

Paramagnetic organometallic liquid crystal polymers

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SUMMARY

We have synthesized a paramagnetic organometallic liquid crystal polymer containing a tetradentate Schiff base complex of copper II. The main chain liquid crystal polymer forms when the functionalized complex is combined at 220°C with the melt of a low molecular weight terpolymer. The terpolymer is a nematic liquid crystal at this temperature and contains oxybenzoate, dioxyphenyl, and pimelate structural units. The organometallic material melts reversibly into a liquid crystalline fluid at a slightly lower temperature than the terpolymer. In external magnetic fields the tendency is for the backbone axis of the organometallic fluid to rotate away from the field direction. This observation suggests that strong interactions between the field and the paramagnetic units dictate the orientation of diamagnetic chemical sequences which normally align parallel to the magnetic field.

INTRODUCTION

A unique property of polymers that exhibit liquid crystallinity is their ability to acquire molecular orientation in magnetic fields. This orientation occurs not only because of anisotropy in magnetic susceptibility but most importantly because of the cooperative nature of liquid crystalline phases. Polymers are usually diamagnetic and we have shown earlier the feasibility of orienting aromatic polyesters in moderately strong magnetic fields (1,2). An exciting possibility in this context is to explore the synthetic opportunities for incorporation of paramagnetic moieties in liquid crystal polymers (LCP's). The most obvious reason for this suggestion is the importance of a strong magnetic interaction in orientational dynamics. Another reason is the possibility of controlling molecular direction with respect to the magnetic field by careful selection of structure and position of paramagnetic units within polymer chains. Finally, in a more distant context it may be possible to observe ferromagnetic ordering in these systems. Synthesis of mesogenic paramagnetic chains can therefore be viewed as important in studies of cooperative dynamics, and with some imagination these macromolecules could be considered technologically attractive systems.

We report here on the synthesis of an organometallic liquid crystal copolymer which contains paramagnetic

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structural units. These structural units contain a tetradentate Schiff base complex of copper (II). Small molecules containing similar complexes have been reported to exhibit paramagnetism with the dominant principal axis nearly perpendicular to the ligand plane(3). Our experimental system has been partially characterized so far and we have also initiated studies on its response to an external magnetic field.

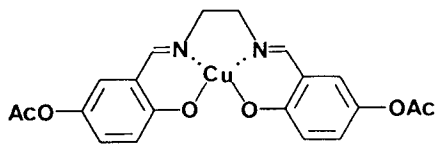
EXPERIMENTAL

The organometallic liquid crystal polymer studied here was synthesized by a transesterification reaction involving a chemically random terpolymer and a functionalized tetradentate copper (II) complex. The terpolymer is a mesomorphic aromatic polyester containing oxybenzoate, dioxyphenyl and pimelate structural units. The synthesis of this terpolymer as well as that of the monomeric copper complex has been described in detail elsewhere(1,4). The transesterification reaction involves mixing 500 mg of the terpolymer and 30-160 mg of the copper complex in a 5 ml pear-shaped flask. This flask is equipped with a distillation head fitted with a gas inlet suitable for bubbling dry nitrogen through the reaction mixture. The flask was immersed in a sand bath held at a temperature of 220°C for a period of one hour under constant nitrogen bubbling. After cooling to room temperature a dark green solid is obtained.

Differential scanning calorimetry (DSC) analysis utilized a Perkin Elmer instrument at a heating rate of 10°C/min under a nitrogen atmosphere. Optical micrographs were obtained with a Leitz Labrolux 12 Pol microscope equipped with a hot stage and Micristar thermal controller. Broad-line ¹H NMR measurements were obtained with a Varian XL-200 instrument equipped with a variable temperature unit. The spectra were recorded at a temperature of 185°C after a period of 120 min.

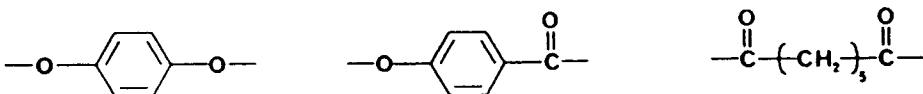
RESULTS AND DISCUSSION

The functionalized organometallic complex used to form the paramagnetic copolymer has the following chemical structure,

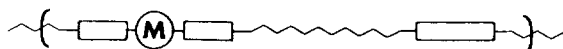


I

and the terpolymer consists of random sequences of the following three structural units,



Thus, assuming that transesterification occurs between carboxylic acid end groups of the terpolymer (pimelic and benzoic) and acetoxy groups in I, the organometallic paramagnetic chain can be envisioned as having the following structure,



where \textcircled{M} represents the magneto-active unit.

Figure 1 shows the DSC scans of the terpolymer and the

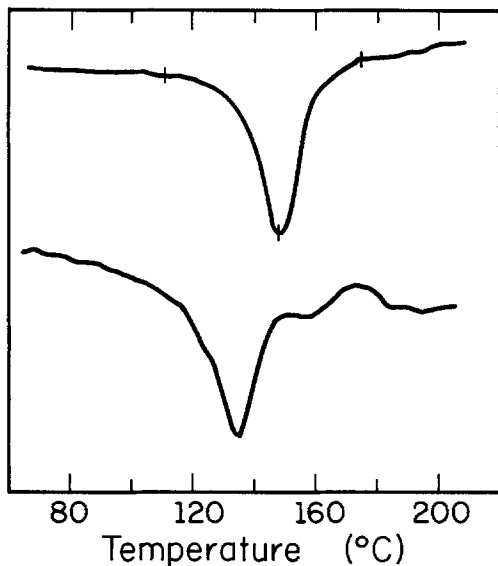


Figure 1. DSC scans of the terpolymer (top) and the paramagnetic copolymer (bottom). The paramagnetic copolymer contained 10% by wt. of the organometallic complex.

organometallic copolymer. The observed endotherm in the terpolymer near 140°C had been previously characterized as a solid to liquid crystal transition. The same transition is observed in the copolymer but shifted to slightly lower temperatures (136°C vs. 142°C). Approximately 20°C above the endotherm one observes an opaque emerald green fluid which can be reversibly solidified and melted. Optical micrographs between cross polars similar to that shown in figure 2 confirm the liquid crystalline nature of the fluid. The Schlieren textures observed indicate that the organometallic system forms nematic phases at temperatures above 180°C. It has been interesting to find that the organometallic unit incorporated in concentrations of the order of 5 to 20 mole% does not disrupt liquid crystalline order of the diamagnetic



Figure 2. Optical micrograph between crossed polars at 185°C of the organometallic copolymer.

terpolymer. This observation would be consistent with the rigid structure and anisotropic geometry of the paramagnetic unit. Furthermore, close examination of the micrographs reveals a tendency toward uniform molecular orientation over considerable distances. This is interesting since it is not uncommon to observe a rather complicated and multichromic texture in the diamagnetic terpolymer. It is surprising that an infusible solid is not formed as a result of donor-acceptor interactions between the organometallic unit and electron rich functional groups in the polymer backbone. Such donor-acceptor interactions involving similar complexes have been documented in the literature(5).

The functionalized copper complex forms an infusible solid in pure form which begins to decompose above 300°C. Therefore, its solubility in the terpolymer at the beginning of our reaction is of great chemical interest. In this context, we must point out that the exact location of all organometallic units in the system remains unknown. For example, transesterification may be incomplete and paramagnetic units may exist as a solute in the polymeric solvent or may be bound to the backbone structure as a guest involved in some type of van der Waals interaction (i.e., donor-acceptor pairs). Detailed studies of structure are currently underway and will be reported at a later date. In any event it is certainly interesting that there is compatibility between the organometallic complex and liquid crystalline order in a main chain system. We describe below

some of our preliminary studies on the response of the copolymer to an external magnetic field. These studies do suggest that some special structural relationship exists between the polymer and the organometallic unit (e.g., covalent incorporation, strong binding through secondary bonding).

Figure 3 shows two broadline proton NMR spectra of the liquid crystal terpolymer and the organometallic system. It is clear that macroscopic molecular orientation in the magnetic field has occurred in both cases. This is revealed by the characteristic dipolar splitting observed in the spectra of the aligned fluids. Alignment of the fluid by a magnetic field is a clear indication that the organometallic system behaves as a liquid crystalline medium. The spectra shown in figure 3 correspond to what appears to be a plateau level of orientation. An important difference between the two spectra is a lower second moment in the organometallic system. The second moment, $\langle \Delta\nu^2 \rangle$, is defined as,

$$\langle \Delta\nu^2 \rangle = \frac{\int_{-\infty}^{\infty} [\nu - \langle \nu \rangle]^2 g(\nu) d\nu}{\int_{-\infty}^{\infty} g(\nu) d\nu} \quad (1)$$

where ν is the frequency, $\langle \nu \rangle$ is the average frequency and $g(\nu)$ represents the functional form of the NMR lineshape. $\langle \Delta\nu^2 \rangle$ is proportional to $\langle S_{z,z}^2 \rangle$, the square of the average macroscopic order parameter. The method used to calculate $\langle S_{z,z}^2 \rangle$ is also described in our previous publication on the liquid crystal terpolymer(2). Table I shows plateau values of $\langle S_{z,z}^2 \rangle$ for both materials. The fact that $\langle S_{z,z}^2 \rangle$ is lower in the organometallic system is an indication that the paramagnetic unit is able to disrupt the uniaxial alignment that would otherwise be acquired by the diamagnetic liquid crystal terpolymer. This observation is consistent with the strong paramagnetic moment of the organometallic unit perpendicular to the molecular director. The disruption in orientation implies that the organometallic unit is either incorporated covalently in the backbone of the polymer or that its solvation in the liquid crystalline medium is able to dictate the orientation of the host polymer. Further studies of these issues are currently underway.

TABLE I

Plateau Values of $\langle S_{z,z}^2 \rangle$

Sample	$\langle S_{z,z}^2 \rangle$
Terpolymer	1.00
Organometallic System ^a	0.69

^aContains 10.0 wt. % organometallic complex.

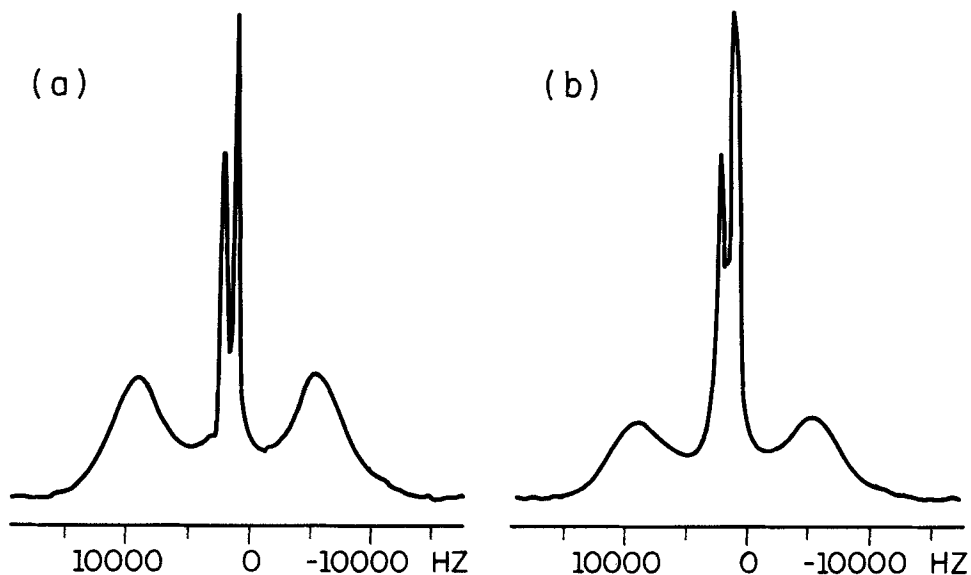


Figure 3. Broadline proton NMR spectra of magnetically oriented samples at 185°C. Spectrum (a) corresponds to the diamagnetic terpolymer and spectrum (b) corresponds to the paramagnetic copolymer containing 10% by wt. of the organometallic complex.

ACKNOWLEDGEMENTS

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REFERENCES

- 1) Moore, J.S.; Stupp, S.I.; *Macromolecules*, **20**, 273 (1987).
- 2) Moore, J.S.; Stupp, S.I.; *Macromolecules*, **20**, 282 (1987).
- 3) Scullane, M.I.; Allen, H.C.; *J. Coord. Chem.*, **4**, 255 (1975).
- 4) Moore, J.S.; Stupp, S.I. (In preparation).
- 5) Tanaka, T.; *Bull. Chem. Soc. Jap.* **33**, 259 (1960).