarwal and S. Russo), Pergamon Press, Oxford, 1992, Chapter 14

6 Percec, V. and Tomazos, D. *Adv. Mater.* 1992, **4**, 548

7 Böeffel, C. and Spiess, H.-W. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie and Sons, Glasgow, 1989, Chapter 8

8 Haws, C. M., Clark, M. G. and Attard, G. S. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie and Sons, Glasgow, 1989, Chapter 7

9 Luckhurst, G. R. in 'Liquid Crystals and Plastic Crystals' (Eds G. W. Gray and P. A. Winsor), Ellis Horwood, Chichester, 1974, Chapter 7

10 Freed, J. H., Nayeem, A. and Rananavare, S. in 'Molecular Dynamics of Liquid Crystals' (Eds G. R. Luckhurst and C. A. Veracini), Vol. 431, NATO ASI Series, Ser. C, 1994, Chapters 12–15

11 Cameron, G. G. in 'Comprehensive Polymer Science Volume 1' (Eds C. Booth and C. Price), Pergamon Press, Oxford, 1989, Chapter 23

12 Wassmer, K.-H., Ohmes, E., Portugall, M., Ringsdorf, H. and Kothe, G. *J. Am. Chem. Soc.* 1985, **107**, 1511

13 Lembicz, F. *Polymer* 1991, **32**, 2898

14 Andreozzi, L., Chiellini, E., Giordano, M. and Leporini, D. *Liq. Cryst.* 1993, **14**, 1529

15 Lee, S. H., Surendranath, V., Kim, Y. C. and Gelerinter, E. *Liq. Cryst.* 1995, **18**, 495

16 Allgaier, J. and Finkelmann, H. *Macromol. Chem. Phys.* 1994, **195**, 1017

17 Morishima, Y., Fujita, J., Ikeda, T. and Kamachi, M. *Chem. Lett.* 1994, 557

18 Steinstrasser, R. and Pohl, L. *Z. Naturforsch* 1971, **26b**, 577

19 Attard, G. S., Imrie, C. T. and Karasz, F. E. *Chem. Mater.* 1992, **4**, 1246

20 Craig, A. A. and Imrie, C. T. *J. Mater. Chem.* 1994, **4**, 1705

21 Craig, A. A. and Imrie, C. T. *J. Polym. Sci., Polym. Chem. Edn.* 1996, **34**, 421

22 Imrie, C. T., Karasz, F. E. and Attard, G. S. *J. Macromol. Sci.-Pure Appl. Chem.* 1994, **A31**, 1221

23 Cameron, G. G., Miles, I. S. and Bullock, A. T. *Brit. Polym. J.* 1987, **19**, 129

24 Rabold, G. P. *J. Polym. Sci. A-1* 1969, **7**, 1203

25 Boyer, R. F. *Macromolecules* 1973, **6**, 288

26 Kumler, P. L. and Boyer, R. F. *Macromolecules* 1976, **9**, 903

27 Boyer, R. F. *Polymer* 1976, **17**, 996

28 Cameron, G. G., Miles, I. S. and Bullock, A. T. *Polymer* 1988, **29**, 1282

29 Kusumoto, N., Sano, S., Zaitsu, N. and Motozato, Y. *Polymer* 1976, **17**, 448

30 Braun, D., Törmälä, P. and Weber, G. *Polymer* 1978, **19**, 598

31 Noirez, L., Keller, P. and Cotton, J. P. *Liq. Cryst.* 1995, **18**, 129