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A small angle neutron scattering study of the conformation of a side chain liquid crystal poly(methacrylate) in the smectic C phase

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The conformation of the backbone in the side chain liquid crystal polymer poly[ω -(4'-methoxybiphenyl-4-yloxy)butyl methacrylate] has been studied in the smectic C and nematic phases. Small angle neutron scattering experiments were performed on mixtures of molecules with perdeuteriated backbones and unlabelled molecules. The polymer is found to adopt an oblate conformation in the smectic C phase. The components of the radius of gyration parallel and perpendicular to the director are determined as a function of temperature from Guinier plots of the SANS data. The radii of gyration do not vary across the smectic phase and are found to be $R_{g,\parallel} = (27 \pm 1) \text{ \AA}$, $R_{g,\perp} = (42 \pm 1) \text{ \AA}$. These results are compared with recent SANS results for other side chain liquid crystal polymers.

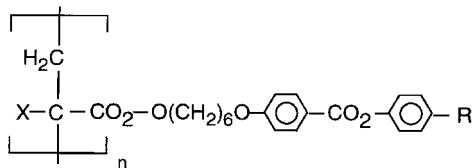
1. Introduction

There has been considerable technological interest recently in side chain liquid crystal polymers (SCLCPs) because they can exhibit both typical polymer properties, for example a glass transition temperature, as well as the electro-optical and non-linear optical properties characteristic of low molar mass materials [1, 2]. In device applications these materials must possess a high glass transition temperature, to ensure the stability of stored information, for example, SCLCPs with a poly(methacrylate) backbone meet this requirement and a number of these materials have been prepared and extensively characterized [3–5].

There have been a number of recent small angle neutron scattering (SANS) studies of side chain liquid crystal polymers by Noirez and coworkers [6, 7], and a neutron diffraction study of the detailed localization of

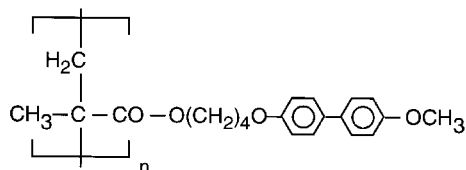
the backbones in the smectic layers [8]. These neutron scattering results have recently been summarized in a review [9]. Noirez *et al.* find that the backbone conformation in the smectic phases that they have investigated is described by an oblate radius of gyration ellipsoid. In other words the backbone tends to be normal to the magnetic field used to orient the mesogens in the side group. In contrast, when the polymer has only a nematic phase, the backbone adopts a prolate conformation, whereas for a polymer with a smectic–nematic transition, the backbone assumes a slightly oblate conformation in the nematic phase which they ascribe to smectic fluctuations. X-ray diffraction by side chain liquid crystal polymers has recently been reviewed by Davidson and Levelut [10]. They point out that it is possible to determine the localization of the backbone in smectic phases from the relative intensities of the Bragg reflections from the layers. They studied poly(acrylate) and poly(methacrylate) side chain liquid crystal polymers with the generic formula

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where $X = \text{H}$, CH_3 and $R = \text{OCH}_3$, OC_4H_9 . They find that the anisotropy of the backbone radius of gyration determined from SANS is correlated to the extent of smectic ordering, deduced from the number of Bragg reflections in the X-ray experiment. Richardson and coworkers performed SANS experiments on a series of poly(siloxane) SCLCPs with a $(\text{CH}_2)_3\text{O}$ flexible spacer and a benzoate ester mesogenic unit, and differing in the terminal group [11]. They found an oblate conformation of the backbone in the smectic and nematic phases. They also studied the mesogenic packing in the smectic phase by measuring the Bragg scattering from mixtures containing selectively deuteriated mesogens. An interdigitated structure of the mesogens was deduced from these measurements.

In this work, we study the backbone conformation of the poly(methacrylate)



by performing SANS on a mixture of materials with unlabelled chains and chains labelled with perdeuteriated backbones. Due to the contrast thus introduced in the material, this gives scattering at low scattering vectors $q = 4\pi \sin \theta / \lambda$ (where 2θ is the scattering angle, and λ is the wavelength) that is related to the conformation of the polymer backbone [12]. In particular, the radius of gyration, R_g , can be extracted in a Guinier plot which is valid in the region $qR_g < 1$. For an anisotropic conformation, the radius of gyration tensor components are no longer equal. Experiments were performed on samples oriented off-line in a magnetic field where the mesogens orient parallel to the field and the components $R_{g,\parallel}$ and $R_{g,\perp}$ were measured. This paper is organized as follows. We first discuss the synthetic methods used to prepare the polymers and the sample characterization techniques employed. Details of the neutron scattering experiments are also provided. A brief outline of the theory appropriate to SANS from a binary blend of polymers is then presented for use in extracting the radius of gyration from Guinier plots. The results are then discussed and finally summarized.

2. Experimental

The deuteriated polymer was prepared using the synthetic route shown in the Scheme.

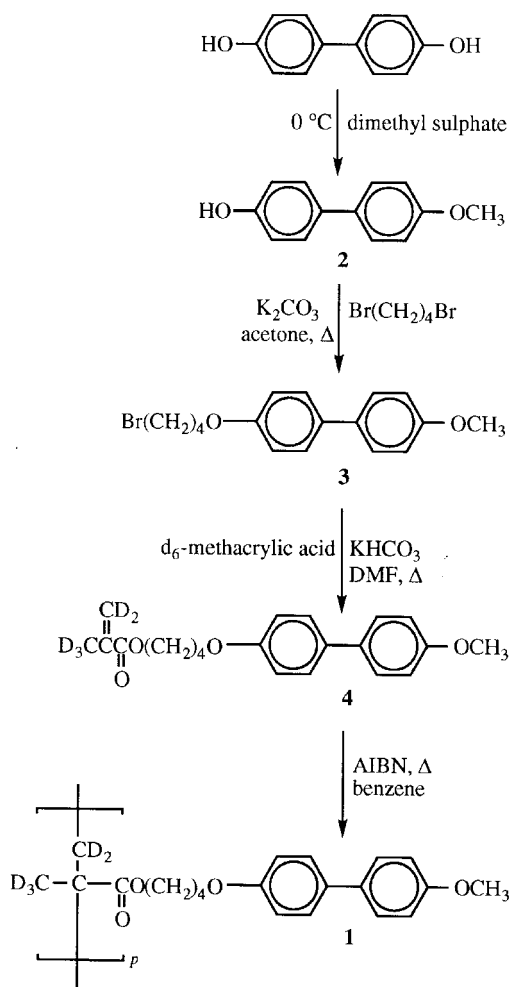
2.1. Materials

2.1.1. Reagents

1,4-dibromobutane (Aldrich) was distilled under reduced pressure using a Kugelrohr apparatus immediately prior to use. Benzene and tetrahydrofuran (THF) were distilled over calcium hydride. AIBN was purified by recrystallization from toluene, washed with petroleum spirits (80–100°C) and dried under vacuum. 4,4'-dihydroxybiphenyl, dimethyl sulphate, dry acetone, hydroquinone and *N,N'*-dimethylformamide were all used as received (Aldrich). Methacrylic acid- d_6 was obtained from C/D/N Isotopes Inc.

2.1.2. 4-Hydroxy-4'-methoxybiphenyl, 2

The preparation of compound 2 has been described in detail elsewhere [3].



Scheme

2.1.3. 1-Bromo-4-(4-methoxybiphenyl-4'-yloxy)butane, **3**

Compound **3** was prepared using the procedure described by Craig and Imrie [3] and was recrystallized twice from ethanol with hot filtration. Melting Point: 129–131°C. ¹H NMR (CDCl₃) δ: 6.9, 7.5 (m, 8H, aromatic), 4.0 (t, 2H, *J* 5.9, OCH₂), 3.8 (s, 3H, OCH₃), 3.5 (t, 2H, *J* 6.5, CH₂Br), 1.9–2.1 (m, 4H, OCH₂CH₂, CH₂CH₂Br).

2.1.4. 4-(4-Methoxybiphenyl-4'-yloxy)butyl methacrylate-d₅, **4**

Compound **4** was synthesized using the method described by Craig and Imrie [3]. Methacrylic acid-d₆ (1 g, 10.9 mmol) was stirred with potassium hydrogen carbonate (1.5 g, 10.9 mmol) at room temperature for five minutes to form the potassium methacrylate salt. To this was added compound **3** (2.9 g, 8.6 mmol), hydroquinone (0.034 g, 0.32 mmol) and *N,N'*-dimethylformamide (100 ml) and the reaction mixture was stirred at 100°C overnight. On cooling, the mixture was poured into water (c. 300 ml) and stirred to coagulate the resulting precipitate which was then collected by suction filtration and dissolved in dichloromethane. The organic solution was washed with 5% aqueous sodium hydroxide and water. The organic layer was dried over anhydrous magnesium sulphate, filtered and the solvent removed. The crude product was recrystallized twice from ethanol. Yield: 2.4 g, 82%. Melting point: 99–8°C. ¹H NMR (CDCl₃) δ: 6.9, 7.5 (m, 8H, aromatic), 4.2 (t, 2H, *J* 6.1, H₂COC(O)), 4.0 (t, 2H, *J* 5.9, OCH₂), 3.8 (s, 3H, OCH₃), 1.8–2.0 (m, 4H, OCH₂CH₂, CH₂CH₂OC(O)).

2.1.5. Poly[ω-(4-methoxybiphenyl-4'-yloxy)alkyl methacrylate-d₅]

Monomer **4** (1.44 g) was dissolved in benzene (10 ml) and 1 mol % of AIBN added as initiator. The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60°C to initiate the polymerization. After 48 h the reaction was terminated by the addition of THF (15 ml) and the polymer precipitated into a large amount of cold methanol. The product was redissolved in THF and reprecipitated into methanol in order to remove excess of monomer. Yield: 1.17 g, 81%. ¹H NMR (CDCl₃) δ: 6.9, 7.4 (m, 8H, aromatic), 3.8–4.0 (m, 4H, OCH₂), 3.7 (s, 3H, OCH₃), 1.6–1.9 (m, 4H, CH₂).

2.2. Characterization

The structures of all the compounds were verified using ¹H NMR spectroscopy (Bruker AC-F 250 MHz NMR spectrometer). The molecular masses of the polymers were measured using gel permeation chromatography (GPC) using a Knauer Instruments chromatograph equipped with 2 PL gel 10 mm mixed

columns controlled by Polymer Laboratories GPC SEC V5-1 Software. Chloroform was used as the eluent and polystyrene standards were used to obtain a calibration curve. For the protonated polymer $M_w = 106 \text{ kg mol}^{-1}$, $M_n = 30 \text{ kg mol}^{-1}$, whilst for the polymer with deuteriated backbone $M_w = 50 \text{ kg mol}^{-1}$, $M_n = 13 \text{ kg mol}^{-1}$.

The thermal behaviour of the polymer was characterized by differential scanning calorimetry using a Mettler-Toledo DSC 820 system equipped with an intracooler accessory and calibrated using an indium standard. Phase identification was obtained by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit. Clear, characteristic textures were obtained by cooling the samples from the isotropic phase at 0.2 or 0.1°C min⁻¹.

2.3. Blends

Blends of labelled and unlabelled polymers were prepared for DSC studies to check the absence of phase separation. The polymers were dissolved in chloroform in equal weights, and the solvent removed under vacuum; the blend was then dried under vacuum.

2.4. Sample alignment

The sample was cooled in a 9.4 T magnetic field from 170°C to 110°C at 0.8°C min⁻¹, and then allowed to cool more rapidly (over 15 min) to 30–40°C before removing from the field.

2.5. Small angle neutron scattering experiments

Small angle neutron scattering experiments were performed using the SANS instrument at Risø National Laboratory, Denmark and on the LOQ instrument at the ISIS facility, Rutherford Appleton Laboratory, U.K. The former is a reactor source, with a fixed neutron wavelength, whereas the latter is a pulsed source where the scattering pattern is obtained from the time-of-flight spectrum which results from the range of incident neutron wavelengths.

At Risø, experiments were performed with $\lambda = 3 \text{ \AA}$ and a wavelength distribution $\Delta\lambda/\lambda = 0.14$. Collimator distances of 1, 3 and 6 m were used to cover the q range 0.008–0.6 Å⁻¹. All measurements were made at room temperature on the sample which had previously been oriented off-line in a magnetic field. The experiments on LOQ were performed with wavelengths selected in the range 2.611–6.674 Å and with a distribution $\Delta\lambda/\lambda = 0.04$; this gives an accessible q range extending from 0.012 to 0.24 Å⁻¹. The sample was contained in a quartz Hellma cell which was heated using two cartridge heaters mounted on either side that were connected to a Eurotherm temperature controller, the temperature

being measured with a Pt resistance thermocouple. Following equilibration (for at least one hour), the temperature variations did not exceed $\pm 1^\circ\text{C}$. The data from the work at both Risø and ISIS were collected using area detectors and were corrected for detector efficiency, sample transmission and background, using standard procedures. The data were put on an absolute scale using water standards.

3. Theory

The inverse structure factor for a mixture with a volume fraction, ϕ_D , of deuterium labelled polymers and $\phi_H = (1 - \phi_D)$ hydrogenous polymers with different molecular weights is given in the Random Phase Approximation by [13]

$$S(q)^{-1} = S_D(q)^{-1} + S_H(q)^{-1} - 2\chi_F \quad (1)$$

Here $S_{D(H)}(q)$ is the structure factor of the labelled (unlabelled) chains, respectively, and χ_F is the Flory–Huggins interaction parameter. In the limit of small q and neglecting interactions between the deuterium labelled and protonated polymers ($\chi_F = 0$), this expression simplifies to [14]

$$S(q)^{-1} = \frac{1}{N_{\text{wd}}} \left(\frac{1}{\phi_D} + \frac{1}{(1 - \phi_D)(1 + \Delta w)} \right) + \frac{q^2 a^2}{18} \frac{N_{zD}}{N_{\text{wd}}} \left(\frac{1}{\phi_D} + \frac{1 + \Delta z}{(1 - \phi_D)(1 + \Delta w)} \right), \quad (2)$$

where a is a segment length and the degrees of polymerization of the hydrogenous polymer are related to those of the deuterated polymer by

$$N_{nH} = N_{nD}(1 + \Delta n), \quad (3a)$$

$$N_{wH} = N_{wD}(1 + \Delta w), \quad (3b)$$

$$N_{zH} = N_{zD}(1 + \Delta z). \quad (3c)$$

The apparent radius of gyration, $R_{g,\text{app}}$, is then related to the radius of gyration of the labelled chain, $R_{g,D}$ by [14]

$$\begin{aligned} R_{g,\text{app}}^2 &= \frac{N_{zD} a^2}{6} \left(1 + \frac{\phi_D \Delta z}{1 + (1 - \phi_D) \Delta w} \right) \\ &= R_{g,D}^2 \left(1 + \frac{\phi_D \Delta z}{1 + (1 - \phi_D) \Delta w} \right). \end{aligned} \quad (4)$$

Due to the large difference in molecular masses of our polymers, this correction is significant. For our polymers, $\phi_D = 0.5$, $\Delta z = 1.2$, $\Delta w = 1.3$, thus

$$R_{g,\text{app}}^2 = 1.36 R_{g,D}^2, \quad (5)$$

and this correction has been used to determine $R_{g,D}$ from the data presented in the following section.

4. Results and discussion

The molecular mass of the deuterated polymer is sufficiently high to ensure that its thermal properties lie outside the molecular weight dependent regime [15]. The polymer exhibited a nematic–isotropic transition at 143°C ($\Delta H = 0.80 \text{ kJ mol}^{-1}$) and a smectic C–nematic transition at 127°C ($\Delta H = 4.29 \text{ kJ mol}^{-1}$); the phases were assigned on the basis of optical textures observed using the polarized light microscope. The texture of the SmC phase was closely similar to that of the schlieren texture depicted in figure 4 of ref [3] for the SmC phase of the unlabelled polymer of the same structure. The phase sequence is identical to that exhibited by the unlabelled polymer and the transition temperatures of the deuterated sample are just $c. 4^\circ\text{C}$ higher than those of the unlabelled sample. An X-ray diffraction study of the unlabelled sample revealed that annealing at temperatures $< 100^\circ\text{C}$ yields a highly ordered smectic phase [16]; this is presumably kinetically suppressed by the cooling rates used in the DSC experiments. Similar behaviour would be expected for the deuterated sample. The absence of phase separation in the blends was confirmed by DSC experiments with heating rates from 0.5 to $10^\circ\text{C min}^{-1}$. No evidence was found of distinct phase transitions from the blends.

Small angle neutron scattering patterns obtained at Risø National Laboratory with the sample at room temperature are presented in figure 1. Figure 1(a) was obtained with a sample-to-detector distance of 3 m and 1 m collimation, and shows that the sample was highly oriented, with two orders of Bragg reflections from the smectic structure on the meridian. From the location of the maxima of the peaks, the smectic layer spacing is obtained as $d = 2\pi / (0.25 \text{ \AA}^{-1}) = 25 \text{ \AA}$. Because the Bragg peaks in the smectic C phase are located on the meridian, it is evident that the layers are oriented normal to the field, and so the mesogens are tilted with respect to the magnetic field. Figures 1(b) and 1(c) show the anisotropic scattering from the polymer backbone. Because the scattering is concentrated on the major axis of an ellipse parallel to the field alignment, the polymer backbone must adopt an oblate conformation, i.e. the radius of gyration normal to the layers is smaller than that parallel to the layers.

The anisotropy of the small-angle scattering data obtained at ISIS was analysed in the Guinier region as a function of temperature. A representative Zimm plot of the scattering in the Guinier region is shown in figure 2. The difference in gradient of the two lines for sectors of the data parallel and perpendicular to the alignment direction is directly related to the difference in radii of gyration in orthogonal directions, whilst the intercept is a function of polymer molecular mass [14]

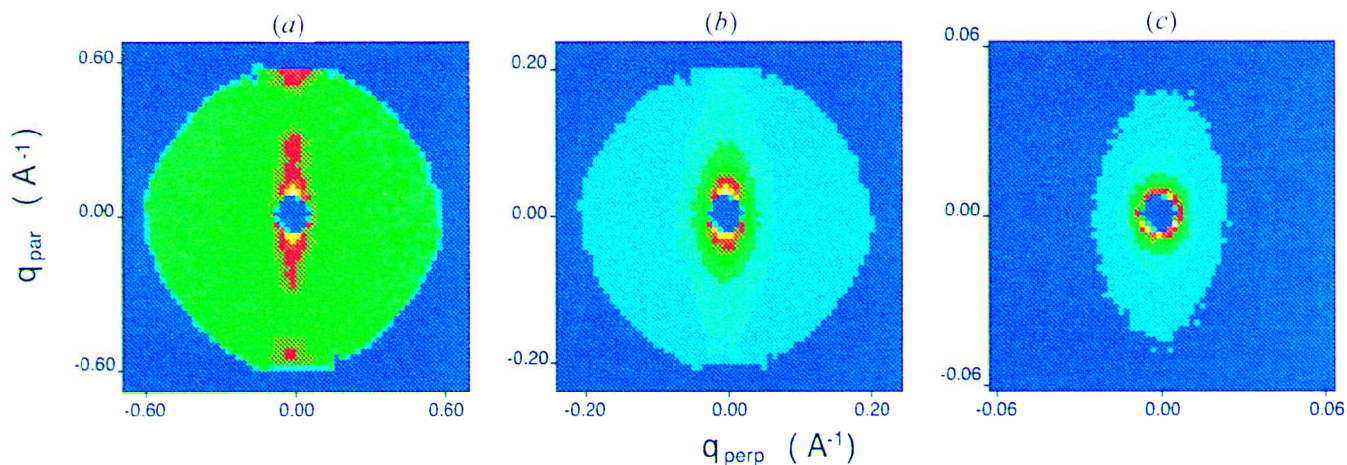


Figure 1. Small Angle Neutron Scattering patterns obtained at Risø National Laboratory at room temperature with (a) 1 m collimation, (b) 3 m collimation, (c) 6 m collimation.

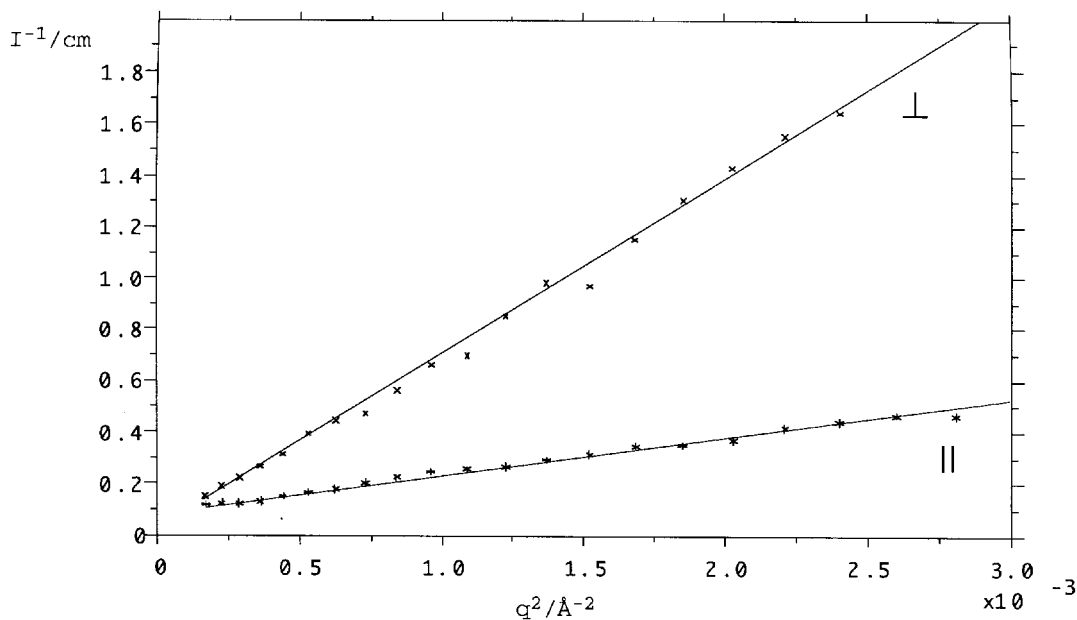


Figure 2. Zimm plot of the inverse SANS intensity at 120°C showing the anisotropy of the radius of gyration parallel (∥) and perpendicular (⊥) to the aligning magnetic field.

and is the same for Zimm plots from sectors of data sets from the same sample.

The radii of gyration extracted from the scattering ellipses in the Guinier region are plotted for a series of temperatures in figure 3. It is evident that the oblate anisotropy for the smectic C phase is essentially independent of temperature. However, upon heating into the nematic phase this anisotropy was largely lost, the small residual difference between the radii of gyration suggesting an oblate conformation in the nematic phase also. Upon cooling back into the smectic phase (closed symbols) the oblate conformation of the backbones is

retained; however the ratio of parallel to perpendicular radii of gyration does not return to its value before heating into the nematic phase. This suggests that the sample lost macroscopic order when heated into the nematic phase and this is not surprising given the absence of an *in situ* magnetic field to align the mesogens in this fluid phase. It is interesting to note that the radius of gyration parallel to the layer normals is approximately equal to one layer spacing. This suggests that, on average, the backbones are confined within a single layer. This is in agreement with the results from SANS experiments obtained by Noirez *et al.* from a

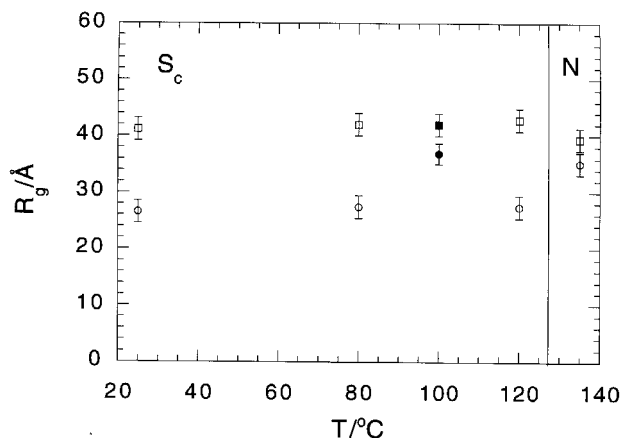


Figure 3. Radii of gyration obtained from SANS data in the Guinier region. (○) $R_{g,\parallel}$ obtained on heating, (●) $R_{g,\parallel}$ obtained on cooling from 135°C, (□) $R_{g,\perp}$ obtained on heating, (■) $R_{g,\perp}$ obtained on cooling from 135°C.

series of smectic side chain LCPs [9]. For our polymer, the backbone is not so confined between mesogens and spacers to form a strongly segregated 'microphase separated' state [17], in contrast to some polymers studied by Noirez *et al.* where $R_{g,\parallel} \ll d$. The values for the radii of gyration obtained from our polymer are comparable to those from side chain LCPs of similar degrees of polymerization in a smectic phase [9].

Noirez *et al.* observed that the backbone conformation is always oblate in smectic side chain LCPs [9], and our results are in agreement with this rule. Furthermore, they observed that this anisotropy is greater than in a nematic phase when present at high temperature, and this is also observed by us.

5. Summary

In summary we have observed, using small angle neutron scattering experiments on mixtures containing labelled chains, that the poly(methacrylate) backbone of a side chain liquid crystal polymer adopts an oblate conformation in the smectic C phase, in agreement with earlier observations [9]. The radii of gyration were found to be approximately constant across the smectic C

phase, but the anisotropy decreased in the nematic phase. The radius of gyration parallel to the layer normals is found to be approximately equal to one layer spacing, showing that the backbone is confined within a single layer. These observations provide further evidence of the dramatic influence of mesogenic side groups on the conformation of polymer chains.

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