

# Fibers from Flexible Liquid Crystal Main-Chain Polymers. II. Functional Copolymers Based on the 4,4'-Dihydroxy-2,2'-Dimethylazoxybenzene Mesogen and Spacers Based on 2-Dodecenedioic and Nonanedioic Acids

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## Synopsis

Fibers spun from liquid crystalline solutions or melts are characterized by a high degree of chain alignment which promotes high values of tenacity and tensile modulus in the direction of fiber axis but lower values in the transversal direction. Structural modifications are introduced into the flexible moiety and the mesogenic group to alleviate this shortcoming. The incorporation of a spacer based on 2-dodecenedioic acids into a thermotropic liquid crystalline polyester was studied. A phase diagram was established to optimize the composition of such copolyesters. A significant increase in mechanical properties on crosslinking through UV irradiation was observed. A remarkable property of such systems is the retention of molecular chain order in spite of temperatures in excess of  $T_g$ . This is valid for both crosslinked and uncrosslinked systems. Remarkable also is the crystallization on annealing of a number of copolymer compositions in spite of a structural difference between the comonomer units.

## INTRODUCTION

It is well known that fibers obtained from nematic solutions of rigid and semirigid macromolecules such as those based on aromatic polyamids (Kevlar)<sup>1,2</sup> and cellulose triacetate,<sup>3</sup> give high values of tensile strength and tensile modulus. This phenomenon is due to the high degree of chain orientation achieved when a nematic mesophase containing domains of ordered main chains is submitted to an elongational flow in the spinnerette.

The main difficulty in obtaining fibers of such rigid polymers is their poor solubility and a very high melting temperature. In addition, the weak cohesive strength (in the direction transversal to the fiber axis) is detrimental to the overall quality of the fiber. Studies of feasibility of spinning nematic melts of inherently flexible macromolecules are therefore of value as such compounds melt at temperatures significantly below their decomposition or below the temperature of chemical changes in their structure.

In the previous work,<sup>4</sup> we have shown that low melting, flexible thermotropic polyesters can be spun from nematic melts to give fibers characterized by a

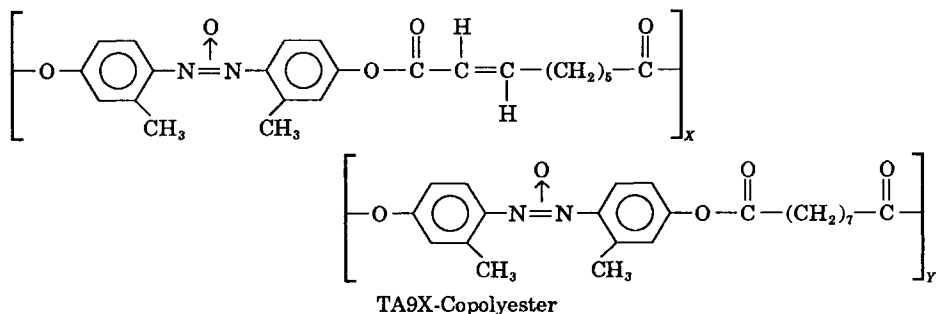
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high orientational order of individual chains and values of tenacity and modulus ( $E$ ) significantly above the ones expected of flexible polyesters spun from the isotropic phase. The values of tenacity and  $E$  were the highest for fibers spun at temperatures closest to the crystal/nematic transition temperature. This is understandable as the chain experiences an increasing degree of extension on cooling throughout the nematic interval. This was directly observed by recent neutron scattering studies.<sup>5</sup> A similar behavior was also recently described by Müller et al.<sup>6</sup> for flexible thermotropic nematic polyethers. These findings dispute the claim often put forward that the existence of a flexible sequence in the main chain makes such macromolecules inherently incapable of giving fibers with high values of tenacity and  $E$ .

The difficulty encountered with such flexible polymer systems is the low value of  $T_g$ . Nevertheless, the fiber described by us in Ref. 4 displayed a remarkably long retention of order at temperatures of about 10–20°C above  $T_g$ . This was explained by strong interchain interactions operating between aligned chains in the nematic fiber.

In addition to a low  $T_g$  a common characteristic of fibers spun from a nematic mesophase is the lack of lateral strength. This can be alleviated by crystallization in homopolymers. If crystallization is suppressed, the chain experiences creep and relaxation of orientation under stress. In this work we examine the feasibility of an approach consisting of incorporation into the main chain of functional groups (here a conjugated double bond) and stabilization of the chain orientation through irradiation-crosslinking. The copolyester studied here is based on: 4,4'-dihydroxy-2,2'-dimethylazoxybenzene mesogen with 2-dodecenedioic acids and nonanedioic acids spacers:



The choice of the mesogen and spacers was dictated by the excellent processing properties of this system and the knowledge of its mesomorphic properties.

## EXPERIMENTAL

### Synthesis of Polyesters and Copolyesters

The mesogen Diol-9 (4,4'-dihydroxy-2,2'-dimethylazoxybenzene) was prepared from *p*-nitrosophenol by reductive coupling<sup>7</sup> and purified by recrystallization. The chloride of nonanedioic acid (azelaic acid) was purified by distillation under reduced pressure. 2-Dodecenedioic acid chloride was prepared by

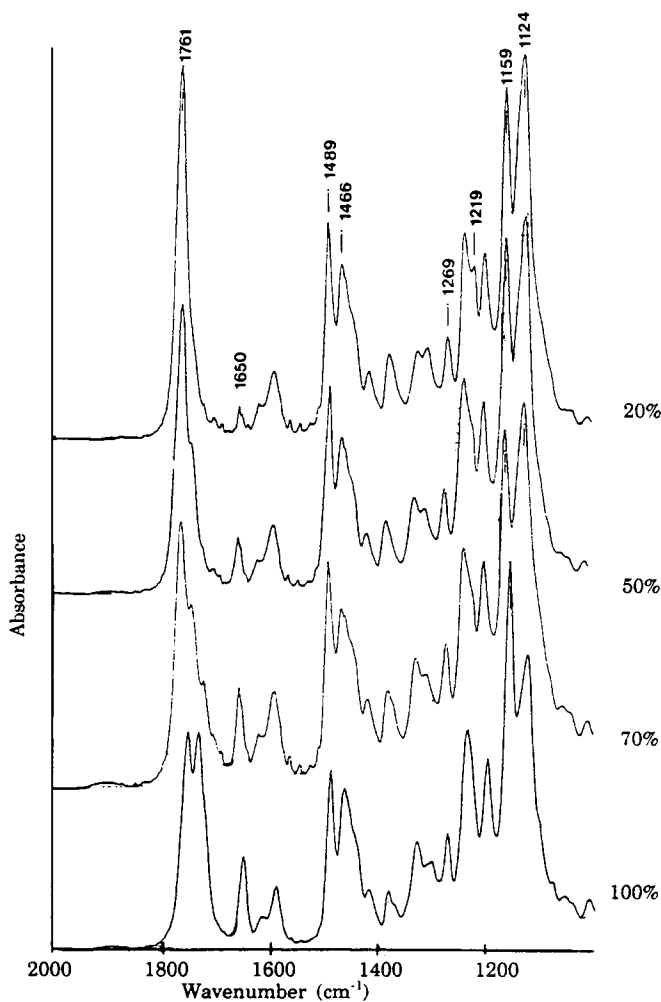


Fig. 1. FT-IR absorption spectra of copolyesters TA9X films. From top to bottom are 20, 50, 70, and 100% traumatic acid, respectively.

chlorination of 2-dodecenedioic acid [traumatic acid (TA)]. It was refluxed with oxalyl chloride and distilled under vacuum. The copolyester of traumatic acid, azelaic acid, and mesogen 9 (TA9X) was prepared by interfacial polycondensation and purified by precipitation according to a procedure described previously.<sup>8</sup>

Films of copolyester (TA9X) were cast on KBr crystal (25 mm diameter, 4 mm thickness) from 1% of chloroform solution and thickness was controlled at about 5  $\mu\text{m}$ .

### Characterization of Polyesters and Copolyesters

The inherent viscosity of the copolyesters TA9X at concentration of 0.5 g/dL was measured in 1,1,2,2-tetrachloroethane at 30°C. Phase transition tem-

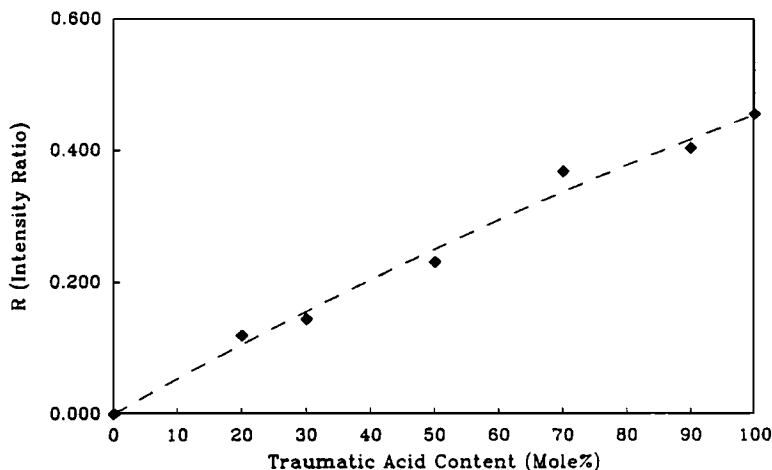


Fig. 2. Intensity ratio ( $R = I_{\text{C}=\text{C}}^{1650, \text{cm}^{-1}} / I_{\text{C}-\text{H}}^{1466, \text{cm}^{-1}}$ ) vs. traumatic acid contents (mol %).

peratures were obtained by thermal analysis using Perkin-Elmer DSC-2C thermal analyzer and data station. The heating and cooling rate was 20°C/min. DSC data were supplemented by polarizing microscopy using Leitz Ortholux II cross-polarizing microscope equipped with Mettler FP5 heating stage.

Figure 2 obtained from FTIR spectra (Fig. 1) shows that the relationship between the composition of the copolymer and that of the feed is linear. This can also be confirmed from Table I which gives the results of elemental analysis for the copolymer system. One can see that the expected and experimental results are quite similar. Figure 3 shows a typical GPC trace of the copolymer (here 20 mol % TA). The shape of the peak suggests that no abrupt changes in the composition of the copolymer takes place.

TABLE I  
Elemental Analysis of the TA9X Copolyesters<sup>a</sup>

Polymer	Expected (%)			Experimental (%)		
	C	H	N	C	H	N
TA90	67.30	6.38	6.82	67.11	6.40	6.71
TA91	67.54	6.42	6.75	67.37	6.45	6.60
TA92	67.75	6.46	6.69	67.39	6.50	6.54
TA93	67.94	6.49	6.63	67.41	6.49	6.37
TA94	68.13	6.52	6.57	67.51	6.57	6.31
TA95	68.35	6.56	6.50	67.64	6.70	6.26
TA96	68.74	6.62	6.39	68.21	6.75	6.02
TA97	69.12	6.68	6.28	68.68	6.77	6.05
TA98	69.32	6.71	6.21	69.06	6.89	5.82

<sup>a</sup> Note: Content of TA (traumatic acid) is shown in Table II.

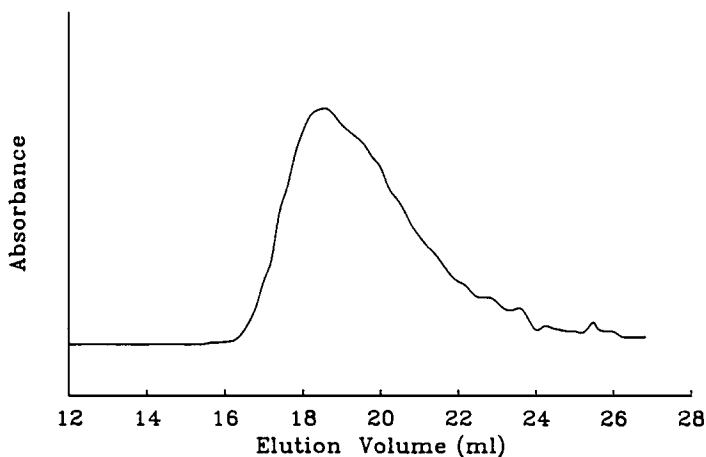


Fig. 3. GPC trace of TA92 (20 mol %) copolyester.

### Fiber Spinning and Testing

Melt spinning of TA9X copolyesters in the mesophase was performed by a monofilament spinneret developed for small experimental samples of polymer.<sup>4</sup> The diameter of fibers was dependent on the extrusion conditions. For TA9-10 sample the diameter was approximately 45  $\mu\text{m}$ ; for TA9-20 it was 25  $\mu\text{m}$ . The spun fiber was stored at low temperature ( $-5^\circ\text{C}$ ) until the time of testing to prevent relaxation of orientation.

The tenacity, tensile modulus, and elongation of TA9X copolyester fibers were tested by means of an Instron tensile tester (Model TTC) under conditions previously described.<sup>4</sup>

### Crosslinking

Crosslinking was effected via the double bond opening for copolyesters using UV irradiation of the fibers. The transparency (or opacity) of the TA9 copolyester to UV irradiation was studied. It was found from the UV absorption spectra that wavelengths of UV radiation between 250 and 300 nm are the least absorbed by the polymer system. The wavelength of 2537  $\text{\AA}$  was used.

The UV irradiation was performed in a reactor equipped with a medium pressure mercury UV lamp emitting at 2537  $\text{\AA}$  (Rayonet photochemical chamber reactor). The fiber was wound around a wire holder and placed in a quartz tube swept by dry and cold nitrogen. The fiber temperature did not exceed  $10^\circ\text{C}$  and was at least  $10^\circ\text{C}$  below its  $T_g$ . The irradiation intensity was measured with a radiometer (model: International Light, IL-1700 Research Radiometer). It was in all cases 2.83  $\text{J}/\text{cm}^2 \text{ h}$ .

The crosslinking process was followed by determination of the double bond contents by FT-IR. IBM FT-IR (Model IR/90) was used. The ratio  $R$  of the intensity of the  $\text{C}=\text{C}$  stretching at  $1650 \text{ cm}^{-1}$  and of the internal reference peak at  $1466 \text{ cm}^{-1}$  corresponding to the  $\text{C}-\text{H}$  scissor vibrations ( $R = I_{\text{C}=\text{C}}/I_{\text{C}-\text{H}}$ ) was followed. Figure 1 gives the FTIR spectra of the TA9X copolyester

system and its evolution with the composition and the double bond content. In Figure 2 is plotted the ratio  $R$  against mol % of traumatic acid. A linear relationship is apparent. Films of copolyester were cast on KBr pellets from 1% chloroform solution (to check the effectiveness of irradiation on the double bond opening and crosslinking of the polymer). These were irradiated for a variable time and FTIR spectra recorded. Figure 4 gives  $R$  as a function of irradiation time for 20, 30, and 70 mol % contents of TA. It is apparent from these curves that UV irradiation (intensity =  $2.83 \text{ J/cm}^2 \text{ hr}$  and  $\lambda = 254 \text{ nm}$ ) beyond 4 h does not contribute to appreciable decrease in the double bond content. For fibers the estimation of crosslinking from the disappearance of the double bond is much more difficult than for films because the fiber diameter (of  $20\text{--}50 \mu\text{m}$ ) is 4–10 times the thickness of the film. Consequently, the FTIR study of the UV irradiated films can be taken only as a qualitative indication of the feasibility of fiber crosslinking.

### X-Ray Scattering

Pictures of WAX scattering of fibers were taken with the help of a Laue camera mounted on Rigaku generator operating at 40 kV and 25 mA using Ni filtered  $\text{Cu-K}\alpha$  radiation of wavelength  $1.54 \text{ \AA}$ .

## RESULTS AND DISCUSSION

Table II gives the transition temperatures obtained after thermal cycling of the TA9X copolyester. These data are plotted in Figure 5 which provides a phase diagram of the unannealed copolymer system and can be used as a guide to the spinning operation. It shows some crystallinity developing for extreme compositions on both sides of the diagram (10 mol % TA and 90 mol % TA). As expected, the medium compositions do not display crystallinity (when in-

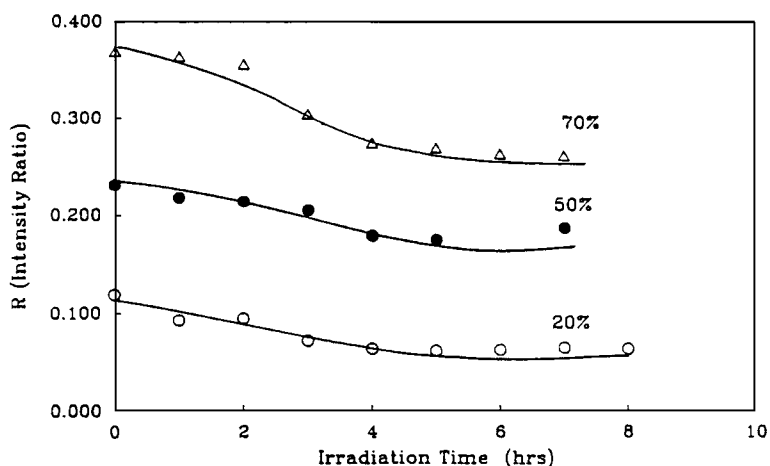


Fig. 4. Intensity ratio ( $R = I_{\text{C}=\text{C}}^{1650 \text{ cm}^{-1}} / I_{\text{C}-\text{H}}^{1466 \text{ cm}^{-1}}$ ) vs. irradiation time of 20, 50, and 70% traumatic acid content copolyesters.

TABLE II  
 Properties of TA9X Copolyesters

Polymer	TA <sup>a</sup> content (mol %)	$\eta_{inh}$ (dL/g)	$T_g$ (°C)	Thermal transition (°C) <sup>b</sup>	
				Heating	Cooling
TA90	0	0.33	20.1	C77.7N143.4I	I137.3N69.8C
TA91	11	0.54	18.9	C74.3N152.6I	I145.6N65.9C
TA92	21	0.45	16.7	N151.7I	I144.9N
TA93	30	0.32	13.6	N145.7I	I140.0N
TA94	39	0.30	11.2	N145.6I	I139.5N
TA95	50	0.47	11.4	N174.1I	I162.2N
TA96	70	0.32	6.0	N159.5I	I152.4N
TA97	90	0.48	4.0	C <sub>1</sub> 77.6C <sub>2</sub> 107.6N183.9I	I174.6N32.4C
TA98	100	0.43	1.0	C114.5N183.0I	I172.5N70.3C
TA9-10 <sup>c</sup>	10	0.89	19.3	C76.5N162.2I	I148.9N57.4C
TA9-20	20	0.78	18.1	N166.1I	I158.3N
TA9-25	25	0.82	18.2	N168.2I	I156.9N
TA9-31	31	1.20	17.5	N178.5I	I166.9N
TA9-81	81	1.13	13.2	N200.2I	I184.3N

<sup>a</sup> TA is the traumatic acid feed in mol %.

<sup>b</sup> Thermal transition temperatures are taken from DSC second cycle, heating/cooling rate at 20°C/min.

<sup>c</sup> TA9-10 to TA9-81 are the copolymers used in fiber spinning.

vestigated by DSC or X-ray diffraction). Annealing for 60 h at 62–64°C introduces changes in the crystallization profile of the copolymer. For lower composition (10 mol % TA) the former crystal melting peak is replaced with two peaks at 80–100°C, respectively. For 30 mol % TA composition these peaks merge into one small peak before disappearing for higher compositions. At the opposite end of compositions (80–90 mol % TA), one observes multiple exotherms and endotherms (possibly indicating multiple melting and recrystallization phenomena). This can be seen in Figure 6, in which DSC scans of unannealed and annealed copolymers of 10 and 90 mol % TA compositions are compared. For median compositions (as expected) no crystallinity either before or after annealing could be detected. The extent of this phenomenon can be seen in Figure 7, in which the sum of crystallization enthalpies is plotted against the copolymer composition after extensive annealing. It is interesting that appreciable crystallinity is present in copolymers with composition below 30 mol % and above 70 mol % despite a difference in the length and structure (conjugated double bond vs a sequence of methylene groups) of the spacers in the comonomer. The copolyester between 20 and 70 mol % supercools easily. The N/I peaks are broad and broaden with the increase in compositional heterogeneity, which is at its maximum in the range of 40–70 mol % composition. Although we have taken for the transition temperature the temperature corresponding to the maximum of the peak, it is obvious from the breadth of the peak that a biphasic is present. This biphasic can extend over temperature intervals exceeding 20–40°C for both the N/I and C/N transitions. At the bottom of Table II are given values of N/I transition temperatures of some samples

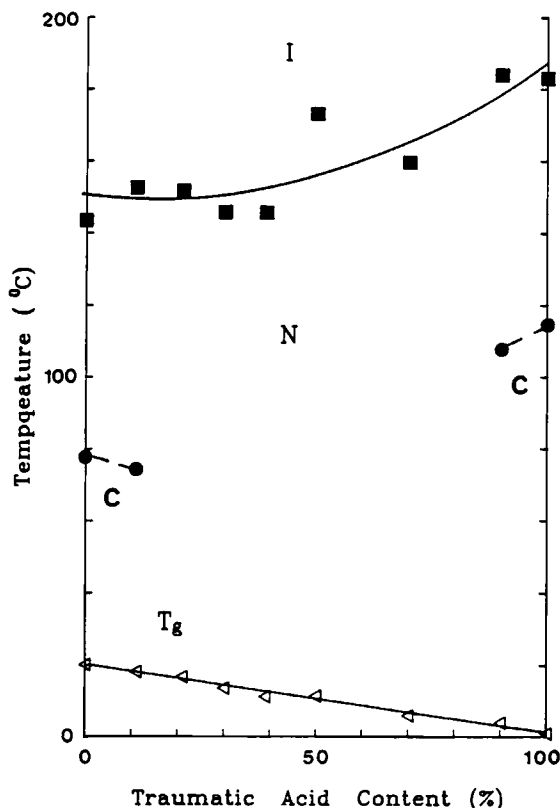


Fig. 5. Phase diagram for the TA9X copolymer system (the data obtained after 2nd heating at 20°/min).

with significantly higher molecular masses than the samples for which the phase diagram was constructed. For these higher masses the N/I transition temperature is increased and so is the nematic interval resulting in an upward translation of the N/I transition boundary. The general shape of the phase diagram of Figure 5 is however unchanged.

Table III gives the results of mechanical testing on fibers from TA9X polyesters. The spinning temperature was set to a value such that the biphasic was avoided and the  $T_s - T_m$  was kept in a similar range (here  $T_m$  representing the induced crystallization temperature and  $T_s$  representing the spinning temperature). As it was shown by Müller et al.,<sup>6</sup>  $T_s - T_m$  is the spinning parameter related directly to the chain order parameter  $S_{zz}$ . From our previous studies of chain extension of such polymers by NMR<sup>9</sup> and neutron scattering,<sup>5</sup> it appears that it is desirable (in order to realize a full extension of the flexible spacer) to operate as closely as possible to  $T_m$ .

It is apparent from Table III that crosslinking produced by irradiation of fibers with up to 31% of traumatic acid significantly enhances the tensile modulus  $E$  and the tenacity of the fiber. Interestingly this process of reinforcement takes place in the first 1–2 h of irradiation and then levels off or even reverses. For high compositions of traumatic acid there is a steady decrease of fiber



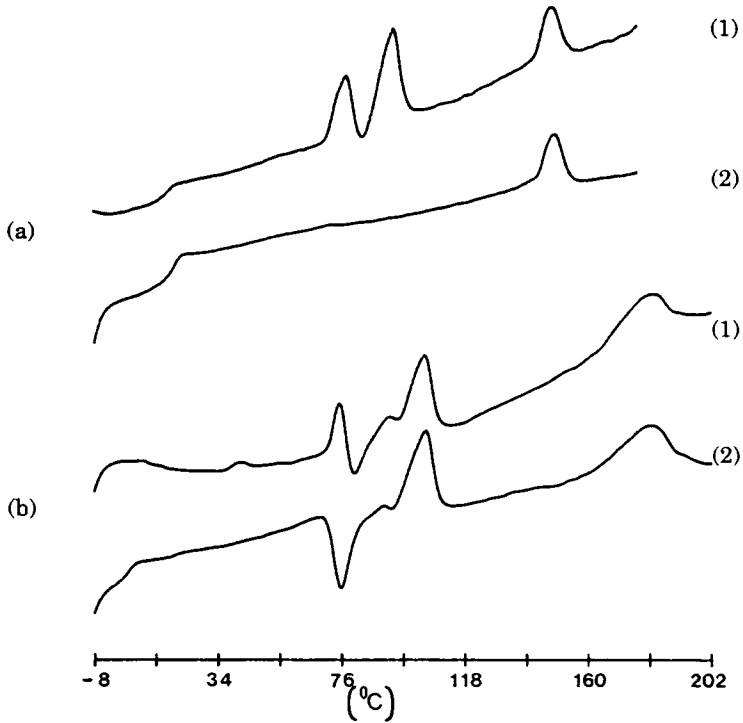


Fig. 6. DSC thermograms of TA9X copolyester (a) 10 mol % TA and (b) 90 mol % TA [(1) annealed at 62–64°C for 60 h; (2) unannealed].

tensile properties on irradiation. This is graphically represented in Figure 8; Figures 9(a) and 9(b) summarize the results given in Table III.

One can see from Figure 9 that the tenacity and modulus of the unirradiated copolymer fiber decreases with the TA content. The crystallinity also decreases

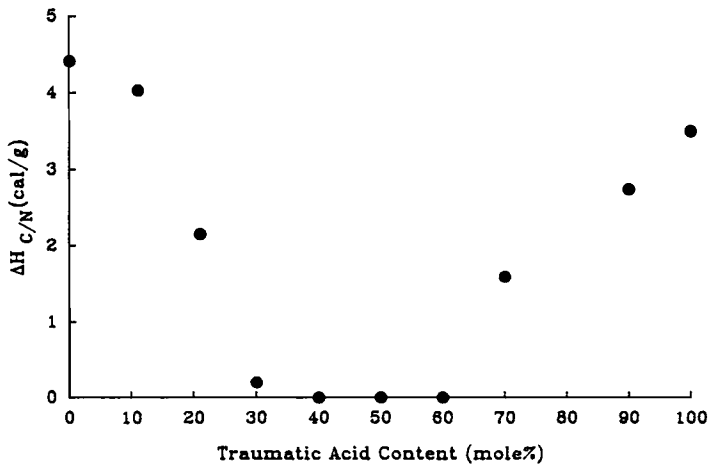


Fig. 7. The sum of crystallization enthalpies vs. TA9X copolymer compositions.

TABLE III  
Mechanical Properties of Copolyesters TA9-X Fibers<sup>a</sup>

Polymer	Spun temp (°C)	Irradiation <sup>b</sup> time (h)	Tenacity (g/den)	Modulus (g/den)	Elongation at break (%)
TA9-10	110	0	1.41	31.2	7.4
		1	3.31	68.9	6.3
		2	2.71	63.9	6.3
		3	3.12	60.3	6.3
		4	3.00	57.6	5.5
TA9-20	104	0	1.29	26.7	5.9
		1	2.07	57.4	6.5
		2	2.66	55.4	6.5
		3	2.49	54.7	5.9
		4	2.23	46.5	5.9
TA9-25	93	0	1.15	26.8	5.8
		1	1.60	43.9	5.8
		2	1.31	39.3	6.2
		3	1.35	33.9	5.6
		4	0.97	27.7	5.2
TA9-31	85	0	0.84	18.5	7.2
		1	0.94	33.0	3.9
		2	1.12	33.2	3.5
		3	1.15	40.6	2.9
		4	0.68	26.8	2.3
TA9-81	123	0	1.39	50.5	3.5
		1	1.00	34.1	3.2
		3	1.11	37.4	3.4
		4	0.96	35.0	2.8

<sup>a</sup>  $T_s - T_m \approx 30^\circ\text{C}$ ;  $T_s$  and  $T_m$  are the spinning temperature and the induced crystallization temperature, respectively.

<sup>b</sup> Irradiation intensity is  $2.83 \text{ J/cm}^2$ , h, and at  $\lambda = 254 \text{ nm}$ .

up to 60 mol % (see Fig. 7) with most of the decrease taking place for the first 20–30 mol % of TA in the copolymer. We believe therefore that the rapid decrease of tenacity [Fig. 9(a)] and modulus [Fig. 9(b)] of the unirradiated fiber is mainly due to the decrease in crystallinity.

After irradiation the picture changes. The mechanical properties first increase dramatically, then decrease slowly as a function of irradiation time (Fig. 9). For example, for 10 mol % of TA the modulus increases from 31 to 69 g/den and then slowly decreases to 57–58 g/den. The disappearance of the absorption at  $1650 \text{ cm}^{-1}$  of the TA9X films during the first 2 h of irradiation makes us think that the enhancement of mechanical properties is due to formation of lateral chain bonding through crosslinking. The decline of mechanical properties on further irradiation appears to be related to a degradation process. This can be inferred from the comparison between the sets of points corresponding to 0 and 1 h irradiation in Figure 9. Although the tenacity and (to a lesser extent) modulus decline only very moderately with TA content for the unirradiated sample, these properties decrease sharply with TA content for the irradiated ones. This suggests that the degradation process is accelerated by the increase

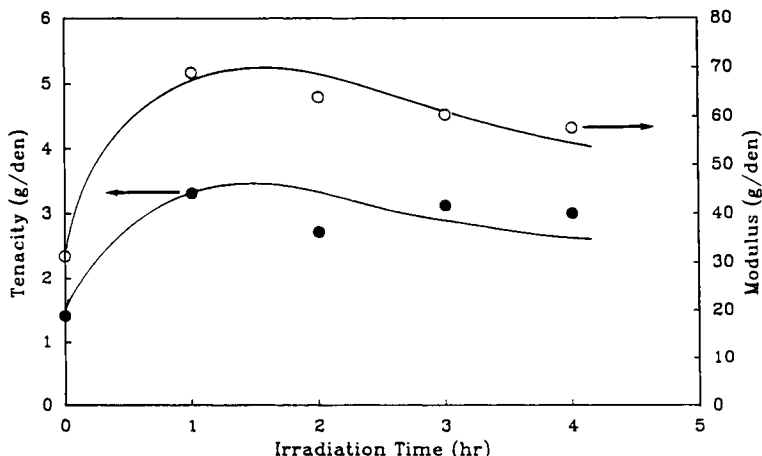


Fig. 8. Tenacity and tensile modulus of TA9-10 fibers vs. UV irradiation time.

in the double bond content of the copolymer. This is apparent from the FTIR spectra displaying a progressive decrease of the  $1650\text{ cm}^{-1}$  band corresponding to the opening of the double bond of traumatic acid. Large changes occur also in the region  $1124\text{--}1269\text{ cm}^{-1}$ . Particularly visible is the decrease of absorption peaks at  $1269$  and  $1179\text{ cm}^{-1}$  (possibly related to the N—O and C—N stretching). All these changes increase in intensity with the increase in composition of traumatic acid of the copolymer. The copolymers are vulnerable to UV irradiation.

The degree of chain orientation in the fiber after extrusion was studied by X-ray scattering. Given the  $T_g$  of  $15\text{--}20^\circ\text{C}$  for this system, X-ray pictures have been taken for (1) the as-spun fiber maintained at room temperature, (2) the as-spun fiber heated to  $40^\circ\text{C}$  for 20 h and (3) to  $65^\circ\text{C}$  for 60 h. The same experiments were also performed on fibers previously irradiated for 2 h by UV radiation. Figures 10(a) and 10(b) show these X-ray pictures. It is apparent that the extruded nematic fibers are characterized by an orientation which persists for 20 h at  $40^\circ\text{C}$ . If the fiber is kept at  $65^\circ\text{C}$  (for 60 h), crystallization takes place and the macroscopic orientation of chains is decreased but not completely relaxed. The irradiated fiber displays similar X-ray characteristics to the unirradiated; however, the annealed irradiated fiber ( $65^\circ\text{C}$ , 60 h) is more oriented. The relaxation of orientation is consequently smaller in the cross-linked fiber.

The above study of fibers spun from rigid-flexible nematic copolyesters has shown that a reinforcing effect on the modulus  $E$  and tenacity can be reached by reacting some of the functional groups (here double bonds) incorporated into the main chain. The crosslinking appears, however, in this case accompanied by a simultaneous degradation reaction. It is therefore not astonishing that the reinforcing effect decreases with the composition of the traumatic acid in the spacer as evidenced by Figures 10(a) and (b) and that the reinforcing effect is reversed for the copolymer of 80 mol % of traumatic acid. The strongest reinforcing effect is noted for the smallest composition of traumatic acid (10%)

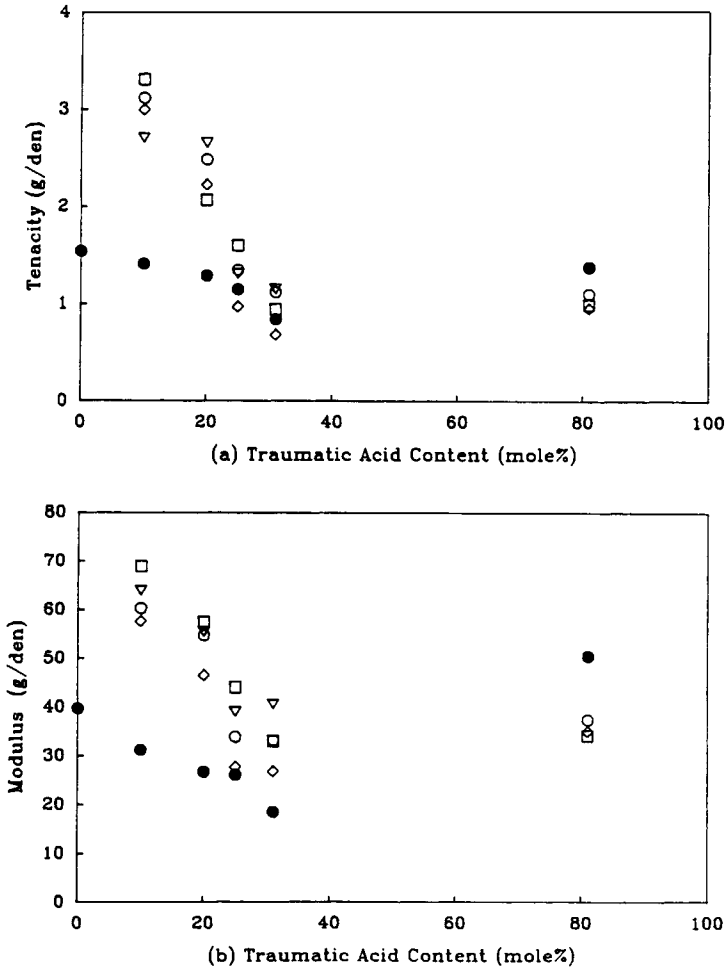


Fig. 9. Mechanical properties (a) tenacity and (b) modulus of copolyester fibers vs. traumatic acid (TA) content (●: unirradiated, □, ▽, ○, ◇: irradiated at 1, 2, 3, and 4 h, respectively).

for 2 h of UV irradiation. At this point the fiber placed in a good solvent, such as tetrachloroethane, loses approximately 80% of its weight by dissolution but preserves its fibrillar shape despite of swelling. The crosslinking is consequently far from complete and yet the modulus and tenacity are comparable to some of the strongest flexible commercial fibers. Based on these findings, one could predict a strong reinforcing effect for a uniformly crosslinked fiber of the same type.

For both crosslinked and uncrosslinked fibers the molecular order of chain is retained in spite of temperatures 20–30°C in excess of  $T_g$ . This can be seen clearly in Fig. 10(1a,b) and (2a,b). The span of the arc of the diffraction halo does not significantly change with annealing to 40°C for 20 h. Annealing at 65°C for 60 h produces crystallization. Partial order persists after crystallization. This can be seen from Figure 10(3a,b) and from the arc patterns of the X-ray diffraction pictures. From these one can infer that the orientation of chains is

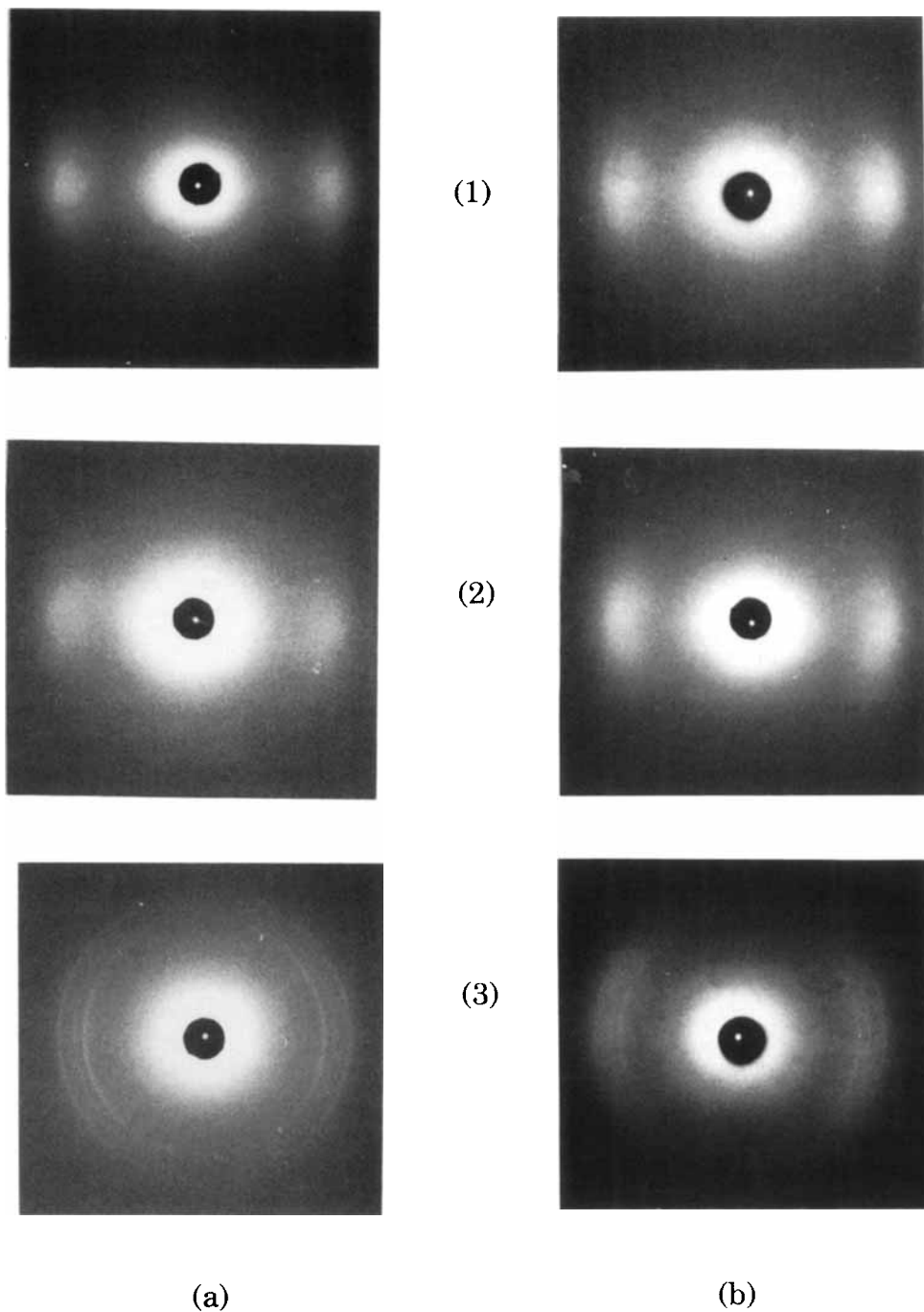


Fig. 10. X-ray diffraction pictures of fibers of TA9-31 (a) unirradiated; (b) UV irradiated for 2 h [(1) fibers "as spun"; (2) fibers annealed at 40°C for 20 h; (3) fibers annealed at 65°C for 60 h]. See text.

better preserved in the crosslinked than the uncrosslinked fibers. It is only on melting of the crystallites and longer annealing (close to the N/I boundary) that orientation is lost. The crystallization on annealing of a number of copolymer compositions is remarkable because it occurs in spite of a certain mismatch in length (approximately 2 Å) and a difference in structure of the flexible spacers in copolymer, the even spacer containing a conjugated double bond and the odd spacer containing a methylene sequence (2-dodecenedioic acid compared to nonanedioic acids).

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