

# Fibers from Flexible Liquid Crystal Main-Chain Polymers. I. Polymers Based on 4,4'-Dihydroxy-2,2'-Dimethylazoxybenzene and Alkyl Dicarboxylic Acids and Alkyl Dihalides

A. BLUMSTEIN,\* C. H. LIN, A. K. MITHAL,<sup>†</sup> and A. TAYEBI,<sup>†</sup> *Polymer Science Program, Department of Chemistry, and <sup>†</sup>Department of Plastics Engineering, University of Lowell, Lowell, Massachusetts 01854*

## Synopsis

The anisotropic properties of thermotropic liquid crystalline polymers are paramount to the development of highly oriented and extended polymer chains in a fiber spinning process. Fibers from liquid crystalline polymers were spun above the mesophase transition temperature. Linear thermotropic liquid crystalline polymers based on 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and alkyl dicarboxylic acids and alkyl dihalides have been previously studied by different techniques and their conformational properties are well established. In this work the mechanical properties of fibers based on such polymers were studied. High values of tenacity and tensile moduli were obtained. These values increase with molecular mass, but decrease with the length of the flexible spacer moiety. The spinning temperature is also an important parameter.

## INTRODUCTION

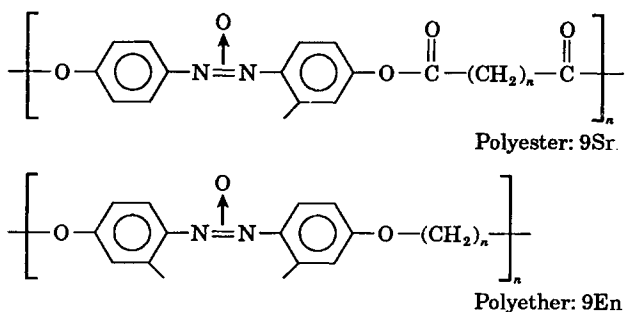
Thermotropic liquid crystalline main chain polymers containing long methylene sequences (flexible spacers) in the backbone are generally not considered as processing materials for fibers. The main reason often given is the existence of conformational disorder in the flexible spacer conducive to chain misalignment and flaws in the morphology of the fiber. However, recent conformational studies performed on polyesters of this type have suggested that a progressive extension of the flexible methylene spacer on cooling throughout the nematic phase takes place.<sup>1,2</sup> One may therefore ask the question, can a fiber spun from nematic melts of such polymers lead to rigorous chain alignment accompanied by conformational extension of the spacer? The appeal of such a system is obvious as it would combine high values of tensile moduli and tenacity of chain aligned fibers with easy processability.

Very little work was done in this field. Krigbaum et al.<sup>3</sup> have spun and tested fibers using rigid-flexible polyesters based on the rigid 4'-hydroxyphenyl-4-hydroxybenzoate moiety and suberic acid. The highest value of modulus recorded was some 3.5 GPa ( $\approx 33$  g/den), a respectable value given the flexible nature of the polymer. More recently, Müller and co-workers<sup>4</sup> have attained tensile moduli of 10–20 GPa ( $\approx 90$ –180 g/den) and tenacities of 0.1–0.3 GPa ( $\approx 1$ –

\* To whom correspondence should be addressed.

3 g/den) with a nematic thermotropic rigid-flexible polyether:poly[1-[4-[4-[(4-oxybenzoyl)oxy]chlorophenoxy]-carbonyl]phenoxy]-1,1,10,10-tetradecane]. These authors concluded that the high modulus and tensile strength was due to high chain orientation on a molecular and supermolecular levels. These results encourage more work in order to investigate the structural and conformational as well as processing characteristics of rigid-flexible thermotropic main-chain polymers.

In this paper we describe some preliminary results obtained with rigid-flexible polyesters and polyethers based on 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene mesogen (Me 9) and aliphatic spacers (Sn)<sup>5</sup>. Some structure-property correlations are discussed. A spinneret accommodating small laboratory scale samples of polymer (0.5–5 g) was used for the fiber spinning process. The two polymer structures investigated are given below:



Fibers from both types of thermotropic flexible liquid crystalline polymers were spun from a wide range of temperatures within the enantiotropic nematic phase. The molecular mass of the polymer, length, parity, and structure of the spacer were taken as structural parameters and their influence on mechanical properties was investigated. Because of substantially narrower mesomorphic intervals of polyethers, the temperature sweep range for these polymers was limited to one or two spinning temperatures.

## EXPERIMENTAL

### Materials

The mesogen 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene was prepared from 3-methyl-4-nitrosophenol by reductive coupling according to Leonard and Curry.<sup>6</sup> The polyesters 9S4, 9S6, 9S7, 9S8, and 9S10 were prepared by an interfacial polycondensation reaction.<sup>7</sup> The polyethers 9E7 and 9E9 were prepared by solution polycondensation reaction at 70°C.<sup>8</sup> 9S7 and 9S10 were fractionated by a nonsolvent addition method; for 9S7 the DMF/methanol mixture was used as the solvent/nonsolvent couple,<sup>9</sup> and for 9S10 fractionation dichloromethane/methanol was selected. The structure and composition of all specimens has been ascertained by elemental analysis and N.M.R. spectroscopy.

### Characterization of Polymers

The polyesters 9S7 and 9S10 were characterized by their molecular mass distribution obtained from GPC (5 wt % of sample was dissolved in chloroform,

using Water's ultrastyrigel columns—500,  $10^3$ , and  $10^4$  Å connected in series) and their inherent viscosity at concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane were measured using the Cannon-Ubbelohde viscometers at 30.0°C. Inherent viscosity in tetrachloroethane was also used to characterize all other polyester specimen. Polyether 9E7 was dissolved in 1,1,1,3,3,3 hexafluoro-2-propanol while 9E9 was dissolved in 1 : 1 mixture of tetrachloroethane and *m*-cresol. In this last case, the inherent viscosity was measured at 40.0°C.

The thermal properties were investigated using a Perkin-Elmer DSC-2C instrument equipped with a thermal analysis data station. The heating/cooling rate was 20°C/min. Textures and phase transitions were observed between slide and cover slip using a Leitz Ortholux II polarizing microscope with a Mettler FP5 hot stage.

The X-ray patterns of polymer fibers were recorded with a Laue camera mounted on a Rigaku generator operating at 40 kV and 25 mA using nickel-filtered Cu-K $\alpha$  radiation of wavelength 1.54 Å.

### Fiber Spinning

Melt spinning of these inherently flexible thermotropic liquid crystalline polymers over a wide range of temperatures within the mesophase was performed using a piston driven monofilament spinneret. This spinneret was designed by us to accommodate small experimental samples (0.5 g) of polymer.

In this study the following conical die geometry was used: entrance angle  $\theta = 45^\circ$ ,  $L/D = 2$ , and  $D = 0.8$  mm, where  $L$  is the length of the narrow cylindrical outlet and  $D$  is its diameter. In a typical extrusion operation, the polymer is placed in the sample chamber and heated until the desired temperature is reached. The pressure is applied progressively. The polymer melt is then extruded through the die and the extruded fiber is picked up by a roller and wound at constant velocity  $V_f$ . In our experiments the take up roller was placed at 1 m distance from the orifice of the die. The spin draw ratio was estimated by measuring the decrease in the diameter of the fiber by microscopy using the relation  $S = V_f/V_0 = (D_0/D_f)^2$ , where  $V_f/V_0$  is the pickup velocity/average extrusion velocity and  $D_0/D_f$  is the diameter of the die orifice/diameter of fiber at roller.<sup>10</sup>

The optimum values of  $V_f/V_0$  for a given fiber spinning operation was determined by increasing progressively the pickup speeds for a given extrusion pressure. This value was dependent not only on the nature of the polymer but also on its molecular mass and extrusion temperature. At low values of spin draw ratios the fiber diameter was not uniform; at high spin draw ratios the fiber had a tendency to break on winding. Typical optimum values of  $V_f/V_0$  ranged from 300 to 700 for different polymers and extrusion pressures. For example 9S7-H was spun at pressure of 160 psi and at a pickup speed ( $V_f$ ) of 38 m/min (with a spin draw ratio of 500). The 9S10-H was spun at a  $V_f = 70$  m/min, and at a 240 psi pressure with a spin draw ratio of 700. Efforts were made to cool the fiber rapidly below  $T_g$  and thereby quench the orientation achieved during the spinning. This was done by making the fiber pass in an ice-water bath (at 0°C) before winding. However, as is shown in this work, the orientation of chains for these polymers is easy to preserve even above  $T_g$ .

### Mechanical Properties

The tenacity, modulus and elongation at break were tested with an Instron tensile tester (Model TTC). The initial specimen length was 12 in. The gauge length was 5 in. and the strain rate was 2 in./min. The initial modulus, tensile strength, and elongation at break were the average values of at least five testing results.

## RESULTS AND DISCUSSION

Table I gives the main characteristics of the samples used. One can see that the polyesters are characterized by broad nematic intervals while the polyethers have a narrower mesomorphic nematic range. This is also true of the biphasic (N + I) interval. In the spinning operation we have tried to avoid the biphasic. Spinning was conducted from temperature below the disappearance of the isotropic component under microscope and at temperatures superior to the disappearance of the crystalline component.

It can be also seen from Table I that the glass transition temperature ( $T_g$ ) of the polymers investigated is in the room temperature range. We have tried to quench the ordering of chains in the fiber by passing it through an ice-water bath at 0°C. The bath was kept at a distance of 30 cm from the die exit (it took the fiber typically less than a second to reach the bath). From that time onwards the fiber was kept below  $T_g$  until mechanical testing.

Table II gives the mechanical properties of polyesters 9S7, 9S10 and polyethers 9E7, 9E9. The values of the tensile modulus and of the tenacity in both polyesters 9S7 and 9S10 are comparable despite of the fact that *in situ* 9S7 does not crystallize. Nevertheless, as we can see from DSC thermograms for powder and fibers of 9S7 (Fig. 1), a substantial amount of 9S7 crystallizes when the fiber is drawn. The amount of crystallinity in 9S7 fiber is, however,

TABLE I  
Properties of Liquid Crystalline Polymers

Polymer	Inherent viscosity (dL/g)	$T_g$ (°C)	Transition <sup>a</sup> (°C)	
			Heating	Cooling
9S4	0.50	37.0	C187.8N247I <sup>b</sup>	I233.3N121.4N
9S6-H	0.90	23.3	C155.7N230.1I	I204.3N
9S6-L	0.39	14.7	C164N218.8I	I200.4N51.4C
9S7-H	0.81	21.7	C90.6N160.6I	I151.4N84.2C
9S7-L	0.33	20.1	C77.7N143.4I	I137.3N69.8C
9S8	0.61	18.4	C <sub>1</sub> 125.9C <sub>2</sub> 142N196I	I177N103.1C <sub>2</sub> 68.5C <sub>1</sub>
9S10-H	0.80	18.9	C123.2N166.2I	I154.9N73.8C
9S10-L	0.51	15.9	C121.1N160.7I	I151.9N86.1C
9E7	0.67	29.7	C133.2N142.5I	I131.6N93.5C
9E9	0.69	26.7	C <sub>1</sub> 105.5C <sub>2</sub> 110.3N126.5I	I119.3N <sup>c</sup>

<sup>a</sup> C = crystalline, N = nematic, and I = isotropic phase.

<sup>b</sup> Partial decomposition.

<sup>c</sup> Supercooling.

TABLE II  
Mechanical Properties of Rigid-Flexible Liquid Crystalline Polymers

Polymer	$T_s$ ( $\Delta H_{C/N}$ , cal/g)	$T_s - T_m^a$ (°C)	Tenacity <sup>c</sup> (g/den)	Modulus <sup>c</sup> (g/den)	Elongation at break (%)
9S7-H	99 (3.88)	8.4	2.21	54.5	7.2
	104 (3.80)	13.4	2.10	51.8	7.1
	118	27.4	1.73	43.6	5.8
	120 (3.64)	29.4	1.72	42.4	5.4
	136 (3.42)	45.4	1.44	39.7	11.7 <sup>b</sup>
9S7-L	142 (3.28)	51.4	1.41	36.2	8.4 <sup>b</sup>
	90	12.4	0.22	13.4	2.9
	100	22.4	0.18	13.3	2.8
	107	29.4	0.18	12.9	2.8
	118	40.4	0.16	12.6	2.7
9S10-H	130	52.4	0.14	7.9	2.7
	126 (4.39)	2.6	1.98	69.9	3.1
	134 (4.38)	10.6	1.40	58.7	3.2
	136 (4.26)	12.6	1.26	55.7	3.2
	142 (4.37)	18.6	1.22	44.6	3.3
9S10-L	147 (4.15)	23.6	1.16	41.9	3.1
	153	29.6	0.97	38.5	3.1
	131	9.7	0.50	34.0	1.6
	135	13.7	0.40	27.6	1.5
	141	19.7	0.33	25.6	1.5
9S4	207	20.0	1.48	77.4	1.5
	217	30.0	1.16	71.2	1.5
9S6-H	166	12.3	2.43	77.3	3.5
	173	19.3	2.16	70.6	3.0
	184	30.3	1.62	54.6	2.8
9S6-L	176	12.3	0.56	48.3	1.2
	180	16.3	0.38	30.0	1.2
9S8	154	12.0	1.18	53.9	1.6
	158	16.0	0.96	50.3	1.5
9E7	138	5.0	2.40	57.4	4.0
9E9	118	7.7	2.41	52.7	5.1
	123	12.7	1.20	30.7	3.7

<sup>a</sup>  $T_s$  = spinning temperature,  $T_m$  = crystalline to nematic transition temperature,  $T_s - T_m$  = temperature difference.

<sup>b</sup> Yield behavior occurred.

<sup>c</sup> Unit for tenacity and modulus is g/den. To convert to N/tex, multiply by 0.0883; N/tex · density = GPa.

smaller than in the 9S10 fiber, a fact which can be explained by the more ordered nature of the cybotactic nematic phase of 9S10 as compared to the ordinary nematic mesophase of 9S7<sup>5</sup>. It is apparent from Figure 1 that the X-ray irradiation has little influence on the thermal behavior of 9S7 and 9S10.

The mechanical properties are strongly influenced by the spinning temperature. The effect of spinning temperature is given in Table II. For both polyesters the closer this temperature is to the crystallization temperature, the higher the tenacity and the modulus of the fiber. This can be understood in the light of recent studies of chain conformation for both polyesters<sup>1,2</sup> by NMR and by

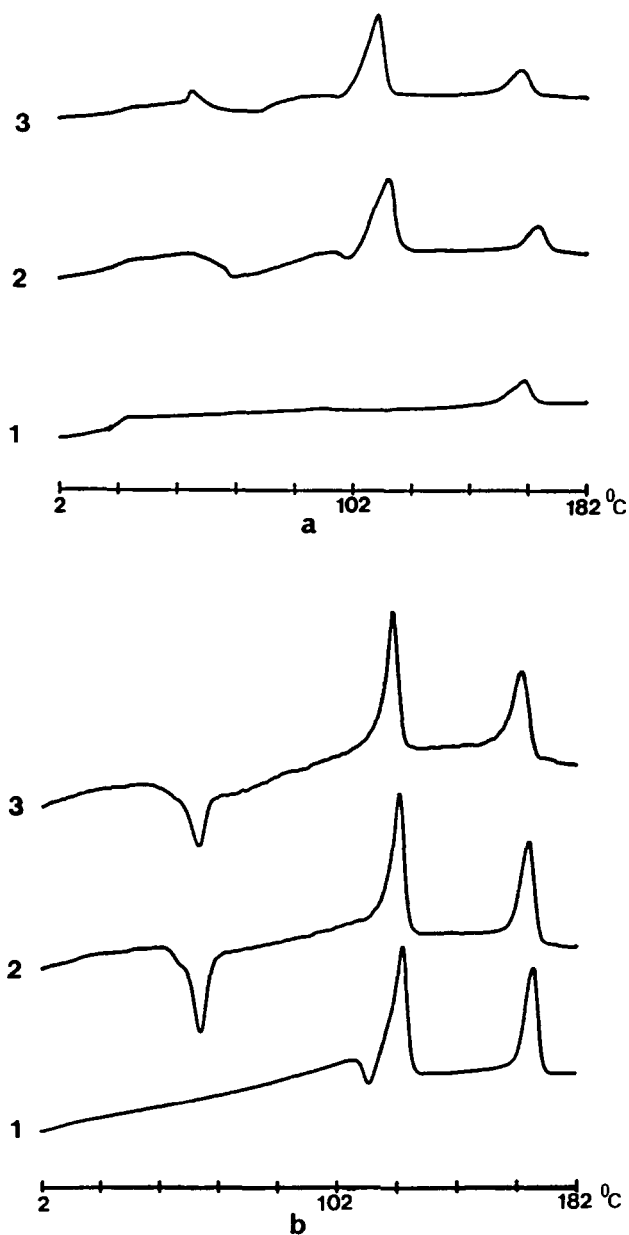


Fig. 1. (a) DSC thermograms of 9S7-H fiber (spun at 120°C,  $T_s$ - $T_m$  = 29.4°C and (b) DSC thermograms of 9S10-H fiber (spun at 126°C,  $T_s$ - $T_m$  = 2.4°C. Heating rate = 20°C/min. (1) Original powder sample; (2) spun fiber; and (3) fiber after x-ray exposure (4 h).

neutron scattering, which unequivocally indicate a progressive chain extension on cooling throughout the nematic mesophase. The largest chain extension is taking place just above the crystallization of the nematic mesophase. This finding also confirms the recently published results on fibers from rigid-flexible main chain polyethers in which a similar effect was observed by Müller et al.<sup>4</sup>

Table II in addition to spinning temperatures gives also the mechanical properties for fibers made of polyesters with flexible spacers of different length (9S4, 9S6, and 9S8 as well as polyethers 9E7 and 9E9) and different molecular mass  $M$  ( $L = \text{low}$  and  $H = \text{high}$ ). Figures 2, 4, and 5 illustrate these effects; in Figure 2 the tensile modulus  $E$  and tenacity are plotted for 9S7-H and 9S10-H against the difference between the spinning and the melting temperatures ( $T_s - T_m$ ). The effects of  $T_s - T_m$  are apparent. A decrease in  $T_s - T_m$  produces an increase in tensile properties. This increase is especially strong for the 9S10 fibers.

In order to investigate the extent of crystallinity and its contribution to the enhancement of tensile properties, the fiber samples of 9S10-H and 9S7-H were submitted to thermal scans. The crystal-nematic transition enthalpy was recorded and plotted as a function of the spinning temperature differential  $T_s - T_m$ . Figure 3 shows the result of such measurements. It is apparent from Figure 3 that the extent of crystallinity in 9S10-H does not change significantly with the spinning temperature while the change in 9S7-H is moderate. The tenacity (open circles and triangles), however, decreases significantly with  $T_s - T_m$ . These data point toward a stronger dependence of mechanical properties of fibers of flexible liquid crystalline polymers on chain orientation rather than on the extent of crystallinity. In contrast the extent of crystallinity in conventional fibers, made from thermoplastic polymers, has a dramatic influence on mechanical properties. This is illustrated in the insert of Figure 3 representing tenacity as a function of the extent of crystallinity for a poly(ethylene terephthalate) (PET) fiber after heat treatment and drawing.<sup>11</sup>

Table III and Figure 4 give the modulus as a function of molecular mass for a number of sharp fraction ( $M_w/M_n = 1.1$ ) of 9S10.<sup>7</sup> It is apparent that  $E$  and

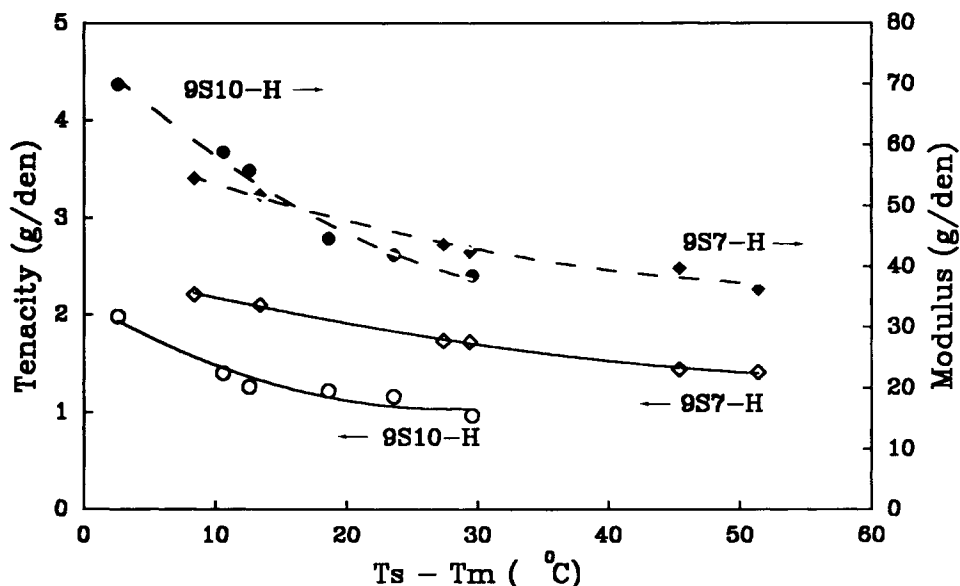


Fig. 2. Mechanical properties of 9S7-H and 9S10-H fibers at different spinning temperatures: (—) tenacity; (---) modulus.

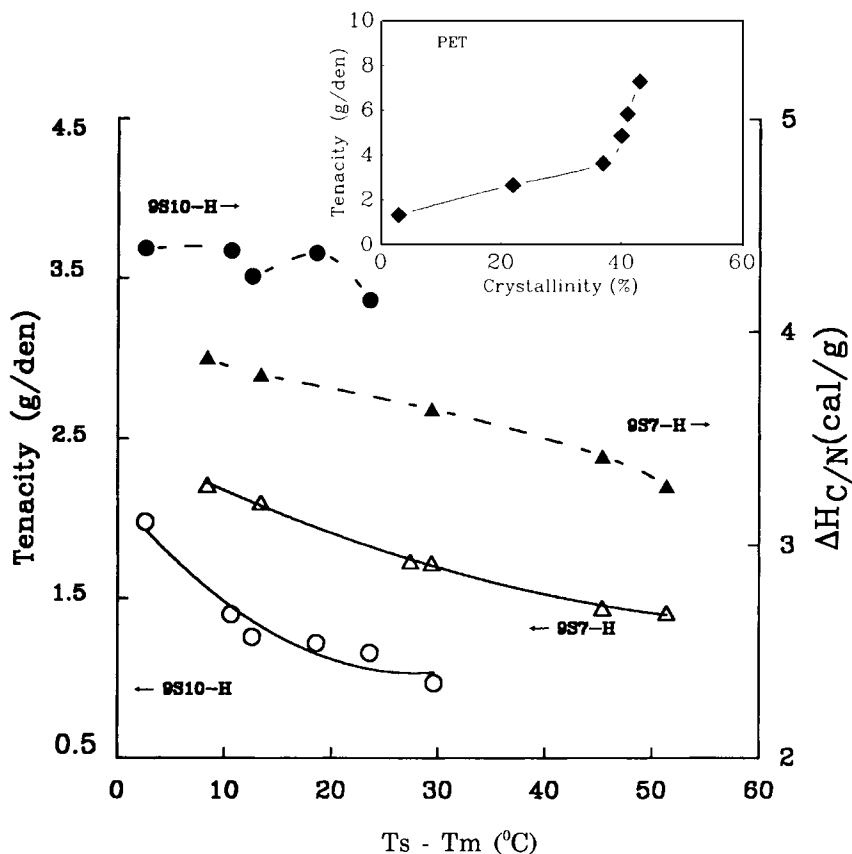


Fig. 3. Tenacity and  $\Delta H_{c/N}$  of 9S7-H and 9S10-H fibers vs.  $T_s - T_m$ . For comparison, data for PET fibers are shown at top right.

tenacity increases with molecular mass first slowly and then fast (for  $M_n > 15,000$ ).

The tensile modulus for all of specimen with  $M$  between 15,000 and 20,000 is in the range of 30–70 g/den, a rather high value for polymers with a flexible backbone. The values of tenacity and  $E$  given in Table II are slightly higher for 9S10 than 9S7. This difference may be due to the more extensive crystallinity of the 9S10.

TABLE III  
Modulus vs. Molecular Mass of 9S10 Polyesters at Similar Spinning Temperatures

$\bar{M}_n$	$T_{spun}$ (°C)	Modulus (g/den)
20,000	144	86.8
17,200	143	36.8
16,000	144	29.1
13,000	140	13.8
9400	140	11.3



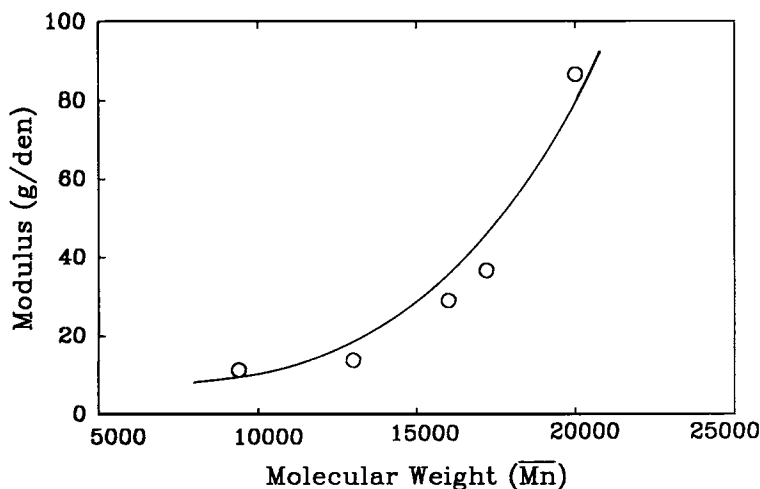


Fig. 4. Modulus vs. different mass 9S10 fibers.

The lower values of tenacity and  $E$  for 9S7 and 9S10 in comparison with the values of Müller et al.<sup>4</sup> may be due to several factors. One factor could be the geometry of the die. The spinneret described in Ref. 4 has a conical die with an entrance angle of  $13^\circ$  and a diameter of 0.4 mm. The conical die used in this study has an entrance angle of  $45^\circ$  with an outlet diameter of 0.8 mm. One may expect that in a narrower conical die the liquid crystalline polymeric melt is submitted to higher elongational forces. Another factor could be the structural difference between polymers described in Ref. 4 and in this study. Polyethers described in Ref. 4 have a longer three member ring mesogenic core resulting in a significantly higher  $T_g$  ( $40^\circ\text{C}$ ). This leads possibly to higher stabilization of the chain extension.

The influence of the spacer length on mechanical properties for samples with the same mesogenic core and similar molecular masses is shown by a rather sharp fall followed by a leveling off of the modulus  $E$  for spacers exceeding in

TABLE IV  
Mechanical Properties of Polyesters with the Same Mesogenic Core  
and Different Spacer Length

Polymer	$\eta_{inh}$ (dL/g)	$T_s - T_m$ ( $^\circ\text{C}$ )	Tenacity (g/den)	Modulus (g/den)	Elongation at break (%)
9S4	0.50	20.0	1.48	77.4	1.7
9S6-L	0.39	16.3	0.38	30.5	1.2
9S7-L	0.33	22.4	0.18	13.3	2.8
9S10-L	0.51	19.7	0.33	25.6	1.5
9S6-H	0.90	12.3	2.43	77.3	3.5
9S7-H	0.81	13.4	2.10	51.8	7.0
9S8	0.63	12.0	1.18	53.9	1.6
9S10-H	0.80	12.6	1.26	55.7	3.2

length 7 or 8 methylene groups (Table IV and Fig. 5). In most cases the extrusion temperature ( $T_s - T_m$ ) and the extrusion pressure were held as close as possible in order to maintain similar spinning conditions. However, the pickup speed was optimized for each sample and varied from sample to sample in order to maintain a similar diameter of the fiber.

The drop in the tensile properties with the spacer length ( $n$ ) may be due to the increase of structural defects in the fiber itself, which is a consequence of higher disorder of longer methylene chains. A similar effect has also been reported by Jackson,<sup>12</sup> who observed for the 4,4'-(alkylenedioxy)-dibenzoic acid polyester system a decrease in  $E$  and tenacity with the increase in the length of the alkylene moiety.

Figures 6 and 7 give X-ray diffraction pictures of 9S10 and 9S7 fibers extruded at increasing  $T_s - T_m$ . It is apparent from Figures 6 and 7 that although crys-

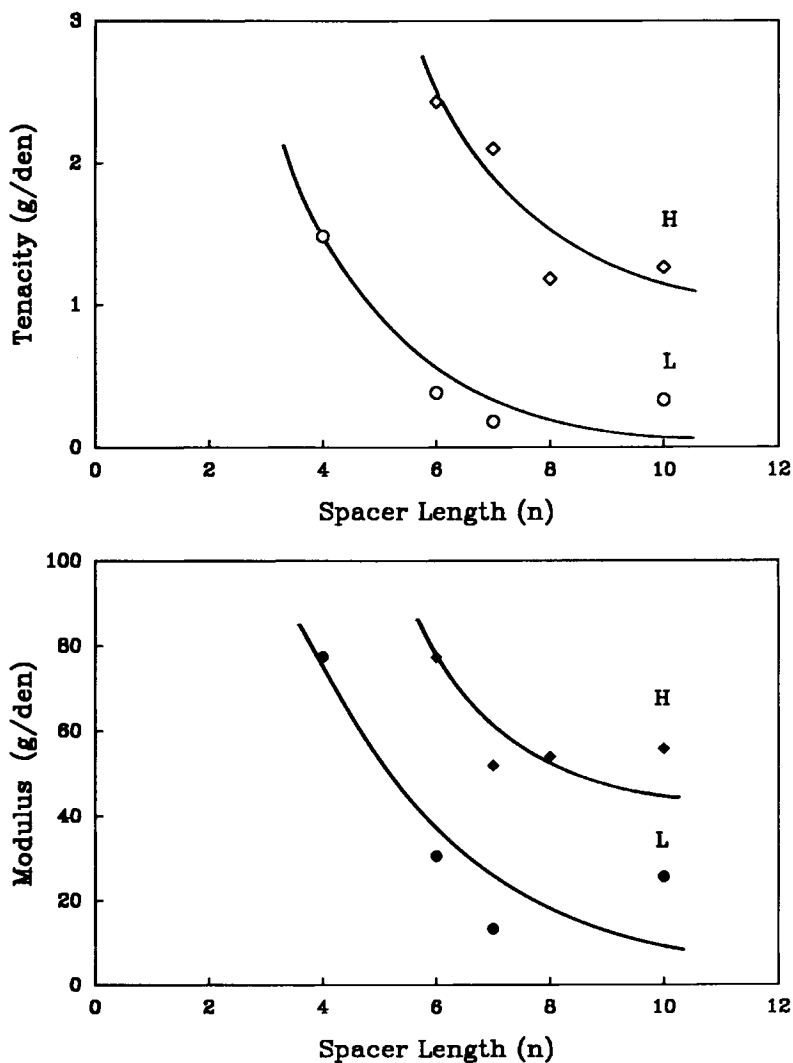


Fig. 5. Mechanical properties of 9S $n$  polyesters vs. spacer lengths.

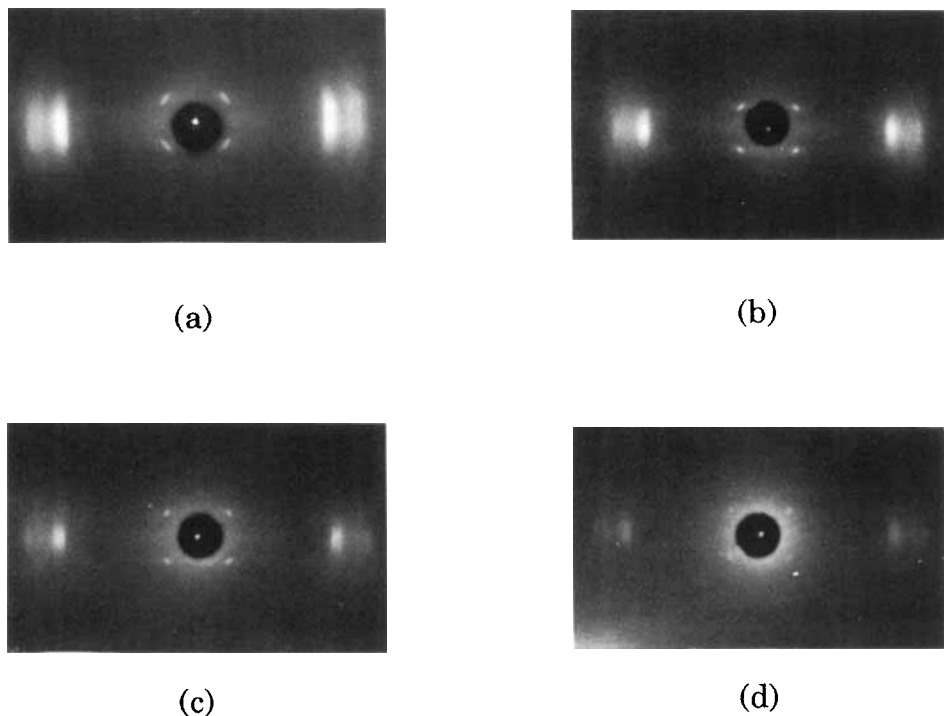


Fig. 6. X-ray diffraction patterns of 9S10-H fiber. Fiber spun at (a) 126°C [ $T_s - T_m = 2.6^\circ\text{C}$ ]; (b) 134°C [ $10.6^\circ\text{C}$ ]; (c) 142°C [ $18.6^\circ\text{C}$ ]; and (d) 147°C [ $23.6^\circ\text{C}$ ].

tallization takes place in both polyesters on extrusion, the polyester with even parity (9S10) displays a significantly higher orientation of crystallites than the polyester of the odd parity of the spacer (9S7). The low angle diffraction picture is also very different. In the case of 9S10 it displays, regardless of extrusion temperature, the four sharp reflections (at approx.  $15.3 \text{ \AA}$ ) characteristic of the "cybotactic" nature of the chain arrangement.<sup>5</sup> In the case of 9S7 there is no reflections at  $15.3 \text{ \AA}$  but orientation of crystallites is apparent. Crystallinity in 9S7 disappears altogether for fibers extruded at  $142^\circ\text{C}$  and above. Such fibers are nematic glasses [Fig. 7(d)]. It is interesting to point out that crystallinity does not appear to affect overwhelmingly the high tensile properties of liquid crystalline polyesters of this type. The polyester 9S7 in its solid *in situ* state is not crystalline (crystallization in this case is a result either of lengthy annealing around  $60^\circ\text{C}$  or flow alignment of chains during extrusion and subsequent quenching by cooling). 9S10 is markedly more crystalline *in situ* and crystallizes up to 50% rather easily (possibly as a result of its higher order parameter and cybotactic nematic structure). The comparison of Figures 6(d) and 7(d) and values of  $E$  in Table II shows that 9S7 and 9S10 whereas differing by the absence of crystallinity in the 9S7 sample give similar values of  $E$ , 35 g/den and 42 g/den, respectively.

The above series of flexible liquid crystalline polyesters provide fibers with "as spun" values of modulus and tenacity significantly higher than the corresponding values of commercial fibers from nonliquid crystalline polymers. For

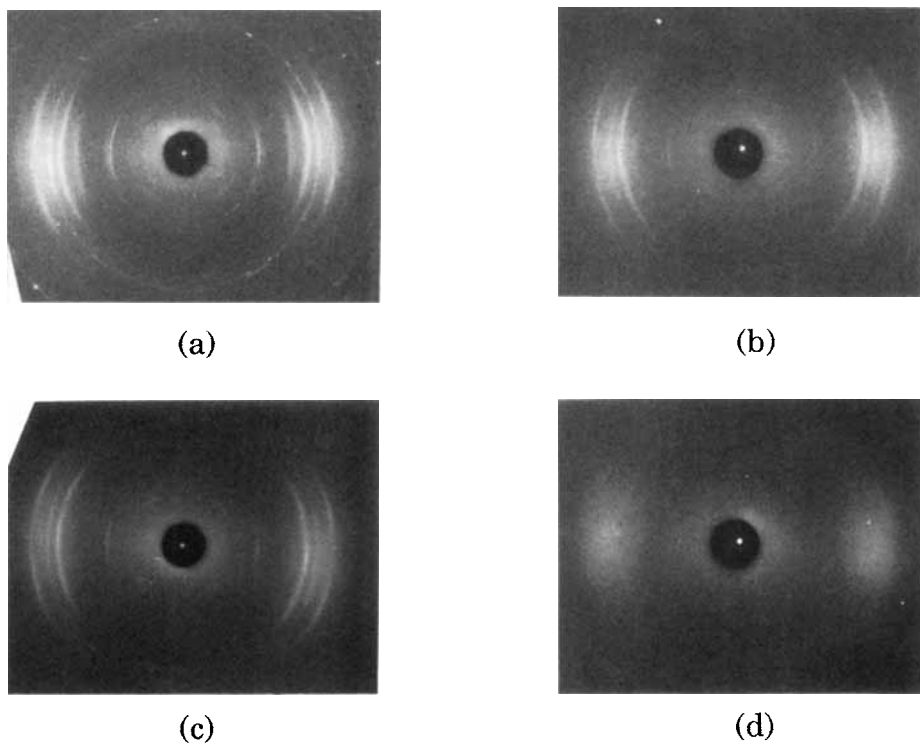


Fig. 7. X-ray diffraction patterns of 9S7-H fiber. Fiber spun at (a) 104°C [ $T_s - T_m = 13.4^\circ\text{C}$ ]; (b) 120°C [ $29.4^\circ\text{C}$ ]; (c) 136°C [ $45.4^\circ\text{C}$ ]; and (d) 142°C [ $51.4^\circ\text{C}$ ].

example, the fiber from 9S7 gives a value of tenacity 2.21 g/den and a modulus of 54.2 g/den (see Table II). The commercial poly(ethylene terephthalate) gives typically values for the "as spun" fiber of 0.8 and 15 g/den for tenacity and  $E$ , respectively, which can still be improved by post-treatment (drawing and heat treatment) and a concomitant crystallization to values in the range of 2.3–5.6 and 30–70 g/den, respectively.

As can be seen in Figures 6 and 7, despite exposing the sample to X-rays for 4 h at temperatures  $10^\circ\text{C}$  above  $T_g$  of the polymer, the diffractograms remain essentially those of oriented fibers and it appears at least in the case of 9S10 that no significant relaxation of chain alignment takes place. It is remarkable that such high values of tensile properties are recorded for 9Sn fibers of low crystallinity tested above their glass transition temperature. These values are comparable to that of tensile properties of highly crystalline fibers tested below  $T_g$  and spun from isotropic polymers. This phenomenon appears to be a consequence of spontaneous individual chain extension and orientation in the nematic phase assisted by elongational flow<sup>2,4</sup> during the extrusion process.

The authors wish to acknowledge the support of the NSF Polymer Science Program under Grant DMR-8600029; thanks are due to Polysar Inc. for a fellowship and to Dr. S. Kumar for providing the polyether samples and to Dr. S. Clough for advice and assistance with X-ray measurements.

### References

1. E. T. Samulski, M. M. Gauthier, R. B. Blumstein, and A. Blumstein, *Macromolecules*, **17**, 479 (1984).
2. J. F. d'Allest, P. Sixou, A. Blumstein, R. B. Blumstein, J. Texeira, and L. Noiret, *Mol. Cryst. Liq. Cryst.*, **155B**, 581 (1988).
3. W. R. Krigbaum, A. Cifferri, and D. Acierno, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **41**, 293 (1985).
4. K. Müller, A. Schleicher, E. Ohmes, A. Ferrarini, and G. Kothe, *Macromolecules*, **20**, 2761 (1987).
5. (a) A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough, R. B. Blumstein, and G. Maret, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 877 (1982); (b) A. Blumstein, O. Thomas, J. Asrar, P. Makris, and S. B. Clough, *J. Polym. Sci. Polym. Lett. Ed.*, **22**, 13 (1984); (c) A. Blumstein, *Polym. J.*, **17**, 277 (1985).
6. N. J. Leonard and J. W. Curry, *J. Org. Chem.*, **17**, 1071 (1952).
7. O. Thomas, Ph.D thesis, University of Lowell, Lowell, MA, 1984.
8. R. S. Kumar, Ph.D thesis, University of Lowell, Lowell, MA, 1986.
9. A. Kotera, in *Polymer Fractionation*, M. J. R. Cantow, Ed., Academic, New York 1967.
10. A. Ziabicki, in *Man-Made Fibers, Science and Technology*, H. F. Mark, S. M. Atlas, and E. Cernia, Eds., Wiley-Interscience, New York, 1967, Vol. 1.
11. D. W. Van Kreelen and P. J. Hoftyzer, *Properties of Polymers*, Elsevier/North-Holland, New York, 1980, p. 318.
12. W. J. Jackson, Jr., *Br. Polym. J.*, **12**, 154 (1980).

Received June 1989

Accepted November 6, 1989