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# Mechanical Properties and Characterization of the Crystalline Structure in Annealed Thermotropic Poly(azomethines)

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ABSTRACT: Fibers of a poly(azomethine) having hydroxyl groups within the mesogenic core have been melt extruded from the nematic phase. The polymer obtained by condensation of 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane and 2-methyl-1,4-phenylenediamine has a $T_g$ of 54 °C and exhibits a nematic phase from 178 to 341 °C. Due to an observed increase in the melt viscosity upon heating above 200 °C, the processing temperature (190 °C) has been closely controlled above $T_m$. Fibers have been subjected to thermal annealing at 100 °C, i.e., above $T_g$ and below $T_m$, either in a relaxed state or under an external force along the longitudinal fiber axis. Fibers have been studied by simultaneous TG-DTA, DSC, and X-ray scattering, and the mechanical properties have been measured. As-spun fibers show good thermal stability and good orientation along the fiber axis; the values of the elastic modulus and tensile strength are 8.9 GPa and 252 MPa, respectively, and the elongation at break is 3.3%. The mechanical properties improve after annealing in a relaxed state. After 90 min at 100 °C, the values of the elastic modulus and tensile strength increase to 11 GPa and 283 MPa, respectively, and the elongation at break is 2.5%. Longer heat treatments do not seem to significantly affect the properties; however, a gradual but remarkable increase in the degree of crystallinity is promoted. A highly crystalline phase is achieved after annealing on a stressed state. It consists of a primitive triclinic lattice where the chains are packed side-by-side with the alkyl chains in an *all-trans* conformation. After 12 h at 100 °C, an increase in the molecular weight is determined from the inherent viscosity values, but relaxation of the molecular orientation is not observed. All of these effects lead to an improvement in the tensile properties: the values of the elastic modulus and tensile strength increase to 18.4 GPa and 388 MPa, respectively, and the elongation at break is 2.2%.

## Introduction

Liquid crystal polymers have been the subject of increasing interest due to their particular unique combination of properties.[1] From them, thermotropic liquid crystal polymers that can be melt-spun into high stiffness and high-strength fibers have been offered as alternatives to lyotropic liquid crystal polymers that require costly and dangerous processing methods.[2] The main advantage of liquid crystal polymers is that the polymeric chains spontaneously align parallel to each other in the mesophase, giving rise to fibers with good degrees of molecular orientation in the direction of the flow, even in the as-spun state. Consequently, excellent mechanical properties in the longitudinal direction of the fiber are expected.[3]

From the considerable amount of thermotropic systems, several examples of fibers from wholly aromatic thermotropic liquid crystal polyesters have been reported in the literature.[4−7] Melt processing conditions and thermal treatments to improve mechanical properties have been explored. In particular, thermal annealing of well-oriented fibers under specific conditions led to an improvement in the tensile properties ascribed to an increase in the molecular weight due to further polymerization and to a higher degree of crystallinity. The main disadvantage of all rigid polymers is their high melting temperatures, which sometimes prevent their processing. To reduce transition temperatures, several different alternatives are available and the introduction of flexible segments in the main chain has proved to be very efficient.[8] Accordingly, there are several examples in the literature of fibers extruded from semiflexible polyesters.[9−11] The values of the reported properties are lower than those of the corresponding rigid polyesters. This is ascribed to lower orientation degrees, short relaxation times, and differences in the degree of crystallinity. Furthermore, depending on the drawing conditions when they are extruded, tensile properties of fibers from these semiflexible polyesters might be improved by annealing.

Compared to polyesters, fibers obtained from poly(azomethines) have received less attention, mainly due to their poor solubility in common organic solvents and nonfusibility. However, an in-depth study of some of these systems has been carried out at Du Pont.[12,13] High-tenacity and high-modulus fibers from wholly aromatic poly- and copoly(azomethines) have been reported, and these properties are susceptible to improvement after gradual thermal annealing. The improvement is related to an increase in the molecular weight, accompanied by increases in the melting temperature, molecular orientation, and crystallinity. Analogous studies of fibers have been reported for a series of semiflexible poly(azomethines) obtained by the reaction of 1,*n*-bis(4-amino-3-methylphenoxy)alkanes (where $n$ = 1−10, 12, 14, and 16) and terephthalaldehyde.[14] In that work, the properties of the fibers are correlated with the length of the flexible spacer. Upon annealing under particular conditions, it is possible to improve the

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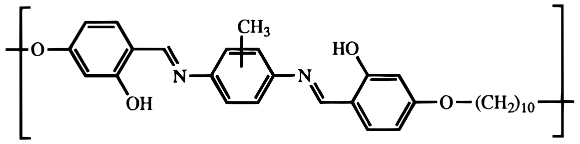

**Figure 1.** Molecular structure of the target poly(azomethine).

tensile properties of fibers with a low even *n*, accompanied by substantial increases in crystallinity and orientation.

In a recent paper, we have described the synthesis and characterization of a series of hydroxy-functionalized liquid crystal poly(azomethines).[15] The paper reported the most appropriate structures to achieve low transition temperatures and high stability. Here, the aim of the work is to obtain fibers from these poly(azomethines) and to study their properties. From the previously described structures, we selected a poly(azomethine) obtained from the complex dialdehyde, 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane, and 2-methyl-1,4-phenylenediamine (Figure 1).

The presence of a lateral methyl substituent on the central benzene ring and a flexible spacer within the repeating unit gave rise to moderate melting temperatures that favored the melt-spinning processing procedures to obtain oriented fibers. However, the novel aspect of this poly(azomethine), as well as the rest of the examples reported, is the presence of hydroxyl groups within the mesogenic core. A hydroxyl group in the *ortho* position of the imine function gives rise to the formation of a chelate ring by means of a hydrogen bond that increases the planarity of the mesogenic core, thus favoring the mesogenic properties. In addition, the chelate ring offers a suitable site to introduce transition metals by complexation.[16] Furthermore, when molecular chains are oriented along the fiber, the presence of the hydroxyl group might lead to an improvement in the transverse properties of the fibers mainly by avoiding defibrillation.[17]

The aim of the present work is to study the properties of melt-extruded fibers and the modifications of these fibers upon thermal annealing, as well as to correlate the results with modifications in the molecular weight, orientation, and crystallinity of the material.

## Experimental Section

**Materials.** The complex dialdehyde 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane was obtained as reported elsewhere.[18] The diamine, 2-methyl-1,4-phenylenediamine, was obtained from its commercially available quaternary ammonium salt, 2-methyl-1,4-phenylenediammonium sulfate. *N*,*N*-Dimethylacetamide was distilled under reduced pressure and collected over molecular sieves (type 4 Å). Lithium chloride (LiCl) was dried under vacuum at 80 °C for 20 h and at 100 °C for 1 h.

**Polymerization Procedure.** To a solution of LiCl (2.5 g) in *N*,*N*-dimethylacetamide (50 mL) under a nitrogen atmosphere at room temperature was added 2-methyl-1,4-phenylenediamine (3.05 g, 25 mmol). When the mixture became clear, 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane (10.35 g, 25 mmol) was added. The reddish solution was kept away from light and stirred at room temperature for 16 h. Water was added to the resulting suspension, and the yellow solid was isolated by filtration and thoroughly washed several times with water and methanol. The product was extracted by using a Soxhlet apparatus with acetone for 24 h and finally dried under vacuum over $P_2O_5$ for 24 h at 80 °C to yield the poly(azomethine) (10.73 g, 86%): IR (KBr disk) 1607 $cm^{-1}$ ($\nu_{C=N}$); inherent viscosity in methanesulfonic acid at 40 °C, 0.41 g/dL; $^1$H NMR ($CF_3COOD$) $\delta$ 9.53 (ArC*H*=O end group), 8.76 (ArC*H*=NAr), 7.57 (Ar*H*), 6.74 (Ar*H*), 6.52 (Ar*H* end group), 4.15 ($OCH_2CH_2(CH_2)_6$), 2.52 ($ArCH_3$), 1.83 ($CH_2(CH_2)_6$), 1.37 ($CH_2(CH_2)_6CH_2$). Anal. Calcd for $C_{31}H_{36}N_2O_4$: C, 74.37; H, 7.25; N, 5.60. Found: C, 73.80; H, 7.46; N, 5.33.

**Fiber Formation Procedure.** Fibers were prepared by a melt-spinning process using a capillary viscosimeter CEAST-Modular-Flow-Index MFI-6542 modified to have lateral flow and equipped with a single-hole spinneret. The exit die presents a conical inlet with an angle of 45°, followed by a short circular channel of 0.474 mm diameter and 0.8 mm length. Approximately 3 g of the poly(azomethine) was loaded, and the molten polymer was extruded in the nematic state at 190 ± 2 °C. Pressure was applied by a hydraulically driven piston using a 10 kg weight. The resulting monofilament solidified at the die exit upon contact with air at room temperature.

**Fiber Annealing Procedure.** Fibers of about 10 cm length cut from the filaments extruded at 190 °C were heat treated under different conditions. Thermal annealing was accomplished at 100 °C, just above the glass transition temperature and below the melting temperature. Fibers were suspended from one end in an oven for 90 min or 4 h or 12 h. Fiber samples were also annealed under tension at 100 °C for 12 h by suspending a weight of 110 g from the free end. Length, diameter, and weight of the fibers were determined before and after thermal treatment.

**Techniques.** Elemental analysis was carried out with a Perkin-Elmer 240C microanalyzer, and IR spectra were measured from KBr pellets on a Perkin-Elmer FTIR 1600. $^1$H NMR spectra were performed using a Bruker ARX 300 in deuterated trifluoroacetic acid. The inherent viscosity of poly(azomethines) was measured at a concentration of 0.5 g/dL in methanesulfonic acid at 40 °C using a Cannon-Fenske viscosimeter. Samples were used immediately after preparation; however, in most of the cases a manifest lowering of the solution flow times in consecutive measurements was detected. This is almost certainly due to degradation of the polymer in methanesulfonic acid at 40 °C. When this was the case, the longest time was used to determine the values of the inherent viscosity.[12]

Mesogenic behavior was confirmed by optical microscopy using a Nikon polarizing microscope fitted with a Mettler FP-82 hot stage and a Mettler FP-80 control unit.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions, which were read as the maximum or minimum of the peaks at a scanning rate of 10 °C/min. Glass transition temperatures were taken as the midpoint of the baseline jump. Both transition temperatures and enthalpy changes were determined by using indium and tin as calibration standards.

Thermogravimetric analysis was performed using a TA Instrument STD 2960 simultaneous DTA-TGA at a rate of 10 °C/min in nitrogen. TGA data were given as the onset of the decomposition curve. Additionally, DTGA data were read. Thermal transitions were read as the maximum or minimum of the peaks.

Mechanical properties of the fibers were determined by using an Instron mod Zwick 1445 at an elongation rate of 10 mm/min at room temperature. Precision on the measurements was ±0.05 N. Fiber diameters were measured by using a laser gauge BETA LG1005/L1800-4FA.

X-ray diffraction diagrams were obtained by using a modified Staton Camera (W. H. Warhus,Wilmington, DE) using nickel-filtered Cu K$\alpha$ radiation of wavelength 0.1542 nm and internally calibrated with molybdenum sulfide.

## Results and Discussion

**Synthesis and Characterization of the Poly(azomethine).** The synthesis and characterization of the target poly(azomethine) have already been described.[19] In the previous work, the polymer was prepared by direct acid-catalyzed polycondensation of the dialdehyde with the diamine in absolute ethanol under reflux using acetic acid as a catalyst, as described

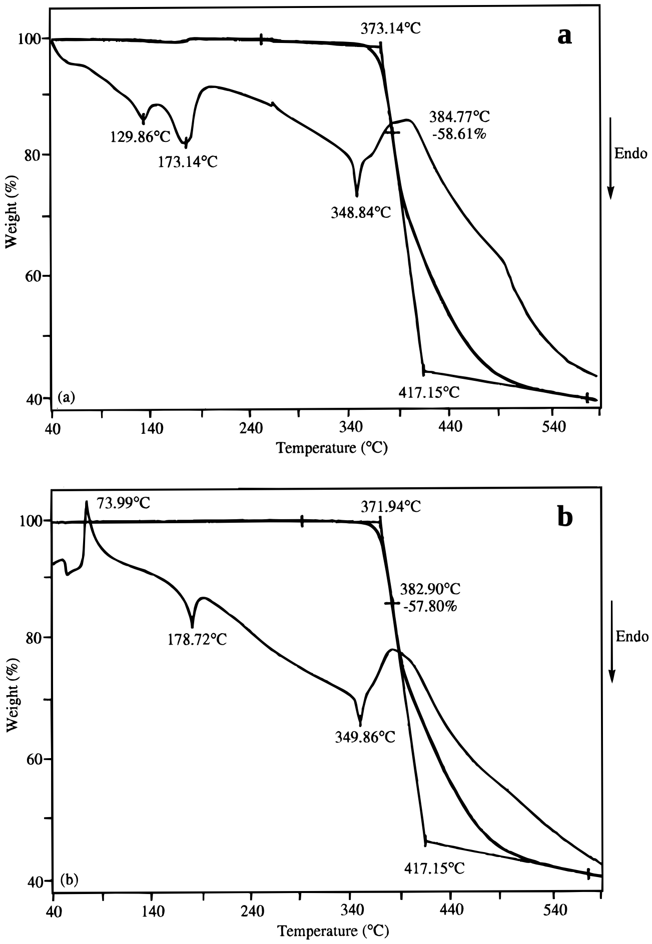

**Figure 2.** TGA-DTA curves for the original polymer (a) and the as-spun fiber extruded at 190 °C (b).

by D'Alelio.[20] The low solubility of the dialdehyde in absolute ethanol makes it difficult to obtain the large amounts of the polymer necessary to draw fibers. Therefore, new reaction conditions were tested. The polycondensation was carried out by using a water-free solvent such as *N*,*N*-dimethylacetamide at room temperature.[12] In this case, the presence of the acid catalyst was not necessary, but anhydrous lithium chloride was used to promote the polymerization by removing the water formed during the reaction.

The yield of the polymerization under these new conditions was identical to that previously reported using D'Alelio's method. Values of the inherent viscosity, 0.41 *versus* 0.45 dL/g, indicate a similar degree of polymerization in each case. IR, $^1$H NMR, and microanalysis of the polymer are in accordance with the proposed structure.

The newly synthesized polymer was carefully characterized by TGA-DTA, optical microscopy, and DSC due to the fact that the melting point would determine its processing temperature. The polymer shows good thermal stability, as can be observed in the TGA-DTA curves reproduced in Figure 2 (see also Table 1). Two endothermic transitions are observed at 130 and 173 °C, the second one corresponding to the melting point as identified by microscopy. No loss of weight is detected for these transitions. An endotherm corresponding to the isotropic transition is observed at 349 °C, followed by decomposition of the sample. The onset of the decomposition takes place at 373 °C.

Observations by polarized light microscopy revealed the presence of a fluid nematic mesophase at 178 °C.

**Table 1. Thermogravimetric and DTA Data of the Original Poly(azomethine) and the As-Spun Fiber Extruded at 190 °C**

| | temperature (°C) | | |
|---|---|---|---|
| | DTA | TGA | DTGA |
| powder poly(azomethine) | 130 | *a* | *a* |
| | 173 | *a* | *a* |
| | 349 | 373 | 385 |
| fiber as spun at 190 °C | 74[b] | *a* | *a* |
| | 179 | *a* | *a* |
| | 350 | 372 | 383 |

[a] No associated loss of weight. [b] Exothermal transition.

As the temperature increased above the melting point, a gradual, but remarkable, increase in the viscosity of the molten polymer was observed above 200 °C. It is well-known that poly(azomethines) may undergo further polymerization in the molten state, and melt viscosity is strongly dependent on the molecular weight. The increase in the viscosity observed by microscopy might be related to an increase of the degree of polymerization. This would be an important factor to be taken into consideration when melt-spinning was carried out. The poly(azomethine) should be extruded in the nematic phase to achieve good orientation along the fiber axis, but at temperatures low enough (i.e., below 200 °C) to avoid a large increase in the viscosity of the melt.

Accordingly, the thermal behavior of the poly(azomethine) was studied by DSC (Table 2). The powdery polymer was subjected to thermal annealing at 190 °C over different periods of time. To determine the glass transition temperature, a sample of the polymer was heated in a sealed DSC pan at 190 °C for 5 min and then quenched at liquid nitrogen temperature. The DSC curve obtained upon heating the quenched sample was typical for a semicrystalline polymer upon heating from low temperatures: the glass transition temperature ($T_g$) was observed at 54 °C followed by an exotherm associated with a cold crystallization process at 79 °C (Figure 3). The endotherm corresponding to the nematic transition ($T_m$) was observed at 178 °C.

Furthermore, different samples of the untreated polymer were heated at 10 °C/min to 190 °C and held at this temperature for different periods of time (5, 10, 30, or 60 min). The samples were cooled down to 0 °C at the same rate, kept at this temperature for 15 min, and reheated. Data for the second heating scans are given in Table 2. The same tendency is observed upon either cooling and heating. In general, values of $T_g$ increase and those of $T_m$ decrease slightly with annealing, and cold crystallization is not observed. However, when annealing is prolonged to 1 h, the DSC curve proved to be more complicated. The glass transition cannot be detected and a broad peak is observed from 48 to 98 °C in the second heating scan. In addition, the melting peak is less defined and presents a shoulder. This behavior can be assigned to a remarkable increase in the molecular weight upon such a prolonged thermal treatment. Endotherms corresponding to the isotropic transition are measured at 341−345 °C for all of the samples and are followed by decomposition.

**Preparation of Fibers.** For this work, fibers of the poly(azomethine) with high anisotropy were obtained by using the melt-spinning technique. The polymer melt was extruded in the liquid crystalline state, and spontaneous molecular alignment of the polymeric chains gave rise to final structures having a high degree of molecular orientation in the direction of flow, espe-

**Table 2. DSC Data of the Original Poly(azomethine) and Fibers**

| | glass transition | cold crystallization | | melting transition | | | | isotropic transition | |
|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $T$ (°C) | $\Delta H$ (kJ/mru)[c] | $T_{m1}$ (°C) | $\Delta H$ (kJ/mru) | $T_m$ (°C) | $\Delta H$ (kJ/mru) | $T_i$ (°C) | $\Delta H$ (kJ/mru) |
| powder poly(azomethine)[a] | | | | | | | | | |
| 190 °C, 5 min (quenched in liquid nitrogen) | 54 | 79 | −6.32 | | | 178 | 13.70 | *d* | |
| 190 °C, 5 min | 55 | | | | | 176 | 14.10 | 341 | 4.61 |
| 190 °C, 10 min | 59 | | | | | 173 | 11.25 | 343 | 5.65 |
| 190 °C, 30 min | 59 | | | | | 170 | 9.51 | 345 | 6.02 |
| 190 °C, 60 min | | | | | | 179[e] | 14.08 | *d* | |
| fibers[b] | | | | | | | | | |
| as spun | 49 | 74 | −6.33 | | | 179 | 6.65 | *f* | |
| annealed at 100 °C | | | | | | | | | |
| 90 min | *g* | *g* | *g* | 114 | 0.46 | 180 | 11.81 | 338 | 9.23 |
| 4 h | *g* | *g* | *g* | 115 | 0.53 | 180 | 10.47 | 338 | 10.15 |
| 12 h | *g* | *g* | *g* | 119 | 0.63 | 180 | 10.22 | 337 | 11.25 |
| 12 h under tension | *g* | *g* | *g* | 117 | 0.48 | 180 | 11.52 | 337 | 8.70 |

[a] Data from a second heating scan after annealing of the sample at the denoted conditions. [b] Data from a first heating scan. [c] kJ/mru: kilojoules per mole of repeating unit. [d] Decomposition. [e] Melting peak gives a shoulder. [f] Isotropization temperature above 320 °C . [g] Not measurable.

**Table 3. Observed and Calculated Spacings (nm) of the Diffraction Diagram from the Fiber Annealed for 12 h at 100 °C under Tension**

| layer line ($l$) | $d_{obsd}$[a] | $d_{calcd}$[b] | $hk$ |
|---|---|---|---|
| 0 | 0.533 | 0.536 | 10 |
| | 0.456 | 0.451 | 01 |
| | 0.375 | 0.371 | 11 |
| | 0.320 | 0.324 | 11 |
| | 0.266 | 0.268 | 20 |
| | 0.230 | 0.225 | 02 |
| 1 | 2.560 | 2.588 | 00 |
| | 0.577 | 0.582 | 10 |
| | 0.477 | 0.482 | 10 |
| | 0.423 | 0.430 | 01 |
| | 0.388 | 0.395 | 11 |
| | 0.328 | 0.327 | 11 |
| 2 | 1.280 | 1.294 | 00 |
| | 0.602 | 0.607 | 10 |
| | 0.396 | 0.402 | 01 |
| 3 | 0.367 | 0.371 | 01 |
| 4 | 0.64 | 0.647 | 00 |
| 5 | 0.514 | 0.517 | 00 |
| 6 | 0.42 | 0.431 | 00 |
| 9 | 0.289 | 0.286 | 00 |
| | 0.335 | 0.325 | 10 |
| 13 | 0.225 | 0.224 | 10 |
| 14 | 0.207 | 0.207 | 10 |

[a] Only highly intense reflections are listed. [b] Calculated and indexed on the basis of a triclinic crystal lattice with parameters $a_o = 0.630$, $b_o = 0.476$, $c_o = 3.067$, $\alpha = 73°$, $\beta = 59°$, and $\gamma = 74.7°$.

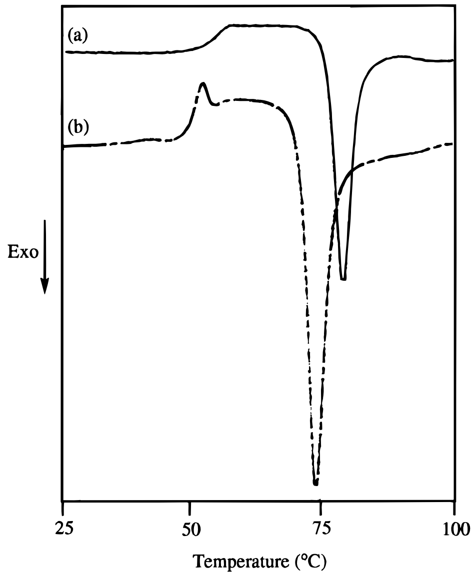

**Figure 3.** DSC curve for the original powder heated at 190 °C and quickly cooled down in liquid nitrogen (a) and the as-spun fiber extruded at 190 °C (b).

cially when conical exit dies are used in the capillary viscosimeter.[10]

We have already mentioned that microscopical observations reveal a nematic mesophase between 178 and 340 °C, accompained by an abrupt increase in the viscosity of the nematic melt as the temperature increases above the melting temperature. As spinning would be difficult if the viscosity was too high, the processing temperature was controlled to be slightly above the melting point. Fibers were first extruded at 180 °C, and the yellow filaments collected had a creased appearance. Hence, fibers were extruded at slightly higher temperatures. At 185 °C, smooth orange filaments were obtained, and similar filaments were also formed at 190 °C.

If poly(azomethines) are indeed susceptible to further polymerization in the molten state, a gain in molecular weight would be likely to occur inside the capillary viscosimeter where the poly(azomethine) is in the nematic state. This was confirmed by inherent viscosity measurements and $^1$H NMR studies. The inherent viscosity of the original polymer was 0.41, and the value rises to 1.22 and 1.33 for the as-spun fibers obtained at 185 and 190 °C, respectively. $^1$H NMR spectra were recorded for the polymer obtained and the as-spun fiber extruded at 190 °C. The possibility of assuming that the aldehyde is the main end group in the polymeric chains has been described.[15] This is based on the fact that the IR spectrum does not show a signal corresponding to $NH_2$ end groups. However, $^1$H NMR spectra show a significantly large signal at 9.53 ppm corresponding to aldehyde end groups. The ratio between the integration values of the peaks of the terminal aldehyde group ($ArCH{=}O$, 9.53 ppm) and the imine group ($ArCH{=}NAr$, 8.76 ppm) might give an idea of the relative molecular weights. Hence, the ratio of integration values for $ArCH{=}NAr/ArCH{=}O$ rises from 6 for the original polymer to 13 for the as-spun fiber. It is interesting to note that, as there were no new peaks in the $^1$H NMR spectrum of the fiber, thermal cross-linking is unlikely to occur during the extrusion process.

**Thermal Annealing of the Fibers.** Fibers cut from the monofilament extruded at 190 °C were annealed

**Table 4. Mechanical Properties and Inherent Viscosity Numbers of the Melt-Spun Fibers**

| fibers | elastic modulus (GPa) | tensile strength (MPa) | elongation at break (%) | $L/L_o$[a] | inherent viscosity (g/dL) |
|---|---|---|---|---|---|
| as spun | | | | | |
| 185 °C | 6.1 | 214 | 3.7 | | 1.22 |
| 190 °C | 8.9 | 252 | 3.3 | | 1.31 |
| annealed at 100 °C | | | | | |
| 90 min | 11.0 | 283 | 2.6 | 1 | 1.30 |
| 4 h | 12.2 | 261 | 2.4 | 1 | >1.31[b] |
| 12 h | 9.8 | 268 | 2.9 | 1 | >1.58[c] |
| 12 h under tension | 18.4 | 388 | 2.2 | 1.32 | >1.65[c] |

[a] $L_o$, length of the fiber before annealing; $L$, length of the fiber after annealing. [b] About 6% of the sample remains insoluble. [c] About 24% of the sample remains insoluble.

under different conditions. Thermal treatment was carried out at 100 °C, above the glass transition temperature and the cold crystallization temperature and below the melting point. This temperature was chosen for a particular reason. Prolonged heat treatments at temperatures approaching the melting point give higher molecular weights. This is one of the main factors in attaining fibers with good tensile properties.[21] However, at these temperatures, softening and deformation of the fiber are possible, which result in a loss of orientation.[14] At temperatures above the glass transition but below the melting temperature, the gain in molecular weight will probably be less important than in the molten state. However, at these temperatures the polymeric chains have sufficient mobility to acquire higher degrees of molecular orientation and crystallinity. As a consequence, an improvement in the properties of the fibers will also be expected. To determine the influence of the thermal treatment on the final properties, fibers were heated in a relaxed state during different time periods (90 min or 4 or 12 h). As-spun fibers were also heated at 100 °C under tension, as it is well documented that crystallinity can be enhanced when fibers are subjected to cold stretching.[22]

It might be deduced from the inherent viscosity values of the fibers that a gain in molecular weight is achieved when thermal treatment takes place (see Table 4). The increase in the molecular weight is only remarkable when annealing is continued up to 12 h. At the same time, the solubility in methanesulfonic acid of the samples annealed for such a long time becomes lower, and about 24% of the sample, when a concentration of 0.5 g/dL is required, remains insoluble. Length and diameter of the fibers were almost unaltered when fibers were annealed in a relaxed state. However, as would be expected, when fibers were heat treated under mechanical stress, the length of the fiber was around 32% longer than the as-spun fibers, which is in contrast to what has been observed previously for similar structures.[14] Diameters were reduced by around 15% under these conditions. When annealing is prolonged, some weight loss in the fibers is observed. It is difficult to determine the origin of this minor loss, however, when polymerization takes place during thermal annealing at 100 °C, water will be evaporated.

**Thermal Studies of the Fibers.** As-spun fibers show good thermal stability, as does the original polymer (Table 1). DTA-TGA curves reproduced in Figure 2 show an exothermal transition at 74 °C corresponding to a cold crystallization and an exothermal transition at 179 °C due to melting into the nematic state as determined by microscopy. No loss of weight is associated with these transitions. The transition to the isotropic state occurs at 350 °C, followed by decomposition of the sample. The onset of the loss of weight takes place at 372 °C.

Application of DSC to the study of fibers is useful to determine physical transitions such as the glass transition, melting, and crystallization.[23] Samples were prepared by cutting the fiber into short lengths. Whereas the data for the original powdery poly(azomethine) correspond to the second heating cycle, the data reported in Table 2 for the fibers correspond to the first heating scans from −25 to 200 °C at 10 °C/min. The reason for giving data from a first scan is that the fibers have a thermal history related to the processing conditions that would otherwise be hidden.

The as-spun fiber shows a DSC curve that is closely related to that obtained for the original poly(azomethine) quenched in liquid nitrogen. DSC traces of both are compared in Figure 3. The glass transition appears at slightly lower temperatures in the fiber sample due to the fact that the experimental conditions and thermal history of the polymer significantly affect $T_g$. An endotherm overlapped with the $T_g$ is observed in the DSC of the fiber, but not in the DSC of the original quenched polymer. The effect known as *recovery structure* has been observed for samples that have been heated to their equilibrium melt, quickly cooled down below $T_g$, and isothermally annealed for different time periods.[24] In our case, the presence of these effects is due to the particular processing conditions. The polymer was melted inside the spinneret, and the extruded filament suddenly cooled down at the exit die and was stored at room temperature. The exotherm due to cold crystallization during heating was also observed.

DSC data measured from the first heating curves of the annealed fibers are given in Table 2. All of the thermally treated fibers show similar DSC scans on consecutive heating and cooling cycles, and there are several points worth mentioning. To illustrate the thermal behavior of the annealed fibers, DSC traces of the fiber annealed at 100 °C in the relaxed state for 12 h are reproduced in Figure 4.

Neither the $T_g$ nor the cold crystallization exotherm was detected for these thermally annealed fibers. The glass transition and the corresponding cold crystallization could only be discerned for the fiber annealed for 12 h, but enthalpies could not be measured. In polymers, chains tend to adopt the minimum energy conformation and they tend to pack so that maximum interaction is possible.[24] Above the glass transition, the polymer chains have enough mobility and it is possible for a process such as crystallization to occur. The as-spun fiber was only partially crystalline, as determined by the cold crystallization exotherm, which gives an idea of the amorphous fraction. When oriented fibers are annealed, increases in the degree of crystallinity and perfection of the crystals are expected.[5] When fibers are annealed under the same thermal conditions, but subjected to elongation forces, the increase in crystallinity during the heat treatment should be larger. In

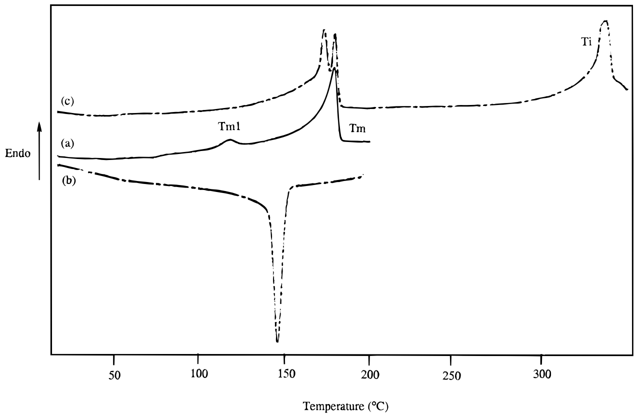

**Figure 4.** DSC curves for the fiber annealed at 100 °C in the relaxed state for 12 h: (a) first heating scan; (b) first cooling scan; and (c) second heating scan.

our case, this is confirmed by the substantial decrease in the enthalpy value of the exotherm corresponding to the cold crystallization process and by the increase in the enthalpy corresponding to the melting process when values of the as-spun fibers and the fibers annealed at 100 °C are compared. Also, as the sample becomes highly crystalline and the amorphous content decreases, the magnitudes of the phenomena associated with the glass transition decrease and become more difficult to detect.[25]

Upon annealing the fibers, a small endothermal peak, indicated as $T_{m1}$, was observed at 114−119 °C before the melting point. This peak was not detected for the as-spun fibers (see Table 2). The transition does not appear upon subsequent heating scans. Endotherms at temperatures either lower or higher than the main melting temperature have been described in thermal studies of fibers by several authors.[26] The peaks have been related to the melting of small crystallites formed during annealing in the amorphous region of the fiber microstructure. In this case, $T_{m1}$ increases slightly with annealing time; however, the melting temperature ($T_m$) remains constant. The area of $T_{m1}$ increases upon annealing (see Table 2). When annealing is carried out under tension, both $T_{m1}$ and its area decrease. As is mentioned later, this is certainly related to the development of crystallinity.

All of the fibers, either as-spun or annealed, were the subject of subsequent cooling and reheating cycles (up to 350 °C). In all cases, double melting behavior was observed: two peaks appeared at temperatures of about 174 and 180 °C. Multiple melting behavior has been previously detected, mainly in liquid crystal polyesters.[27] The phenomenon has been explained as due to a recrystallization of the polymeric chains. The first endotherm corresponds to the melting of the polymer, which immediately recrystallizes to a higher temperature solid form.[28] Peaks corresponding to the isotropic liquid transition were at about 337 °C and were followed by decomposition.

**X-ray Analysis of the Fibers.** The effects of the thermal treatment on the orientation and crystallinity of the extruded fibers may be followed by X-ray diffraction, as illustrated in Figure 5. An oriented texture consisting of molecules aligned along the spinning direction, but not showing any sign of crystallization, is present in the as-spun fiber. This is largely expected for a fiber prepared by extrusion of a nematic phase with a rather slow relaxation time. A considerable degree of crystallization, which gradually increases with the time of the thermal treatment, is promoted by annealing. Furthermore, a highly crystalline phase is achieved after 12 h of thermal treatment under stress at the same temperature. A comparative inspection of the diffraction patterns, including both medium and wide angle regions, reveals that side-by-side rearrangement of molecules should be the process essentially occurring in the crystallization taking place during annealing.

The whole diffraction diagram obtained from the fiber annealed under tension for 12 h is reproduced in Figure 6. Whereas only discrete reflections are found on the equator ($l = 0$), some sharp streaks are observed on the other layer lines, indicating that a certain disorder of chain rotations and translations is still present in the sample. In this context, it should be noted that a microstructure without regular orientation should be expected for this poly(azomethine) due to the unsymmetrical nature of the 2-methyl-1,4-phenylenediamine used as the monomer for the synthesis. Nevertheless, the diagram contains more than 35 reflections, which may be satisfactorily indexed on the basis of a primitive triclinic lattice with parameters $a_o = 0.630$ nm, $b_o = 0.476$ nm, $c_o = 3.067$ nm, $\alpha = 73°$, $\beta = 59°$, and $\gamma = 75.7°$. The density calculated for this structure is 1.11 g/mL, which is in good agreement with the experimental value of 1.13 g/mL obtained by the flotation method in aqueous KBr solution. Observed and calculated spacings for the higher intensity reflections appearing in the diagram are compared in Table 3.

The geometry of the crystal lattice determined for the poly(azomethine) corresponds to a structure composed of molecules in a fully extended conformation aligned along the *c* axis of the crystal. This is consistent with the planarity predicted for the rigid aromatic core and implies that the poly(methylene) segment must be crystallized in an *all-trans* conformation. Since the chains are packed together with a determined axial stagger, no separation of the aliphatic and aromatic moieties in a bilayer structure is expected to occur. On the other hand, since the polymer chain is adirectional, no upside-down arrangement should be required to satisfy the presumed folding of the molecules in the crystal. Therefore, a primitive lattice consistent with our diffraction data seems to be sufficient at this stage to represent the crystal structure of the poly(azomethine).

**Mechanical Properties of the Fibers.** Elastic modulus, tensile strength, and elongation measured for the as-spun and thermally annealed fibers along the longitudinal fiber axis are reported in Table 4. Mechanical properties are strongly dependent on factors such as chemical structure, molecular weight, crystallinity, and molecular orientation. By comparing the mechanical properties of the fibers spun at 185 and 190 °C, we observe that an increase of 5 °C in the spinning temperature gives rise to an improvement in the tensile properties and a slight decrease in the value of the elongation, probably due to a slightly higher molecular weight.

It is well established that, upon heat treatment, the tensile properties of the fibers are increased.[4] Tensile strength basically increases in the first stages of the thermal annealing. Hence, after 90 min an improvement in the tensile strength from 252 to 283 MPa is observed, which is about 12%. When the thermal treatment is extended, the tensile strength is affected only slightly and the differences in the values displayed in Table 4 might be due only to experimental factors or

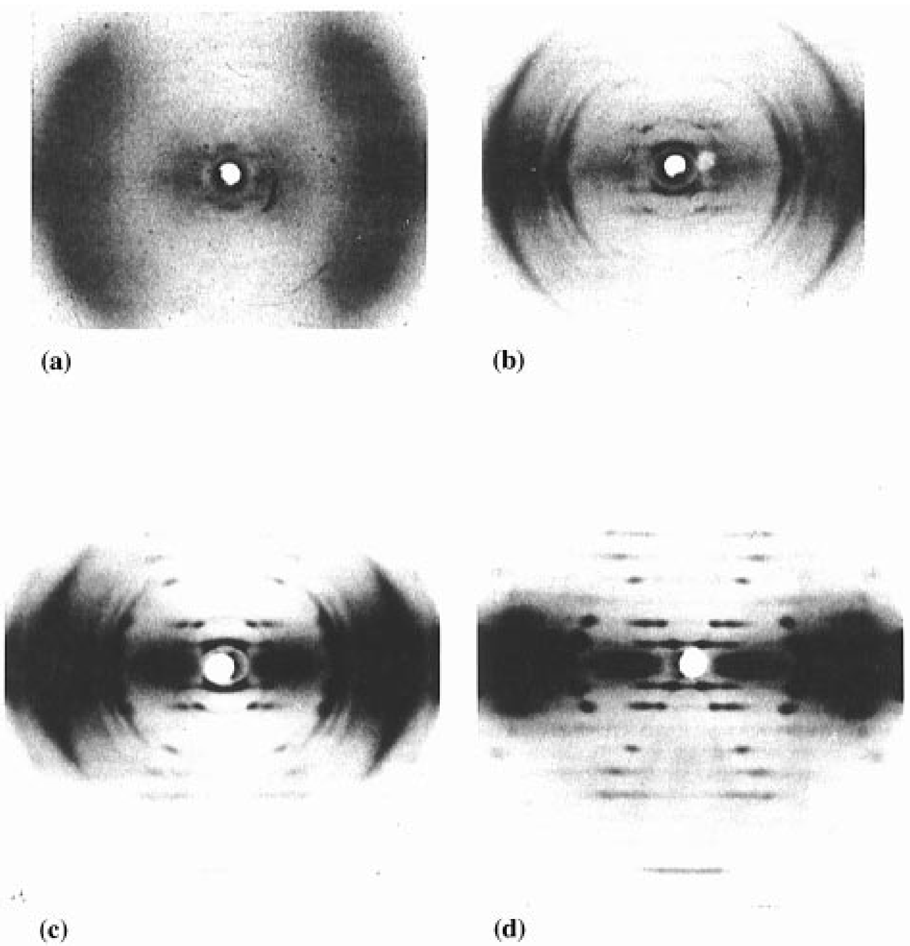
(a) (b) (c) (d)

**Figure 5.** X-ray diffraction patterns of the as-spun fiber (a), the fiber annealed in a relaxed state at 100 °C for 90 min (b), the fiber annealed in a relaxed state at 100 °C for 12 h (c), and the fiber annealed under tension at 100 °C for 12 h (d).

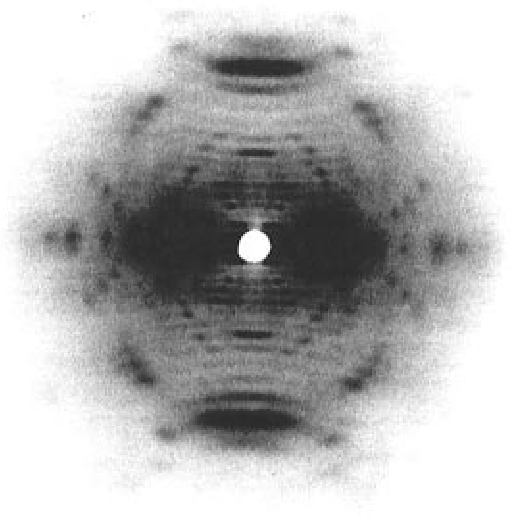

**Figure 6.** Whole diffraction diagram obtained from the fiber annealed at 100 °C under tension for 12 h.

uniformity in the fiber structure. The maximum tensile strength values are achieved when fibers are heated under mechanical strain. In these cases, the value of this tensile property increases up to 388 MPa, which is 54% higher than that of the as-spun fiber at 190 °C.

The elastic modulus follows a similar trend. When the fibers are annealed in a relaxed state, the elastic modulus shows an increase in the first stages of the thermal treatment. An improvement of 25% in the elastic modulus is observed after 90 min of thermal annealing. When annealing is performed for longer than 90 min, the value of the elastic modulus appears to vary unevenly. Therefore, the improvement in the property is less remarkable after the first stages of annealing. The highest value of the elastic modulus is reached when fibers are subjected to cold stretching. Fibers then show about a 105% increase in the value of the elastic modulus.

Elongation at break is related to both the tensile strength and the initial modulus and follows an opposite trend compared to the tensile properties. The values of elongation decreased when fibers were thermally annealed. The values varied smoothly as the time of thermal treatment was extended, even when tension was applied.

We have concluded from DSC and X-ray studies that heat-treated fibers are considerably more crystalline than as-spun fibers. Due to the mesogenic nature of the poly(azomethine) and the processing conditions, the as-spun fibers have a high degree of molecular orientation along the fiber axis, which increases after annealing, especially when the thermal treatment has been carried out under external stress. Furthermore, from the inherent viscosity values, we have concluded that an increase in the molecular weight is noticeable when annealing is extended to 12 h. Molecular orientation, crystallinity, and molecular weight certainly are all factors that contribute to the improvement in the tensile properties of the annealed fibers compared to the as-spun fibers. During the first stages of thermal annealing, when the increase in the molecular weight is not

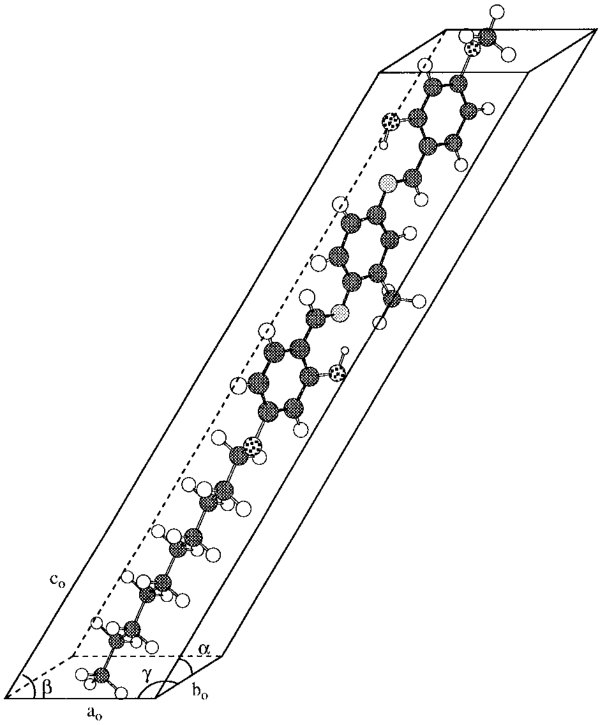

**Figure 7.** Representation of the primitive triclinic lattice and the repeating unit of the target poly(azomethine). Parameter values of the primitive triclinic lattice: $a_o = 0.630$ nm, $b_o = 0.476$ nm, $c_o = 3.067$ nm, $\alpha = 73°$, $\beta = 59°$, and $\gamma = 75.7°$.

particularly remarkable, the improvement in the mechanical properties is mainly related to rearrangements of the molecules, giving rise to the development of crystallinity and molecular orientation. As the heat treatment time is prolonged, the mechanical properties largely are not affected, even if the molecular weight increases. However, cold stretching of the fibers above $T_g$ promotes a remarkable improvement in the tensile properties. This certainly correlates to the highly crystalline phase obtained after 12 h at 100 °C under stress, bearing in mind that the increase in the molecular weight will also play a role.

The mechanical properties of melt-spun fibers of poly(azomethines) with similar molecular structures have been reported.[14] Fibers were melt spun at 205 °C from the polymer obtained by the reaction of 1,10-bis(4-amino-3-methylphenoxy)decane and terephthalaldehyde (melting temperature was 190 °C). Values of the tensile strength and elongation at break reported for the as-spun fibers (136 MPa and 2.1%, respectively) are lower than those reported here, but they have a higher elastic modulus (9.41 GPa). The highest values for the tensile properties were achieved by the author when annealing of the fibers in a relaxed state was carried out below the melting point (4 h at 170 °C; 13.89 GPa, 291 MPa, and 2.5% for the elastic modulus, tensile strength, and elongation at break, respectively). When annealing was performed above the melting point, adverse effects were observed, especially for the value of the elastic modulus, and these were attributed to a loss in crystallinity and orientation of the fiber at high temperatures. However, an increase in the elongation at break when fibers were subjected to the aforementioned thermal treatments was detected. In contrast to what we have observed, the improvement in the properties is not as significant when the thermal treatment is performed under tension at 150 °C (15.04 GPa, 165 MPa, and 1.7% for the elastic modulus, tensile strength, and elongation at break, respectively). Furthermore, the author reports a reduction of about 0.2% in the length of the annealed fiber. To conclude, we have shown that the tensile properties of the fibers of our particular poly(azomethine) can be markedly improved by cold stretching due to the development of molecular orientation and crystallinity. Comparison between these data should take into account the fact that 5% excess of diamine is added during polymerization to control the molecular weight and to prevent chain growth and viscosity increases during polymerization. In the present work, the increase in the molecular weight during spinning and annealing has not been so high as to require the addition of a capping agent.

Reported semiflexible polyesters show, in general, lower values of the tensile properties than poly(azomethines). For instance, a polyester obtained by the condensation of hydroquinone, 4-hydroxybenzoic acid, and suberic acid gave values of the elastic modulus between 3 and 3.5 GPa, a tensile strength of 60−110 MPa, and elongation at break of 1.5−3%.[9]

As expected, the properties of the fibers reported here are lower than those of wholly aromatic liquid crystal poly(azomethines).[12,13] Values reported for the as-spun fibers of the polymer obtained by the reaction of methyl-1,4-phenyldiamine and terephthalaldehyde are 99 GPa, 798 MPa, and 1.67% for the elastic modulus, tensile strength, and elongation at break, respectively. The values can be improved after thermal annealing. For polyesters, the differences in the values between all rigid and semiflexible polymers have been attributed to the lower molecular orientation of the fibers during melt spinning and differences in the degree of crystallization of semiflexible polyesters when compared to wholly rigid analogues.[9,10]

## Concluding Remarks

As expected, well-oriented fibers can be melt-extruded from semiflexible poly(azomethines) having hydroxyl groups in the main chain. Upon annealing of the as-spun fibers in an unstressed state below $T_m$ and above $T_g$, relaxation of the molecular orientation is not observed, but a gradually higher degree of crystallinity is promoted, as can be followed by DSC and X-ray. Fibers do not shrink after annealing, and the molecular weight increases only when thermal treatment is extended for 12 h. Mechanical properties improve on the first stage of annealing, and parameter values seem to reach a plateau after this first increase. This improvement might be associated with the development of crystallinity and orientation under these conditions, rather than to the growth of the molecular chain, which probably would have been more important if annealing were carried out at temperatures closer to $T_m$.

Annealing under an external force along the fiber axis for 12 h below $T_m$, known as cold stretching, results in the development of a highly crystalline phase where some degree of disorder is still present due to the flexibility of the alkyl chains. Nevertheless, the characteristics of the X-ray diffraction patterns for the sample allow the determination of the geometry of the crystal lattice. The molecules, in a fully extended *all-trans* conformation, are arranged side-by-side along the *c* axis of a primitive triclinic lattice. Cold stretching at 100 °C carried out for 12 h is accompanied by an elongation of the fiber length and an increase in the molecular weight. All of these factors give rise to substantial improvements in the mechanical properties.

It is interesting to note the possibility of improving mechanical properties upon annealing below $T_m$. Therefore, the weakening of the tensile properties when annealing is performed at high temperatures, attributed to relaxation of the structure by fiber softening, can be avoided.

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