

The Effect of Temperature on Optical and Viscoelastic Properties of a Homogeneous Thermotropic Liquid Crystalline Polymer

Paul DRISCOLL, Ken-ichi FUJIWARA, Toshiro MASUDA,
Akira FURUKAWA,* and Robert W. LENZ**

*Research Center for Medical Polymers and Biomaterials, Kyoto University,
Shogoin, Sakyo-ku, Kyoto 606, Japan*

**R and D Laboratory for Photomaterials, Mitsubishi Paper Mills, Ltd.,
1-6-6 Kaiden, Nagaokakyo-shi, Kyoto 617, Japan*

***Polymer Science and Engineering Department, University of Massachusetts,
Amherst, MA 01003, U.S.A.*

(Received September 30, 1987)

ABSTRACT: Dynamic viscoelastic properties of a newly synthesized thermotropic liquid crystalline homo-polymer with relatively low transition temperatures were measured over a range of temperatures with a Rheometrics Mechanical Spectrometer (RMS). The unique behavior of this material, highlighted by an intermediate temperature minimum in the $|\eta^*|$ vs. T curve in the temperature range explored, is indicative of a liquid crystal nature, and may be related to structural differences. Viscoelastic results were therefore compared with optical micrographs taken in the static state over the range of temperatures. Polarized light optical microscopy identifies the so-called isotropitization temperature which signals the beginning of the isotropic rheological behaviour, but optical micrographs show little apparent corresponding structure change below this temperature, in the range where the intermediate temperature rheological transition is located.

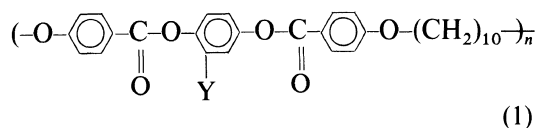
KEY WORDS Thermotropic Liquid Crystalline Polymer / Dynamic Viscoelasticity / Optical Microscopy / Effect of Temperature on Domain Structure /

Polymer liquid crystal research has been dominated by the study of lyotropic systems and copolyester thermotropic systems. This is related to the relative abundance of these materials, because of their actual and perceived commercial importance. Recently, homogeneous liquid crystalline polymers have been synthesized. This class of materials has a less complicated structure than thermotropic copolyester counterparts, potentially giving insight into the nature of thermotropic liquid crystals.¹⁾ In this paper we examine the temperature dependence of the structure and of the dynamic viscoelastic properties of one of these materials.

Previous experiments seem to indicate that the rheology of thermotropic liquid crystalline

polymers (TLCP) is closely related to their structure (for example see ref 2 and 3). For this reason it was desirable to compare structure as revealed by optical microscopy with dynamic viscoelastic properties as a function of temperature.

We have synthesized materials of this class offering considerably lower LC transition temperatures than the well known thermotropic copolyesters.⁴ The general structure is:



(1)

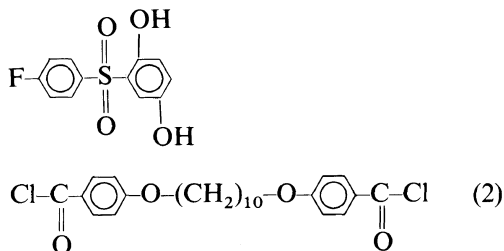
In this case, the polymer is of the structure where $Y = \text{SO}_2\text{---} \langle \text{benzene ring} \rangle \text{---F}$.

In this article dynamic viscoelastic properties as measured by a Rheometrics Mechanical Spectrometer (RMS) are compared with the structure observed by optical microscopy over a similar temperature range. No doubt there may be danger in drawing conclusions from the results because of the limitations of these tests, some of which are discussed in ref 5. Nonetheless some basic structural and rheological information is provided by this combination of experiments.

EXPERIMENTAL

Preparation of Polymer

Preparation of (1) was carried out by melt polycondensation of the two monomers:



A well-ground mixture of these monomers was heated to 120°C to obtain a melt mixture and stirred under a constant flow of dry nitrogen gas. Then, the temperature was gradually raised to 180°C and the reaction was continued at this temperature for 3 hours. The polymerization was completed under reduced pressure at 240°C for an additional 2 hours. After cooling to room temperature, the polymer was dissolved in 1,1,2,2-tetrachloroeth-

ane, precipitated in a 10-fold volume of acetone, filtered, washed well with methanol, water, and acetone, and dried under reduced pressure overnight.

Characterization

The inherent viscosity of this polymer was found to be 0.66 in tetrachloroethane (0.5 g/100 ml) at 45°C. Gel Permeation Chromatography (GPC) measurements shown in Figure 1 revealed that this polymer has a molecular weight of about 80000 at the peak position, when compared to a polystyrene standard. (A 80000 molecular weight polystyrene had an elution volume of about 26.3 ml.) Although, of course, actual molecular weight averages were impossible to obtain because of a lack of standards for the experimental polymer, the polydispersity (\bar{M}_w/\bar{M}_n) was determined to be 4.1 from the GPC curve. We currently are able to offer no explanation for this wide molecular weight distribution, and present these findings only as an experimental observation.

Differential Scanning Calorimetry (DSC) at a rate of 20°C min⁻¹ is seen in Figure 2. Peaks are revealed on heating, (more well defined on the second heating), which separate an isotropic liquid phase, from a nematic liquid crystalline phase at about 180°C, with the next transition to a crystal+(supercooled) nematic liquid crystal phase at about 129°C, and finally a transition to a crystal+nematic glass phase at about 93°C. These distinct thermal transition peaks seem to be a characteristic of homogeneous liquid crystalline polymers; they

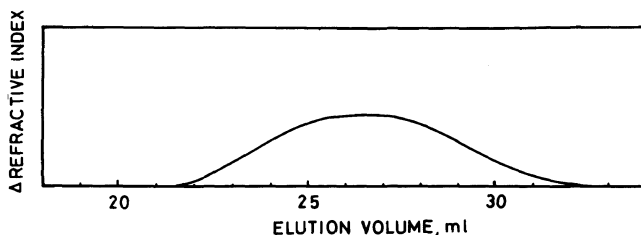


Figure 1. GPC curve for the TLCP showing a single uniformly shaped peak.

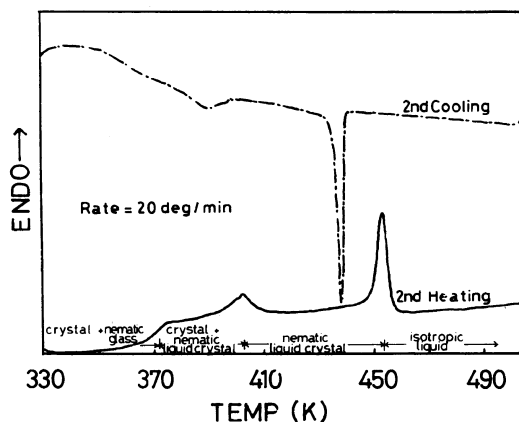


Figure 2. DSC heating and cooling curves for the TLCP, measured at a scanning rate of $20^{\circ}\text{C min}^{-1}$.

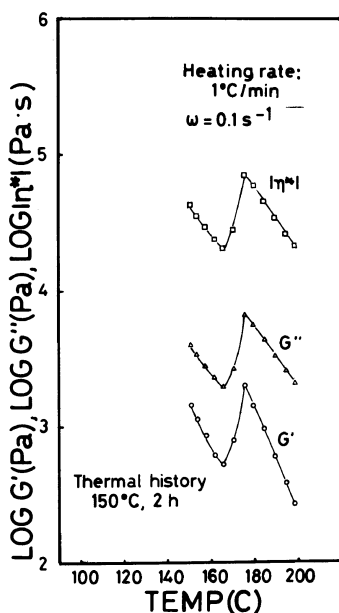


Figure 3. For heating at $1^{\circ}\text{C min}^{-1}$, temperature dependence of dynamic viscoelastic functions G' , G'' , and $|\eta^*|$ for the TLCP measured at $\omega = 0.1 \text{ s}^{-1}$ and $\gamma_0 = 6\%$.

are not observed in thermotropic copolyesters.^{3,6} According to our current thinking most of the above-mentioned nematic liquid crystalline phase on cooling is able to transform to a crystal phase. A certain amount of material is supercooled (the amount increasing with increasing cooling rate), therefore we label this temperature range crystal+nematic liquid

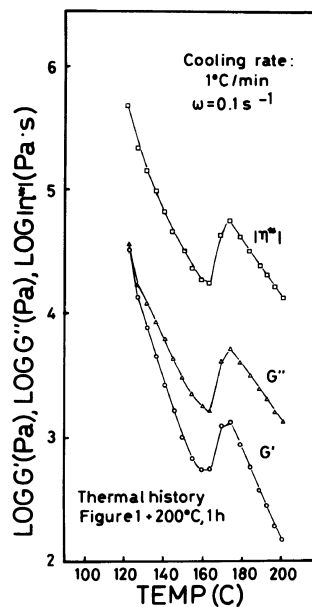


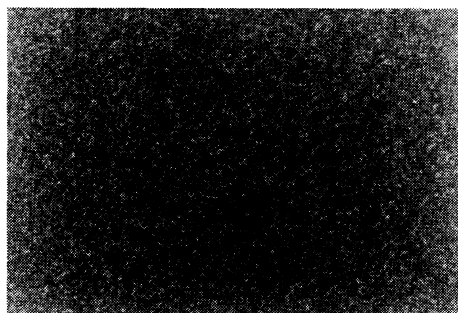
Figure 4. For cooling at $1^{\circ}\text{C min}^{-1}$, temperature dependence of dynamic viscoelastic functions G' , G'' , and $|\eta^*|$ for the TLCP measured at $\omega = 0.1 \text{ s}^{-1}$ and $\gamma_0 = 5\%$.

crystalline. Given enough time (possibly until infinity), this material would be able to form a crystal phase. If the material is further cooled below the glass transition temperature, any remaining supercooled material forms a nematic glass.

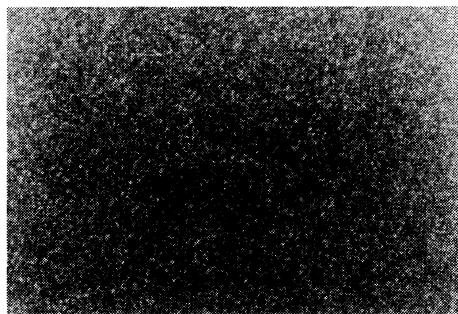
Sample Preparation and Measurement

RMS sample preparation consisted of drying the polymer under vacuum at 105°C for at least 6 hours, before further preparation was done. Compression molding of RMS samples was then performed at 200°C .

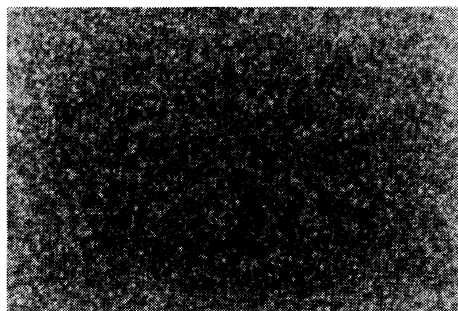
Dynamic viscoelastic properties were measured using a Rheometrics RMS-605. Data were obtained in dynamic mode using 50 mm diameter parallel-plate in an extremely dry air atmosphere. The sample thickness was approximately 1.75 mm. The gap was initially set at 230°C , where it could be quickly adjusted to 1 mm. At 150°C no effect of strain amplitude was seen between $1\% < \gamma_0 < 8\%$ at $\omega = 1 \text{ s}^{-1}$; subsequent measurements were per-



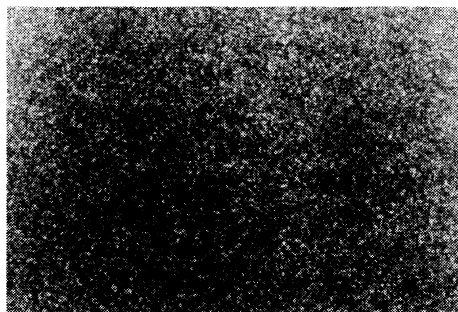
(a)



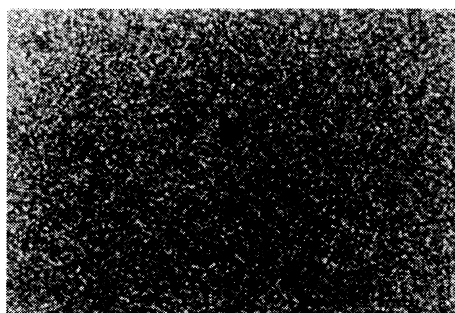
(b)



(c)



(d)



(e)

Figure 5. Photomicrographs for the TLCP between crossed polars at various temperatures. (a) 130°C; (b) 145°C; (c) 160°C; (d) 167°C; (e) 172°C. (a)—(c) were taken in succession as part of a heating program, whereas (d) and (e) were obtained by reheating a cooled melt. Further thermal history details are presented in the text.

formed at $\gamma_0 = 5$ or 6%.

Texture observation was made with a polarizing microscope equipped with a hot stage. Microscopy samples were limited in thickness because of the lack of transparency of the sample. Samples were between 35—50 microns in thickness, on the same order of those used in other TLCP optical microscopy investigations.⁶⁻⁸

RESULTS AND DISCUSSION

Viscoelastic Properties

Figure 3 shows the temperature dependent curves of storage modulus G' , loss modulus G'' , and the absolute value of the complex viscosity $|\eta^*|$ for the experimental polymer. Measurements were performed at a constant $\omega = 0.1 \text{ s}^{-1}$, and a heating of 1°C min^{-1} was used. Indication of an intermediate temperature minimum is seen in this curve.

A subsequent run with decreasing temperature is seen in Figure 4. A cooling rate of 1°C min^{-1} was used. Here the measurements were extended to lower temperatures. It is believed that the intermediate temperature minimum is related to a structural change in the polymer.

Direct comparison of Figures 3 and 4 shows a decrease in the viscoelastic parameters in Figure 4. This is believed to be related to the degradation of the sample in the isotropic state caused by the extended period at 200°C. Although certainly a quantitative concern, this does not effect the results qualitatively; namely, the intermediate temperature minimum in the viscoelastic parameters is still present.

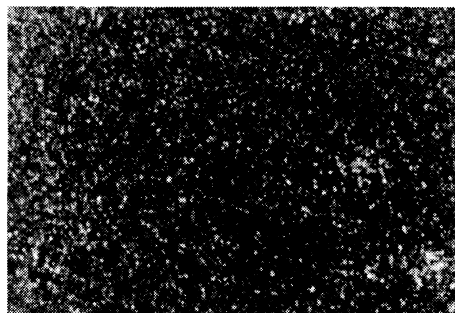
Optical Microscopy

Hot stage optical microscopy was used to investigate the structural characteristics of this polymer over a similar temperature range as was used for the RMS measurements. Initial work examined the texture of a sample at constant temperatures from 130 to 172°C. Under crossed polars photomicrographs are shown in Figure 5. Each temperature was maintained for at least 5 minutes before the picture was taken. Increase of temperature was accomplished by heating at 10°C min⁻¹ between pauses at 15°C intervals. This procedure was followed for pictures until 160°C (Figures 5a—c), but the sample lost all its birefringence before 175°C was reached. Therefore the sample was cooled, and then held at 167°C (Figure 5d) for the picture, then heated at 10°C min⁻¹ to 172°C (Figure 5e) and held again. Comparing the 167°C picture to the 160°C photomicrograph, there is little evidence of coalescence of the regions of birefringent structure after so-called "isotropitization",⁴ followed by subsequent cooling. The texture of the 172°C photo, on the other hand, is representative of the beginnings of the isotropitization transformation.

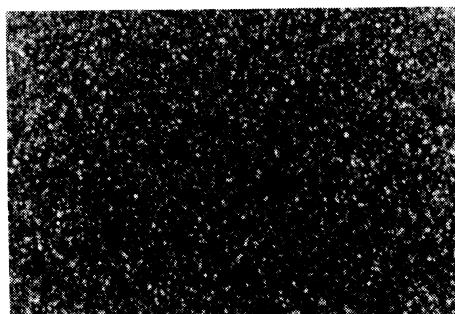
In the next experiment, photomicrographs were taken during a constant heating at 3°C min⁻¹ from 140 until 170.5°C. Structure observed under these experimental conditions was similar to that observed in the previous set of pictures. Transformation appeared to be beginning at approximately 170°C so heating was halted nominally at 170.5°C where pic-



(a)



(b)



(c)

Figure 6. Photomicrographs for the TLCP between crossed polars during a heating from 140 until 170.5°C at 3°C min⁻¹. (a) 170.5°C at 0 min; (b) 170.5°C after 3 min; (d) 170.5°C after 55 min.

tures were then taken as a function of time (Figures 6a—c). Undoubtedly there was some overshoot exposing the sample temporarily to temperatures above 170.5°C. This apparently activated the transformation process, but with time, there was an eventual return to a texture similar to those originally seen in Figure 5. It

should be noted that no apparent coalescence of the birefringent regions occurred (therefore the domain size, and consequently the domain boundaries, must remain about the same). Transformation at first must involve the reorganization of material within these regions, the boundaries remaining intact, at least initially for small heatings above the birefringence transition.

There is little evidence in these static optical microscopy results of a drastic change of structure in the range of the minimum in the $|\eta^*|$ vs. ω curve. Nevertheless optical microscopy was useful in verifying that the isotropitization transition of this polymer is between 170.5 and 173°C, which agrees well with the DSC results considering the lower heating rates used for microscopy.

CONCLUSIONS

An intermediate temperature minimum in the dynamic viscoelastic properties G' , G'' , and $|\eta^*|$ is evidence of the liquid crystalline nature of this thermotropic liquid polymer. Further indication of the liquid crystallinity is the DSC results which show well defined peaks

which can be related to LC transitions. Little change in texture is apparent for the quiescent sample when heated through this temperature range. The rheological anomalies, therefore seem to be a more complicated structural phenomenon than standard optical microscopy was able to reveal. For this reason direct observation and rheological measurement during shear is desirable, and will be examined in a subsequent paper.

REFERENCES

1. A. Blumstein, O. Thomas, and S. Kumar, *J. Polym. Sci., Phys. Ed.*, **24**, 27 (1986).
2. A. Bickel, M. T. Snow, and E. T. Samulski, *J. Rheol.*, **28**, 653 (1984).
3. T. Masuda, M. Takahashi, and K. Fujiwara, submitted to *J. Polym. Sci., Phys. Ed.*
4. For a review see, R. W. Lenz, *Faraday Dis.*, **79**, 21 (1985).
5. A. E. Zachariades, P. Navard, and J. A. Logan, *Mol. Cryst. Liq. Cryst.*, **110**, 93 (1984).
6. D. J. Graziano and M. R. Mackley, *Mol. Cryst. Liq. Cryst.*, **106**, 73 (1984).
7. A. M. Donald, C. Viney, and A. H. Windle, *Polymer*, **24**, 155 (1983).
8. C. Viney, A. M. Donald, and A. H. Windle, *J. Mater. Sci.*, **18**, 1136 (1983).