Thermal and Rheological Properties of a Liquid-Crystalline Polyurethane

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ABSTRACT: A novel liquid-crystalline polyurethane (LCPU) was synthesized by the condensation of 2,4-toluenediisocyanate and 4,4′-bis(6-hydroxyhexoxy)biphenyl. Solution polymerization in dimethylformamide produced intrinsic viscosities in the range 0.30–0.57 dL/g. Differential scanning calorimetry shows a crystalline melting transition that is highly dependent on molecular weight and thermal history and a clearing transition that is virtually independent of both. Parallel-plate rheometry results are consistent with the presence of a liquid-crystalline phase, coexisting with a small amount of three-dimensional crystallinity, between 152 and 166 °C. Dynamic mechanical measurements reveal an unusually high elastic modulus of 180 MPa in the plateau region above T_g, compared with 6 MPa for an amorphous polyurethane with a chemical structure based on 1,4-butanediol.

Introduction

In recent years considerable interest has developed in the rheological properties of thermotropic liquid-crystalline polymers.[1] This is a consequence of their potential application as high-strength fibers and plastics and their unusual properties in the melt due to structural order in the fluid phase. Some of the main rheological phenomena present in these melts include unusually long relaxation times, apparent yield stresses, minima in viscosity as a function of temperature, considerably lower viscosities than comparable amorphous polymers, and negative values of the first normal stress difference.[2-5]

Most of the studies of the rheological properties of these polymers have been done on thermotropic polyesters,[2,3,5,6-9] mainly copolymers of ethylene terephthalate and *p*-hydroxybenzoic acid (HBA/PET). In contrast, no rheological work has been reported for polyurethane liquid-crystalline polymers. This is a consequence of the difficulties involved in obtaining such polymers with appropriate transitions occurring at temperatures below those at which they undergo considerable degradation. The first liquid-crystalline polyurethanes were synthesized by Iimura et al.[10] who reported only the thermal properties of these materials.

In this work we report the synthesis, structural characterization, and mechanical and rheological properties of a polyurethane, first synthesized by Jadhav et al.,[11] obtained by the condensation of 4,4′-bis(6-hydroxyhexoxy)-biphenyl with 2,4-toluenediisocyanate. Tanaka and Nakaya[12] synthesized a related polyurethane based on toluenediisocyanate (TDI) (unspecified isomer) and 4,4′-bis(2-hydroxyethoxy)biphenyl, which they reported to be liquid-crystalline, but they obtained only low molecular weights ($[\eta] = 0.13$ dL/g). Our polymer has the structure shown in Figure 1 and will be referred to in this paper as LCPU. Samples of two different molecular weights were studied in detail, and these will be referred to as LCPU-1 ("low molecular weight") and LCPU-2 ("high molecular weight"). It is shown that the rheological behavior of this polyurethane is dependent on the presence of liquid-crystalline order in the fluid phase as well as on the presence of a small amount of three-dimensional crystallinity.

Experimental Section

Materials. Starting materials were obtained from Aldrich Chemical Co. except as indicated. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1-butanol, and 2,4-toluenediisocyanate (2,4-TDI) were purified by vacuum distillation. All other starting materials were used as received.

Mesogenic Diol. The diol, 4,4′-bis(6-hydroxyhexoxy)biphenyl (BHHBP), was prepared as follows: Sodium hydroxide (32.00 g, 0.800 mol) and 4,4′-dihydroxybiphenyl (37.2 g, 0.200 mol) were stirred into 400 mL of ethanol. The resulting slurry was heated under reflux, and 6-chlorohexanol (120.2 g, 0.880 mol) was added dropwise. The reaction mixture was refluxed for 24 h and poured into cold water. The precipitated solid was filtered and recrystallized twice, first from a 3:1 mixture of ethanol and DMF and then from 1-butanol, to give 68.3 g of BHHBP, mp 176 °C, yield 88%. This compound was previously synthesized with a reported melting point of 167–170 °C.[13]

Liquid-Crystalline Polyurethanes. Polyurethanes were synthesized by the reaction of BHHBP with 2,4-TDI (Fluka Chemical Corp.). A slight excess (0.5–1.0%) of the latter was used to compensate for side reactions involving isocyanate groups. The reaction was run on several scales, ranging from 10 to 100 g. Higher molecular weights were obtained in the larger scale polymerizations, probably because the influence of impurities and side reactions was decreased. The procedure described hereafter is for the largest scale preparation; similar procedures were used in the others.

BHHBP (67.98 g, 0.1759 mol) was dissolved in 200 mL of DMF in a heat-dried five-necked round-bottom flask fitted with a condenser, mechanical stirrer, thermometer, and addition funnels charged with DMF and 2,4-TDI. Nitrogen was kept flowing through the system continuously. 2,4-TDI (30.90 g, 0.1774 mol) was added dropwise to the solution, and the temperature was raised to 80 °C and held there for 20 h. As the reaction proceeded, DMF was added as needed to keep the solution viscosity low enough to allow stirring. By the end of the reaction period, 500 mL of additional DMF had been added.

The hot, viscous solution was poured into cold methanol to precipitate the polymer in the form of a white, fibrous material. The polymer was filtered, washed with fresh methanol, and subsequently dried under vacuum at 90 °C for 72 h. The yield was 94.71 g (96%). ^{1}H NMR (reported as follows: chemical shift, multiplicity, integration, assignment in Figure 1) δ 9.51 (s, 1 H, a), 8.75 (s, 1 H, b), 7.47 (m, 5 H, c), 6.96 (m, 6 H, d), 3.96 (m, 8 H, e), 2.09 (s, 3 H, f), 1.65 (m, 8 H, g), 1.40 (m, 8 H, h). Anal. Calcd for $(C_{32}H_{38}N_2O_6)_n$: C, 70.69; H, 7.19; N, 5.00. Found for LCPU-1: C, 70.44; H, 6.97; N, 5.18. Found for LCPU-2: C, 70.74; H, 7.22; N, 5.00.

1,4-Butanediol/2,4-TDI Polyurethane. A homopolymer of 1,4-butanediol and 2,4-TDI was synthesized as follows: In a round-bottom flask, fitted with a condenser and nitrogen inlet and outlet, 1,4-butanediol (1.49 g, 0.201 mol) was dissolved in DMF (40 mL), and 2,4-TDI (3.51 g, 0.201 mol) was added dropwise. The reaction was allowed to proceed at 80 °C for 24 h. The polymer was precipitated in methanol, filtered, washed with methanol, and vacuum dried at 65 °C for 24 h. The yield was 4.64 g (93%).

Polymer Characterization. The intrinsic viscosities of the polymers were determined at 30 °C in DMSO by using a Cannon-Ubbelohde viscometer. Molecular weights relative to poly-

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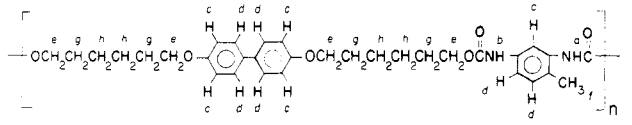

Figure 1. Structure of LCPU. Lower case letters refer to ^1H NMR results (see Experimental Section).

styrene standards were determined in a Waters Model 590 gel permeation chromatograph equipped with four Ultrastyragel columns (500, 10^3, 10^4, and 10^5 Å), using DMF as eluent at 45 °C. A flux of 1 mL/min was maintained in all runs. NMR spectra were recorded on a Varian XL-200 spectrometer, operating at 200 MHz, in perdeuterated DMSO. Calorimetric measurements were conducted in a Perkin-Elmer DSC 7, using indium standards for calibration.

Wide-angle X-ray scattering patterns were obtained in a Statton X-ray camera using a pinhole-collimated Cu Kα source. Polymer samples were placed in a 1.5-mm glass tube which was sealed and placed in a heating chamber in the path of the X-ray beam. The scattering patterns were recorded on photographic film; exposure times ranged from 4 to 5 h.

Optical textures were studied with a Zeiss polarizing optical microscope equipped with a Linkam hot stage and a Polaroid camera. The polymer sample was placed between glass slides and heated to the isotropic melt, and the slides were then sheared to produce a thin layer of melted polymer. The sample was then cooled at 10 °C/min to 145 °C and photographed at that temperature.

Dynamic mechanical properties of the solid polymers were obtained by using a Polymer Laboratories dynamic mechanical thermal analyzer at a frequency of 1 Hz in the double-cantilever mode. The polymer samples were rectangular films with dimensions of 0.6 × 7.0 × 25.0 mm. Nitrogen was circulated continuously during testing to minimize degradation.

Rheological measurements were made in a Rheometrics dynamic spectrometer in the parallel-plate mode using 25-mm serrated disks. Frequency sweeps were carried out at temperature intervals of approximately 10 °C. Parallel-plate geometry was preferred to cone-and-plate because the former is less sensitive to small variations in the gap width caused by thermal expansion of the stainless steel fixtures. The wide gap also minimizes the effect of orientation of the melt at the surfaces of the plates. Nitrogen was continuously circulated in the rheometer chamber. The LCPU was molded in a hot press to obtain disks 25 mm in diameter and approximately 2 mm thick. The disks were placed in the rheometer and heated to 190 °C to allow the marks of the serrated fixtures to penetrate the LCPU. This procedure assured nonslip conditions at the plates, which was especially important for the low-temperature measurements, because high torques were generated during deformation of the samples. The nonslip condition was verified by running the samples at different strains and observing no strain dependence in the measurements. After the gap was adjusted between the plates, the LCPU was cooled to 50 °C and then heated to 140 °C, where the first frequency sweep was performed. The heating was done slowly to avoid temperature overshoots in the environmental chamber. All the runs at temperatures below 160 °C were performed at 1% strain and corrected for stiffness because there was some transducer deflection due to the high torques generated. At higher temperatures, strains up to 5% were applied to the melt. In all cases it was verified by running the sample at different strains that the viscoelastic behavior of the LCPU was well within the linear region.

Tensile tests were performed in an Instron Model 4202 universal testing machine. The LCPU was molded at 175 °C into thin sheets between 0.2 and 0.3 mm thick, and these sheets were cut into rectangular strips, 5 mm wide and 70 mm long. The strips were strained to failure at a rate of 1 mm/min, at room temperature. Reproducibility in the tensile tests was obtained only after a procedure was developed to eliminate all traces of residual solvent from the precipitated LCPU. To do this, about 5 g was molded in a press at 175 °C to obtain thin films with thicknesses varying from 0.10 and 0.30 mm. These films were then cut into rectangles about 15 mm wide and 70 mm long and placed in a Sohxlet extractor. Methanol was used as refluxing solvent. The films were extracted for 48 h and dried in a vacuum oven at 80 °C for 24 h. These films were subsequently used in the tensile measurements or remelted to prepare thicker rectangular samples for the DMTA or disks for the rheological measurements.

Table I
Molecular Weight Characterization of Liquid-Crystalline Polyurethanes

polymer	intrinsic viscosity, dL/g	gel permeation chromatography		
		M_n	M_w	P^a
LCPU-1	0.32	35 100	50 000	1.42
LCPU-2	0.57	75 000	140 200	1.87

[a] P = polydispersity.

Table II
Thermal Properties of Liquid-Crystalline Polyurethanes and Mesogenic Diol by Differential Scanning Calorimetry

	phase transition temp, °C			transition enthalpies, J/g	
	T_g	T_m	T_i	ΔH_m	ΔH_i
LCPU-1	95	152	166	4.1	41.4
LCPU-2	95		169		43.7
BHHBP[a]		96	174	52.9	110.9

[a] 4,4′-Bis(6-hydroxyhexoxy)biphenyl.

Results and Discussion

Molecular Weight Characterization. Table I contains intrinsic viscosity and gel permeation chromatography results for the "low" and "high" molecular weight LCPUs. The GPC molecular weights reported here are only useful for comparisons between the two LCPUs because the calibration of the columns was based on polystyrene standards. Nevertheless, it is apparent from these relative measurements that a reasonably high degree of polymerization was reached.

Thermal Characterization. All the scans for the thermal analysis of the LCPUs were carried out at a rate of 10 °C/min. Reproducible transition temperatures were obtained by first heating to 190 °C (approximately 20 °C above the highest transition temperature) and then cooling to room temperature at the same rate. By this procedure all subsequent scans were virtually identical.

Table II lists the basic thermal properties of both LCPUs. The reported T_m and T_i correspond to the peak maxima, but it should be noted that both transitions extend at least 8 °C higher. It is worthwhile to point out that the clearing enthalpy (ΔH_i) is larger than the enthalpy of fusion (ΔH_m) for both LCPUs and for the mesogenic diol.

DSC thermograms for LCPU-1 are shown in Figure 2. On heating at 10 °C/min the glass transition (T_g) is observed at 90 °C (Figure 2a). Two sharp endotherms appear at 152 and 166 °C, corresponding respectively to melting (T_m) and to the clearing transition (T_i). T_i was found to be virtually independent of annealing, quenching, heating rate, and molecular weight.

On cooling at 10 °C/min, both T_i and T_m are observed, but they are shifted toward lower temperatures (Figure 2b). The T_i exotherm occurs at 128 °C and the T_m exotherm at 105 °C. Supercooling for these transitions is on the order of 40 °C. Similar behavior has been found in other liquid-crystalline polymers. This is in contrast to the behavior of low molecular weight liquid crystals where usually little or no supercooling is observed.[14,15]

After LCPU-1 is annealed for 6 h at 149 °C, quenched, and then reheated, only one endothermic peak (167 °C) is observed in the DSC scan (Figure 2c). At first glance it would appear that this thermal treatment has produced

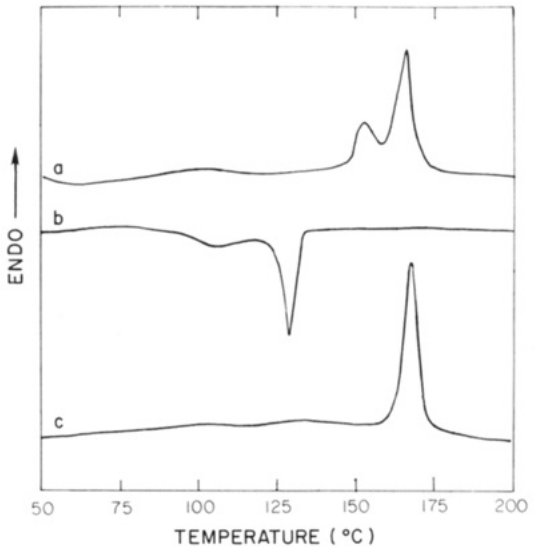

Figure 2. DSC thermograms for LCPU-1 at 10 °C/min: (a) heating after cooling to room temperature from 190 °C; (b) second cooling from 190 °C; (c) heating after annealing for 6 h at 149 °C followed by quenching to room temperature.

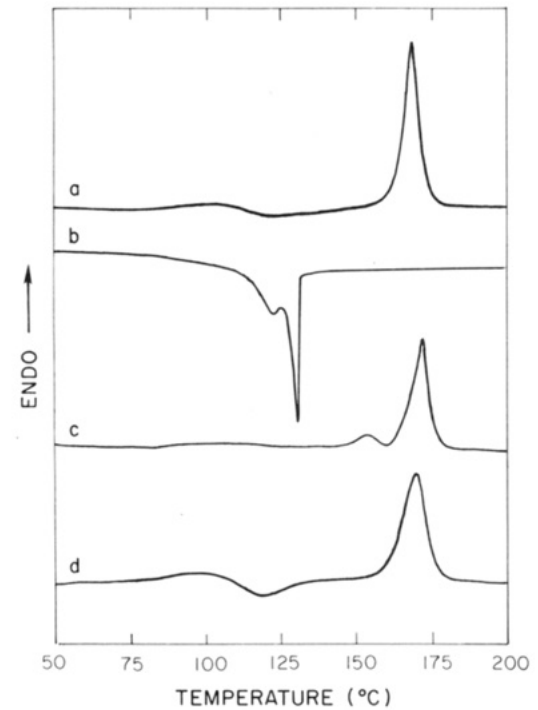

Figure 3. DSC thermograms for LCPU-2 at 10 °C/min: (a and b) same conditions as in Figure 2; (c) heating after annealing for 2 h at 141 °C followed by quenching to room temperature; (d) heating after quenching from the isotropic melt.

a liquid-crystalline glass, but X-ray measurements have shown that three-dimensional crystallinity still exists in this sample. So apparently the annealing process has raised T_m so that it is approximately equal to T_i. Subsequent studies have shown that annealing can raise T_m to as much as 10 °C higher than T_i.[16]

Similar behavior occurs in LCPU-2, except that the DSC scan shows only one endotherm even without annealing (Figure 3a). The glass transition is now more clearly observed at 95 °C, and T_i is found at 169 °C. Again a 40 °C supercooling occurs upon cooling, with T_i appearing at 131 °C and T_m at 123 °C (Figure 3b). Figure 3c shows the DSC scan obtained after annealing LCPU-2 for 2 h at 141 °C. A small crystalline melting peak is detected at 154 °C,

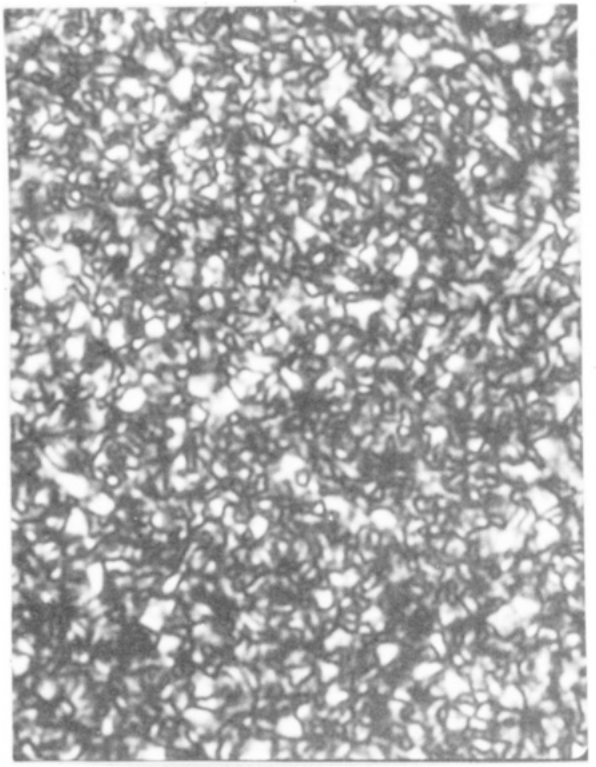

Figure 4. Polarizing optical microphotograph of LCPU-1 at 145 °C between crossed polars.

and T_i shifts slightly to 172 °C. When LCPU-2 is quenched from the isotropic melt and then reheated, a very well-defined glass transition is observed accompanied by a broad exothermic peak at 118 °C (Figure 3d). This is assigned to crystallization, which begins to take place when a sufficient degree of chain mobility is attained.

From the DSC experiments we can conclude that the crystalline melting point, but not the clearing temperature, depends strongly on molecular weight and thermal history.

Polarizing Optical Microscopy. Figure 4 shows a polarizing optical microphotograph of a sample of LCPU-1, which was cooled from the isotropic melt (180 °C) to 145 °C. The threaded texture is typical of nematic polymers.[17]

Wide-Angle X-ray Scattering. X-ray diffraction photographs were taken of a fiber of LCPU-2 drawn from the isotropic melt at 178 °C. The DSC scan of this fiber is similar to Figure 3d. At 24 °C with no thermal treatment, the diffraction pattern (Figure 5a) is characteristic of a nematic A phase.[18,19] The diffuse equatorial reflection corresponding to interchain spacing occurs at 4.0–4.8 Å. The meridional reflections occur at 15.4 and 31 Å, suggesting a nearly extended chain.

When the fiber is annealed for 14 h at 132 °C (just above the crystallization exotherm in Figure 3d), the diffraction pattern shows crystalline order (Figure 5b). The interchain spacing is now resolved into three distinct reflections, at 4.0, 4.3, and 4.6 Å, with the 4.3-Å reflection occurring at an angle of 59° with respect to the chain axis. The axial reflections have shifted to 12.9 and 28 Å, indicating a less extended chain conformation.

Dynamic Mechanical Thermal Analysis. Figures 6 and 7 represent the temperature dependence of E' and tan δ, respectively, at 1 Hz for LCPU-2. Figure 6a is obtained with a film cooled from 195 °C at a rate of 40 °C/min, which was the highest cooling rate attained in the press where the samples were molded. A dynamic modulus (E') of 1600 MPa is measured at temperatures below T_g, taken as the maximum in tan δ (Figure 7) and occurring at 104 °C. E' decreases by 1 order of magnitude immediately

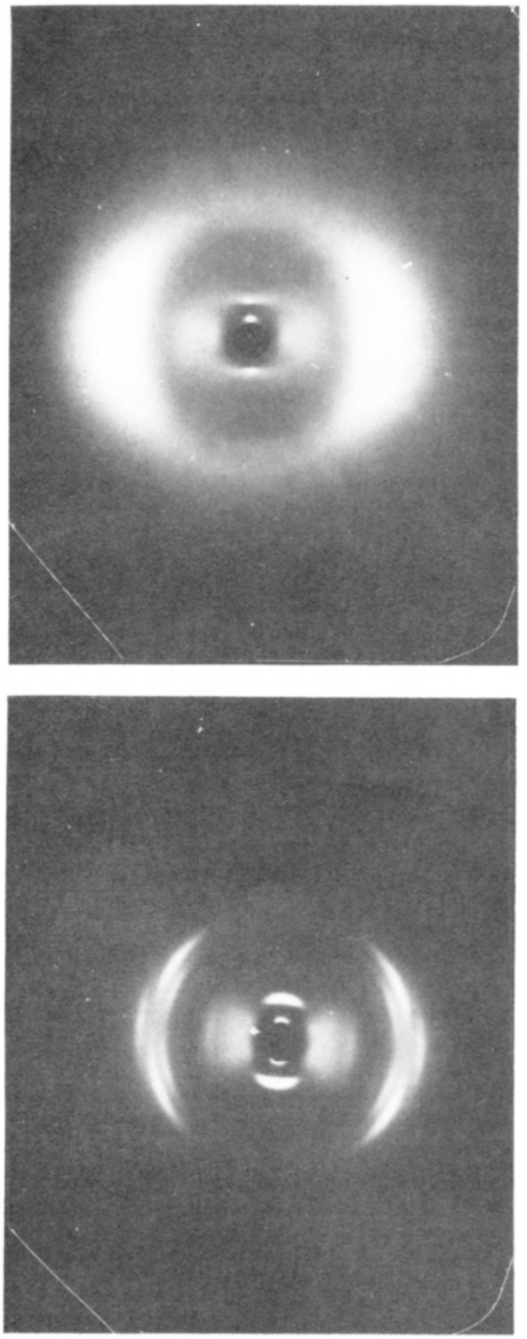

Figure 5. Wide-angle X-ray scattering patterns of a melt-drawn fiber of LCPU-2: (a) without thermal treatment; (b) annealed 14 h at 132 °C.

above T_g and then increases slightly to reach a very flat and stable plateau of quite high modulus ($E' = 180$ MPa).

The depression and subsequent elevation of the modulus above T_g are assigned to the onset of crystallization. (Such behavior is sometimes caused by slippage in the grips due to relaxations above T_g. It is believed that this is not the case here because the phenomenon was quite reproducible in scans performed on different samples.) DSC scans carried out after cooling LCPU-2 from 195 °C at 40 °C/min (the same rate used in molding the sample) appear similar to the one shown in Figure 3d, which, as we mentioned, is consistent with partially inhibited crystallization due to rapid cooling. Finally, close to 170 °C, E' decreases dramatically as LCPU-2 goes through the clearing transition.

Figure 6b shows the change in dynamic mechanical behavior when LCPU-2 is annealed for 2 h at 141 °C (the same thermal treatment as sample c in Figure 3). Now a more gradual decrease in E' is observed, and T_g decreases by almost 10 °C to 95 °C. E' reaches the same value as that of the rapidly cooled sample at approximately 155 °C. This is very close to the T_m of the annealed LCPU-2 in the DSC study.

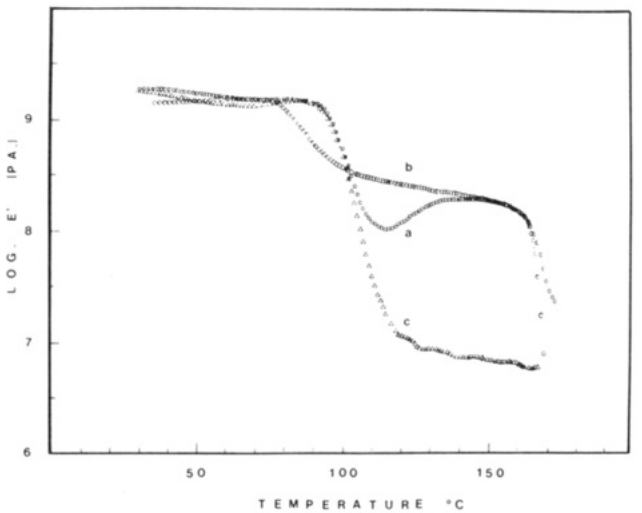

Figure 6. Temperature dependence of the storage modulus (E') at 1 Hz by DMTA: (a) LCPU-2 after cooling from 195 °C at 40 °C/min; (b) LCPU-2 after annealing for 2 h at 141 °C and cooling to room temperature; (c) a polyurethane obtained from 2,4-TDI and 1,4-butanediol after cooling from 195 °C at 40 °C/min.

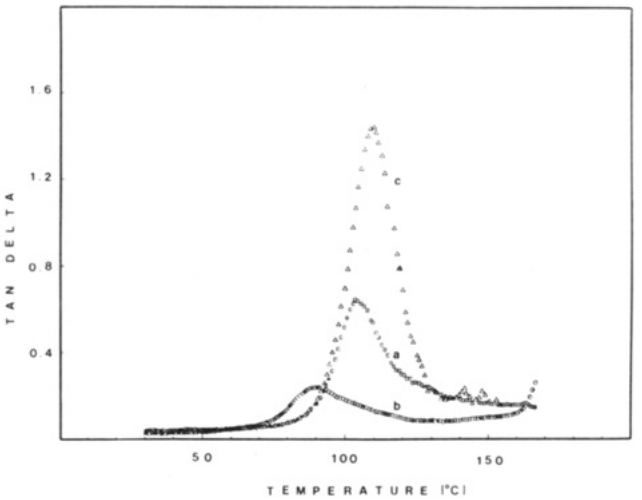

Figure 7. Temperature dependence of tan δ at 1 Hz: (a) LCPU-2 after cooling from 195 °C at 40 °C/min; (b) LCPU-2 after annealing for 2 h at 141 °C and cooling to room temperature; (c) a polyurethane obtained from 2,4-TDI and 1,4-butanediol after cooling from 195 °C at 40 °C/min.

GPC measurements on the annealed LCPU-2 used in the DMTA experiments indicate that annealing in the press considerably reduces the molecular weight. The weight-average molecular weight, relative to polystyrene, decreased from 140 200 to 76 900. This decrease in molecular weight probably accounts for the observed decrease in T_g. (When DSC and rheological experiments were carried out under nitrogen, no significant decrease in molecular weight was observed.)

The results shown in Figure 6c are for a polyurethane obtained by polymerizing 2,4-toluenediisocyanate with 1,4-butanediol. This polymer has the same modulus below T_g as LCPU-2 but is completely amorphous. E' for this polymer decreases by almost 3 orders of magnitude above T_g to a plateau value of about 6 MPa. This is in marked contrast to the behavior of LCPU-2 and is clear evidence

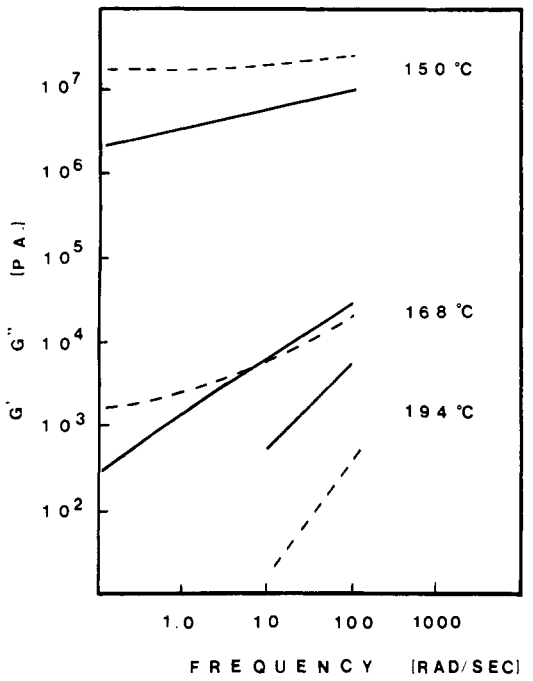

Figure 8. Storage modulus (- - -) and loss modulus (—) versus frequency for LCPU-1.

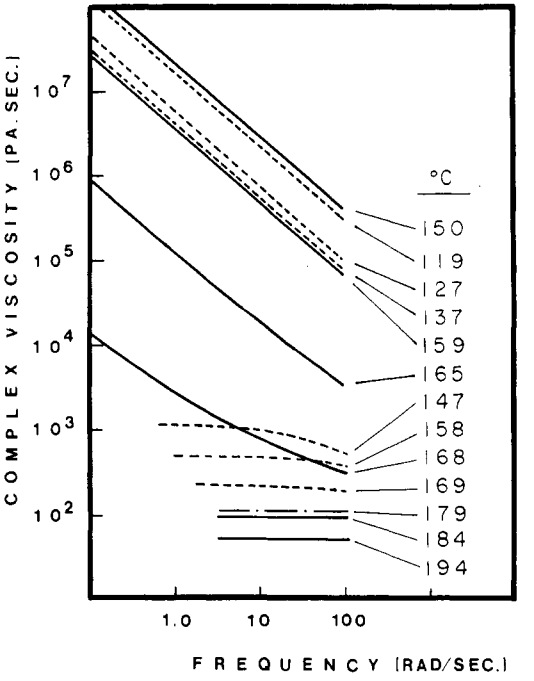

Figure 9. Complex viscosity versus frequency for LCPU-1: (—) heated from room temperature; (- - -) cooled from 194 °C; (-·-) results obtained at 179 °C, which were the same on heating as on cooling.

for the existence of three-dimensional order in the latter.

Rheological Measurements. We will first discuss the behavior of LCPU-1. Below 150 °C its viscoelastic properties did not change significantly. This temperature region corresponds to the flat plateau zone observed in the DMTA experiments (Figure 6a). As shown in Figure 8, G' is independent of frequency with a value of 30 MPa at low frequencies, and there is a strong dependence of the complex viscosity on frequency (d log η^*/d log ω = −0.9), which is typical of solidlike behavior (Figure 9).

To avoid confusion in the plot, only the curves corresponding to 150, 168, and 194 °C are shown in Figure 8 while the curves of η^* for all the temperatures are shown in Figure 9. The three temperatures in Figure 8 correspond to typical solidlike behavior, liquidlike behavior, and intermediate behavior, as explained below.

Measurements were taken at three temperatures in the vicinity of T_m and T_i. The first, 159 °C, is only 7 °C above T_m. It is expected that at this temperature a considerable amount of residual crystalline order remains in LCPU-1. The rheological data reveal a decrease in G' of about 1 order of magnitude to 4.40 MPa at low frequencies. The complex viscosity plot still exhibits the properties of a highly elastic material with a slope of −0.9. This reflects the fact that the loss modulus is consistently lower than the storage modulus by about 1 order of magnitude.

At 165 °C, 13 °C above T_m, the elastic modulus decreases by another 1.5 orders of magnitude, and the complex viscosity follows the same trend. Now the frequency dependence of η^* is lower (d log η^*/d log ω = −0.84) at frequencies below 3.16 rad/s. It is still lower at frequencies higher than 3.16 rad/s (d log η^*/d log ω = −0.73). The behavior of the melt is now more like that of a lightly cross-linked rubber.

A significant change in behavior is observed at 168 °C, just above T_i. At this temperature G' shows a greater dependence on frequency. The η^* curve shows a marked concavity upwards from an initial slope of −0.67 at low frequencies to a final slope of −0.37 for frequencies between 10 and 100 rad/s. This indicates a frequency-dependent change from elastic behavior to viscous behavior. This is also reflected in the fact that G' and G'' intersect at 10 rad/s, so that G'' is greater than G' at high frequencies (Figure 8). The shapes of the η^* and G' curves at this temperature are similar to what has been observed in HBA/PET liquid-crystalline copolyesters[2,3,6] and in concentrated (9–10%) anisotropic solutions of poly(*p*-phenyleneterephthalamide),[20,21] where particular care has been taken to protect the solutions from undesirable moisture effects.

Finally, at temperatures above T_i, the behavior is more like that of a typical polymer melt. At 179 °C the melt, which was opaque at lower temperatures, is completely transparent. There is a very slight dependence of the complex viscosity on frequency, and the frequency dependence of the loss modulus is d log G''/d log ω = 1. G'' is now about 1 order of magnitude higher than G'. At 184 and 194 °C the results are similar, except that the Newtonian behavior extends to the highest frequencies obtained in the rheometer.

It should be noted that, in contrast to what has been observed in some other liquid-crystalline polymers, the clearing transition in the LCPU is not accompanied by an increase in viscosity.[7,9] Such an increase in viscosity at T_i in liquid-crystalline polymers is not general and seems to depend on the shear rate regime at which the viscosity is measured.[2,7,22] The observed behavior of the LCPU may then be due to the fact that the comparison of viscosities in the isotropic and liquid-crystalline states has been made only at low shear rates. The 40 °C supercooling observed in the DSC scans and in the rheological measurements (see below) allows one to compare the frequency dependence of the viscosity at 168 °C in the mesophase (solid line in Figure 9) and at essentially the same temperature (169 °C) in the isotropic melt (dotted line in Figure 9). If these two curves are extrapolated to higher frequencies, it appears that they may intersect, with the viscosity of the liquid-crystalline phase becoming lower than that of the isotropic phase. It should also be pointed out that these are dynamic measurements and not steady-state shearing measurements, where higher degrees of orientation may be achieved.

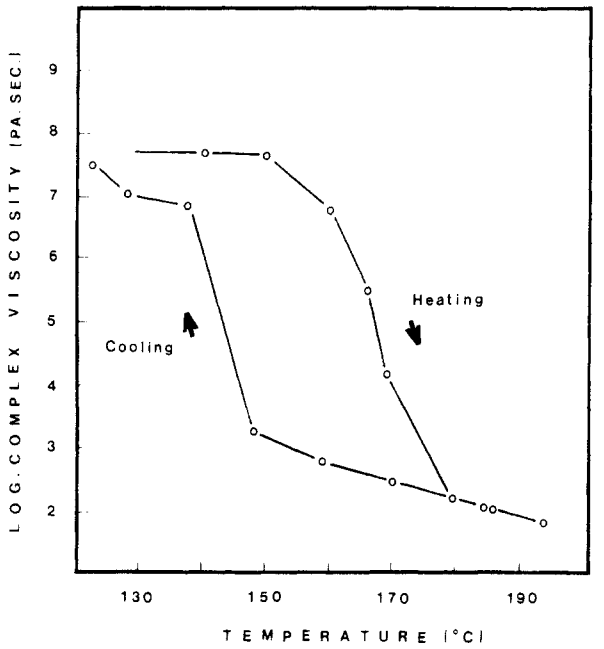

Figure 10. Hysteresis curves for complex viscosity versus temperature at 1 rad/s (LCPU-1).

Another plausible explanation for the observed phenomena, which is independent of the above arguments, is that, because there is only a 14 °C difference between T_m and T_i, a considerable amount of three-dimensional crystallinity may coexist with the liquid-crystalline phase up to T_i. (Preliminary X-ray observations indicate that this is the case.) This residual crystallinity could considerably increase the viscosity in the liquid-crystalline phase.

When the rheological properties are measured as LCP-U-1 is cooled from the isotropic melt, a completely different pattern emerges. Measurements were taken at 179, 169, 158, and 147 °C (Figure 9), and at these temperatures the response of LCPU-1 is that of an isotropic melt. This is consistent with the DSC measurements, which show a considerable degree of supercooling with T_i occurring at 131 °C.

An Arrhenius temperature dependence for viscous flow is typical of single-phase polymer melts. In this temperature range a plot of log η^* versus $1/T$ gives an activation energy of 11.5 kcal/mol with a very slight departure from linearity at temperatures below 158 °C. This value is similar to those found for liquid-crystalline polyesters.[2]

At 137 °C LCPU-1 again exhibits the rheological response of a solid, and as the temperature is decreased to 121 °C, the behavior gradually approaches that observed after slow heating from temperatures below T_g. The hysteresis effect of thermal history on the rheological properties is clearly evident from the temperature dependence of the viscosity measured at 1 rad/s, as shown in Figure 10. A wide range of behavior, ranging from solid to viscous flow, and complex viscosities that differ by up to 4 orders of magnitude, is observed at the same temperature, depending on the thermal history of the sample.

It appears from these results that the drastic changes in the rheological properties of LCPU-1 arise at least partially from the presence of crystallites that form a three-dimensional physical network. The network seems to be slowly destroyed in a range of at least 10 °C between 155 and 165 °C. At 168 °C the frequency dependence of the viscosity is very similar to that of other liquid-crystalline polymers. Above T_i the melt behaves like a typical low molecular weight polymer melt with almost no shear thinning.

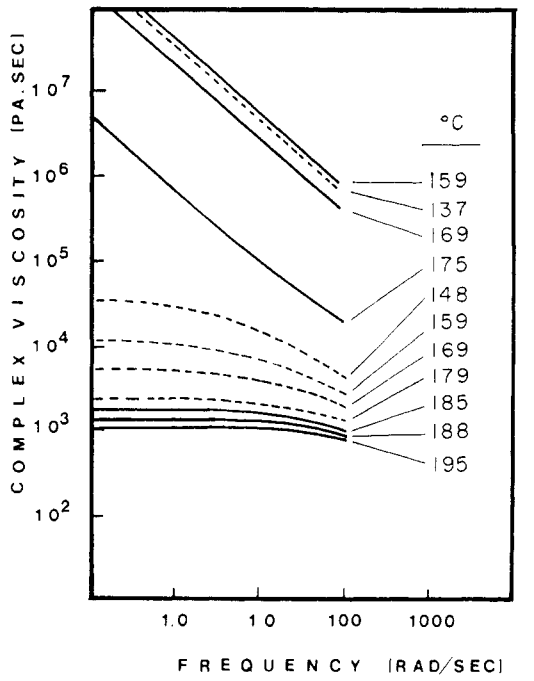

Figure 11. Complex viscosity versus frequency for LCPU-2. The convention followed for the curves is the same as in Figure 7.

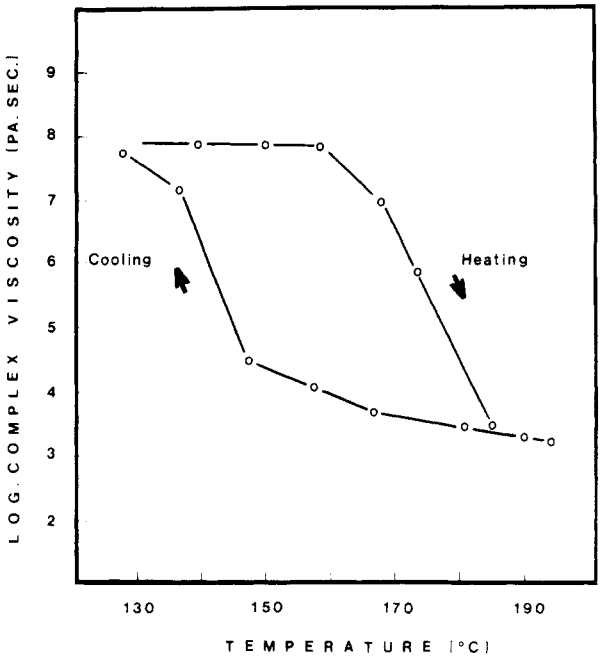

Figure 12. Hysteresis curves for complex viscosity versus temperature at 1 rad/s (LCPU-2).

For LCPU-2 the same main features are observed in the solidlike region below 159 °C (Figure 11). The modulus is again approximately 30 MPa. At 168 °C, very close to the T_i found in the DSC analysis (Figure 3a), G' and η^* begin to decrease but maintain solidlike behavior. At 175 °C the response resembles that found at 165 °C for LCP-U-1.

At 179 °C the melt is transparent, and the rheological behavior is again typical of an isotropic polymer melt. On cooling, LCPU-2 shows a very high degree of hysteresis (Figure 12). The activation energy of the melt is the same as for LCPU-1, but the departure from Arrhenius behavior occurs at lower temperatures. The viscosity versus shear rate curves (Figure 11) now show a greater shear rate dependence, which is a consequence of the higher molecular

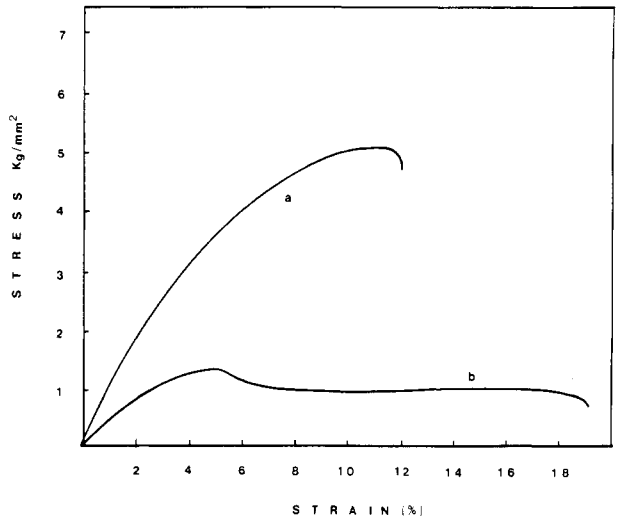

Figure 13. Stress–strain curves for LCPU-2: (a) after extraction of residual solvent; (b) before extraction of solvent.

weight. The curves at 137 and 128 °C are solidlike and approach the high-modulus plateau.

These results are again very consistent with the DSC measurements. The slight differences observed for the transition temperatures on heating and cooling with the two techniques are attributed not only to the different natures of the measurements but also to the different rates of heating and cooling employed in each case.

Tensile Tests. Several rectangular samples were tensile tested after treatment, as indicated in the Experimental Section. The results were quite reproducible, indicating high initial modulus (taken as the slope of the stress/strain curve at zero strain) in the linear region, with values between 800 and 1200 MPa for LCPU-2. The samples show moderate ductility with elongations at break ranging from 8% to 14% (Figure 13a).

When small amounts of solvent remain, a different stress–strain behavior is observed. LCPU-2 shows a lower initial modulus (approximately 600 MPa), upper and lower yield points, and elongations at break of about 20% (Figure 13b).

Conclusions

The synthesized LCPU exhibits phenomena consistent with the presence of a liquid-crystalline phase at temperatures between 152 and 166 °C. The fact that the low-temperature peak in the DSC scans is highly dependent on molecular weight and thermal history, while the high-temperature peak is virtually independent of both, strongly suggests that the former corresponds to a crystalline melting transition and the latter to a clearing transition. The shear rate dependence of the complex viscosity between the transition temperatures is similar to that found in other liquid-crystalline polymers. A considerable degree of three-dimensional crystallinity appears to coexist with the liquid-crystalline phase up to the clearing temperature. Wide-angle X-ray scattering of melt-drawn fibers indicates the existence of a mesophase which crystallizes upon annealing. Polarizing optical microscopy shows textures which are also characteristic of a mesophase.

The presence of three-dimensional crystallinity in the LCPU is surprising in view of the asymmetry of the 2,4-toluenediisocyanate linkage. Other polyurethanes based on 2,4-TDI have been found to be completely amorphous. It is likely that interaction between biphenyl mesogens on adjacent chains provides a strong driving force for crystallization. Infrared spectroscopy studies to be published will examine the hydrogen-bonding properties of the LCPU.

The dynamic mechanical and tensile measurements show interesting mechanical properties for the LCPU. Further investigations will focus on its use as a component in blends and copolymers.

Acknowledgment. We are grateful to the Center for UMass–Industry Research in Polymers (CUMIRP) and to the Army Materials and Mechanics Research Center in Watertown, MA, for support of this research.

Registry No. (2,4-TDI)(BHHBP) (copolymer), 117252-65-0; (2,4-TDI)(BHHBP) (SRU), 117308-04-0.

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