(16) Torkelson, J. M.; Lipsky, S.; Tirrell, M. *Macromolecules* **1981**, *14*, 1601.
(17) Torkelson, J. M.; Lipsky, S.; Tirrell, M.; Tirrell, D. A. *Macromolecules* **1983**, *16*, 326.
(18) Abuin, E.; Lissi, E.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1984**, *20*, 105.
(19) Lindsell, W. E.; Robertson, F. C.; Soutar, I. *Eur. Polym. J.* **1981**, *17*, 203.
(20) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1973**, *9*, 1315.
(21) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.
(22) Turro, N. J.; Okubo, T. *J. Phys. Chem.* **1982**, *86*, 1485.
(23) Ander, P.; Mahmoudhagh, M. K. *Macromolecules* **1982**, *15*, 214.
(24) Major, M. D.; Torkelson, J. M. *Macromolecules* **1986**, *19*, 2801.
(25) Frank, C. W.; Semerak, S. N. *Adv. Polym. Sci.* **1984**, *54*, 31.
(26) Oyama, H. T.; Tang, W. T.; Frank, C. W. *Macromolecules* **1987**, *20*, 474.
(27) Morishima, Y.f Kobayashi, T.; Nozakura, S.; Webber, S. E. *Macromolecules* **1987**, *20*, 807.
(28) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic: New York, 1973; p 114.

Formation of a High Melting Crystal in a Thermotropic Aromatic Copolyester

Y. G. Lin and H. H. Winter*

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received September 28, 1987*

ABSTRACT: The formation of a high melting crystal during melt annealing is observed for a thermotropic liquid crystalline polymer (LCP), VECTRA A900 of Celanese Corp. When the polymer is heated to 290 °C, i.e. just above its nominal DSC melting temperature of about 280 °C, it melts rapidly, displaying a low complex modulus of about 10^3 Pa. However, during annealing at this same temperature, the nematic melt slowly crystallizes and undergoes a liquid/solid transition, as shown by a gradual increase in the complex modulus by 3 orders of magnitude in 200 min. For DSC and X-ray studies, a discrete set of samples were prepared with increasing time of annealing at 290 °C and subsequent cooling to room temperature. Wide-angle X-ray scattering patterns of these samples shows an additional reflection ring with d = 3.8 Å. In the DSC first heating scan, the annealed samples display two separated endothermic peaks. The first peak is about 280 °C; the second peak is 20–30 K above the annealing temperature. The unannealed samples have only the first peak. As the annealing time increases, the first peak decays and the second peak grows and moves from 305 to 315 °C. The growth of the complex modulus is found to be proportional to the area under the second endothermic peak. All these observations indicate a gradual formation of a high melting crystal with a higher degree of order. The formation of the high melting crystal is thermoreversible. After being heated to a temperature above the DSC second endothermic peak, the annealed samples return to their initial state before annealing, displaying once again low complex modulus and a single endothermic peak. The rate of the crystallization depends on annealing temperature and on mechanical and thermal histories of the samples. Higher annealing temperature leads to slower crystallization. At 290 °C, stretched samples exhibit accelerated crystallization. It is interesting to note that samples which have been subjected to a prior heating to 320 °C do not show significant crystallization at 290 °C. This indicates that the crystallization is a nucleation and growth process and that the nuclei melt during the preheating to 320 °C.

Introduction

The crystallization behavior of liquid crystalline polymers (LCPs) has been the subject of several recent publications.[1-6] It is well-known that for flexible polymers the crystallization process can be quite rapid[7,8] because the flexible molecular chains can readily adjust their sequences into a growing crystalline structure. However, it is much more difficult for the rigid molecular chains of LCPs to diffuse appropriate sequences into a crystal growing location.[1] In the nematic melt state, rigid molecular chains arrange into a polydomain texture with high local order and long-range random orientation.[9-16] The local order determines the crystallization process. The crystals have little long-range order.[1] A matter worthy of note is that thermal and mechanical treatments can alter the local order[5,6,12-15] and hence can change the ability of crystallization of LCPs. These characteristics of LCPs complicate the phase behavior and the rheology in a wide temperature range.

Severe time dependence of rheological properties in the nematic melt state has been recently reported for copolymers of 73 mol % 4-hydroxybenzoic acid and 27 mol % 6-hydroxy-2-naphthoic acid in capillary flow[3] and for a quaterpolymer of chalorhydroquinone, 4,4′-dihydroxydiphenyl, terephthalic acid, and resorcinol in a mole ratio of 40/10/35/15 in dynamic mechanical measurements.[2] In both cases, DSC curves of the annealed samples showed a second endothermic peak at a temperature above the annealing temperatures. It is expected that these changes of rheology resulted from formation of some high melting crystalline structure.

Recently, a commercial liquid crystalline aromatic polyester (VECTRA A900, Celanese Corp.) has been extensively studied in our laboratory.[5,6] When this polymer is kept under isothermal conditions slightly above the melting temperature, its rheological stability depends strongly on prior thermal treatment. After preheating to 320 °C, the polymer melt shows relatively stable rheological properties throughout several hours.[6] However, if the sample is just melted and kept at 290 °C, without prior heating to an elevated temperature, the polymer melt displays a severe increase in the complex modulus. In the present work, these experimental observations are related to a gradual formation of a high melting crystal.

Experimental Section

The liquid crystalline polymer studied, VECTRA A900 (Celanese Corp.), is a random copolymer containing 73 mol % 4-hydroxybenzoic acid (HBA) and 27 mol % 6-hydroxy-2-naphthoic

0024-9297/88/2221-2439$01.50/0

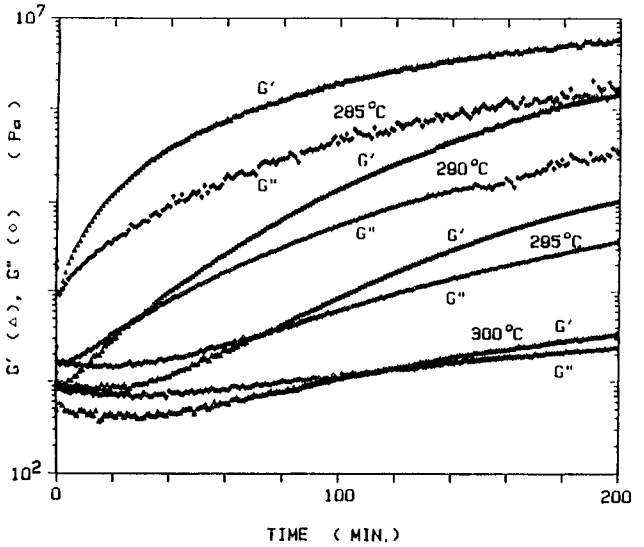

Figure 1. Evolution of apparent storage modulus, G', and apparent loss modulus, G'', at the indicated annealing temperatures. The time sweep started as soon as the sample was heated to the desired temperature, at a frequency of 1 rad/s and a strain amplitude of $\gamma_R = 0.005$.

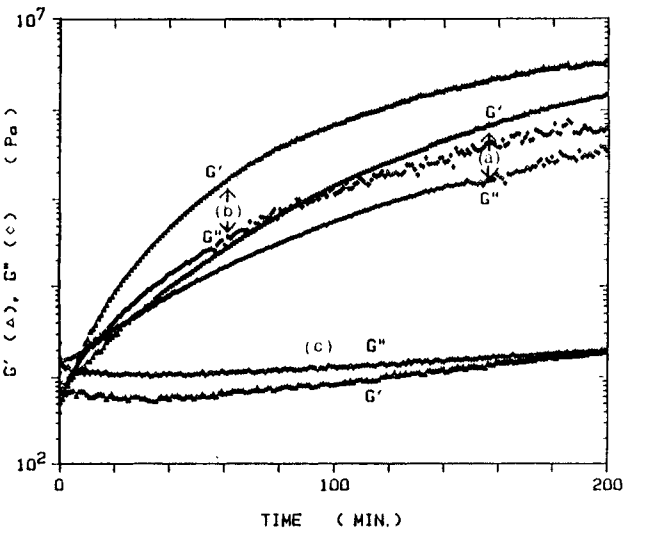

Figure 2. Evolution of apparent storage modulus, G', and apparent loss modulus, G'', during isothermal annealing at 290 °C: (a) molded sample; (b) stretched sample; (c) sample had been subjected to prior heating to 320 °C.

acid (HNA). The nominal DSC melting temperature is about 280 °C, above which the polymer is in a nematic state. The clearing temperature is well above the thermal decomposition temperature.

The received polymer pellets were ground into powder and then dried under vacuum at 120 °C for 20 h. Two kinds of samples were prepared for the study: A first set of samples with no obvious molecular orientation were vacuum molded at 320 °C into disks (d = 25 mm, h = 1 mm) and quiescently cooled to room temperature. A second set of samples with planar molecular orientation were prepared by using the lubricated squeezing technique[5,17,18] on a linear rheometer (Rheometrics RDS-LA). Molded samples with initial thickness of 3.2 mm were quickly heated to 310 °C and then cooled with a rate of about −20 K/min under nitrogen. While cooling, the samples were rapidly stretched at 270 °C to the final thickness of 1.0 mm.

Rheological measurements during isothermal annealing were performed on a Rheometrics dynamic spectrometer (RDS). Placed between two parallel plates of the rheometer, a sample was heated to the desired temperature (285, 290, 295, or 300 °C) and held there for isothermal annealing. The apparent storage modulus G′ and apparent loss modulus G″ were measured at constant frequency (1 rad/s) and a strain amplitude of $\gamma_R = 0.005$. After having annealed for a prescribed time, the sample was cooled (−20 K/min) to room temperature and then taken out from between the plates for X-ray and DSC analyses.

Wide-angle X-ray scattering was made at room temperature, using Cu Kα radiation and a Ni-filtered statton camera. The sample to film distance was 53 mm.

Differential scanning calorimetry was carried out on a Perkin-Elmer calorimeter with Model 3500 data station. The scanning rate was 20 K/min, and the sample weight was about 20 mg.

Results and Discussion

The apparent storage modulus G' and the apparent loss modulus G'' of molded samples increased substantially during isothermal annealing (Figure 1). When a sample was annealed at 290 °C, G' and G'' increased by 3 orders of magnitude in 200 min. As the annealing temperature increased, the sample showed slower increase in the moduli. In each case, G' increased faster than G''; i.e., there was an increase in the relative elasticity. This phenomenon has also been observed when the super-cooled melt of the same polymer was annealed at a constant temperature below the melting temperature.[6] It could indicate the phase transition into the solid state. At 285 °C, the initial moduli were unusually high, indicating that the sample had not been completely melted.

The dynamic mechanical measurement has no effect on the modulus growth during annealing. Samples that were annealed under continuous shear oscillation at small strain amplitude ($\gamma_R = 0.005$) showed the same growth rate as samples that were quiscently annealed.

The growth rate of the moduli depends not only on annealing temperature but also on the mechanical and thermal histories. At 290 °C, a stretched sample, in which lubricated squeezing had induced planar molecular orientation,[5] showed faster increase in the moduli than the molded sample (Figure 2). However, the effect of mechanical history notably abated as the annealing temperature increased. At temperatures above 300 °C, the effect of mechanical history was rather negligible. This phenomenon can be attributed to the fact that the molecular orientation present in a stretched sample relaxes quickly at high temperatures.

The effect of prior heating to an elevated temperature is also shown in Figure 2. In the rheometer, a sample was first heated to 320 °C, held there for 1 min, and then cooled to 290 °C for isothermal annealing. This sample exhibited only slight increase in the moduli in 200 min. In this experiment, molded samples and stretched samples displayed the same behavior, indicating that prior heating to an elevated temperature can erase the effect of mechanical history and result in a relatively stable nematic melt state of the polymer.

The modulus growth which occurs during isothermal annealing is thermoreversible. As shown in Figure 3, a molded sample was annealed at 290 °C for 100 min, then heated to 320 °C, and cooled back to 290 °C for the next 100 min. The moduli G' and G'' of the sample increased by about 2 orders of magnitude in the first 100 min and then dropped to the initial values upon heating. When the temperature restabilized at 290 °C, the moduli grew slowly, as is the case for a sample which had been initially preheated to an elevated temperature (compare with curve c of Figure 2). However, after heating to 320 °C in the end of the first 100 min, if the sample was cooled to a temperature low enough for rapid solidification (e.g. 220 °C) and then heated back to 290 °C for the second time of annealing, it behaved like a fresh sample, displaying a rapid increase in the moduli. This observed thermoreversibility suggests that the modulus growth results from a physical change rather than from a chemical change.

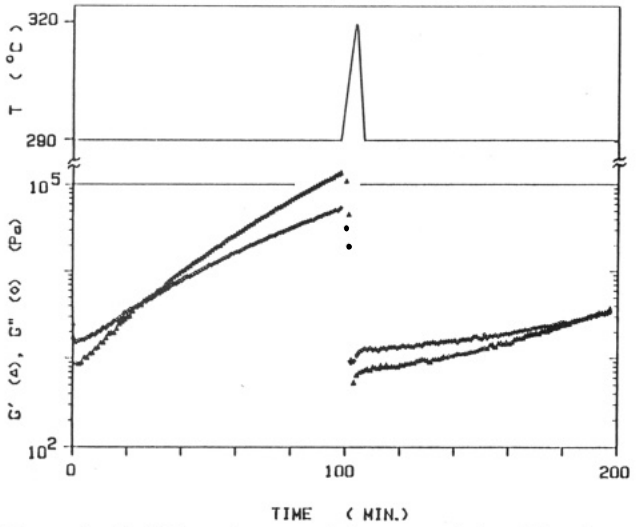

Figure 3. Evolution of apparent storage modulus, G', and apparent loss modulus, G'', of a molded sample annealed at 290 °C. In the end of the first 100 min, the sample was rapidly heated to 320 °C and then cooled back to 290 °C.

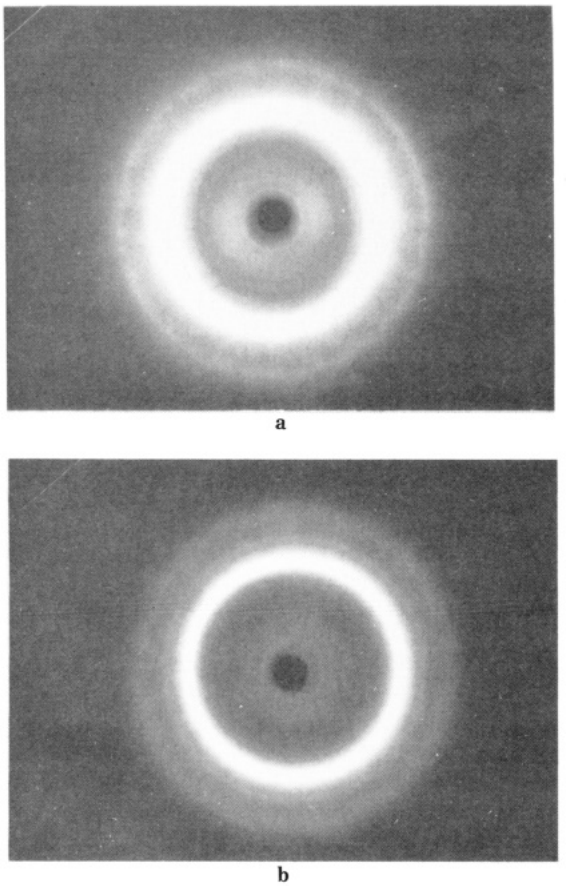

Figure 4. Wide-angle X-ray scattering patterns of (a) molded sample before annealing and (b) molded sample after 200 min isothermal annealing at 290 °C.

In the wide-angle X-ray scattering patterns, the unannealed samples had reflections at d = 6.8, 4.6, 3.3, and 2.1 Å (Figure 4a), conforming with the data reported in the literature for this polymer.[19-22] However, the annealed sample showed an additional reflection ring at d = 3.8 Å (Figure 4b). This observation indicates that perfection of crystalline structure occurred during annealing.

Figure 5 shows the DSC curves of the first heating scan on the molded samples that had been annealed at the indicated temperatures for 200 min. The annealed samples

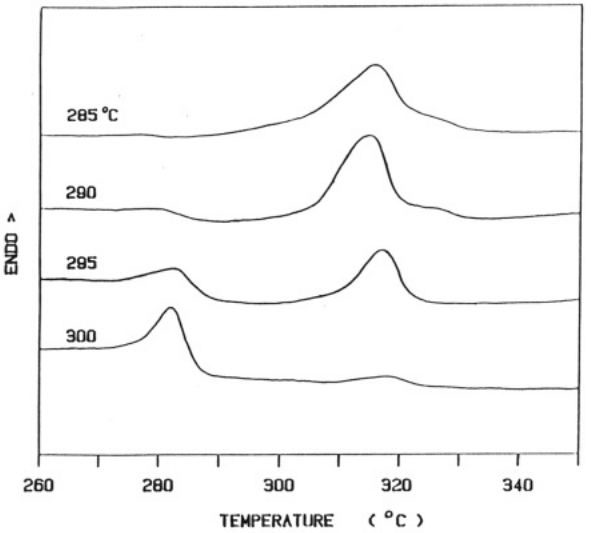

Figure 5. DSC curves of molded samples which had been annealed at the indicated temperature for 200 min and then cooled. The scanning rate was 20 K/min.

displayed two separate endothermic peaks. The first peak is at about 280 °C, corresponding the initial melting temperature of the polymer. The second peak at about 315 °C is believed to be due to the melting of the structure-improved crystal that was formed during annealing. It can be seen that the formation of the high melting crystal depends on annealing temperature. Higher annealing temperature results in a lower rate of the crystallization. A matter worthy of note is that the high melting crystal has a melting point much higher than the annealing temperatures; i.e., a crystalline solid was formed during the isothermal annealing of the nematic melt.

The effect of annealing time on the formation of high melting crystal shows in the DSC curves of Figure 6. As the annealing time increased, the disappearance of the initial structure (melting peak $T_m \approx 280$ °C) and the appearance of the higher ordered structure (melting peak $T_m \approx 315$ °C) is clearly seen. The effect is more pronounced with stretched samples (Figure 6b) than with molded samples (Figure 6a). The area under the DSC second peak increased linearly during the first 150 min of annealing (Figure 7).

The effect of prior heating to a high temperature has been also shown by DSC. After preheating to 320 °C, the followed isothermal annealing at 290 °C did not give rise to significant crystallization; i.e., the second endothermic peak did not appear in the DSC curves of the first heating scan. This result confirms the rheological measurement (see curve c of Figure 2).

The dynamic modulus is a sensitive measure to follow structural changes. However, by itself it does not give any indication about the type of structural change. Figure 8 compares the increasing modulus with the increasing melting heat of the high melting crystal. Two linear regimes are found in the semilogarithmic plot. Both molded samples and stretched samples show the same relations between the moduli G' and G'' and the melting heat ΔH_2. This suggests that when the polymer is annealed at a temperature slightly above its initial melting point, the rate of modulus growth are mainly determined by the rate of crystallization.

Conclusions

After preheating to 320 °C, the melt of VECTRA A900 shows relatively stable rheological properties over long time at temperatures above the melting temperature. This is

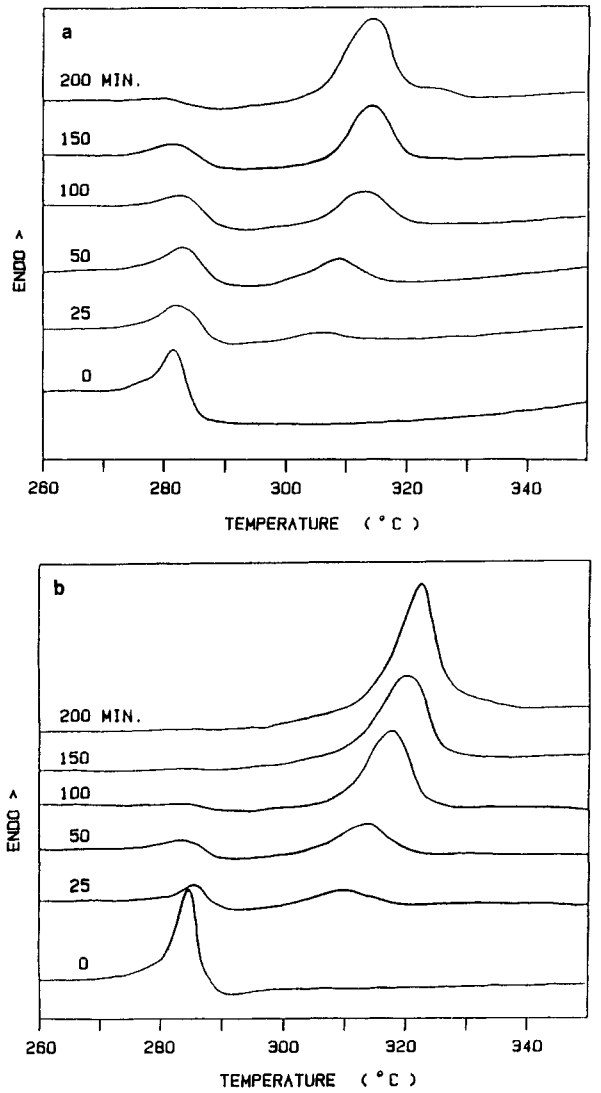

Figure 6. DSC curves of (a) molded samples and (b) stretched samples. Parameter is the isothermal annealing time at 290 °C. The scan rate was 20 K/min.

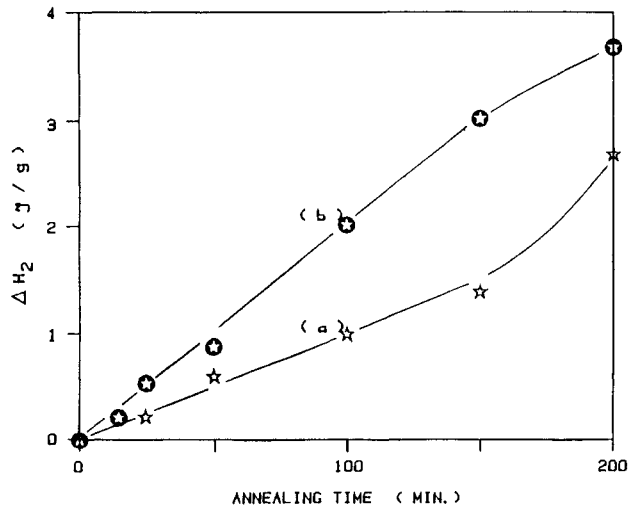

Figure 7. Melting heat of the new crystal, ΔH_2, is plotted as a function of annealing time at 290 °C: (a) molded samples; (b) stretched samples.

in good agreement with our earlier work.[6] However, when the same polymer is annealed at a temperature slightly above the melting point without prior heating to an elevated temperature, it displays a notable growth of the complex modulus and relative elasticity. This decrease in molecular mobility results from a gradual formation of high melting crystals with improved order, as confirmed by an additional reflection ring at d = 3.8 Å in the wide-angle X-ray scattering patterns and by an increased second endothermic peak in the DSC curves. The rate of this crystallization depends on annealing temperature and mechanical history. Higher annealing temperature leads to a slower crystallization. Stretched samples exhibit an accelerated crystallization. The effect of mechanical history is believed to be due to flow-induced molecular orientation, as we found earlier that flow-induced molecular orientation can notably accelerate crystallization in the super-cooled melt of the same polymer.[5]

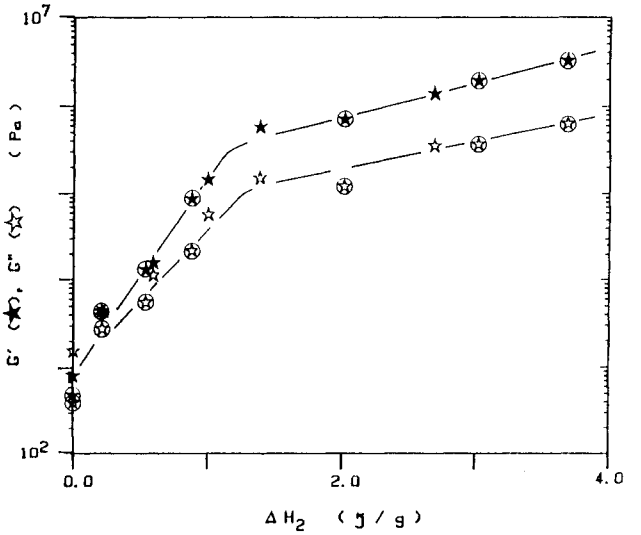

Figure 8. Apparent storage modulus, G', and apparent loss modulus, G'', are plotted as a function of the melting heat of the new crystal. The samples were annealed at 290 °C. The circled points present the data from stretched samples.

The type of higher order in the polymer is not yet known. It can be hypothesized that similar block sequences in chains associate between molecules[1] or the molecules pack into a structure of higher order.

LCPs exhibit a melting temperature range due to the various degrees of local order. We attribute the stabilizing effect of preheating to 320 °C to the melting of all residual crystallites which otherwise would play the role of nuclei of the crystallization above melting temperature. It is expected that the crystallization occurs in two steps, nucleation and growth. The nucleation rate is much lower than the growth rate. After preheating to 320 °C, the crystallization is suppressed due to lack of nuclei. The effect of residual crystallites on the rheological stability of LCPs will be studied further in our laboratory.

It is expected that during annealing at a certain temperature range above the initial melting point, the formation of high melting crystalline structure could occur in a wide variety of LCPs. Further study in this phenomenon will help us to improve the understanding of the unusual rheological behavior of LCPs and to get materials with increased thermal resistance.

Acknowledgment. Financial support through National Science Foundation Grant MSM-860 6223 is gratefully acknowledged. We thank Celanese Corp. for supplying the polymer sample.

Registry No. (HBA)(HNA) (copolymer), 81843-52-9.

References and Notes

(1) Butzbach, G. D.; Wendorff, J. H.; Zimmermann H. J. *Polymer* 1986, 27, 1337.

(2) Gochanour, C. R.; Weinberg, M. *J. Rheol.* **1986**, *30*(3), 601.
(3) Wissbrun, K. F.; Kiss, G.; Cogswell, F. N. *Chem. Eng. Commun.* **1987**, *53*, 149.
(4) Done, D.; Baird, D. G. *Polym. Eng. Sci.* **1987**, *27*(11), 818.
(5) Lin, Y. G.; Winter, H. H.; Lieser, G. *Liq. Cryst.*, in press.
(6) Lin, Y. G.; Winter, H. H. *Liq. Cryst.*, in press.
(7) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.
(8) Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1973; Vols. 1 and 2.
(9) Onogi, S.; Asada, T. *Rheology and Rheo-optics of Polymer Liquid Crystals*; Astariata, G., Marrucci, G., Eds.; Plenum: New York, 1980; vol. 1, p 127 (papers presented at Eighth International Congress on Rheology, Naples, 1980).
(10) Asada, T. *Rheo-optical Studies of Polymer Liquid Crystalline Solution, Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic: New York, 1982; Chapter 9.
(11) Wissbrun, K. F. *Br. Polym. J.* **1980**, 163.
(12) Marrucci, G. Proceedings of the IX International Congress on Rheology, University of Mexico, 1984.
(13) Wissbrun, K. F. *Faraday Discuss., Chem. Soc.* **1985**, *79*, 161.
(14) Graziano, D. J.; Mackley, M. R. *Mol. Liq. Cryst.* **1984**, *106*, 73.
(15) Marrucci, G. *Pure Appl. Chem.* **1985**, *57*, 1545.
(16) Wood, B. A.; Thomas, E. L. *Nature (London)* **1986**, *324*, 655.
(17) Chatraei, S.; Macosko, C. W.; Winter, H. H. *J. Rheol.* **1981**, *25*, 433.
(18) Soskey, P. R.; Winter, H. H. *J. Rheol.* **1985**, *29*, 493.
(19) Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983**, *24*, 937.
(20) Blackwell, J.; Gutierrez, G. A.; Chivers, R. A. *Macromolecules* **1984**, *17*, 1219.
(21) Chivers, R. A.; Blackwell, J.; Gutierrez, G. A. *Polymer* **1984**, *25*, 435.
(22) Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55.

State of Aggregation and Surface Chemical Composition of Composite Thin Films Composed of Poly(vinyl alcohol) and Fluorocarbon Amphiphile

Atsushi Takahara, Nobuyuki Higashi,† Toyoki Kunitake,† and Tisato Kajiyama*

Departments of Applied Chemistry and Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan. *Received October 5, 1987*

ABSTRACT: Structural characterization of composite thin films composed of poly(vinyl alcohol) and a fluorocarbon amphiphile has been carried out. The wide-angle X-ray diffraction study revealed that the fluorocarbon amphiphile in the composite thin film forms bimolecular lamellae. The bimolecular lamellae were oriented parallel to the surface of the composite thin films. X-ray photoelectron spectroscopy showed enrichment of fluorocarbon groups on the surface of the composite thin film owing to the lower surface free energy of fluorocarbon groups compared with that of PVA. The surface of the composite film is completely covered with fluorocarbon amphiphilic molecules even when the weight fraction of fluorocarbon amphiphile is very small.

Introduction

Organic compounds containing fluorocarbon components show unique properties due to the low surface free energy of CF_2 and CF_3 groups. Some fluorocarbons have been used as artificial blood since they dissolve molecular oxygen very well.[1,2] One of the authors succeeded in preparing an oxygen enrichment membrane composed of polymer, liquid crystal, and fluorocarbon monomers.[3,4] One of the most important industrial application of organic compounds containing fluorine is the surface treatment of textiles and plastics by utilizing the surface-active effect of fluorocarbon groups.[5] As adhesion between a fluorocarbon surface and other compounds is very weak, such surfaces show nonadhesive properties. Therefore, the characteristic property for preventing contamination of surfaces is obtained by adding a small amount of surfactant containing fluorocarbon groups.[3]

A series of amphiphiles containing fluorocarbon have been synthesized by Kunitake and co-workers.[6,7] Fluorocarbon amphiphiles form a bilayer structure in water and exhibit phase transition behavior similar to that observed for biological lipids or other artificial hydrocarbon amphiphiles.[8-10] The fluorocarbon amphiphiles can be immobilized by casting a water solution of amphiphile with aqueous poly(vinyl alcohol). A gas permeation experiment through this immobilized film revealed that the permeation rate of oxygen was 2.4–2.7 times as fast as that of nitrogen.[11] This oxygen-enriching property was observed even when the weight content of fluorocarbon amphiphile was less than 10%.

In this paper, the surface chemical composition of the composite thin film composed of poly(vinyl alcohol) and fluorocarbon amphiphile has been studied by X-ray photoelectron spectroscopy. Also, the state of aggregation of the components was investigated on the basis of X-ray diffraction studies and morphological observation.

Experimental Section

1. Sample Preparation. The fluorocarbon amphiphile and polymer used in this study are shown in Figure 1. The amphiphile containing fluorine was prepared by the standard procedure.[6,7] The fluorocarbon amphiphile forms a stable bilayer membrane in water. The fluorocarbon amphiphile was dispersed in water by sonication and the dispersion was mixed with a water solution of poly(vinyl alcohol) (PVA) (MW = 154 000). The composite thin film was prepared by casting a water solution of PVA with the fluorocarbon amphiphile on a clean glass plate at room temperature; the cast film was then extensively dried in vacuo. The weight fraction of the fluorocarbon amphiphile in the composite thin film was varied from 19 to 83 wt %.

2. Measurements. In order to characterize the state of aggregation of PVA and the fluorocarbon amphiphile in the composite thin films, scanning electron micrograph (SEM) observation and X-ray diffraction study were carried out. The morphological observation of the composite thin film was carried out by using

* Author to whom correspondence should be addressed.
† Departments of Applied Chemistry and Organic Synthesis.

0024-9297/88/2221-2443$01.50/0