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Influence of Hydroxy Functionalization and Metal Cross-Linking on Fiber Properties of Liquid-Crystalline Polyazomethines

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ABSTRACT: A number of semiflexible liquid-crystalline polyazomethines have been synthesized by condensation of two dialdehyde monomers (1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane or 1,10-bis-[(4-formylphenyl)oxy]decane) with two diamines (2-methyl-1,4-phenylenediamine or 3,3′-dimethoxybenzidine). Polyazomethines having a hydroxyl group at the ortho position of the imine bond have higher degrees of polymerization and a remarkable tendency to show an increase in their molecular weight upon postpolymerization thermal treatments. These hydroxy-functionalized polymers have been coordinated with copper(II) ions to give rise to metallomesogenic cross-linked polymers. Fiber spinning of both organic and copper(II)-complexed polymers has been carried out, and the structure, orientation, and morphology of the fibers have been studied by X-ray diffraction, electron paramagnetic resonance, and scanning electron microscopy. The mechanical properties have also been evaluated. Hydroxy functionalization and copper(II) complexation are the key strategies to obtain highly oriented fibers with good mechanical properties and strong intermolecular cohesive forces. A highly oriented crystalline phase with improved mechanical properties could be developed by thermal annealing of “as-spun fibers”.

Introduction

Main-chain thermotropic liquid-crystal polymers (LCPs) have received considerable academic and industrial attention because of the excellent thermal and mechanical properties of products obtained from their anisotropic melts.[1−4] Melt spinning of a thermotropic polymeric mesophase—the nematic is the most suitable for this purpose—is a common technique where the spontaneous alignment of the molecules is turned into high-stiffness and high-strength fibers with the polymeric chains uniaxially oriented. In these nematic fibers the polymer chains are well oriented in the flow direction, even in the as-spun state, producing self-reinforced fibers with excellent mechanical properties along the longitudinal direction.[5]

Most research efforts in this area concern the synthesis and characterization of wholly aromatic polyesters in which the backbone stiffness is responsible for the good mechanical properties.[6−8] However, this rigidity is also responsible for the high melting points of the polymers, a property that might limit the suitability of the process. The introduction of structural irregularities such as kinks, bends, or lateral substituents within the polymeric backbone is a very effective strategy to reduce melting temperatures. A different alternative is the design of semiflexible polymers where the presence of flexible segments lowers the melting temperatures.[9−11] However, this approach also gives an adverse effect as regards the mechanical behavior.

Polyazomethines, also known as polyimines or Schiff base polymers, exhibit good thermal stability and environmental resistance, and they are promising materials in optoelectronic and photonic applications.[12] Many of these polymers form mesophases on heating, but the high melting points and low solubilities make both their characterization and processing difficult. Despite these disadvantages, fibers of thermotropic polyazomethines have been reported[13] with generally higher tenacities than thermotropic polyesters.[14,15] Most of these examples are either academic or industrial contributions and concern wholly aromatic polyazomethines derived from terephthaldehyde.[16] A remarkable characteristic of polyazomethines is their tendency to increase in molecular weight and crystallinity upon thermal annealing, a process that usually brings about an improvement in the mechanical properties of derived fibers.[17]

In recent papers we have described the synthesis and properties of a series of polyazomethines, derived from 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane, with the general formula shown in Scheme 1 where X = OH.[18,19] Different diamines were tested in order to obtain polymers with low transition temperatures and high stabilities.

The principal feature of these polyazomethines is the presence of the hydroxyl group in the ortho position of the imine bond, which introduces an extra functionality on the rigid core of the polymers. In particular, salicylaldimines can be coordinated with metal ions to give metal complexes that have been reported as excellent metal-containing liquid crystals, also known as metallomesogens.[20] For this reason, hydroxy-functionalized polyazomethines with the aforementioned structure can be easily complexed to metal ions, for instance Cu(II), leading to partially cross-linked materials in which the cross-linking density can be tuned by controlling the percentage of metal ions used in the coordination reaction.[21] These metallomesogenic cross-linking sites, with a square-planar geometry, can be oriented in the nematic state when the polymers are processed into

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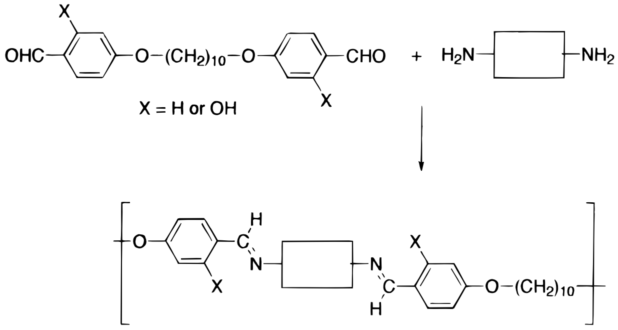
Scheme 1. Schematic Representation of the Synthetic Strategy Applied To Obtain Polyazomethines



fibers, enhancing their mechanical properties and reinforcing the cohesive lateral interactions.[22]

As a continuation of these studies, we now report the preparation, properties, and processing of several polymers in order to evaluate and compare the overall influence of several factors on the mechanical properties, structure, and morphology of fibers processed from the mesomorphic melt. The chemical structure of these polymers is shown in Figure 1. The different structural modifications have been introduced in order to gain information about the effect of the following: (i) the presence or absence of hydroxyl groups in the ortho position of the imine bond, (ii) the structure of the diamine used in the synthesis of the polymers, and (iii) metal coordination with low percentages of Cu(II).

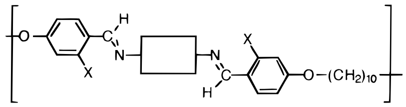
Fibers prepared from these polymers have been subjected to different thermal treatments in order to gain an insight into thermal annealing on the aforementioned factors. We pay particular attention to the importance of hydroxy functionalization on the design of versatile and easily processed polyazomethines and on metallomesogenic cross-linking as a way of tuning the mechanical properties of the fibers.

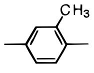
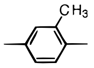
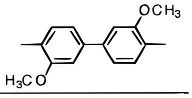
To obtain fibers from small amounts of polymer, ca. 500−600 mg, we designed a small-scale melt-spinning setup in which commercial dies used for processing engineering polymers were adapted. It is known that the fiber properties are influenced not only by the physical properties of the polymer (e.g., molecular weight or molecular weight distribution)[23] but also by the spinning conditions;[24] however, the results were similar to those previously obtained from fibers extruded on commercial spinning equipment, fitted with conical exit dies designed for LCPs.[25]

Experimental Section

Materials. The dialdehydes used in the synthesis of the polymers, 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane and 1,10-bis[(4-formylphenyl)oxy]decane, were obtained by a previously reported procedure.[26] 2-Methyl-1,4-phenylenediamine was obtained from the commercially available 2-methyl-1,4-phenylenediammonium sulfate (Aldrich) and purified prior to use by vacuum distillation. 3,3′-Dimethoxybenzidine (Aldrich) was purified by successive recrystallizations from ethyl acetate/hexane. *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.

Polymers. Polyazomethines were synthesized by solution polycondensation of the appropriate diamine and dialdehyde according to a previously reported method.[25] 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 or 3,3′-dimethoxybenzidine (25 mmol). When the mixture became transparent, the dialdehyde 1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane or 1,10-bis[(4-formylphenyl)oxy]decane (25 mmol) was added. The solution was kept away from light and stirred at room temperature for 16 h. Water was added to the resulting suspension, and the solid was isolated by filtration and thoroughly washed with water and methanol. The product was extracted using a Soxhlet apparatus with acetone for 24 h and finally dried under vacuum over P_2O_5 at 80 °C to yield the corresponding polyazomethine.



Nomenclature	% Cu[a]	X	
pF(CH_3)-**OH**, pF(CH_3)-**H**	--	**OH**, **H** (respectively)	
pF(CH_3)-**2**-Cu, pF(CH_3)-**5**-Cu	**2**, **5** (respectively)	OH	
DMB-**OH**, DMB-**H**	--	**OH**, **H** (respectively)	

[a] Molar ratio of the metal related to the repeating unit

Figure 1. Repeating unit and nomenclature of the synthesized polyazomethines.

Metal complexation of the polymers was carried out by addition of a solution of copper(II) acetate to a suspension of the corresponding polyazomethine in 1,4-dioxane. A description of the procedure is given for polymer pF(CH_3)−2-Cu as an example: Polyazomethine pF(CH_3)−OH (250 mg) was suspended with mechanical stirring in freshly distilled 1,4-dioxane (20 mL) at reflux temperature. Copper(II) acetate (2 mg, ca. 2 mol of Cu(II) ions per 100 mol of repeating unit) in hot 1,4-dioxane (10 mL) was added dropwise to the above suspension. The suspension was stirred for 2 h under a nitrogen atmosphere. After cooling the reaction mixture, the solid was filtered off and successively washed with 1,4-dioxane, hot water, and methanol. The product was extracted 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 polymer.

Fiber Spinning and Annealing. Fiber preparation was carried out by loading between 500 and 600 mg of polymer in a small-scale melt-spinning unit specially designed in our laboratory. The setup consists of a special steel (F155 Cr-Mo) block with a central orifice of 5 mm diameter and 90 mm length were the polymer is introduced. The block is heated by a bracket resistor (400 W) and thermally isolated by a Termalite jacket. The exit die was a commercial single-hole spinneret for engineering polymers of 0.45 mm diameter fixed at the lower end of the block. The spinning temperature was selected according to the melting temperature of the polymer as determined by DSC. Pressure was applied by a driven piston using a weight that was varied depending on the viscosity of the extruded polymer. The filament was spun into air at room temperature either by falling from the end coming from the exit die under its own weight or by suspending the minimun weight necessary to avoid windup of the fibers. Fibers of selected polyazomethines were heat treated in an oven for 12 h while applying a longitudinal tension by suspending a weight of 110 g from the free end.

Techniques. Elemental analyses were carried out using a Perkin-Elmer 240C microanalyzer. FTIR spectra were performed on a Perkin-Elmer FTIR 1600 using KBr disks dried under vacuum for 1 h. The copper content was determined by inductively coupled plasma (ICP) atomic emission spectroscopy using a Perkin-Elmer P-40 spectrometer.

Table 1. Characterization Data of the Synthesized Polyazomethines and Copper(II) Complexed Polymers

polymer	% C found (calcd)	% H found (calcd)	% N found (calcd)	% Cu found (calcd)	C=N(st), cm^{-1}	$-$CH=N$-$R δ/ppm
pF(CH_3)$-$OH	74.03 (74.40)	7.18 (7.20)	5.68 (5.60)		1608	8.76
pF(CH_3)$-$H	78.00 (79.48)	7.62 (7.69)	5.90 (5.98)		1602	8.86
DMB$-$OH	72.97 (73.30)	7.35 (6.75)	4.31 (4.50)		1616	*a*
DMB$-$H	76.93 (77.28)	7.51 (7.12)	4.10 (4.74)		1608	8.90
pF(CH_3)$-$2-Cu	74.03 (74.21)	6.60 (6.78)	5.60 (5.58)	0.86 (1.99)[b]	1607	*a*
pF(CH_3)$-$5-Cu	73.80 (73.95)	6.62 (6.75)	5.60 (5.56)	3.59 (4.95)[c]	1601	*a*

[a] Insoluble in trifluoroacetic acid. [b] 44% of Cu initial introduced determined by ICP atomic emission spectroscopy. [c] 72% of Cu initial introduced determined by ICP atomic emission spectroscopy.

^{1}H NMR measurements on polymer solutions were performed with a Varian Unity-300 spectrometer operating at 300 MHz using deuterated trifluoroacetic acid as a solvent. Measurements were made on solutions immediately after preparation in order to avoid degradation.

The inherent viscosities (η_{inh}) of the polyazomethines were measured at a concentration of 0.5 g/dL in methanesulfonic acid at 40 °C using a Cannon-Fenske viscometer. Samples were used immediately after preparation in order to avoid degradation.

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, and temperatures were read at the maximum of the peaks at a scanning rate of 10 °C/min. Glass transition temperatures were measured at the midpoint of the baseline jump.

Thermogravimetric analysis was performed using a TA STD 2960 simultaneous DTA-TGA instrument at a heating rate of 10 °C/min in the range 40$-$600 °C under a nitrogen atmosphere.

Wide-angle X-ray patterns of fibers were obtained using a modified Statton camera (W. H. Warhus, Wilmington, DE) using nickel-filtered Cu$-$Kα radiation of wavelength 0.1542 nm and internally calibrated with molybdenum sulfide.

EPR measurements were performed at room temperature with a Bruker ESP-380 spectrometer working in the X-band. The fibers were aligned by fixing them using Scotch tape and then mounting them on a rotation setup attached to a goniometer as described elsewhere.[27]

The mechanical properties of the fibers were measured at room temperature on an Instron Zwick 1445 machine at a crosshead speed of 10 mm/min using single filaments of about 10 cm length. Values are averages over at least five individual determinations. Fiber diameters were measured by using a laser gauge BETA LG1005/L1800-4FA.

Morphological studies by electron scanning microscopy of the as-spun and annealed fibers were performed using JSM 6400 equipment. Two specimens were studied: fibers fractured on the Instron machine in order to study the tensile fracture surface and fibers prepared by the peel-back method.[28] Samples prepared by this last method were obtained by initially cutting the fiber with a razor blade at an oblique angle halfway into the fiber, followed by a cut either along or parallel to the fiber axis. This second cut, which is below the first, is peeled back with forceps to provide a thin section of material aligned parallel to the fiber axis.

Results and Discussion

Synthesis and Characterization of Polymers. The polymers were prepared in good yields by solution polycondensation using freshly distilled *N*,*N*-dimethylacetamide and anhydrous LiCl to remove the water formed during the reaction. The copper(II) complexes were derived from the polyazomethine pF(CH_3)$-$OH since the high melt viscosity of polymer DMB$-$OH made its metal cross-linking inadvisable. These complexes were synthesized using 1,4-dioxane under reflux. Only low theoretical percentages of copper content (2 or 5%) were introduced because higher percentages would considerably increase the viscosity of the melt, making the processing difficult.

Table 2. Thermal Stability[a] and Thermal Transition Data (DSC)[b] of the Organic Polyazomethines and the Copper(II)-Coordinated Polyazomethines

polymer	TGA (°C)	DTGA (°C)	T_g (°C)	T_m (°C)	T_i (°C)
pF(CH_3)$-$OH	373	385	52	173[c]	349
pF(CH_3)$-$H	417	438	39	150[d]	315
DMB$-$OH	366	378, 430 (sh)	77	206[c]	>320 dec
DMB$-$H	398	415, 464	59	146[d]	>300 dec
pF(CH_3)$-$2-Cu	366	382	57	172[c]	347
pF(CH_3)$-$5-Cu	357	379	56	169[c]	331

[a] TGA: onset of the weight loss in thermogravimetric analysis. DTGA: derivative thermogravimetric analysis. [b] T_g: glass transition temperature. T_m: melting temperature. T_i: isotropization temperature. [c] Annealed at 150 °C for 1 h. [d] Annealed at 120 °C for 1 h.

The materials were characterized by IR, ^{1}H NMR, and microanalysis and the results collected in Table 1 are in accordance with the proposed structures. The IR spectra of pF(CH_3)$-$H and DMB$-$H display bands corresponding to end groups that were not visible in the spectra of related polymers with $-$OH groups. This fact, together with the values of η_{inh} (see Table 3), indicates that in the absence of $-$OH groups lower degrees of polymerization were obtained. This situation does not prevent, a priori, processing of the polymers because even though an optimum degree of polymerization is required for LC polymers to be processed, very high degrees of polymerization can also be inconvenient due to the higher viscosity of the molten polymers.[29]

The thermal stability and phase transitions of the polymers were studied by thermogravimetric analysis under a nitrogen atmosphere, DSC, and optical microscopy. Table 2 summarizes the results. All the polymers showed good thermal stability with decomposition temperatures above 350 °C. The fact that hydroxy-functionalized polyazomethines exhibit lower degradation temperatures is due to the presence of additional oxygen atoms at which thermal degradation may be initiated.[26] The copper(II) complexation slightly decreases the thermal stability in comparison with the parent polymer.

The polarized light microscopy study revealed the presence of a nematic mesophase, identified by its typical schlieren and threaded textures, for all the polymers. The only exception was the polyazomethine DMB$-$OH where the high viscosity of the molten polymer hindered the development of well-defined textures. However, the granular-type texture observed in this case was assigned to a nematic mesophase in accordance with X-ray diffraction of oriented samples (see below). Samples of this polymer synthesized by an alternative method with a lower degree of polymerization showed a transition from the N to the S_C phase after annealing at the mesophase temperature for more

Table 3. Processing and Annealing Conditions of Fibers; Comparison of η_{Inh} of Virgin Polymer, As-Spun Fibers, and Fibers after Annealing

polymer	processing temp (°C)[a]	temp at exit die (°C)[b]	annealing temp (°C)	η_{inh} virgin polymer	as-spun fibers	annealed fibers
pF(CH_3)−OH	225−235	195	100[c]	0.5	1.25	>1.60
pF(CH_3)−H	165	145	100	0.3	0.30	0.65
DMB−OH	245−270	220	140[c]	*d*	*d*	*d*
DMB−H	135	120	100	0.11	0.12	0.30
pF(CH_3)−2-Cu	230−245	200	110[c]	*d*	*d*	*d*

[a] Temperature selected in the control heating. On hydroxy polyazomethines, the processing temperature was increased during processing in order to ensure a continuous fiber extrusion. [b] Initial temperature measured at the exit die when the fiber is obtained. [c] A weight of 110 g was put at the end of the fiber. [d] Insoluble in methanesulfonic acid.

than 1 h.[18] When polymer DMB−OH was annealed at the mesophase temperature, an increase in the melt viscosity was observed under the optical microscope. However, the initial texture prevailed, and the aforementioned transition could not be detected.

The transition temperatures of the polyazomethines (T_g, T_m, and T_i) were determined by DSC. The polymers have moderate melting temperatures and wide mesophase temperature ranges. Transition temperatures of the hydroxy-functionalized polyazomethines are higher than those of polymers without OH groups due to their higher degree of polymerization and stronger intermolecular interactions.[26] Copper(II) complexation does not modify the transition temperatures but greatly increases the viscosity of the nematic molten state.

Fiber Processing. The polymers were processed into anisotropic fibers by melt spinning in the liquid-crystalline state. Several attempts were carried out to select the optimum processing temperature, taking into account the thermal transition detected by DSC. For hydroxy-functionalized polyazomethines, the initial processing temperature was about 20−40 °C above T_m (see Table 3). However, due to the rapid increase in melt viscosity on heating, it was necessary to increase the temperature (approximately 10−15 °C) while processing in order to ensure a continuous fiber extrusion. Despite this, the high melt viscosity of polymer DMB−OH gave rise to irregularities in the final fibers. The processing temperature of polymers without hydroxyl groups (pF(CH_3)−H, DMB−H) was close to T_m (±5 °C) since the low viscosity of these polymers made it impossible to process them at higher temperatures. Fibers extruded from these polymers were extremely fragile, and they broke under manipulation.

Good-quality fibers were easily obtained from the nematic phase from pF(CH_3)−2-Cu, but when the copper content was increased up to 5% in pF(CH_3)−5-Cu, the melt viscosity showed such a marked increase that processing was impossible.

It has been reported that thermal annealing of fibers of polyazomethines gives rise to an increase in molecular weight as a consequence of their reactivity in the solid state and also induces crystallinity, which improves mechanical properties.[15] The latter effect is favored when a longitudinal tension is applied during the treatment. For this reason, fiber samples of all these polymers were heated at temperatures approximately 50−60 °C above the T_g of the virgin polymer under tension except for fibers derived from nonfunctionalized polymers that, due to their extreme fragility, were annealed in a relaxed state.

The η_{inh} values of the as-spun and thermally annealed fibers were determined in order to analyze the influence of processing and thermal annealing on the polymer size. The results are shown in Table 3. Unfortunately, values for DMB−OH, pF(CH_3)−2-Cu, and their fibers could not be determined due to their insolubility in methanesulfonic acid. On the other hand, the values for polyazomethines without −OH groups (pF(CH_3)−H, DMB−H) do not show a significant variation after processing or annealing. In contrast, η_{inh} values are markedly affected by these factors when −OH groups are present, as in pF(CH_3)−OH. The increase in η_{inh} values can be correlated with the increase in the melt viscosity observed during extrusion of the polymer, pointing to a gain in molecular weight due to the fact that the possibility of cross-linking or other side reactions was rejected on the basis of IR and ^{1}H NMR analysis (see for instance Figure 2). Therefore, we can infer that −OH groups have a crucial influence on both polymerization and postpolymerization reactions, with a notable increase in the molecular weight of the polymer.

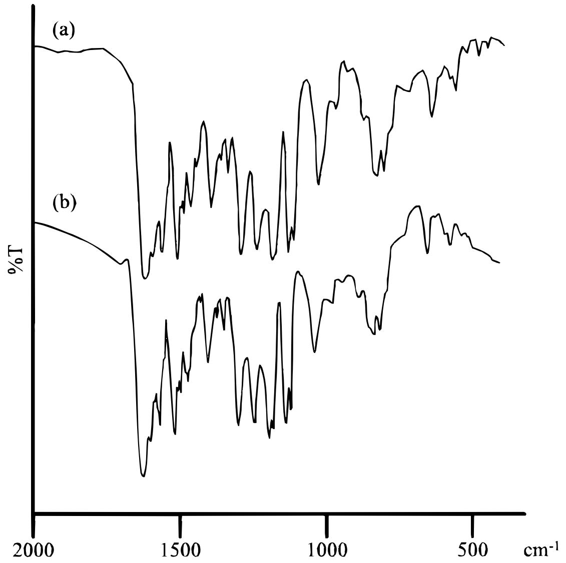


Figure 2. FTIR of films of the polyazomethine DMB−OH before being annealed (a) and after annealing at 275 °C for 1 h in air an atmosphere (b). No significant chemical changes can be observed.

Thermal Properties of the Fibers. The thermal stabilities and transitions of the materials were analyzed by simultaneous DTA−TGA and by DSC, and the results are summarized in Table 4. It can be seen that as-spun and annealed fibers had thermal stabilities similar to those of the parent polymers. The DSC data gathered in Table 4 correspond to the first heating data of as-spun fibers before or after thermal annealing (heat-treated fibers, denoted by the symbol “T”) in order to relate results with the thermal history of the samples.

A different thermal behavior is observed on comparing the DSC traces of fibers derived from hydroxy-function-

Table 4. Thermal Stability[a] and Thermal Transition Data (DSC)[b] of the As-Spun and Annealed Fibers

fibers	TGA (°C)	DTGA (°C)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (kJ/mru)[c]
pF(CH_3)−OH	369	380	55	90	170	4.59
pF(CH_3)−OH-T[d]	369	380	55		166	6.89
pF(CH_3)−H	428	443	39		169, 180	6.56
pF(CH_3)−H-T[e]	417	439			169, 179	6.55
DMB−OH	362	377	84	132	203	4.92
DMB−OH-T[d]	362	375	88		189	9.09
DMB−H	384	421, 455	42	100	148	8.26
DMB−H-T[e]	396	414, 463	42	100	148	9.98
pF(CH_3)−2-Cu	369	380	56	126	162	0.17
pF(CH_3)−2-Cu-T[d]	369	381			156	8.07

[a] TGA: onset of the weight loss in thermogravimetric analysis. DTGA: derivative thermogravimetric analysis. [b] T_g: glass transition temperature. T_c: cold crystallization temperature. T_m: melting transition temperature. [c] ΔH_m given in kilojoules per mole of repeating unit. [d] Fibers annealed under tension ("T" indicate fiber undergone to thermal treatment). [e] Fibers annealed in a relaxed state ("T" indicate fiber undergone to thermal treatment).

alized polyazomethines and those derived from nonfunctionalized polyazomethines. In fact, the processing of pF(CH_3)−OH or DMB−OH from the nematic melt gives rise to fibers where the nematic order has been frozen that exhibit a glass transition at a slightly higher temperature than that of the original polymer. This phenomenon is a consequence of the aforementioned increase in molecular weight. At temperatures above the glass transition they exhibit an exotherm corresponding to the cold crystallization of the amorphous material, which finally melts to give the nematic phase. However, the fiber derived from the nonfunctionalized polyazomethine pF(CH_3)−H is obtained as a semicrystalline material that displays a glass transition but no cold crystallization before finally melting to give the nematic phase. DMB−H exhibits a similar DSC trace to DMB−OH although the thermal treatment, as in the case of pF(CH_3)−H, has a minor influence on the thermal behavior. These results indicate that the non-hydroxy-functionalized polymers processed from the nematic melt give rise to semicrystalline fibers in which the nematic order has not been frozen. Furthermore, the thermal annealing does not afford a noticeable increase in crystallinity.

In the cases of the hydroxy-functionalized polymers and the copper(II) derivative, the thermal annealing above T_g under tension modifies the thermal behavior. First, the glass transition is hardly detected, and no cold crystallization of the amorphous content is achieved. Second, the enthalpy corresponding to the melting of crystalline regions formed upon annealing increases with respect to the as-spun fibers. This effect is remarkable in the copper(II)-complexed polymers. The as-spun fibers of pF(CH_3)−2-Cu exhibit a low melting enthalpy due to their low tendency to crystallize above the T_g (cold crystallization) because of their cross-linked nature. In contrast, the thermal annealing under tension strongly induces crystallization.

The melting temperature T_m slightly decreases in fibers in comparison to untreated samples, especially when they have been subjected to thermal annealing. However, it must be taken into account that fibers show sharper melting peaks than the original polymer, a fact that could affect the value taken for the calculated maximum.

Structural Study of the Fibers. A study regarding the influence of the structure and thermal annealing on the orientation and crystallinity of the fibers was carried out by X-ray diffraction. The comparison of X-ray diffraction patterns revealed significant differences between fibers derived from functionalized and nonfunctionalized polymers.

As illustrated in Figure 3a for the case of polyazomethine pF(CH_3)−H, Debye−Sherrer diagrams consisting of a fair number of sharp intense rings characteristic of an isotropic crystalline material were produced by as-spun fibers made of nonfunctionalized polymers. Only weak changes in crystallization and orientation (Figure 3b) were observed when those fibers were subjected to thermal annealing.

In contrast, the X-ray analysis of as-spun fibers obtained from functionalized polymers reveals the presence of a well-oriented nematic structure with the polymer chains aligned along the spinning direction but without showing the evidence of crystallization that would be expected for fibers prepared by extrusion of a nematic melt with a rather slow relaxation time. Thermal annealing under tension dramatically modifies the X-ray pattern, and this shows that a highly crystalline phase that retains the high orientation is present in the unheated fibers.

Figure 4a shows the X-ray pattern of the as-spun fiber of DMB−OH. This pattern appears to correspond to a well-oriented nematic structure. Thermal annealing induces a large increase in crystallinity (Figure 4b), and the diagram may be indexed, on a preliminary basis, as belonging to a primitive triclinic lattice with parameters $a = 15.40$ Å, $b = 8.65$ Å, $c = 34.20$ Å, $\alpha = 81.1°$, $\beta = 80.5°$, and $\gamma = 117.4°$ containing four monomeric units in the unit cell. The density calculated for this structure is 1.07, which is consistent with the value found experimentally by the flotation method.

On the other hand, X-ray diffraction data obtained from both as-spun and annealed fibers of pF(CH_3)−OH are fully consistent with those previously reported for fibers of the same polymer obtained using commercial extrusion equipment.[25] The diagrams may be satisfactorily indexed on the basis of a primitive triclinic lattice with parameters $a = 6.30$ Å, $b = 4.76$ Å, $c = 30.67$ Å, $\alpha = 73°$, $\beta = 59°$, and $\gamma = 75.7°$ but containing only one repeating unit. The as-spun fiber of the copper-complexed polymer pF(CH_3)−2-Cu also exhibits a pattern typical of a well-oriented nematic structure (Figure 5a), and the thermal annealing induces a crystalline phase (Figure 5b) with reflections coinciding with those appearing on the patterns given by the parent polyazomethine pF(CH_3)−OH.

Electron paramagnetic resonance (EPR) has proved to be a very useful tool in the study of paramagnetic metallomesogenic polymers[30,31] and, in particular, in the microstructural study of fibers.[27] In a preliminary communication we briefly described the EPR spectra of fibers of polymer pF(CH_3)−2-Cu using fibers drawn from the nematic melt with preheated tweezers.[22] The

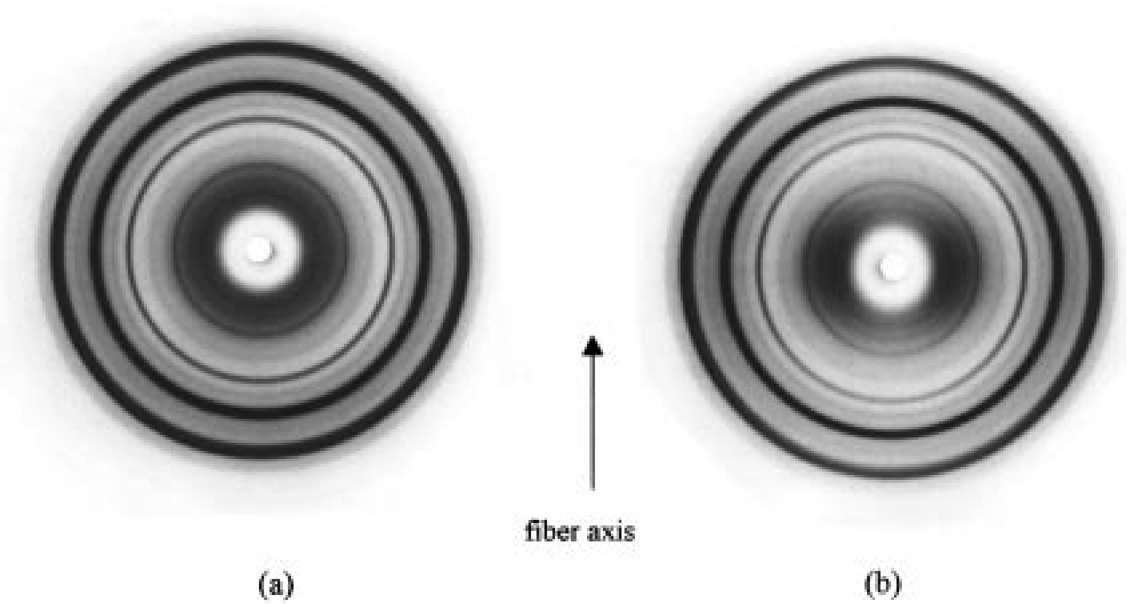


Figure 3. X-ray diffraction pattern of the fibers derived from polyazomethine pF(CH_3)−H: as-spun fiber (a) and annealed at 100 °C for 12 h (b).

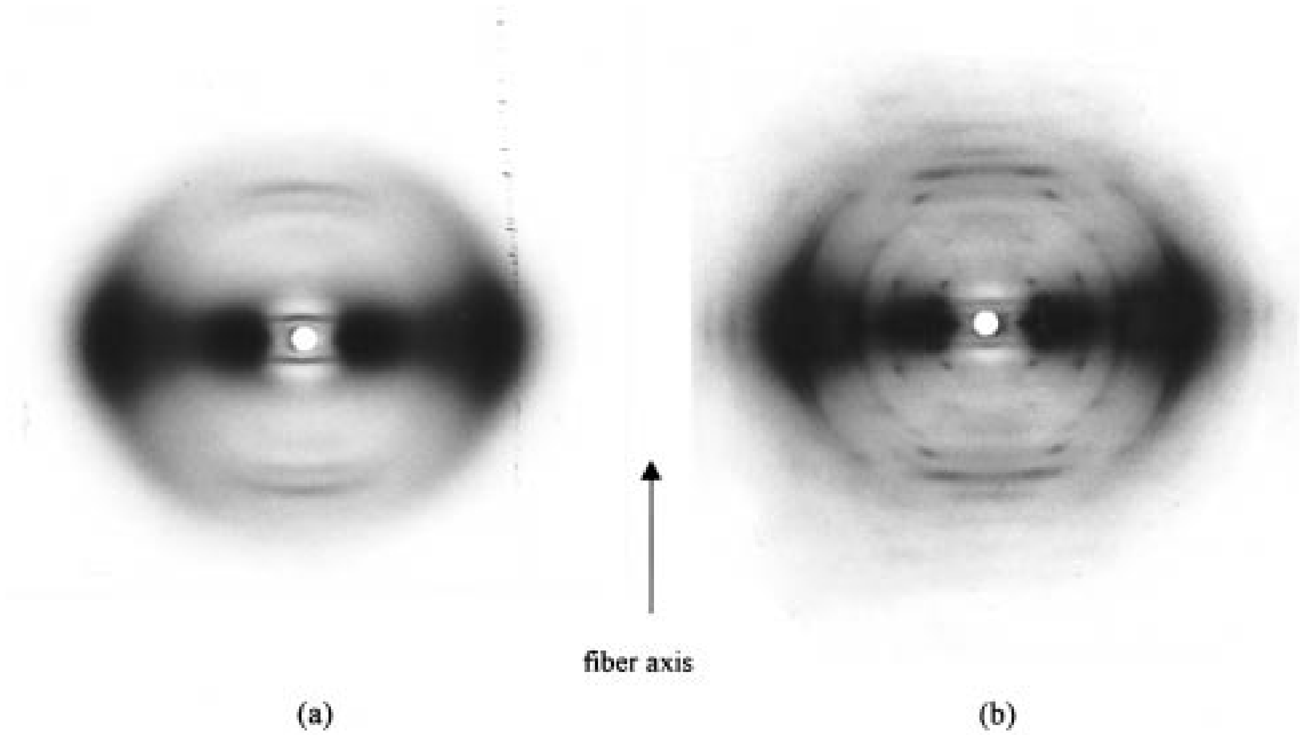
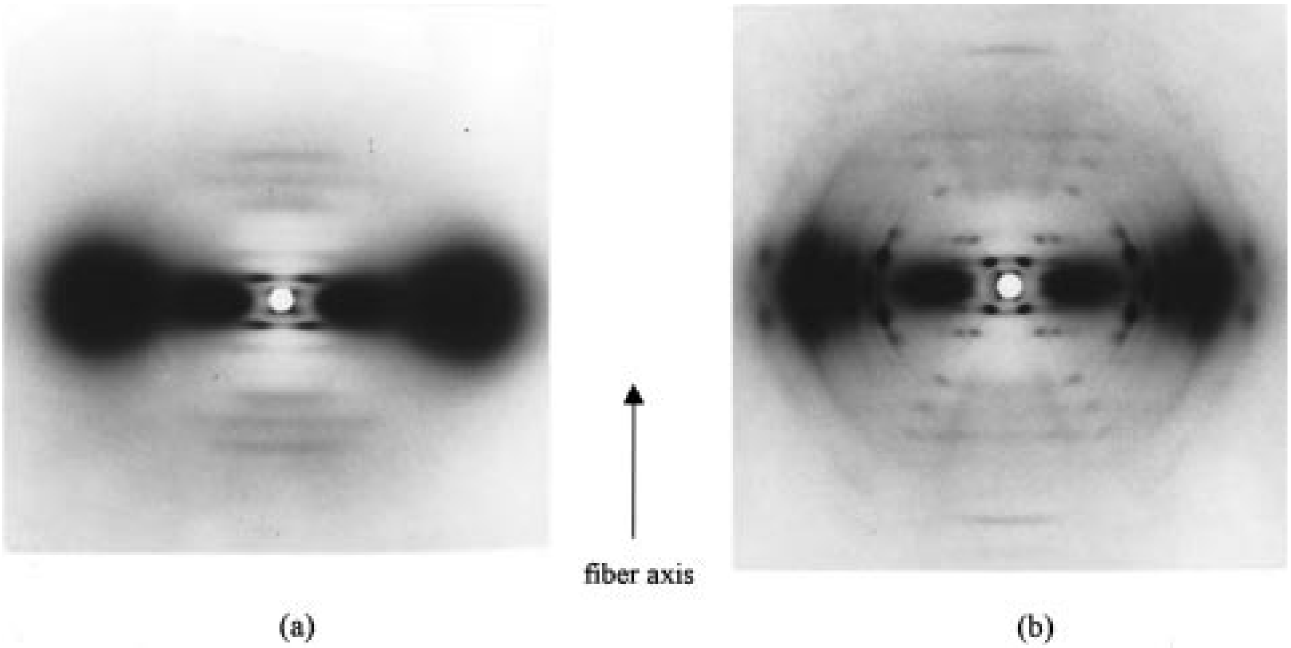


Figure 4. X-ray diffraction pattern of the fibers derived from polyazomethine DMB−OH: as-spun fiber (a) and annealed at 100 °C for 12 h (b).

fibers obtained in this way exhibit a high anisotropy, which is interpreted to be a consequence of the nematic orientation of the square-planar coordination, as has been shown previously for other similar metal-complexed polymers.[21,32]

Fibers processed in the melt-spinning unit have now been studied by EPR, and the spectra are quite similar to those previously mentioned and highly dependent on the angle (ψ) between the magnetic field and the fiber axis. The spectra of this fiber have been explained by considering that the fiber axis lies in the square-planar Cu coordination plane, while the normal to this plane is randomly oriented in the plane normal to the fiber. Such a high anisotropy reflects the nematic orientation of the copper(II) cross-links.

Mechanical Properties. The mechanical parameters of the fibers extruded from the anisotropic melt, including the elastic modulus, tensile strength, and elongation at break along the fiber axis, are collected in Table 5. The mechanical properties of fibers derived from pF(CH_3)−OH were first reported for fibers processed by using commercial extrusion equipment fitted with an exit die specially designed for LCPs.[25] We have now used an exit die that is not specifically designed for LCPs in our experimental setup. However, the mechanical properties of the fibers obtained from both



(a) (b)

Figure 5. X-ray diffraction pattern of the fibers derived from polyazomethine pF(CH$_3$)−2-Cu: as-spun fiber (a) and annealed at 100 °C for 12 h (b).

Table 5. Mechanical Properties of the Melt-Spun Fibers

fibers	elastic modulus (GPa)	tensile strength (MPa)	elongation at break (%)
pF(CH$_3$)−OH	8	239	3.3
pF(CH$_3$)−OH-T[b]	12	309	2.6
pF(CH$_3$)−H-T[c]	[a]	[a]	[a]
DMB−OH	3	167	3.4
DMB−OH-T[b]	7	178	2.4
DMB−H-T[c]	[a]	[a]	[a]
pF(CH$_3$)−2-Cu	8	445	6.4
pF(CH$_3$)−2-Cu-T[b]	16	840	5.6
Vectra A950[d]	20	512	4.5

[a] Fibers were too fragile and could not be measured as they break under manipulation. [b] Fibers annealed under tension. [c] Fibers annealed in a relaxed state. [d] As-spun fibers from the commercial polymer extruded in the designed spinning unit.

sets of equipment are very similar, which confirms the usefulness of the experimental extrusion unit used in this comparative study.

Comparison of the values obtained again provides evidence of the favorable presence of hydroxyl groups. Filaments processed from nonfunctionalized polyazomethines, including those subjected to thermal treatment, are extremely fragile as a consequence of the low degree of polymerization. Therefore, these polymers are not suitable for processing into high-strength fibers.

However, the introduction of hydroxyl groups dramatically modifies the properties of this kind of semiflexible polyazomethine. The hydroxyl groups are responsible for an improvement in the reactivity of the dialdehyde monomer, giving rise to polymers with higher degrees of polymerization, as has been mentioned above. Hydroxyl groups also affect the postpolymerization behavior in the molten state. As a consequence, the polymers can be processed into good-quality nematic fibers that exhibit good mechanical properties, especially if we take into account the presence of a flexible decamethylenic spacer.

An additional factor to be considered is the possibility of intermolecular H-bonding. At first glance, the intramolecular H-bond should be sterically favored. However, preliminary AM1 calculations[33] in related low molecular weight models point out that both inter- and intramolecular H-bonds are energetically favorable. Therefore, the presence of intermolecular H-bonding would increase lateral interactions between polymeric chains, giving rise to better mechanical properties.

The structure of the mesogenic unit also has an influence on mechanical properties. This becomes apparent when we compare properties of the fibers derived from pF(CH$_3$)−OH and DMB−OH. However, differences might also be due to the diameter irregularities observed in fibers processed from the melt of DMB−OH. The large increase in viscosity observed during the processing of DMB−OH favors the appearance of these irregularities, which causes failures where fibers can be easily broken and thus lowers the magnitudes of the properties.

The increase in molecular weight and the development of crystallinity upon thermal annealing also have an influence on the mechanical properties. The mechanical properties of these semiflexible hydroxy-functionalized polyazomethines, and in particular pF(CH$_3$)−OH, are higher than the generally reported semiflexible polyesters[34] or semiflexible nonfunctionalized polyazomethines.

A general drawback of fibers derived from LCPs is the relatively low compressive strength, which is believed to arise from the lack of strong intermolecular bonding.[35,36] Several approaches have been used to enhance lateral interactions. In particular, the introduction of covalent cross-linking within the fibers is expected to improve these interactions. However, thermally activated cross-linking of nematic fibers usually leads to degradative processes or structural imperfections upon processing that decrease tensile mechanical properties.[37]

Metal cross-linking is expected to enhance intermolecular interactions but also makes the processability of the nematic melt difficult. Thus, only the polyazomethine with the lowest metal content, pF(CH$_3$)−2-Cu, was suitable to be processed. Results show that mechanical properties of this polymer are better, and in particular, the tensile strength is 1.9 times higher for the as-spun copper-complexed material than for the original polyazomethine. There is also an increase in the elongation at break, as was expected for cross-linked fibers. When these copper-containing fibers are annealed under tension, the improvement in properties is again outstanding, showing a tensile strength value of 840 MPa, which is 3.5 times higher than the value found for the as-spun fiber. This remarkable improvement by copper complexation is associated with the Cu(II) cross-linking points, which lead to tougher fibers without disrupting the nematic orientation or the development of a highly oriented crystalline structure by annealing.

The mechanical properties of these copper(II) cross-linked fibers are better than those observed for semiflexible liquid-crystal polyesters[34] or copolyesteramides[38] and similar to those exhibited by wholly aromatic LC polyesters. As a comparison, fibers of VECTRA A950 were extruded in our experimental extrusion setup and showed, after annealing, a value of 20 GPa for the elastic modulus, 512 MPa for the tensile strength, and 4.5% for elongation at break.

Fiber Morphology. The morphology of the as-spun and annealed fibers was studied by SEM for the surfaces of both the tensile fractured fibers and specimens prepared by the peel-back method.

Fibers derived from the polyazomethine without hydroxyl groups exhibited a fast brittle fracture morphology (Figure 6a), which is consistent with the oligomeric nature of these polymers and the nonoriented semicrystalline structure analyzed by X-ray diffraction. No changes in morphology were observed by thermal annealing.

Fibers derived from the organic hydroxy-functionalized polymers exhibited a slow energy-absorbing fibrillar fracture that appears woody in texture, as shown in Figure 6b for DMB−OH. Fibers of copper(II)-complexed polymer showed a fibrillar fracture similar to the organic parent polymers (see Figure 6c) (taken from ref 22).

The study of specimens of hydroxy-functionalized polymers prepared by the peel-back method provided evidence of a highly internal fibrillar structure, and there seems to be more coherence within the cross section as shown in Figure 7a (taken from ref 22) for polymer pF(CH_3)−OH. This arrangement is not disturbed by thermal annealing. The introduction of copper cross-links does not disrupt the orientation. (Figure 7b). This morphology provides evidence of strong intermolecular cohesive forces, which may be attributed to the high electronic polarizability of the mesogenic units, intermolecular H-bonds, and metal covalently linked in Cu(II)-containing polymers. The morphologies of LCPs, and in particular LC polyesters, generally exhibit a fibrillar texture with a tendency to fray, as can be observed in Figure 7c for a fiber of VECTRA A950, and this is a consequence of the weak cohesive forces.

Concluding Remarks

Hydroxy functionalization dramatically modifies the properties of semiflexible polyazomethines. The presence of hydroxyl groups influences monomer reactivity, giving rise to polymers with a high degree of polymerization. Furthermore, hydroxy-functionalized polymers exhibit a larger increase in viscosity upon thermal treatment as a consequence of postpolymerization reactions. Therefore, the processing of hydroxy-functionalized semiflexible polyazomethines gives rise to fibers with good mechanical properties whereas non-hydroxy-functionalized polymers give rise to extremely fragile fibers. The presence of functional groups allows the chemical modification of the parent polymers, introducing new expectations on fiber properties. The copper(II) complexation gives rise to metallomesogenic cross-linking sites, and controlling the cross-linking density copper(II)-containing fibers could be processed from the nematic melt. As-spun fibers of functionalized and copper(II)-containing polymers exhibit a high degree of orientation, as was observed by X-ray diffraction. In the case of pF(CH_3)−2-Cu the orientation of the copper cross-links could be monitored by EPR. Furthermore, fibers of these polymers develop a highly crystalline

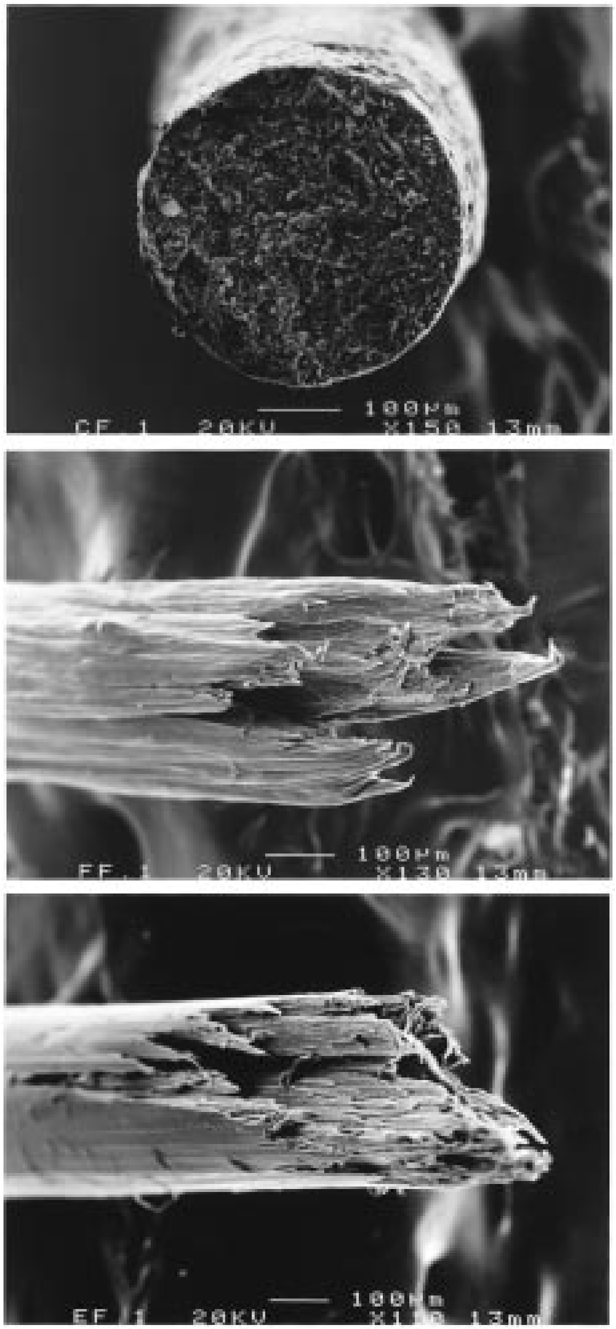


Figure 6. SEM photographs of the polyazomethine fibers: tensile fracture surface of DMB−H (a, top), DMB−OH (b, middle), and pF(CH_3)−2-Cu (c, bottom) (taken from ref 22).

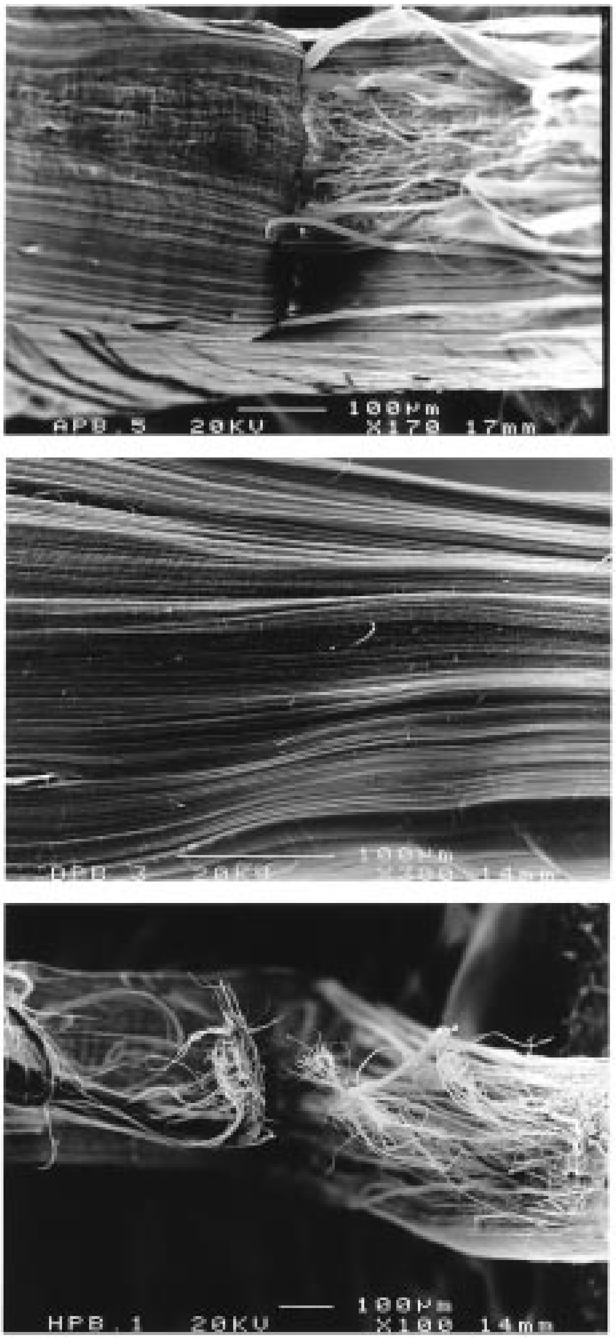


Figure 7. SEM photographs of the polyazomethine fibers: samples prepared by the peel-back method of pF(CH_3)−OH (a, top) (taken from ref 22) and pF(CH_3)−2-Cu (b, middle). Sample of the commercial polymer VECTRA A950 is included for comparison (c, bottom).

phase upon thermal annealing as well as an increase in molecular weight. The mechanical properties of fibers depend on these aspects. Thus, copper(II) cross-linking results in a remarkable improvement in fiber mechanical properties, and this is especially evident after annealing. The study of the morphology of fibers of the hydroxy-functionalized and Cu(II)-modified polymers provides evidence of a highly oriented fibrillar texture with a high interaction between fibrils.

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