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Recognition of a New Type of Main Chain Liquid Crystalline Polymer: Poly(1-olefin sulfones)[1]

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ABSTRACT: By observations with the polarizing microscope and by DSC studies we show that poly(eicosene sulfone), poly(hexadecene sulfone), and a number of copolymers of the latter with cyclohexene are main chain liquid crystalline polymers and have liquid crystalline phases at temperatures between the ambient temperature and 100 °C. The sensitivity of the clearing temperature and a softening point to molecular weight has been measured for poly(hexadecene sulfone) samples. A liquid crystalline *schlieren* texture has been photographed for a copoly(hexadec-1-ene–cyclohexene sulfone) containing 10% of the latter residues. ^{13}C MAS NMR measurements on a high molecular weight poly(hexadecene sulfone) show that there is a dispersion of backbone shifts present at low temperatures (-60 °C) and that this is also present in the liquid crystalline state, indicating conformational stiffness and consistent with a hairy rod model for the polymers.

Liquid crystalline polymers have mesogenic groups either in the main chain or as part of the side chains. Flory showed some time ago that the liquid crystalline state might be obtained with a polymer if the main chain were a stiff rod, provided that the aspect ratio was high enough,[2] since which time there has been a growth in the appreciation of the incidence of such materials. They extend from solutions of the natural molecules DNA[3] and the α helical state of proteins and polypeptides[4] through derivatives of biopolymers such as cellulose[5] to man-made polymers such as the isocyanates[6] and Kevlar[7] and rigid polyesters with flexible side chains.[8] The isocyanates are examples of stiff helical rods, the Kevlar chain is nearly a flat stiff ribbon, possibly with kinks of a minor angle spaced along the chain, and the polyester has a similarly stiff main chain with flexible side chains promoting fluidity, but the side chains render the cellulose derivatives stiff by hindering rotation about the links between the residues to create a fairly large persistence. These polymers may be both thermotropic and lyotropic.

Here we demonstrate that a number of poly(1-olefin sulfone)s,[9] [$-CH_2-CHR-SO_2-$] formed by the free radical reaction of sulfur dioxide with eicos-1-ene ($R = C_{18}H_{37}$) and hexadec-1-ene (but not that with hex-1-ene), are main chain liquid crystalline thermotropic polymers. The discovery was made experimentally when observations on terpolymers were extended from the mesogenic olefin-rich side of phase diagrams[10] to the nonmesogenic side chain side and was anticipated from our knowledge of the helical nature of poly(1-olefin sulfone) chains.[11-13] Within the chains the sulfone dipoles self-assemble through an electrostatic influence to create stiff sections. Long side chains also stabilize the helical structures through a mutually repulsive mean field effect.[13] While completing the work, we learned that a transmission electron microscope investigation of a poly(tetradecene sulfone) had found helices in the image of molecules placed in isolation upon a surface.[14]

To establish the liquid crystalline nature of the materials, we have examined them with the polarizing microscope and differential scanning calorimetry. Some experiments have been performed with ^{13}C MAS NMR spectroscopy on one poly(hexadecene sulfone) sample, JM3, at temperatures within the different phases to investigate chain stiffness.

We start with a sample of poly(eicosene sulfone), a white polymer at ambient temperatures with a molecular weight of 1.3×10^5 (RWD285) (the reported molecular weight values were measured by GPC using THF as solvent and polystyrene standards for calibration). When observed upon the hot stage of a polarizing microscope, the material remained in its normal condition until a temperature of 54 °C was reached, when a slight pressure on the cover slip caused the polymer to spread to form a clear film. This temperature we term a softening point. Under crossed polarizers the polymer showed birefringence, a feature that was removed when the material warmed to 71 °C but which reappeared on cooling. When examined by differential scanning calorimetry (DSC), the curve was reproducible. A typical example is shown in Figure 1, where it is clear that the method has detected two first order transitions, and the clearing temperature value there indicated agrees well with that obtained with the microscope (71 °C). (The values of the peak temperatures and the enthalpies of the transitions were not significantly altered by raising or lowering the rate of heating by a factor of 2.) The lower transition occurs at 37 °C, a temperature below the softening point of 50 °C, of which there is no indication on this plot. The softening temperature, T_s, is not a true thermodynamic quantity defining a phase boundary: as the sample is heated, it is merely the temperature at which the viscosity becomes sufficiently low to allow distortions to take place under a small force.[15]

For a second poly(1-olefin sulfone), that made from hexadec-1-ene, the microscope examination found a liquid crystalline range of 65-70 °C. Thus, shortening the side chain had only a minor effect upon the clearing temperature but did raise the softening temperature, an effect that is consistent with the polymers that have long side chains being rubbers.[16] To examine the effect of molecular weight, we have measured these transition temperatures with the microscope for poly(hexadec-1-ene sulfone) samples that were made using a wide range of proportions of the chain transfer agent bromotrichloromethane, $BrCCl_3$.[9] The values of T_c and of T_s are plotted in Figure 2, where it may be seen that once molecular weights are above 30 000, the two temperatures observed experimentally with the microscope cease to rise with molecular weight. Also on Figure 2 are experimental points obtained

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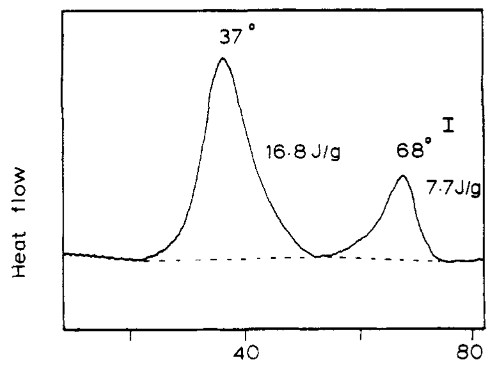

Figure 1. Examination by differential scanning calorimetry of a sample of poly(eicosene sulfone) (RWD285) with $M = 1.3 \times 10^5$. The two endotherms mark the transitions between smectic phases, at 37 °C, and an isotropic melt, at 68 °C. The plot could be reproduced 20 min after cooling the sample. Scanning rate: 10 deg/min when heating and 5 °C/min when cooling.

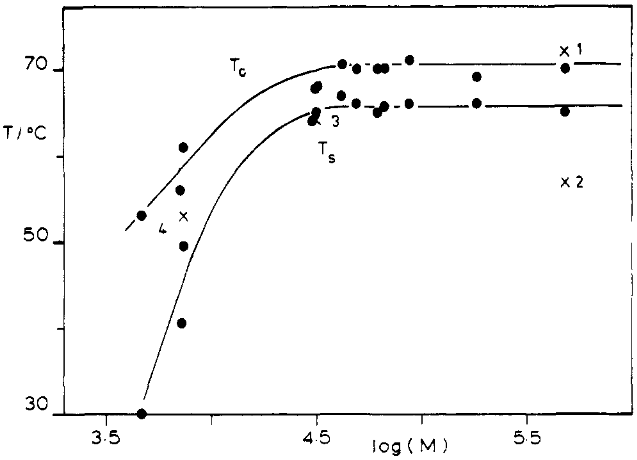

Figure 2. Clearing temperature and softening point of poly(hexadecene sulfone) as a function of molecular weight. The samples were prepared with different proportions of $BrCCl_3$ to control M, which was measured by GPC with solutions in THF using polystyrene standards. The extra points X were measured by DSC (heating and cooling at 5 °C/min); they are endotherm peak maxima and were measured (1) on a fresh sample, (2) after standing for 40 days, and (3) and (4) on fresh samples.

when three samples of differing molecular weights were examined by differential scanning calorimetry (DSC). By this method endotherms were obtained for each polymer with peaks at temperatures within a few degrees of the visually-measured clearing temperatures, confirming that a thermodynamic first order transition is present. The behavior of these polymers was not exactly reproducible; for example the transition temperature of the high molecular weight sample was lower (point 2) when the measurement was repeated, even after 6 weeks.

Next we describe measurements made upon the hex-1-ene polysulfone with $M = 4 \times 10^5$. When examined with the microscope, a softening temperature was found at 88 °C, and the liquid that formed was birefringent. However, on standing, this dispersed and did not reappear upon cooling. The first examination by DSC of the sample that had been precipitated from a solution several years ago found a single endotherm (peak at 84 °C, 7.2 J/g) superimposed upon a small step, but the second scan found only the step of a glass transition temperature at 72 °C, a behavior that is reminiscent of earlier DSC studies[17] on polysulfones. When a similarly obtained sample of a copolysulfone of cyclohexene and hex-1-ene (X93X, $M = 4 \times 10^5$)[11] was first examined by DSC, an endotherm at 88 °C was found, but on subsequent examination only the glass transition temperature was seen (at 77 °C). For this series of polymers the softening points are just above the glass transition temperatures and liquid crystalline behavior is not clearly seen.

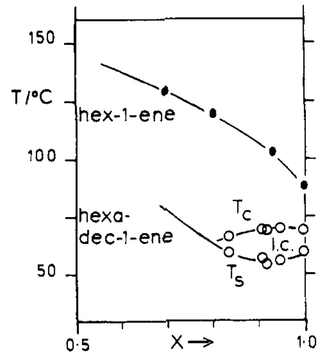

Figure 3. Softening points of a series of terpolymers of hex-1-ene and cyclohexene and SO_2, previously used in ref 11, with molecular weights about 4×10^5 (●). Also shown are clearing temperatures and softening points for terpolymers of hexadec-1-ene and cyclohexene and SO_2 with a more restricted range of compositions (○), showing the extent of a liquid crystalline phase. The temperatures were observed on a polarizing microscope. x is the mole fraction of residues of the 1-olefin, measured from the ^{13}C NMR spectrum.[9]

In our simple theory of the configuration of the poly(1-olefin sulfone) chain, the C–C bonds in the stiff helical sections are in the *gauche* conformation, and a kink or break in the helix occurs when a C–C bond is promoted to the *trans* conformation (thus freeing adjacent sulfone dipoles from a locking electrostatic interaction). The mean length of the helices, $\langle m \rangle$, is related[13] to p, the fraction of C–C bonds in the *trans* state, by $\langle m \rangle = 1/(1 - p)$ in solution. In the bulk we suppose that the chains are in helical conformations which are mesogenic unless the temperature is so high that the helix is disrupted. A higher temperature is known[13] to lower p and so to lower $\langle m \rangle$. The theory thus accounts for the clearing temperature of the polymer as the temperature at which $\langle m \rangle$ falls below the level at which the main chain helices operate as mesogens. The poly(eicosene sulfone) and the poly(hexadecene sulfone)s do have sufficiently long helical sections for them to have a mesogenic character at the temperatures at which they soften, but for poly(hex-1-ene sulfone) this is apparently not so.

The presence of a small fraction of cyclohexene residues in the chain is expected to reduce the mean length of helical sections: then $\langle m \rangle = 1/(1 - px)$, where x is the fraction of 1-olefin residues present.[11] A set of copolysulfones of hexadecene and cyclohexene have been prepared by methods described before,[11] with x in the range 0.8–1.0 according to ^{13}C NMR measurements,[11] to explore the compositional dependence of the liquid crystalline phase. For these copolymers, which have a Bernoullian distribution of olefin residues[11] and whose molecular weights were all above 10^5, a liquid crystalline phase was detected by microscopy at the temperatures shown in Figure 3. The presence of cyclohexene residues does not destroy the mesogenic effect, which is surprising, for $\langle m \rangle$ may be as low as 5–10 in some of these terpolymers. The long side chain effectively counteracts the disrupting effect of the cyclohexene residues in the main chain. We recognize also that it may not be appropriate to neglect entirely effects between chains when considering bulk properties.

The poly(hexadecene sulfone) and the copoly(hexadecene–cyclohexene sulfone) polymers had a small liquid crystalline range of temperatures when examined with

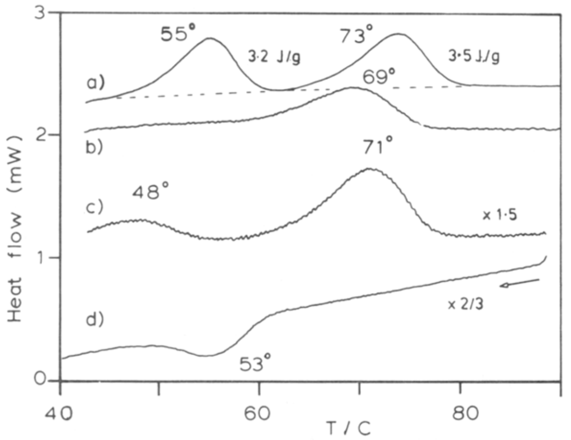

Figure 4. Examination by differential scanning calorimetry of a sample of copoly(hexadecene–cyclohexene sulfone) OAS2, with $M = 0.52 \times 10^5$ and $x = 0.90$: (a) trace obtained when heating after a delay of 6 weeks since the previous examination (two endotherms seen); (b) trace obtained 10 min after trace a; trace obtained after a delay of 2 h; (d) trace obtained on cooling directly. Scanning rate, 5 °C/min; sample weight, 12 mg.

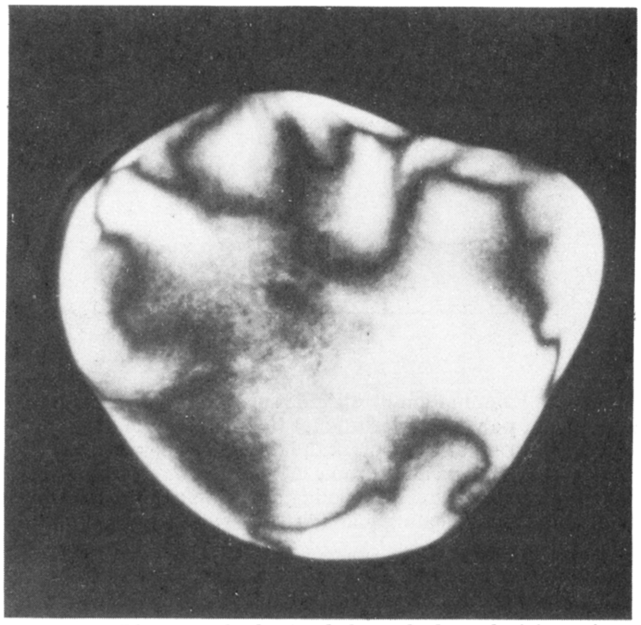

Figure 5. Photograph obtained through the polarizing microscope at ×33.5 magnification of a drop of the copoly(hexadecene–cyclohexene sulfone) OAS2. The sample had been heated to 75 °C and then cooled at a rate of 0.1 °C/min to 71.2 °C. The observed *schlieren* texture was photographed 16 h afterward, though it had developed within a few hours.

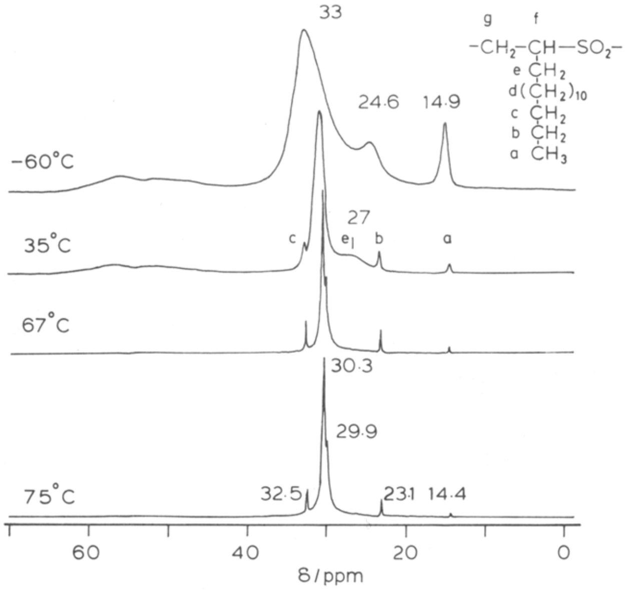

Figure 6. ^{13}C MAS-CP-DD NMR spectra at 75.4 MHz of the poly(hexadecene sulfone) JM3 at the temperatures indicated, recorded as the temperatures were successively lowered. Spectrometer settings: ACQ time 48.9 ms, relaxation delay 1.0 s, CP contact time 1.0 ms, spin rate > 4 kHz, number of scans 27K to 57K. The peaks are assigned to the carbons a–g, as shown in the insert top right. $M = 4.8 \times 10^5$ by GPC.

the microscope. A liquid crystalline phase was present for the polymer with a mole fraction of cyclohexene residues as high as 16%. At the lower temperatures of softening of the hexadecene co- and terpolymers the mesogenic nature of the chain is more effective than that of hex-1-ene at the higher temperature. The length of the side chain apparently stabilizes the helix[14] and so counteracts the tendency of the presumably randomly placed cyclohexene residues to disrupt.[11] The results of a DSC examination are shown in Figure 4 for the hexadecene cyclohexene terpolymer OAS2, with $x = 0.90$. In each study the clearing temperature was observed, though the peak maximum was found at a higher value the longer a period lapsed before the measurement was made. More sensitive to the pretreatment was the behavior of the smaller endotherm near 50 °C. It was not visible if the scan was performed within 10 min of cooling the sample to ambient temperatures (trace b) but could be recognized if a period of 2 h at ambient had lapsed (trace c). The upper but not the lower features appeared as an exotherm on cooling (trace d). This polymer, with shorter side chains than those of poly(eicosene sulfone), is more sensitive to the thermal history. We show in Figure 5 one photograph taken 16 h after the sample had been cooled, within the temperature range of the upper transition as observed with the DSC, from 75 to 70.2 °C at a rate of 0.1 °C/min. A *schlieren* texture has clearly developed, with *noyaux* and brushes visible in this picture. The sample is lying within the span of the endotherms shown in curves a–c on Figure 4 and has a clear and characteristic nematic liquid crystalline texture. Note that, for the copolymers of hex-1-ene and cyclohexene and cyclohexene and SO_2, as x falls, so the softening temperature rises smoothly. We associate this trend with the progressive increase in rigidity of the backbone as covalent cyclic structures become common and restrict the configurations of the backbone. (The softening temperature of poly(cyclohexene sulfone) is about 180 °C.)

Finally, we present the results of some measurements made upon the high molecular weight poly(hexadecene sulfone) sample JM3 using CP-MAS ^{13}C NMR spectroscopy. Spectra that are shown in Figure 6 were obtained at progressively lower temperatures after the sample was heated to 80 °C. The various carbons present have been assigned from the solution spectrum, the most prominent line being from the side chain methylenes. Their shift at 35 °C is at about 30 ppm, consistent with the bonds being in a good proportion of *gauche* conformations,[17] so that they are well coiled as in amorphous polyethylene and incapable of themselves being mesogenic. Between +35° and −60 °C their shift falls from 30 to 33 ppm, indicating that the chains change their conformation toward the *trans* state within that range. The sharpness of the signals from the methyl groups and methylenes (b and c) at the end of the side chain we attribute to their rapid motion; there is a hindering in the motion of the carbons as the backbone is approached and as the temperature is lowered, so the chemical shift anisotropies are not effectively averaged

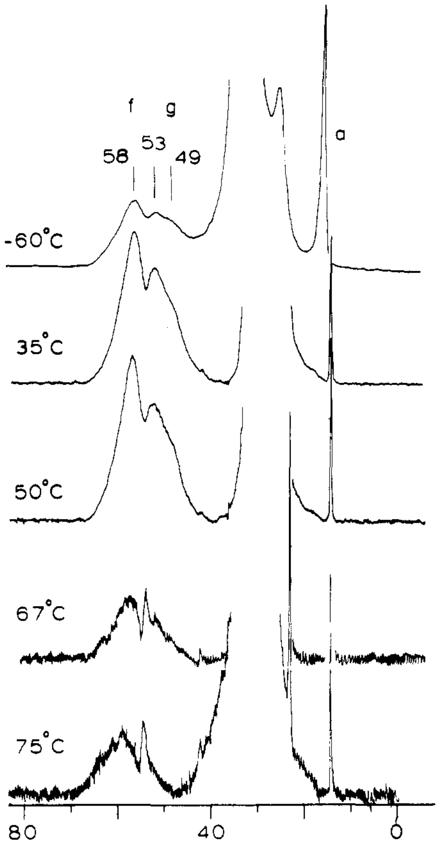

Figure 7. Part of the ^{13}C MAS-CP-DD NMR spectra of the poly(hexadecene sulfone) of Figure 6 enhanced to show the signals from the main chain carbons f and g.

and broad line shapes are seen.[18] There is a significant broadening of the side chain signals between 67 and 35°C; the polymer has probably passed through a transition temperature consistent with it behaving like the terpolymer OAS2 of Figure 4. The terminal methyl and the adjacent methylene signals become broad at −60 °C, when the material is probably in a glassy state. The relative weakness of the sharp signal from the carbons at the end of the side chain is also attributed to their rapid motions; cross-polarization is discriminating against the signals from liquidlike atoms.[18] The signals from the main chain carbons (and from the first side chain carbon C_e) are too broad to be seen at the higher temperatures in these spectra unless the scale is expanded, as has been done for the plots shown in Figure 7. In the presumed glassy state, at −60 °C, the signal from the backbone carbons is well dispersed when compared to the methyl carbon, C_a. Near 50 ppm, the main peak C_g, has a shoulder too removed to be attributed to a microstructure feature,[11,18] and the carbon has clearly a dispersion of shifts because the chain is frozen into more than one conformation (the origin may lie in the γ-gauche effect of a carbon or an oxygen of the sulfone group[19]). This stiffness was present when the temperature was 50 °C, which may lie within the liquid crystalline phase, and even at the two higher temperatures it is noticeable that the signals were relatively broad. This is consistent with the backbone being in a frozen conformation and the liquid crystalline properties being derived from the mesogenic character of the main chain, which is known to adopt a helical configuration in dilute solutions[11-13] and which is evidently effective in the bulk.

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References and Notes

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