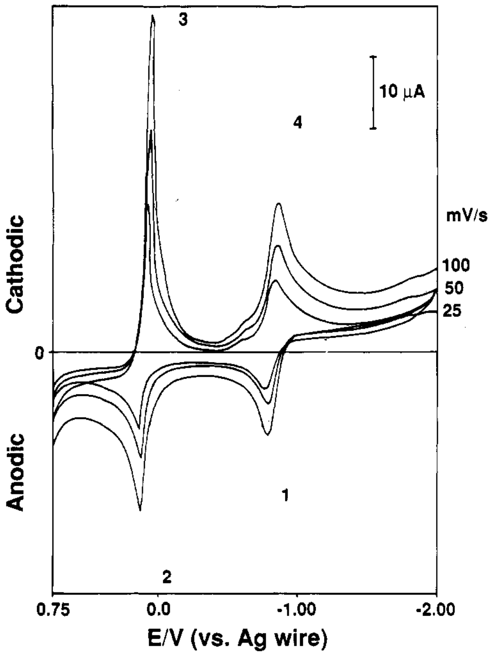

Figure 1. Cyclic voltammogram for PBOSD-Ni (1.6×10^{-3} M) in DMF; 0.1 M $TBAClO_4$ at carbon working electrode.

be reported on further in the near future.

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Fei Wang and John R. Reynolds*
Department of Chemistry
The University of Texas at Arlington
Arlington, Texas 76019

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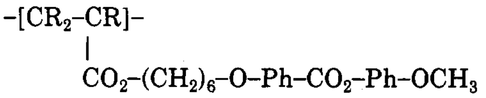
Backbone Conformation of a Mesogenic Side-Chain Polyacrylate

I. Introduction. Small-angle neutron scattering (SANS) is a powerful method for the determination of polymer conformations. It has been extensively used in the melt to access to the backbone conformation of side-chain liquid-crystal polymers by labeling the backbone with deuterium.[1-5] These polymers are different polymethacrylates and polysiloxanes. The nematic phase induces a backbone anisotropy which is always weak and often difficult to determine, but in the smectic phase all SANS experiments conclude that the main chain prefers to orient itself perpendicularly to the mesogenic units and this result may be a general feature. However, recent NMR data about a mesogenic polyacrylate[6,7] seem to indicate that for such a polymer, the backbone is aligned, in the smectic phase, along its mesogenic side chains. Therefore, a small-angle neutron scattering study on the same polymer is of interest. Experimental conditions are specified in section II, and the results are described in section III.

II. Experimental Section. The measure by SANS of the conformation of one polymer backbone in its bulk requires a mixture of similar polyacrylates with hydrogenated and deuteriated backbones.

Both such compounds have been synthetized at the Laboratoire Léon Brillouin according to a method (already used for the polymers of ref 6, 7) described elsewhere.[8] They have the following formula:



$$\begin{array}{l}-[CR_2-CR]- \\ \qquad\;\; | \\ \qquad CO_2-(CH_2)_6-O-Ph-CO_2-Ph-OCH_3\end{array}$$

where R = H or R = D.

These polymers have been characterized by gel permeation chromatography and light scattering on line[9] at the Institut Charles Sadron, Strasbourg, as the coupling of both methods gives the absolute molecular weights without reference samples. The molecular weight of the hydrogenated polymer is 27 000 (weight average) and its polydispersity is 2.6 (M_w/M_n); the deuteriated polymer has a molecular weight of 41 000 (weight average) and a polydispersity of 2.0. These molecular weights are about half of those studied by NMR.[6,7]

The polymer has two mesomorphic phases; a nematic phase at higher temperatures and a monolayer smectic phase determined by X-ray[10] and neutron patterns (Figure 1).

The phase-transition temperatures, shown in Table I, were obtained by DSC.

In order to obtain a maximum scattered intensity we have used a sample containing 50% of deuteriated chains.[11] The intensity detected is that scattered by the backbone alone since this is the only part deuteriated. Therefore, the sizes discussed in the following section correspond to those of the main chain without mesogenic.[12] The sample

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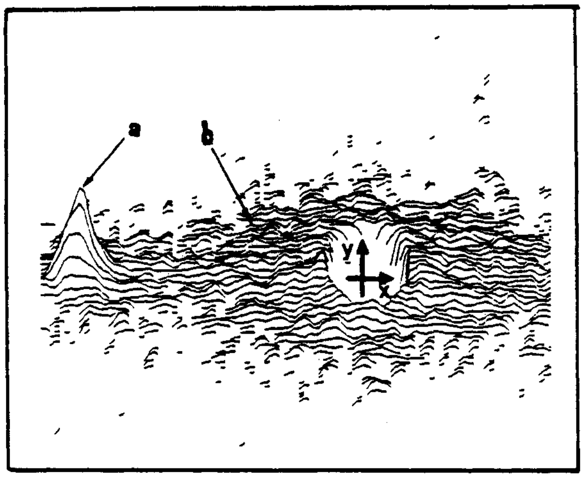

Figure 1. *XY* spectrum at 3.7 Å of the polyacrylate backbone in the smectic phase. *H* is the magnetic field parallel to *x* axis: (a) (001) Bragg peak; (b) anisotropic small-angle scattering (oblate shape in the real space); (+) the origin of the two axes, $q_\parallel$ and $q_\perp$, and corresponds to the direct beam position.

Table I
Characteristic Transition Temperatures of Polyacrylates Obtained by DSC

polymers	phase transition temp, °C						
PA(H)		22		88		116	
	glassy		smectic		nematic		isotropic
PA(D)		23		88		114	

is set in an oven (temperature stability of 0.2 °C), itself placed in the neutron beam, and then slowly cooled (5 °C/h) in situ from the isotropic phase in a magnetic field (1.4 T) in order to obtain aligned nematic and smectic phases. The alignment of the liquid crystal parts is controlled in situ, in the smectic phase, by the observation of the 001 Bragg peak at relatively large angle, $q = 0.25$ Å^{-1} (neutron diffraction).

These neutron experiments have been performed on the SANS spectrometer, PAXY, at the Orphée Reactor (CEN Saclay). An *XY* position multidetector (15 500 cells of 5 × 5 mm^2) allows the measurement of the anisotropic intensity over the required scattering vector range by choosing a suitable wavelength. So, our neutron diffraction experiments were carried out at a wavelength, λ, of 3.7 Å, at a sample–multidetector distance $D = 2m$; the scattering vector, $q \simeq 2\pi(\theta/\lambda)$ (where θ is the scattering angle), takes values between 0.03 Å^{-1} < q < 0.27 Å^{-1}.

In the SANS experiments, the scattering intensity was interpreted from an extension of the Guinier approximation, suitable when there is a difference between the molecular weights of species (labeled and unlabeled) without specific interaction between them:[13]

$$I^{-1}(q_i) \propto \left(\frac{1}{M_D\varphi_D} + \frac{1}{M_H\varphi_H}\right)(1 + q_i^2 R_{i\,\mathrm{app}}^2)$$
$$q_i R_{i\,\mathrm{app}} \leqslant 1 \quad (1)$$

where φ_D and φ_H are the volume fractions and M_D and M_H the molecular weights respectively of deuteriated and hydrogenated chains. $R_{i\,\mathrm{app}}$ is an apparent quadratic size in the direction q_i related to the real size R_i by[15]

$$R_{i\,\mathrm{app}}^2 = R_i^2\left(1 + \frac{\varphi_D}{\varphi_H + M_D/(M_H - M_D)}\right) \quad (2)$$

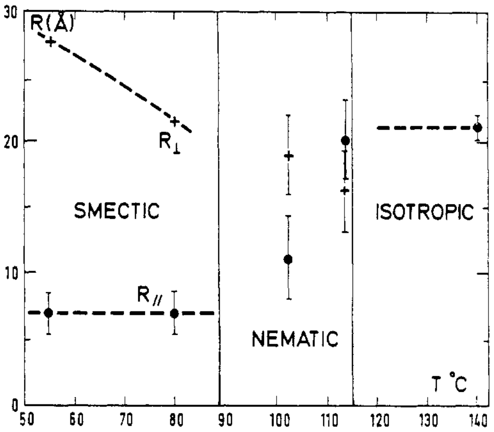

Figure 2. Quadratic sizes of the polyacrylate backbone in directions respectively parallel ($R_\parallel$) and the perpendicular ($R_\perp$) to the magnetic field versus temperature.

R_i is denoted $R_\parallel$ for q_i parallel to the magnetic field and $R_\perp$ for the perpendicular direction. The scattered vector range used for this determination is 8×10^{-3} Å^{-1} < q < 6×10^{-2} Å^{-1}, chosen in order to have a linear dependence of $I^{-1}(q)$ as a function of q^2. This range has been obtained with a wavelength of 15 Å and the same sample–multidetector distance ($d = 2m$).

The values of $R_\parallel$ and $R_\perp$ differ from R_{app} by less than 15%. Notice that eq 2 assumes a Gaussian conformation of the chain; it is a reasonable hypothesis since the corresponding treatment, assuming a rodlike chain, gives similar values far inside the error bars.

III. Results. Figure 1 is the scattering pattern obtained in the smectic phase. It clearly shows an oblate conformation of the polymer backbone, and the lower the temperature, the more pronounced the anisotropy. The backbone size, in the smectic phase in the direction perpendicular to the magnetic field, reaches $R_\perp = 27 \pm 2$ Å at 55 °C, while the size in the parallel direction is $R_\parallel = 7 \pm 2$ Å. This latter value is much smaller than the smectic layer thickness (25 ± 1 Å) or the molecular length of the side chain (about 26 Å). Such a small component of radius of gyration, $R_\parallel$, has not been observed in mesogenic polymethacrylates.[1-4] One must add that the molecular weights of these later are from five to 12 times the molecular weight of the polyacrylate and it may be the reason why their quadratic size $R_\parallel$ is always much larger. It would be of interest to know if the same polyacrylate, but with a higher molecular weight, could be as anisotropic as that studied here.

Such an anisotropy supposes that the polyacrylate is confined between two smectic layers. The probability for a chain to cross the smectic layer is very weak so the backbone, perpendicular to its mesogenic side chains, must stay at the interface of two smectic layers. We have made measurements in the smectic phase at two different temperatures (Figure 2). The size $R_\parallel$ remains constant, indicating that the backbone is probably completely confined, while $R_\perp$ increases significantly. The backbone only extends perpendicularly to its mesogenic units.

Two measurements have also been made in the nematic phase (Figure 2). Their accuracies are not as good as in the smectic phase due to a smaller counting time and probably also to the scattering intensity which is stronger when the polymer is confined. The signal-to-noise ratio increases by a factor 3 from the nematic phase to the smectic one at larger q values in the Guinier range which explains the different confidence ranges shown in Figure 2. The data at 103 °C clearly shows the sense of the anisotropy (oblate) following a decrease of the parallel size from the isotropic state. The other point at 113 °C does not give information about the anisotropy but shows that

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there is a shrinking of the backbone at the isotropic–nematic transition since $R_\perp$ (and $R_\parallel$ probably, within the error range) decrease from the isotropic state. This effect has also been noted for this transition, in the case of mesogenic polymethacrylates.[2-4] This phenomenon could be associated with the volume contraction which can occur for this transition[14] as a decrease of the mesogen specific volume. However, the variation of the specific volume observed for this polyacrylate is only of about 2%[15] from 130 to 113 °C, too weak to explain alone such a decrease of R_i.

IV. Discussion and Conclusions. The liquid-crystal side-chain polymers like polymethacrylates and polyacrylates seem to present, in the nematic and smectic A phases, a similar behavior for homologous mesogenic groups. The more the temperature decreases, the more widely the polymer backbone expands perpendicularly to its mesogenic units and approaches an oblate shape. In contrast to the NMR interpretation, we show that the sense of the global anisotropy is not affected by the steric hindrance of the α-methyl group since the polyacrylate and the polymethacrylate, which bear the same side chains, behave alike. These data confirm a general tendancy for all these types of side-chain polymers with one mesogenic unit per chemical unit of backbone. Indeed, the poly(methylsiloxanes), the polymethacrylates, and now this polyacrylate segregate the mesogenic cores from the backbone building zones of backbones and zones of mesogenic cores, which give rise to the lamellar structure. In addition, this polyacrylate has shown the property that one backbone can be highly confined between two smectic layers.

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Registry No. $H_2C{=}CHCO_2(CH_2)_6OPhCO_2PhOCH_3$ (homopolymer), 82200-54-2; $D_2C{=}CHCO_2(CH_2)_6OPhCO_2PhOCH_3$ (homopolymer), 115512-10-2; neutron, 12586-31-1.

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[†] Centre de Recherche Paul Pascal.
[‡] Institut Charles Sadron.

L. Noirez, J. P. Cotton,* F. Hardouin,† P. Keller, F. Moussa, G. Pêpy, and C. Strazielle‡

Laboratoire Léon Brillouin, CEN Saclay
91191 Gif-sur-Yvette Cedex, France
Centre de Recherche Paul Pascal
33405 Talence Cedex, France
Institut Charles Sadron (CRM-EAHP)
67083 Strasbourg Cedex, France

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On the Screening of Hydrodynamic Interactions in Dilute Polymer Solutions

The concept of screening of hydrodynamic interactions in polymer solutions and the criteria for this effect are well understood.[1-12] The screening length for the hydrodynamic interaction is generally a complicated function of the experimental variables and many different limiting situations of experimental relevance may be identified. By use of the appropriate limits of the hydrodynamic screening length, results of extensive studies of the oscillatory flow birefringence,[13] linear viscoelastic properties,[13] and dielectric relaxation[14] of polymer solutions can be understood. In particular, the concentration dependence of the relaxation times of the internal normal modes of linear chains in dilute solutions have been calculated[7-11] by using the screened hydrodynamic interaction; the results are in reasonable agreement with oscillatory flow birefringence and dielectric dispersion measurements.[13,14]

Recently, a calculation by Shiwa, Oono, and Baldwin[15] has been reported where the authors have derived results which are not only inconsistent with themselves but also in disagreement with the previous theories and a wealth of experimental data. Although Shiwa et al. claim to begin with a new model at a more fundamental level, their formulas for viscosity and mobility are the same[15] as those of the Freed–Edwards theory. Therefore the differences between the work of Shiwa et al. and the previous theories stem from the approximations applied to the various complicated formulas for viscosity, screening length, etc.

We show below that the errors in the work of Shiwa et al. originate from the inconsistent use of formulas for different regimes. For specificity, let us consider the concentration dependence of the relaxation time (τ_p) of the pth normal mode of polymer chains in dilute solutions. The initial concentration dependence of τ_p for linear flexible chains in three dimensions has been derived[7,9,10] to be

$$\frac{\tau_p}{\tau_p{}^\circ} = 1 + \frac{\pi \rho l l_1{}^{3/2}(q)}{(12q)^{1/2}} + ... \qquad (1)$$

where $\tau_p{}^\circ$ is the value of τ_p at infinite dilution, l is the Kuhn step length and $q = 2\pi p/L$. l_1 is a crossover function for the effect of the excluded-volume effect with the limits[6]

$$l_1 \approx q^{-1/5} \qquad \text{good solutions}$$
$$l_1 \approx l \qquad \Theta \text{ solutions} \qquad (2)$$

Therefore, eq 1 can be rewritten as

$$\tau_p/\tau_p{}^\circ = 1 + a\rho(p/L)^{1-d\nu} + ... \qquad (3)$$

where the generalization to arbitrary space dimension[10] is included. In eq 3, a is a known factor with appropriate

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