

Copper-Containing Semiflexible Hydroxypolyazomethines: Metallomesogenic Units Inducing Enhanced Mechanical Properties

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Received February 21, 1997

Investigation of metallomesogens is one of the most promising areas in the field of liquid crystal (LC) research.¹ In this context, metallomesogenic polymers can be considered as hybrid materials which combine the advantages of the anisotropic properties of LCs, the processability of polymers and the electronic properties of metals.² We describe here a new approach to obtain control over and improve the mechanical properties of anisotropic fibers by introducing metallomesogenic units into the structure of LC polymers.

The industrial developments on LC polymers for structural applications mainly concern two types of rigid-rod macromolecules: aramids and aromatic polyesters. Aramids (e.g., KEVLAR, DuPont) form high-strength and high-modulus fibers but must be processed from lyotropic concentrated sulfuric acid solutions at elevated temperatures.³ Recently, Dembek and co-workers have proposed a new approach to process aramids by converting them into soluble metallomesogenic derivatives.⁴ Thermotropic polyesters (e.g., VECTRA, Hoechst-Celanese)⁵ are easily processed from their anisotropic melt which flows easily under shear. However, in comparison with aramids, the intermolecular cohesive forces are drastically reduced, and, consequently, fibers of thermotropic polyesters show poor compressive properties.

As a continuation of our recent research into metallomesogenic polymers, we investigated a new material that would combine melt processability and significant intermolecular interactions. Accordingly to previous results, we chose the semiflexible thermotropic polyazomethine shown in Figure 1.^{6,7} The mesogenic core of this polyazomethine has two chelation centers where metal ions can be introduced to give rise to a partially cross-linked LC polymer (see Figure 1). The cross-linking density in this system can be tuned by controlling the percentage of metal ions. Furthermore, their presence does not disturb the nematic order or the polymer orientation during processing. Metal cross-linking is expected to enhance intermolecular lateral interactions, thus improving fiber-abrasion resistance. This approach is based on similar principles to the reported thermally-activated chemical cross-linking of fibers.⁸ However, this method can lead to degradative processes or structural imperfections in the fiber.

The parent and Cu(II)-complexed polyazomethines were obtained according to a previously described method.⁹ The most

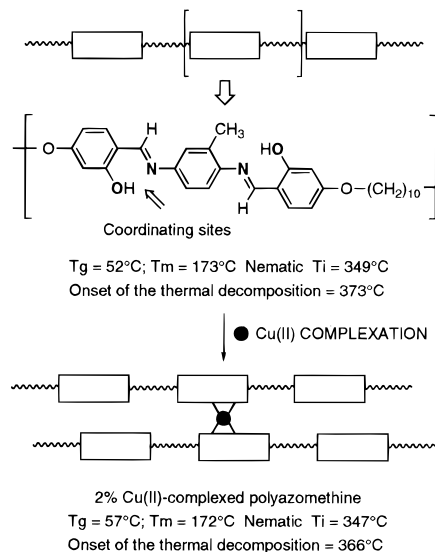


Figure 1. Parent hydroxy-functionalized polyazomethine and schematic representation of the cross-linking introduced by metal complexation.

Table 1. Tensile Fiber Properties^a of the Investigated Parent and Cu(II)-Complexed Polyazomethines

polymer	TS (MPa)	mod (GPa)	elong(%)
parent polyazom./as spun	239	8	3.3
parent polyazom./heat treated (100 °C/12 h/tension)	309	12	2.6
Cu(II)-complex./as spun	445	8	6.4
Cu(II)-complex./heat treated (110 °C/12 h/tension)	840	16	5.6
VECTRA A950/as spun ^b	512	20	4.5

^a TS: tensile strength; Mod: elastic modulus; elong: elongation at break. Average of the measurements obtained from six fibers (elongation rate: 10 mm min⁻¹; room temperature). ^b Literature values for VECTRA fibers can be found in ref 12.

important thermal data are collected in Figure 1. In order to avoid an excessive degree of cross-linking that would result in a high melt viscosity, only a 2% molar ratio of Cu(II) was added (based on the reaction of 1 mol of repeating unit with 1 mol of Cu(II) ion). Fibers of the Cu(II)-chelated polyazomethine were processed from its nematic melt at 200 °C, using a small-scale extrusion apparatus equipped with a commercial die of 0.45 mm diameter. As-spun fibers were further subjected to heat treatment under elongational forces at 110 °C for 12 h. Tension was applied by suspending a 110 g weight from one end of the fiber.

The mechanical properties of the parent polyazomethine have already been described.⁷ However, due to the fact that the Cu(II)-containing polymer was extruded under slightly different conditions, new fibers of the parent polymer were also extruded in order for direct comparisons to be made. As a reference for a comparative study, fibers of the commercial polyester VECTRA A950 were processed under the same conditions. As can be seen in Table 1, Cu(II) complexation produces a significant increase in the tensile strength of as-spun fibers (239 MPa vs 445 MPa). The heat treatment of fibers under tension also increases the tensile strength, giving rise to a value of 840 MPa for the Cu(II)-complexed polymer, which is remarkably higher than the values usually obtained for semiflexible LC polyesters¹⁰ or copolyesteramides.¹¹ Furthermore, this value is of a similar

(9) Oriol, L.; Alonso, P. J.; Martínez, J. I.; Piñol, M.; Serrano, J. L. *Macromolecules* **1994**, *27*, 1869–1874.

(10) Krigbaum, W. R.; Ciferri, A.; Acierno, D. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1985**, *41*, 293–305.

(11) Pedretti, U.; Montani, E.; Città, V.; LaMantia, F. P.; Magagnini, P. *Mol. Cryst. Liq. Cryst.* **1995**, *266*, 121–134.

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(1) *Metallomesogens. Synthesis, Properties and Applications*; Serrano, J. L., Ed.; VCH: Weinheim, 1996.

(2) Oriol, L.; Serrano, J. L. *Adv. Mater.* **1995**, *7*, 348–369.

(3) Tanner, D.; Fitzgerald, J. A.; Philips, B. R. *Angew. Chem., Int. Ed. Engl. Adv. Mater.* **1989**, *28*, 649–654 and references therein.

(4) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087–2089.

(5) De Martino, R. N. *J. Appl. Polym. Sci.* **1983**, *28*, 1805–1810.

(6) Barberá, J.; Oriol, L.; Serrano, J. L. *Liq. Cryst.* **1992**, *12*, 37–47.

(7) Cerrada, P.; Oriol, L.; Piñol, M.; Serrano, J. L.; Iribarren, I.; Muñoz-Guerra, S. *Macromolecules* **1996**, *29*, 2515–2523.

(8) Jiang, T.; Rigney, J.; Jones, M. C. G.; Markoski, L. J.; Spilman, G. E.; Mielewski, D. F.; Martin, D. C. *Macromolecules* **1995**, *28*, 3301–3312.

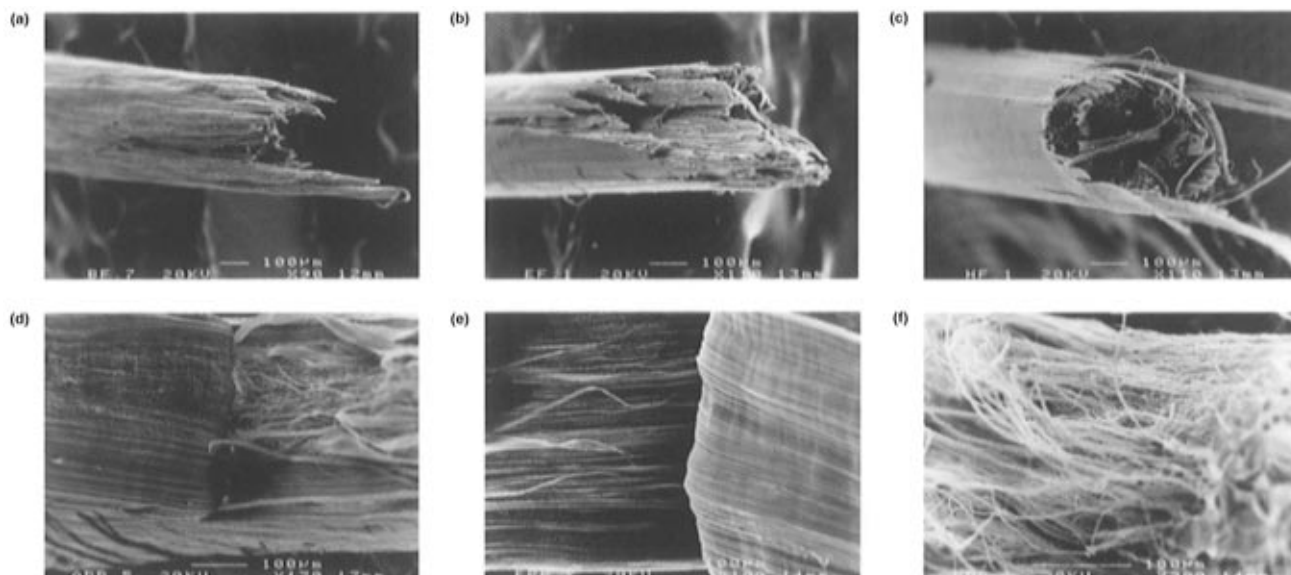


Figure 2. SEM photographs of parent polyazomethine fibers: (a) tensile fracture surface and (d) fiber prepared by the peelback method. SEM photographs of Cu(II)-containing fibers: (b) tensile fracture surface and (e) fiber prepared by the peelback method. SEM photographs of VECTRA A950 fibers: (c) tensile fracture surface and (f) fiber prepared by the peelback method.

order to the tensile strength exhibited by fibers of wholly aromatic LC polyesters, e.g., VECTRA. The tensile moduli of the polyazomethine fibers also increase by a factor of 2 after heat treatment. This improvement in the mechanical properties is a consequence of the increase in the molecular weight as well as the development of a crystalline structure as it has been determined by X-ray diffraction.⁷ The elongation at break of the Cu(II)-containing fibers is higher than that corresponding to the parent polyazomethine due to the Cu(II) cross-links which lead to tougher fibers.

The morphological study by SEM of the tensile fracture surface of both organic and Cu(II)-complexed polymeric fibers reveals a slow, energy-absorbing fibrillar fracture, which appears woody in texture, as shown in Figure 2 (parts a and b). As a reference, Figure 2c shows the tensile fracture surface of the LC polyester VECTRA A950 which exhibits a typical skin-core morphology. Fiber samples prepared by the peelback method¹³ reveal the highly internal fibrillar structure which could be more accurately described by uniaxially oriented sheets (see Figure 2d). This highly fibrillar orientation, promoted by processing from the nematic melt, is not disturbed by Cu(II) complexation or heat-treatment. A remarkable characteristic of these polymers is the low tendency to fray shown by the fibrils, especially the Cu(II)-complexed fibers (see Figure 2e) in comparison with the fibers of wholly aromatic polyesters such as VECTRA A950 (see Figure 2f). This fact provides evidence of strong intermolecular cohesive forces, which may be attributed to the high polarizability of the mesogenic units and also to the formation of intermolecular hydrogen bonds. Furthermore, in the case of Cu(II)-complexed polymers, the metal introduces covalent bonds which help to improve the compressive properties.

The presence of Cu(II) introduces some additional properties related to their electronic structure. Thus, the presence of Cu(II) paramagnetic entities in the fibers allows the use of EPR as a powerful tool to study the fiber orientation. Figure 3 shows

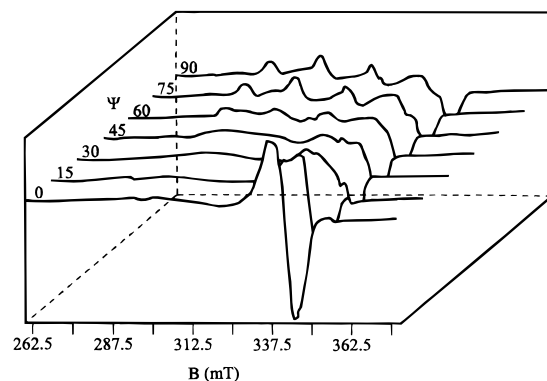


Figure 3. Room temperature EPR spectra of a copper(II) containing fiber measured at different angles (Ψ) between the magnetic field and the fiber axis.

the EPR spectrum of a fiber measured at different angles between the magnetic field and fiber axis. The high anisotropy observed in the EPR spectra is a consequence of the nematic orientation of the square-planar coordination centers.¹⁴

In summary, metal-complexation of polyazomethines provides a method of tuning polymer properties and approaches high-performance anisotropic fibers. Metallomesogenic cross-linking is responsible for the large increase in tensile properties in as-spun and annealed fibers, without loss of orientation and crystallinity. Furthermore, this approach significantly increases the cohesive fibrillar interactions. The electronic structure of Cu(II) complexes also gives rise to additional properties such as paramagnetism. Studies on different polyazomethines, metal atoms, and metal contents are in progress.

Acknowledgment is made to the CICYT (Spain) for financial support under project MAT96-1073-C02-02 and to Prof. P. J. Alonso for the EPR study.

JA970558F

(12) McIntyre, J. E. *Makromol. Chem., Macromol. Symp.* **1993**, 69, 65–73.

(13) Scott, R. G. *ASTM Spec. Tech. Publ. No. 257* **1959**, 121.

(14) Alonso, P. J.; Puértolas, J. A.; Davidson, P.; Martínez, B.; Martínez, J. I.; Oriol, L.; Serrano, J. L. *Macromolecules* **1993**, 26, 4304–4309.