Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Domain Growth in Thermotropic Liquid Crystalline Polymers by Small Angle Light Scattering

Sergio Rojstaczer [a] & Richard S. Stein [a]

[a] Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA, 01003

Version of record first published: 19 Dec 2006.

To cite this article: Sergio Rojstaczer & Richard S. Stein (1988): Domain Growth in Thermotropic Liquid Crystalline Polymers by Small Angle Light Scattering, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 293-301

To link to this article: http://dx.doi.org/10.1080/00268948808080238

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 157, pp. 293–301
Reprints available directly from the publisher.
Photocopying permitted by license only.

Printed in the United States of America

DOMAIN GROWTH IN THERMOTROPIC LIQUID CRYSTALLINE POLYMERS BY SMALL ANGLE LIGHT SCATTERING

SERGIO ROJSTACZER and RICHARD S. STEIN
Polymer Science & Engineering Department, University of Massachusetts, Amherst, MA 01003

Abstract The small angle light scattering from nematic liquid crystalline polymers was studied. The observed patterns are qualitatively interpreted in terms of the concentration of disclinations. Both a stiff chain and a semiflexible liquid crystalline polyester were investigated, and their light scattering patterns recorded at varying annealing times in the mesophase. A "domain growth" process is found to take place in a much shorter time scale for the rigid rod polymer, this being attributed to the relative instability of the disclinations.

INTRODUCTION

In recent years there has been an increasing interest in morphological studies of liquid crystalline polymers due to their ability to be processed into high modulus and high strength fibers. In order to fully understand the deformation mechanisms which lead to high performance materials, a complete characterization of the superstructure or texture of the polydomain state is needed. While most of the morphological features found in polymeric liquid crystals can be fitted under the classifications developed for small molecule liquid crystals, a more complex texture is often observed.[1] Due to the high viscosity of polymeric systems, these textures are in general more stable to external forces than small molecule liquid crystals. Several factors such

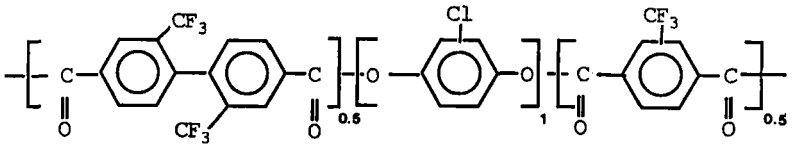
as sample thickness, boundary conditions and thermal history are found to strongly affect the observed textures.

With the development of the continuum theory of curvature elasticity by Oseen[2] and Frank[3], the schlieren texture was interpreted in terms of a continuous director field with singularities at the disclination points. More recently, the role of the spatial distribution and interaction of disclinations has been emphasized in rheological studies of liquid crystalline polymers.[4-5]

In the present study, the small angle light scattering technique is used in investigating the morphological rearrangements that take place by annealing at constant temperature in the nematic phase for two different kinds of polymeric liquid crystals.

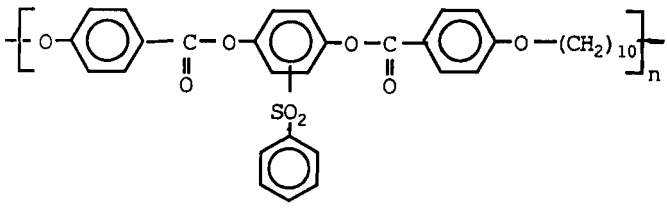
EXPERIMENTAL

Two different kinds of liquid crystalline polymers were investigated. One, which will be referred to as the "rigid rod" polymer, is a wholly aromatic, para-linked polyester, while the second one, the "semiflexible" polymer, is an aromatic polyester with decamethylene spacers. The rigid rod polymer was provided by the Polaroid Corporation and its synthesis and characterization details are described in Ref. 6. The Polaroid polyester has the following structure:



This rigid rod polymer has a glass transition temperature of 106°C and it forms a nematic phase at 170°C. Thermal decomposition takes place at around 460°C, before an isotropic phase develops.

The semiflexible polyester was synthesized and characterized by Furukawa and Lenz.[7] Its structure is the following:



This polymer has a Tg of 70°C, a crystal to nematic transition temperature of 100°C and becomes isotropic at 170°C. Films of both polymer samples were prepared by solution casting from their respective 0.5% THF solutions onto microscope glass slides. The films were about 2 microns thick and these showed no birefringence when observed under a polarizing microscope.

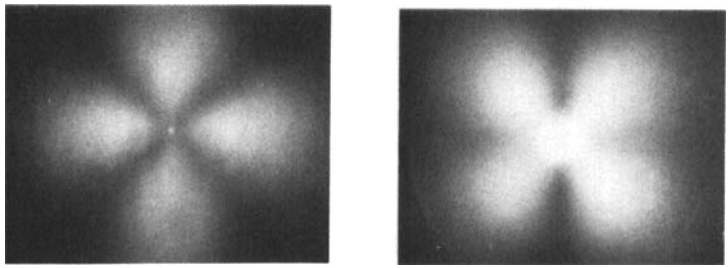
Samples of both polymers were exposed to the nematic phase for different periods of time. This was done differently for each kind of polymer. The semiflexible polymer samples were first heated up into the isotropic phase at 180°C for about 5 minutes, then cooled down to 150°C to form the nematic phase and subsequently quenched to room temperature. Since the rigid rod polymer samples do not become isotropic, they were brought into the nematic phase by exposing the as casted films to a temperature jump to 200°C and subsequently quenching them to room temperature.

The small angle light scattering patterns were recorded on photographic film for the different samples. The H_V and V_V patterns corresponding to crossed and parallel polarization respectively, were measured for a typical sample of the semiflexible liquid crystal. For the annealing studies, only the H_V patterns were recorded.

RESULTS AND DISCUSSION

Figure 1 shows the H_V and V_V patterns obtained from a semiflexible polymer sample. As it can be observed, both H_V and V_V patterns show an azimuthal depence of the intensity with a four-fold symmetry. The H_V pattern shows intensity maxima at azimuthal angles of $\mu = 0°,90°...$ while in the V_V pattern the maxima occur at $\mu = 45°,135°...$ Also, at constant azimuthal angle, the intensity is found to have a maximum at a scattering angle $\theta = \theta_{max}$. Superimposed to the four-leaf clover shape, the V_V pattern shows strong intensity at zero scattering angle ($\theta = 0°$). Most of the above general features were observed for the rigid rod liquid crystal samples, the only difference being a strong intensity spot at $\theta = 0°$ for the H_V case.

The present work will not attempt to interpret the observed angular dependence of the intensity. Theoretical model calculations to account for the angular dependence of the intensity are being carried out at the present time and will be published in the near future. For the purpose of the present study, it can be stated that the small angle light scattering from polydomain nematics is a consequence of the spatial distribution of the director field $\underline{n}(\underline{r})$. The following discussion is concerned with the observed angular range of the scattered intensity which leads information on



(a) (b)

FIGURE 1. H_V (a) and V_V (b) scattering patterns from the semiflexible liquid crystalline polyester (vertical incident polarization).

the orientation correlation length. Even though the word domain is used in this work, rather than relating the orientation correlation length to a physical domain, this length parameter is interpreted in terms of a given concentration of disclination. Thus, a relatively large correlation length will indicate a relatively low concentration of disclinations (or a "large domain") and vice versa.

Figure 2 shows a sequence of H_V patterns obtained for the semiflexible liquid crystal samples annealed in the nematic phase for 30 seconds, 10 minutes and 40 minutes. A similar sequence of patterns is shown in Figure 3 for the rigid rod liquid crystal samples corresponding to samples annealed for 3, 10 and 20 seconds. As it is noticed, the H_V scattered intensity moves to smaller angles, indicating an increase in the orientation correlation length. This means that following the formation of the liquid crystalline

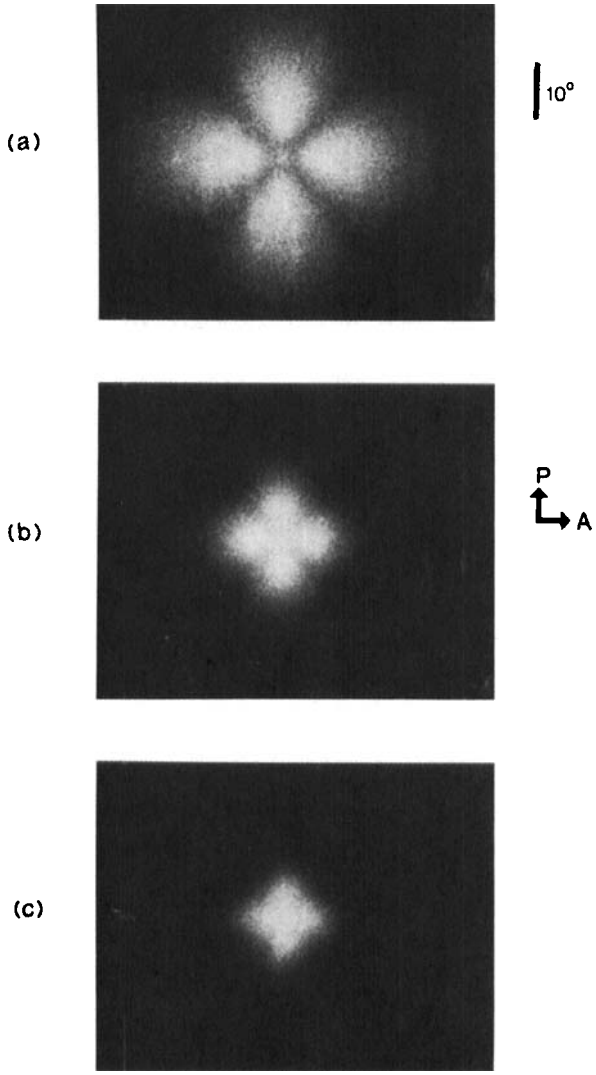


FIGURE 2. H_V scattering patterns from the semiflexible polyester after 30 sec. (a), 10 min. (b) and 40 min. (c) in the nematic phase.

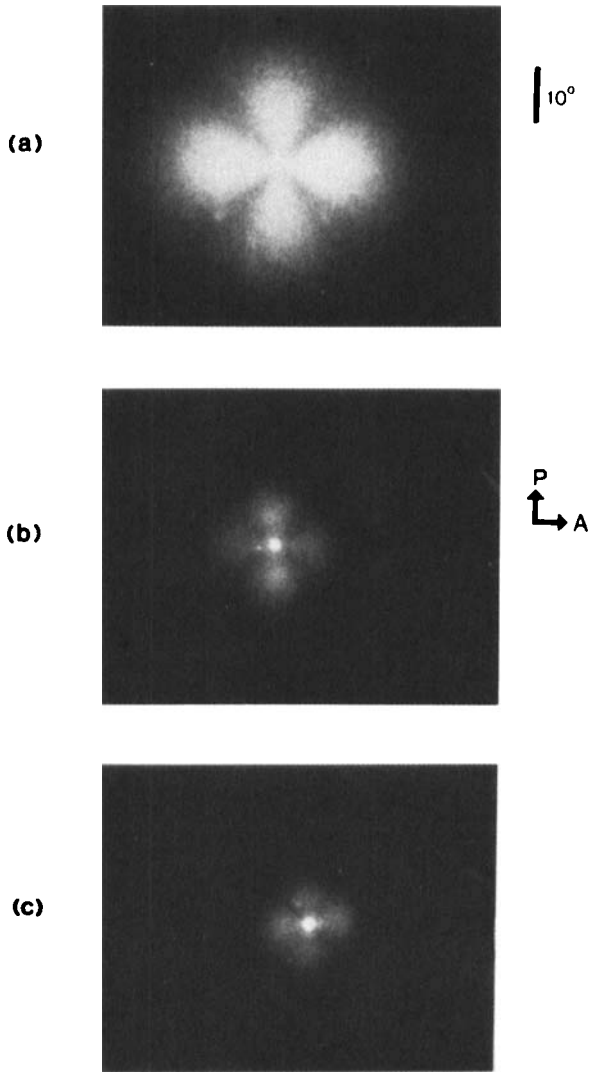


FIGURE 3. H_V scattering patterns from the Polaroid stiff rod polyester after 3 sec. (a), 10 sec. (b) and 20 sec. (c) in the nematic phase.

phase, which occurs almost instantaneously as the samples are brought into the respective temperature range, a morphological rearrangement takes place by annealing at constant temperature. This ordering process can be named a "domain growth" process. More specifically, we believe this process consists of the annihilation of disclinations. It is known that disclinations can merge, either creating a new disclination of strength $S' = S_1 + S_2$ or disappearing, if they are of opposite sign and same absolute value. Since the excess free energy of a disclination is proportional to $|S|^2$, the annihilation of disclinations of opposite sign is the energetically favored process. As a consequence of this, the number of disclinations per unit volume decreases, or in other words, the average distance between two neighboring disclinations increases.

The major difference in comparing the two kinds of polymers studied is the time scale in which the domain growth process occurs. For the semiflexible polymer this process is relatively slow, and changes in the angular range of the scattered intensity could be detected in samples annealed for up to 2 hours. For the rigid rod polymer ths significant changes in the scattering pattern occur in up to one minute. The kinetics of the annihilation of disclinations depends on the mobility of the medium as well as on the thermodynamic driving force. It appears that the striking difference observed in the time scale of the ordering process resides on the latter factor and is related to the nature of the two samples studied. The stiff chain polymer is expected to have larger Frank's elastic constant values and the orientation fluctuations due to the spatial distribution of disclinations will be less stable than for the polymer containing the flexible spacers.

CONCLUSIONS

The topological rearrangements occuring upon the formation of the nematic phase can be followed by the small angle light scattering technique. An increase in the orientation correlation length is observed due to the annihilation of defects. The kinetics of this domain growth process are found to be much faster in the rigid rod kind polymer when compared to the semiflexible one. This is believed to be due to the effect of backbone rigidity on the relative instability of the disclinations.

ACKNOWLEDGEMENTS

The authors appreciate the support of the Materials Research Laboratory of the University of Massachusetts and its grant from the Division of Materials Research of the National Science Foundation as well as from a grant from the Polaroid Corporation.

REFERENCES

1. C. Viney and A.H. Windle, J. Mater. Sci., 17, 2661 (1982).
2. C.W. Oseen, Trans. Faraday Soc., 29, 883 (1933).
3. F.C. Frank, Disc. Faraday Soc., 25, 19 (1958).
4. G. Marrucci, Proc. IX Int. Congr. Rheol. (University of Mexico, 1984).
5. B.A. Wood and E.L. Thomas, Nature, 324, 655 (1986).
6. R. Sinta, R.A. Minns, R.A. Gaudiana and H.G. Rogers, J. Polym. Sci., Polym. Lett. Ed., 25, 11 (1987).
7. A. Furukawa and R.W. Lenz, Macromol. Chem., Macromol. Symp., 2, 3 (1986).