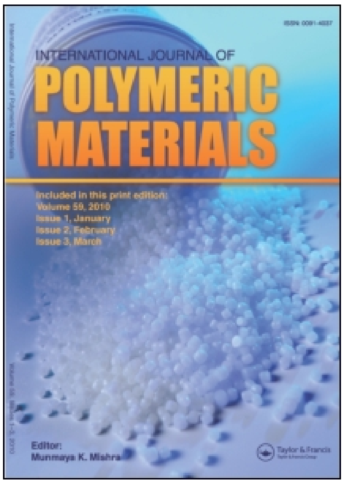

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Effects of Orientation on the Properties of Liquid Crystalline Polymers

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Effects of Orientation on the Properties of Liquid Crystalline Polymers

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Mechanical properties and thermal behavior of liquid crystalline polymers with mesogene groups in the main chain were studied as functions of jet draw ratio. It is shown that tensile strength F and Young's modulus E increase with draw ratio and the maximum E depends mainly on the chemical structure of chain and F is strongly affected by molecular packing that may be improved by heat treatment. The differential thermal analysis, thermal mechanical analysis and thermal acoustic analysis were used to find the spinning conditions for achieving maximum orientation and annealing conditions for macromolecular reconstructions without disorientation.

KEY WORDS Tensile strength, Young's modulus, thermal expansion, shrinkage, liquid crystalline polymers.

INTRODUCTION

It is well known that properties of both flexible- and rigid-chain polymers depend on macromolecular orientation. Especially "sensitive" to orientation are the Young's modulus E, tensile strength F, thermal expansion coefficient and shrinkage. It has been shown that high E and F can be achieved by orienting a molecular bonds' network with a certain junction concentration.[1] For any polymer an optimal network structure may be formed by preparing specimens from the solution of the ultra-high-molecular-weight (UHMW) polymer in a "poor" solvent with the concentration corresponding to molecular weight (MW). If drawing conditions are chosen so that chain scissions, junction destruction and chain slippage do not occur, the highest values of E and F can be achieved, as for example, for ultraoriented UHMW PE fibers ($E = 220$ GPa, $F = 7$ GPa).[1,2] The value of the thermal expansion coefficient α along these fibers ($\alpha = -1.10 \times 10^{-5}$ K^{-1}) is close to that of a PE single crystal along the c-axis ($\alpha = -1.2 \times 10^{-5}$ K^{-1}), and tensile compliance is the lowest obtained for PE ($(1–2)\times10^{-11}$ m^2 N^{-1}, see Reference 2). Unique properties of these fibers were supposed to be caused by close packing of very long well-oriented chains. In accordance with the model[1] a similar structure can be formed only from a low concentration solution of the UHMW polymer in a poor solvent. As for the liquid crystalline polymers (LCP) with mesogene group in the main chain, it is believed that their high orientation can be obtained by melt spinning in mesophase state. Despite a great amount of data on LCP synthesis, structure and properties, the influence of the macromolecular orientation on the LCP properties and also the drawability and the possibility to affect it in a desired way still remain unclear.

The main purpose of this work was to study the influence of the macromolecular orientation on the LCP properties. The roles of crystallinity and technological factors were considered separately and the results were compared with those for flexible-chain polymers studied earlier with the aim of finding the approach to production of high performance materials.

EXPERIMENTAL

The polymers investigated were synthesized as described in Reference 3. They were the wholly aromatic LC polyester polyphenyl-*p*-phenyleneterephthalate (PPT) and related copolyesters denoted as PTT-30 and PTT-40 in accordance with a content of terephthaloyldioxybenzoate and FHR-20, 50, and 80 with successively diminishing content of *m*-phenylene units. The data of differential thermal analysis (DTA), thermal mechanical analysis (TMA) and thermal acoustic analysis[4] (TAA) were used to find optimal spinning conditions. Fibers were formed with laboratory units of a syringe or extruder type. As a rule, a little amount of polymer (1–2 g) was synthesized and fibers were formed with a syringe of 1 cm^3 volume. The possibility of heating under evacuation or inert gas was provided. The pressurized feed rate was ensured by pressure on the syringe piston.

The take up rate was changed from 2 $cm\ s^{-1}$ to 5 $m\ s^{-1}$. Dies were made up of capillary tubes 0.5, 0.75, 0.82, 0.95, and 1.8 mm in diameter and 16, 16, 12.5, 9, and 7 mm in length, respectively. Diameters of the specimens obtained were from 1.9 mm to 10 μm, so that the jet draw ratio X, which was determined as the die to sample diameters ratio, varied from 0.9 to 1000.

The values of MW were estimated from the intrinsic viscosity $[\eta]$ of polymer solution in the mixture of dichloroethane and trifluoroacetic acid (2 : 3).

The magnitudes of E, F, and α were measured as described in Reference 4. The macromolecular orientation was estimated from the value of E of the samples obtained under optimal conditions.[4] The shrinkage ratio S was calculated as the ratio between the initial and final (after shrinking) length of the piece. To observe the LCP shrinkage the LCP pieces were inserted into a liquid heated up to the LC transition temperature T_m or 1–2 dozen degrees above T_m.

RESULTS AND DISCUSSION

The moduli versus X for LCPs of different chemical structures are presented in Figure 1. E is seen to increase with X for all specimens. The ultimate values of E (E_{max}) depend on the chemical structure. E_{max} increases with increasing content of paraphenylene units in the chain. It should be noted that the dependences are obtained for specimens formed

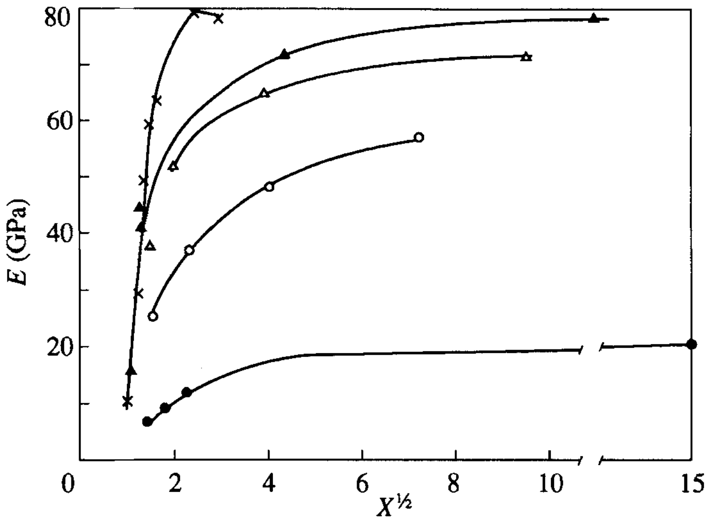

FIGURE 1 Sonic moduli E versus jet draw ratio for FHR-20 (●), FHR-50 (○), FHR-80 (△), PTT-30 (▲), and PTT-40 (×).

under the optimal conditions.[4]

Figure 2 indicates that the strength of PPT fibers (formed also under optimal conditions) increases with X. Fibers were formed from the polymer with the intrinsic viscosity $[\eta] = 5.3$ dl g^{-1}. It is essential because of the effect of $[\eta]$ on E and F (see Reference 4). To achieve the ultimate value of F ($F_{\max}$) the same values of X as for $E_{\max}$ are needed.

The dependences of modulus and strength on X for LCP remind those for the flexible-chain polymers. However, irrespective of the fact that LCP can be drawn up to draw ratio as high as solution-formed UHMW PE fibers, the ultimate strength for PE is substantially higher. This may be due to the imperfection of the LCP fiber structure: chain scissions, a great quantity of end groups, porosity, etc. Let us compare the efficiency of drawing of LCP and PE by analyzing the dependences of E and F on X (see Figure 2a and b) and temperature dependences S (Figure 3). As seen, the higher is the value of E for the oriented samples, the larger is the shrinkage ratio. The S values for LCP are much lower than those for UHMW PE. A low efficiency of LCP orienting is not surprising because of its low MW, if compared with UHMW PE. In addition to this, MW of LCP decreases upon spinning due to chain destruction at high temperatures and under tension. It is confirmed by the reduction in $[\eta]$ of fibers, as compared to nascent polymer.

Since LCPs are typically synthesized by the polycondensation processes, the question arises if it is possible to increase MW by annealing a fiber. Such defects as porosity may also be healed by annealing. However, heat treatment (HT) can lower the orientation due to chain scissions and coiling. Consequently, it is necessary to find the conditions for annealing without disorientation. To this end, we used the DTA and TAA techniques.

DTA curves for LCP with different thermal histories are presented in Figure 4. As seen, both the position and area of the peaks are annealing time t_a and temperature T_a dependent. It may be explained by the ability of polymer chains to form the crystals of different sizes and perfectness depending on T_a and t_a.

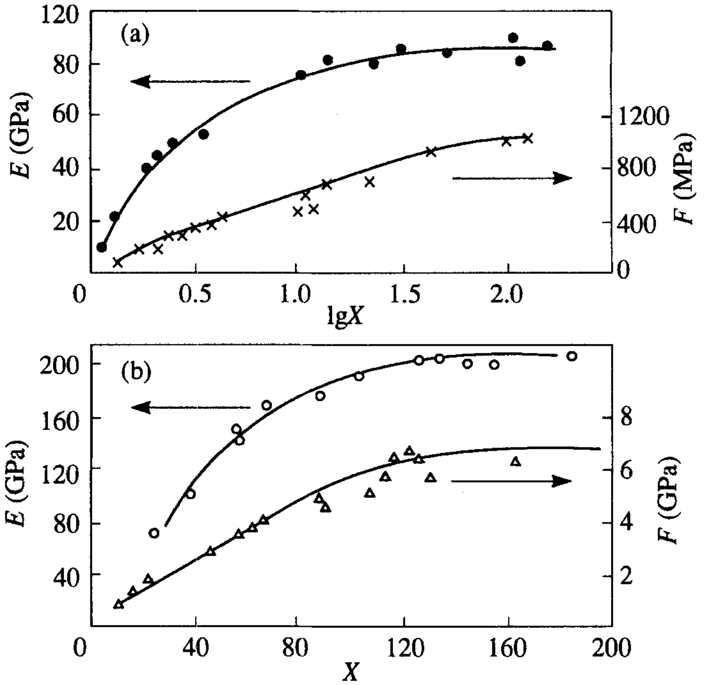

FIGURE 2 Tensile strength F and modulus E versus jet draw ratio for (a) PPT and (b) PE fibers.

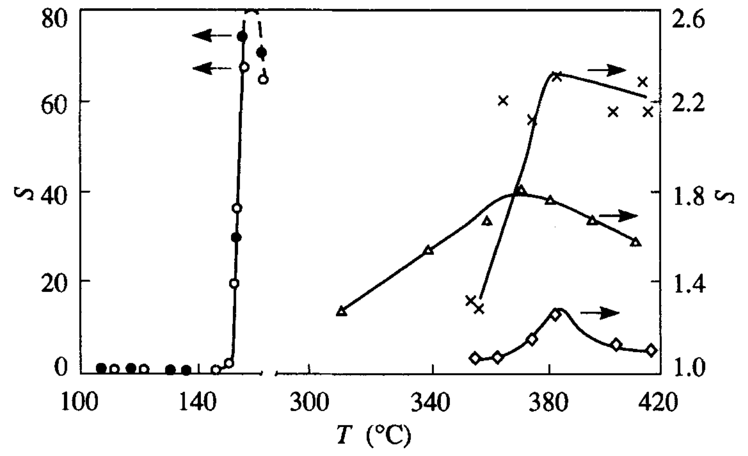

FIGURE 3 Shrinkage ratio as a function of bath temperature for UHMW PE (o, $E = 120$ GPa; •, 200 GPa), PPT (Δ, 67 GPa), and FHR-80 (◇, 17 GPa; ×, 76 GPa) fibers.

TAA curves were used to answer the question how the thermal conditions affect the orientation. Temperature dependences of sound velocity C and transmitted sound intensity I as well as time dependences of I under isothermic conditions are shown in Figure 5. As seen the high-temperature annealing ($T_a > T_m$) decreases the sound velocity C at the temperatures lower than glass transition temperature, which may be due to disorientation

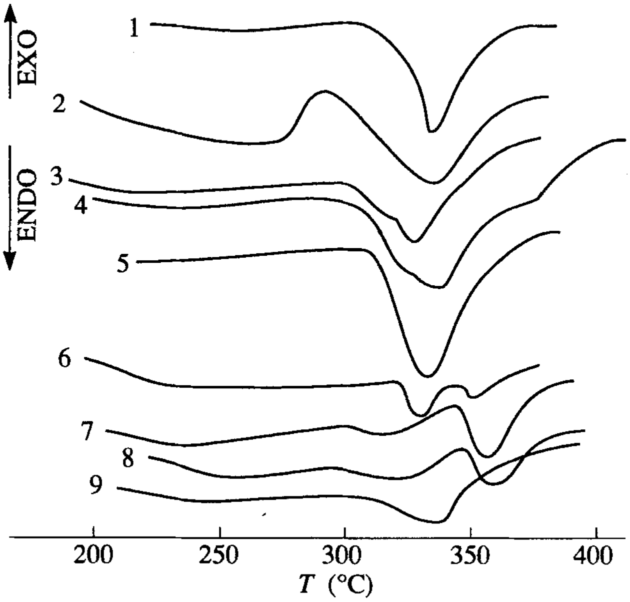

FIGURE 4 DTA curves for PPT with different thermal histories. Nascent polymer or untreated fiber (curve 1), quenched sample (curve 2), fibers annealed at various T_a and t_a (curve 3–9). $T_a = 275°C$, $t_a = 25$ min (curve 3); 275°C, 60 min (curve 4); 275°C, 240 min (curve 5); 325°C, 90 min (curve 6); 275°C, 35 min then 325°C, 90 min (curve 7); 275°C, 120 min, then 325°C, 90 min (curve 8); 345°C, 60 min (curve 9).

of chains. The initial rate of E decrease ($E = C^2\rho$, where ρ is a polymer density) versus $1/T$ is plotted and activation energy is found to be 290 kJ mol^{-1}. This value is close to the energy of molecular scissions, which evidences that disorientation is accompanied by destruction.

Yet it is possible to heat a fiber up to a sufficiently high temperature without decreasing C if it was first annealed at $T_a < T_m$. This phenomenon is easy to understand by considering the curves in Figure 5. There are three different types of annealing conditions for LCP samples. The first is annealing at comparatively low temperatures when the process of MW increase may dominate. Such treatment results in a small increase of C and I (Figure 5b, compare curves 1 and 2, 1′ and 2′) at the temperatures ranging from room temperature to T_m. The second one is annealing at temperatures near the crystallization temperature T_{cr} (see curve 2 in Figure 4). If polymer chains are able to crystallize, there is a significant increase of I with annealing time (Figure 5a). The value of C slightly increases. The subsequent warming up to T_m+(20–40) K results in disappearance of the intensity peak near T_m. As for the temperature dependence of C it remains unaltered, if the highest temperature T_a exceeds T_m only slightly, and C decreases in the whole range up to T_m if T_a is far above T_m.

The estimation of the activation energy from the I increase rate versus $(1/T)$ gives 60 ± 5 kJ mol^{-1}, which points to macromolecular rearrangements of crystallization type. If it is crystallization, the Avraami coefficients at temperatures from 320 to 350°C prove to be 0.50 ± 0.05.

The third type of annealing conditions is realized at high temperatures (for PPT it takes place at $T_a > 360°C$, see Figure 4). There are a slight increase of I and C at high

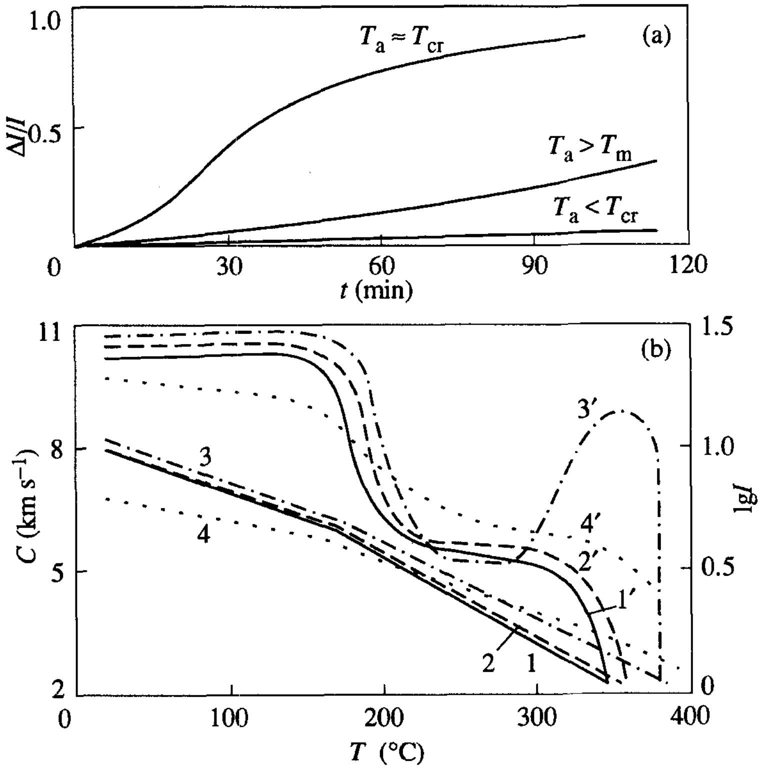

FIGURE 5 TAA curves for LCP fibers. (a) The dependences of relative change in I with annealing time for different T_a. (b) Sound velocity (curves 1–4) and transmitted intensity (curves 1′–4′) as a function of temperature for untreated (curves 1, 1′) and annealed samples: $T_a < T_{cr}$ (curves 2, 2′), $T_a \approx T_{cr}$ (curves 3, 3′) and $T_a > T_m$ (curves 4, 4′).

temperatures and decrease of C at low temperatures (compare curves 1 and 4, curves 1′ and 4′ in Figure 5b). The transmitted intensity at low temperatures can increase or decrease depending on the thermal prehistory of the samples investigated, chemical structure of macromolecules and polymer molecular-weight distribution. The thermal treatment under the conditions that provide a simultaneously increase of I and C results in strengthening (Table I).

The behavior of LCP described above can be explained in terms of the network model of LCP structure. It is the junction network that controls drawability. The network is formed during the synthesis or remelting and is determined in the first turn by the value of MW. Junction concentration grows with MW. Fiber spinning requires optimal junction concentration. Indeed, it is impossible to produce fiber from LCPs with $[\eta] < 0.5$ and $[\eta] > 10$ dl g^{-1}. The higher is $[\eta]$, the higher tension is needed to achieve the maximum orientation. When a fiber is heated, the low molecular weight fractions are the first to become mobile and can react with other chains (short or long) thereby increasing MW and enhancing the chain entanglements. This leads to the yield loss at temperatures above T_m in thermomechanical experiments (Figure 6). In the case of fast heating, the fiber shrinks due to the transition of long chains from an extended state to coiled one.

If the network structure is not destroyed on annealing because of a lower segmental

TABLE I
Properties of LCP fibers before and after heat treatment

			before HT				after HT		
No	Polymer	X	E (GPa)	F (MPa)	$\alpha \times 10^6$ (K^{-1})	S_{max}	E (GPa)	F (MPa)	$\alpha \times 10^6$ (K^{-1})
1	PPT	1.3	17	100	6.0	1.1	16	—	5.4
2	PPT	3.2	55	350	−7.6	1.6	55	—	−8.0
3	PPT	100	80	1000	−8.0	3.1	85	3000	−7.0
4	PTT-40	1.2	10	100	13.2	1.1	11	—	12.8
5	PTT-40	—	54	—	−7.2	1.8	57	—	−9.8
6	PTT-40	25	90	700	—	1.9	95	2200	—
7	FHR-80	1.2	13	—	23.0	1.05	—	—	13.2
8	FHR-80	100	79	850	−8.2	3.0	80	1000	−9.8

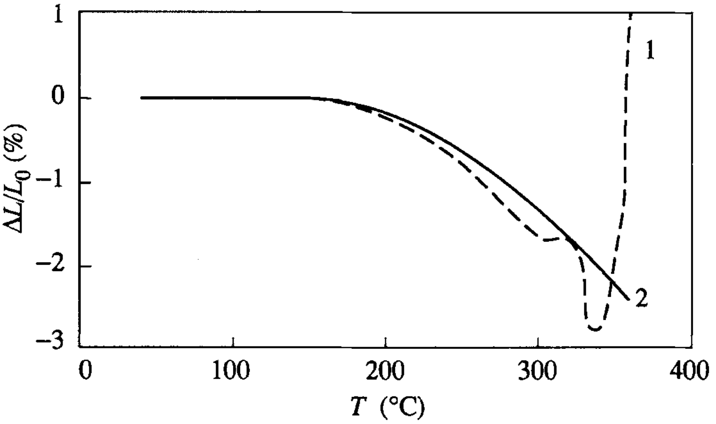

FIGURE 6 Relative change in the sample length $\Delta L / L_0$ versus temperature for untreated fiber (curve 1) and for fiber after thermal treatment (curve 2).

mobility of the chains included into the junctions as compared with the mobility of the short chains which are not included into junctions, E remains unaltered. Crystallization at the temperature near T_m leads to strengthening due to a more dense packing of the chains and morphological units (defects healing or free volume decreasing). Similar structure transformation can affect also the α values (Table I and Figure 7). It should be noted that strengthening is followed by the increase of the activation energy for mechanical destruction,[4] e.g. from 109 to 142 kJ mol^{-1} for PPT.

CONCLUSIONS

(i) Drawability of LCPs is determined by the structure of the macromolecular network that is formed during synthesis or remelting of samples, as in the case of flexible-chain polymers.

(ii) Jet drawing of LCPs is less effective than thermal drawing of flexible-chain polymers.

(iii) The oriented fibers of LCPs have a less perfect structure than the highly oriented

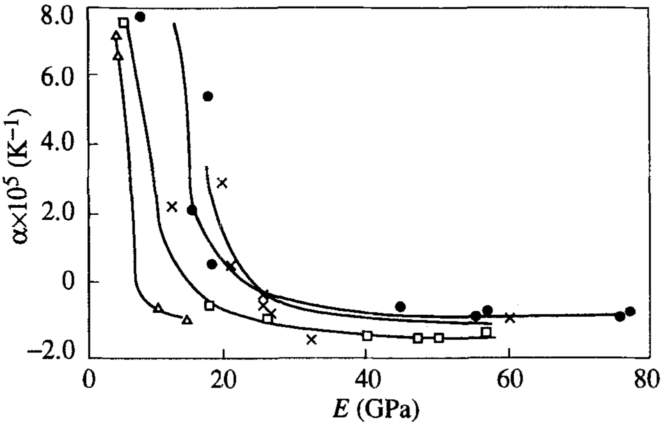

FIGURE 7 Correlation between thermal expansion coefficients α and sonic moduli for PPT (●), FHR-80 (×), FHR-50 (☐) and polycaproamide (△) fibers.

specimens formed from low concentrated solutions of UHMW polymers. A comparatively low tensile strength (about 1 GPa) of LCP fibers may be caused by the imperfection of their structure. Long chains of LCP are included in a great number of LC formations, whose high strength is the reason for breakage of the longest macromolecules during spinning. That is why heat treatment is needed to increase the strength.

(iv) Additional polycondensation, recrystallization and network transformation occur during HT or one of these may be prevailing, depending on the chemical structure of chain, thermal history of the sample and HT conditions. Recrystallization of poly(phenyl-*p*-phenyleneterephthalate) under definite HT conditions enhances the strength from 1 to 3 GPa. It is followed by the increase of activation energy for mechanical destruction from 109 to 142 kJ mol^{-1}.

(v) The DTA, TMA, and TAA techniques can be used to find the conditions of network transformations that will improve the structure without disorientation.

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