Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

BEHAVIOR OF A LIQUID CRYSTAL POLYMER AFTER ELONGATION FLOW TREATMENT

Jiaping Lin[a]; G. Eder[b]; H. Janeschitz-Kriegl[b]
[a] Department of polymer Science and Engineering, East China University of Science and Technology, Shanghai, China [b] Institute of Chemistry, Linz University, Linz, Austria

To cite this Article Lin, Jiaping , Eder, G. and Janeschitz-Kriegl, H.(1999) 'BEHAVIOR OF A LIQUID CRYSTAL POLYMER AFTER ELONGATION FLOW TREATMENT', Journal of Macromolecular Science, Part A, 36: 4, 645 — 652
To link to this Article: DOI: 10.1081/MA-100101554
URL: http://dx.doi.org/10.1081/MA-100101554

J.M.S.—PURE APPL. CHEM., A36(4), pp. 645–652 (1999)

NOTE

BEHAVIOR OF A LIQUID CRYSTAL POLYMER AFTER ELONGATION FLOW TREATMENT

JIAPING LIN,* G. EDER, and H. JANESCHITZ-KRIEGL

Institute of Chemistry
Linz University
A-4040 Linz, Austria

Key Words: Liquid Crystal Polymer, Crystallization, Elongation Flow

ABSTRACT

Crystallization behavior of a liquid crystal copolyester of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) after an elongation flow treatment was investigated by differential scanning calorimeter (DSC), polarized light microscopy (PLM), and an instrument capable of generating elongation flow. DSC heating scans of the elongation flow treated samples exhibit an additional high temperature endothermic peak, suggesting that the high degree of molecular orientation achieved by elongation flow results in a formation of new kind of crystalline structure. The annealing effect including different temperature and time on such stretched samples has also been studied.

---

* Author to whom correspondence should be addressed.

Present address: Department of Polymer Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai (200237), China.

INTRODUCTION

The kinetics of crystallization of liquid crystalline polymers has been a matter of interest in recent time [1, 2]. It is through the investigation of crysallization kinetics that information about the nucleation process and the growth of crystals can be gained, and such information is of great interest from both theoretical and technological standpoints. The crystallization behavior of a kind of liquid crystal polymer, which receives interest widely, is the Vectra copolyesters consisting of HBA and HNA. Cheng *et al*. [3-6] showed by DSC that two transition processes have been found to occur when such copolyesters are cooled from the liquid crystal state: a fast transition process during quenching results in a pseudohexagonal packing, and a slow transition process during annealing results in an orthorhombic packing.

In the nematic melt state of liquid crystal polymers, rigid molecular chains usually arrange into a polydomain texture with high local order and long range random orientation. After an elongation flow treatment, such polydomains can be easily transformed to a monodomain texture with oriented extended chain conformation, [7] thus leading to a change in the ability of the crystallization of the liquid crystal polymers. In this work, elongation flow influence on the crystallization behavior of a liquid crystalline copolyester has been investigated. Shown by the DSC heating curve, the liquid crystal samples crystallized after elongation flow treatment exhibit an additional high temperature endothermic peak, suggesting that a high melting crystalline structure is formed after the elongation treatment. The annealing effect including different temperature and time on the stretched samples has also been studied.

EXPERIMENTAL

The liquid crystal polymer, Vectra A950 (Hoechst Corp.), is a random copolyester containing 73 mol% 4-hydroxybenzoic acid (HBA) and 27 mol% 6-hydroxy-2-naphthoic acid (HNA). The nominal melting temperature of the quiescent sample is 287°C (K→N), above which the polymer is in a nematic state. The cleaning temperature (N→I) is well above the thermal decomposition temperature. The received polymer granules were first dried under vacuum at 110°C for 24 hours, then vacuum molded into rods for various use. The quiescent samples were prepared by heating the DSC pan containing a polymer tablet to 320°C for 30 minutes, then quenching to room temperature.

The stretched samples were obtained with the aid of an instrument developed in our laboratory for the generation of elongation flow [8]. The main part of the instrument is a cylindrical reservoir with a piston inside. First the molded polymer rod was charged into the reservoir, then the it was heated to 320°C, held there for 30 minutes. Finally, the piston was moved down to extrude the fluid through the die where the elongation flow occurred in the entrance region. The elongated liquid crystal melt was quenched to room temperature where the crystallization process took place. The standard nominal elongation rate used in the sample preparation was 23s-1. The thermal properties of the samples were investigated using a Perkin-Elmer DSC-7 differential scanning calorimeter under N2 purger. For the annealing studies, the DSC pan which contained either a quiescent or a stretched sample was first heated to a programmed temperature for a fixed period of time, then quenched into ice water.

RESULTS AND DISCUSSION

Formation of High Melting Crystalline Structures

Shown in curve a of Figure 1 is the DSC heating scan of a quiescent sample. A melting peak located at 287°C with a latent heat of 0.70 J/g is demon-

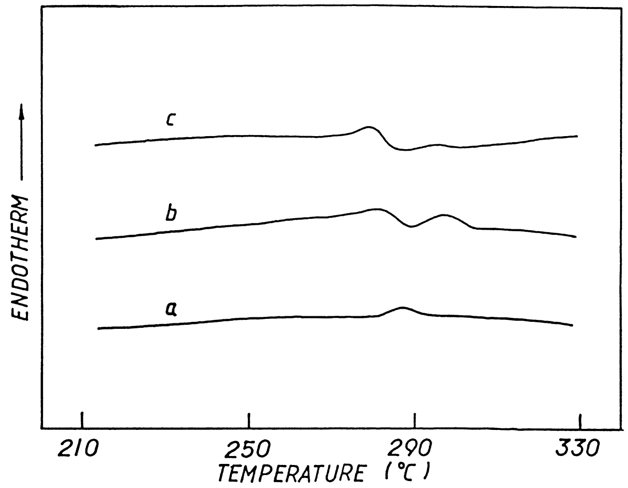

Figure 1. DSC scans at a heating rate of 10°C/min of copolyester samples prepared with different conditions: (a) quiescent sample, (b) stretched sample, and (c) stretched sample after being heated to 320°C, held there for 30 minutes, then quenched to room temperature.

strated. This peak temperature is called nominal melting temperature, above which the polymer is in a nematic state, [9, 10] even if the formation of crystalline structure is not yet completed under the present condition employed. The DSC first heating curve of the stretched sample, shown by curve b of Figure 1, displays two separate endothermic peaks. The first peak is at about 281°C, corresponding to the nominal melting temperature of the polymer. The second peak at about 298°C is believed to be due to the melting of the crystalline structure that is formed after an elongation flow treatment of liquid crystal melt. The fusion heats are 0.83J/g and 0.56J/g for the first and second peaks respectively. The high melting crystal structure formed after elongation treatment is thermally reversible. After heating the stretched sample to 320°C for 30 minutes, then quenching it to room temperature, the high melting peak almost disappears as demonstrated by curve c in Figure 1. The low melting peak in curve c is lower than the quiescent sample. It may be due to the fact that the crystals with such a lower melting temperature formed in the extruding process were not well developed compared to the quiescent sample. The lower peak is for the entire experiment. According to the optical observations, (Figure 1), to the left of the peak the polymer is in the crystal state, while to the right it is in the nematic state. The morphological textures of both stretched and quiescent samples can also be easily observed. Regarding the stretched sample, a homogenous supermolecular structure is obtained with orientation parallel to the extruding direction. The morphology, as obtained with the sample quenched from quiescent melt to room temperature, shows a texture with high birefringence and many small colored domains. For the sample used for curve c, the oriented fibril texture almost disappears an a texture which is more like that of the quiescent sample, is shown.

It is observed that two separate processes exist in the crystallization of most thermotropic liquid crystalline polymers. Studies reported by Cheng *et al.* [3-6] show that two transition processes occur during the transitions from the nematic to solid state for the copolyesters of HBA/HNA. A fast transition process takes place via aggregation of the molecules within a very short time period during quenching, and later, a slow transition process develops gradually. Since the fast cooling rate under the present experimental condition employed could prevent the slow transition process from occurring, the crystals observed in both stretched and quiescent samples are those developed in the fast transition process. Cheng *et al*. attributed the fast process as originating from relatively ordered chains in the nematic state. On the basis of this argument, it is reasonable to expect that changing the nematic order through elongation flow before the rapid cooling should affect the fast crystal formation process. A model proposed by Windle *et al.* [11] suggests that identical sequences in random copoly(HBA/HNA) chains match each other laterally, forming nonperiodic crystals that have three dimensional order. In the present study, where the random copolyester contains 73 mol% HBA, statistical analysis supports the presence of long HBA blocks in the random chains. After an elongation flow treatment, the extended molecular chains are oriented, which would lead to a lower translational energy barrier. Thus, the lateral matching of the identical HBA sequences could be greatly facilitated to form crystallites consisting of sufficiently long HBA repeat units. The high degree of perfection of these crystallites might be responsible for the high melting point crystals.

Annealing Effects

Stretched samples for annealing were first heated to a temperature (T_a), ranging from 260°C to 290°C, kept there for 1 hour, then quenched to ice water. The DSC heating curves of these samples are shown in Figure 2. When Ta is between 260°C and 280°C, the DSC curve shows two melting peaks. The lower temperature peak is identical with the nominal melting peak observed for the quiescent samples and the other melting peak corresponds to the melting peak of the high melting crystal. Within this tempera-

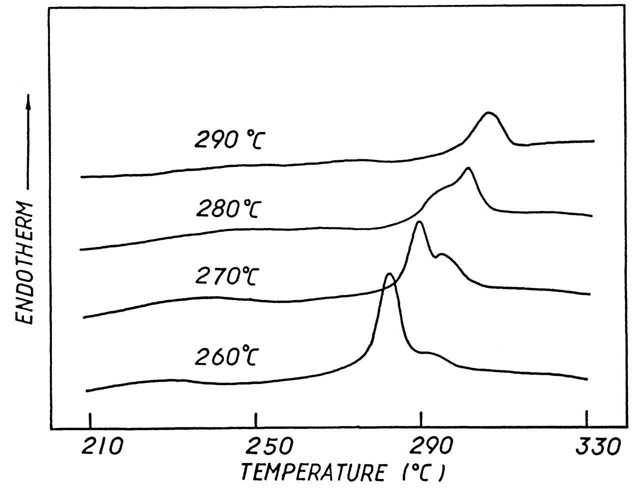

Figure 2. Effect of annealing temperature on the melting behavior of stretched samples. The annealing time was 60 minutes.

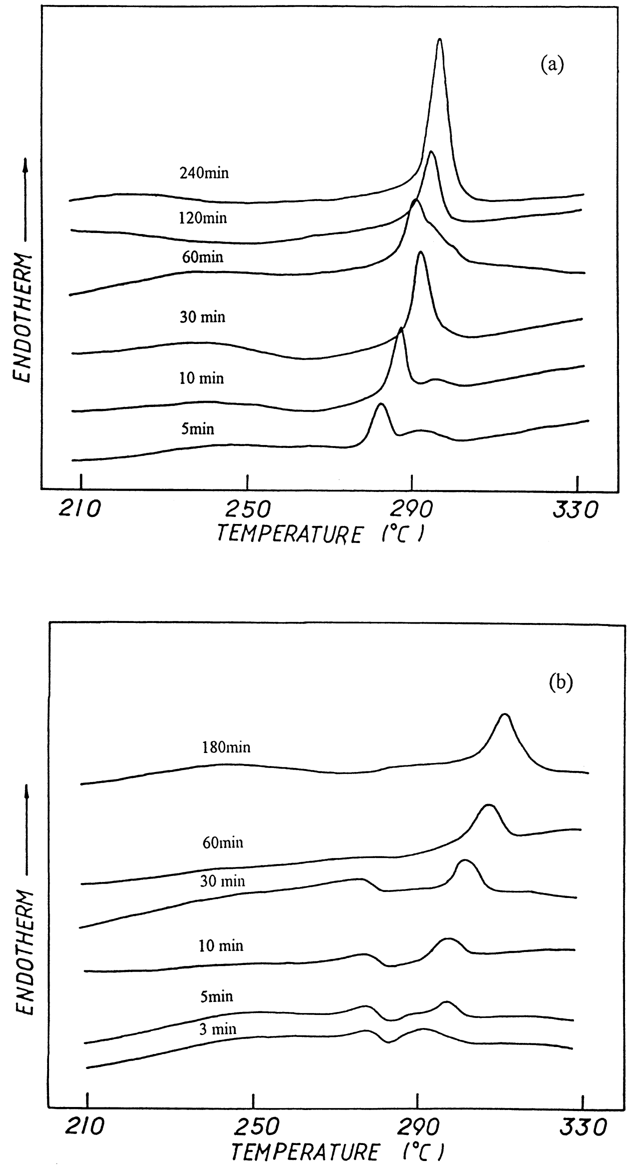

Figure 3. Effect of annealing time on the melting behavior of stretched samples. The annealing temperature was 270°C (a), 290°C (b).

ture range, both melting temperatures increase with annealing temperature. At T_a= 290°C, the nominal melting peak as observed with the quiescent samples almost disappears, and only the melting process of the high melting crystal can be observed.

For further annealing studies, two annealing temperatures were chosen. The first temperature is 270°C, which is below the nominal temperature. The second temperature applied is 290°C, which is between the nominal melting temperature and the melting temperature of the high melting crystal. Figure 3(a) shows a set of DSC melting traces for the stretched samples annealed at 270°C for different lengths of time. With an increase in time, both melting peaks of nominal crystal and high melting crystal continuously shift to high temperatures. However, the annealing effect seems to have less influence on the high melting crystal. After about 1 hour, the two melting peaks eventually overlap completely. Figure 3(b) represents a set of DSC heating traces for the stretched samples which were annealed at 290°C for different annealing times. For short annealing times, it is clear that two peaks contributed by nominal melting and high melting crystal can be observed. With increasing annealing time, the nominal melting peak gradually turns flat and finally disappears. However, the effect on the high melting crystals is more pronounced as it can be seen from Figure 3(b). Since the crystals formed through quenching processes under the present condition employed can be further grown and perfected in annealing, the crystallinity may increase with annealing time. The higher crystallinity achieved in long time annealing (180 minutes) could give rise to an endotherm higher than that for other conditions in Figure 3(b).

CONCLUSION

Crystallization behavior of liquid crystal polymers is a new area of macromolecular research. Interest in this research field is growing rapidly. The knowledge obtained from this study has provided a possible way of obtaining a liquid crystal polymeric material with enhanced thermal resistance and mechanical properties.

ACKNOWLEDGEMENTS

J. Lin takes pleasure in acknowledging his gratitude to the Austria Science Foundation for awarding a Lise-Meitner fellowship.

REFERENCES

[1] J. Grebowicz and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed., 21*, 141 (1983).

[2] G. D. Butzbach, J. H. Wendorff, and H. J. Zimmermann, *Polymer, 27*, 1337 (1986).

[3] S. Z. D. Cheng, *Macromolecules, 21*, 2475.

[4] S. Z. D. Cheng, J. J. Janimak, A. Zhang, and Z. Zhou*, Macromolecules, 22*, 4240 (1989).

[5] S. Z. D. Cheng, A. Zhang, R. L. Johnson, Z. Wu, H. H. Wu, *Macromolecules, 23*, 1196 (1990).

[6] R. L. Johnson and S. Z. D. Cheng, *Macromolecules, 26*, 94 (1993).

[7] T. Asada, in *Polymer Liquid Crystal*, A. Ciferri, W. R. Krigbaum, and R. B. Meyer, Eds., Academic, New York, 1982.

[8] M. E. Mackay, A. M. Dajan, H. Wippel, H. Janeschitz-Kriegl, and M. Lipp, *J. Rheol., 39*, 1 (1995).

[9] Y. G. Lin and H. H. Winter, *Macromolecules, 21*, 2439 (1988).

[10] Y. G. Lin and H. H. Winter, *Macromolecules, 24*, 2877 (1991).

[11] S. Hanna and A. H. Windle, *Polymer, 29*, 207 (1988).

Received May 18, 1998
Revision received December 10, 1998

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 13:27 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081MA100101554