Effect of Thermal History on the Rheological Behavior of a Thermotropic Liquid-Crystalline Polymer

Seung Su Kim and Chang Dae Han*

Department of Chemical Engineering, Polytechnic University, Brooklyn, New York 11201

Received November 24, 1992

ABSTRACT: The effect of thermal history on the rheological behavior of a thermotropic liquid-crystalline polymer was investigated. For the study, an aromatic polyester, poly[(phenylsulfonyl)-*p*-phenylene-1,10-decamethylenebis(4-oxybenzoate)] (PSHQ10), was synthesized. PSHQ10 was found to have (a) a weight-average molecular weight of 35 000 relative to polystyrene standards and the polydispersity index of 2.0, (b) a glass transition temperature of 80 °C, (c) a melting point of 110 °C, and (d) a nematic–isotropic transition temperature (T_{NI}) of 175 °C. Dynamic storage and loss moduli, G' and G'', in the oscillatory shear mode were measured during isothermal annealing for specimens of PSHQ10 having various thermal histories. We found that thermal history had a profound influence on the rheological behavior of PSHQ10; specifically, during isothermal annealing in the nematic region, the values of G', G'', and complex viscosity $|\eta^*|$ of the as-cast specimen increased with time much faster at 130 °C than at 135 and 140 °C, but at temperatures above 140 °C the values of G', G'', and $|\eta^*|$ initially decreased and then increased, finally leveling off after a very long annealing period (for instance, 500 h after the annealing began at 145 °C). Using information obtained from differential scanning calorimetry, we explained the seemingly peculiar behavior in terms of a slow process of "crystal-like phase" formation below ca. 140 °C. However, when the as-cast specimen was first heated to a temperature above T_{NI}, subjected to steady shear flow at $\dot{\gamma}$ = 0.085 s^{-1} for 5 min, and then cooled slowly down to the nematic region, the values of G', G'', and $|\eta^*|$ were found to change little during the subsequent annealing for a long period. Also conducted were light scattering experiments on as-cast specimens of PSHQ10 having different thermal histories. We found that during isothermal annealing the maximum intensity of scattered light increased faster as the annealing temperature increased, and the rate of "domain" coarsening, induced by isothermal annealing in the nematic range, increased as the annealing temperature increased. This finding was corroborated by the micrographs taken with a cross-polarized optical microscope.

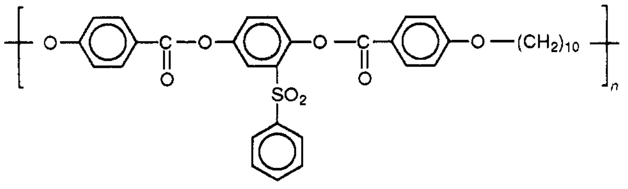
Introduction

The rheological behavior of thermotropic liquid-crystalline polymers (TLCP) is dependent upon the temperature of the melt and the intensity of an applied external flow field. Rheological study of TLCP began with Jackson and Kuhfuss,[1] who in 1976 first reported the synthesis of thermotropic copolyesters of *p*-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET), which exhibit liquid-crystalline behavior over a certain range of copolyester compositions, and the dependence of viscosities on the composition of HBA/PET copolyesters and strong shear-thinning behavior. Subsequently, the synthesis of thermotropic copolyesters of HBA and 6-hydroxy-2-naphthoic acid (HNA) was reported.[2] A number of research groups studied the rheological behavior of HBA/PET copolyesters,[3-10] HBA/HNA copolyesters,[7,11-13] and other types of TLCPs.[14-23]

Some unusual temperature dependency of TLCP has been reported in the literature,[18,21,22] namely, the viscosity in the isotropic state is higher than that in the nematic state although the temperature is higher in the isotropic state. What makes the matter very complicated is that the rheological behavior of TLCPs is greatly influenced by thermal history.[3,7] It should be mentioned that almost all the previous rheological studies mentioned above, with the exception of the study of Wissbrun and Griffin,[15] dealt with polymers that have relatively high crystal–nematic transition temperature (T_{KN}) (also referred to melting temperature, T_m) and high nematic–isotropic transition (also referred to as clearing or isotropization) temperature (T_{NI}) (say, above 350 °C, which is close to thermal degradation temperature). Under such circumstances, it would not be possible for one to erase previous thermal histories associated, for instance, with polymerization by heating the polymer to a temperature above T_{NI} (i.e., to the isotropic state), before subjected to rheological measurements at a temperature in the nematic region ($T_m < T < T_{NI}$).

In an attempt to decrease the T_m and also the T_{NI} of TLCP, flexible aliphatic spacers have been introduced to the main chain of an LCP,[24,25] and the role of these flexible spacer groups within the main chain of an LCP has been studied, theoretically[26-31] and experimentally.[32-36] However, as shown by Antoun et al.,[32] the presence of flexible spacer groups alone within the main chain of an LCP decreases little the value of T_{NI}. On the other hand, it has been reported[25] that introducing lateral substituents into an aromatic ring of a liquid-crystalline compound normally lowers the T_{NI}, which is attributed to a regular decrease in the intermolecular forces with increasing size of the substituent. Thus, the lateral substituents together with flexible spacers on the main chain are expected to decrease both the T_m and T_{NI} of TLCPs.[37]

In the present study, with an intent to investigate transient and steady-state shear flow behavior of TLCP having reasonably low T_m and T_{NI}, we have synthesized a thermotropic liquid-crystalline polyester, with structure[37]



PSHQ10

which will hereafter be referred to as PSHQ10.[38] The unique features of PSHQ10, from the point of view of

---

* To whom correspondence should be addressed at the Department of Polymer Engineering and Institute of Polymer Engineering, The University of Akron, Akron, OH 44325-0301.

0024-9297/93/2226-3176$04.00/0

studying the rheological behavior of TLCPs, are as follows: (a) it has a T_m of ca. 110 °C and a T_{NI} of ca. 175 °C; (b) the range of temperatures between the T_m and the T_{NI} is sufficiently broad, so that the specimens can be annealed at several different temperatures between T_m and T_{NI}; (c) it enables one to measure rheological properties in both the nematic and isotropic states; (d) it can be heated to a temperature above T_{NI}, so that any previous thermal histories associated with polymerization can completely be erased before being subjected to rheological measurements at a temperature in the nematic region ($T_m < T < T_{NI}$). However, we felt that we had to first investigate the effect of thermal history of PSHQ10 on its rheological behavior, so that we would be able to establish initial conditions for transient and steady-state shear flow properties.

The organization of this paper is as follows. Firstly, variations of complex viscosity, $|\eta^*|$, of PSHQ10 in the oscillatory shear mode during isothermal annealing in the nematic region will be presented, using specimens having various thermal histories. In order to help interpret the rheological behavior observed, the results of differential scanning calorimetry and light scattering experiments for specimens having various thermal histories will be presented. Also presented will be the effect of annealing temperature on "domain" coarsening of PSHQ10 as determined by cross-polarized optical microscopy. Secondly, the effect of thermal treatment in the isotropic region on the oscillatory shear flow properties of PSHQ10 in the nematic region will be discussed.

Experimental Section

Materials. The polymer employed in this study was poly[(phenylsulfonyl)-*p*-phenylene-1,10-decamethylenebis(4-oxybenzoate)] (PSHQ10), which was synthesized, via solution polymerization, in our laboratory, by preparing two monomers, 2-(phenylsulfonyl)-1,4-hydroquinone and 4,4′-dichloroformyl-1,10-diphenoxydecane. The details of the method of synthesis are given in previous papers.[37,39] We have determined using gel permeation chromatography the weight-average molecular weight of PSHQ10 to be 35 000 relative to polystyrene standards, and the polydispersity index to be 2.[40]

Sample Preparation. Specimens for rheological and DSC measurements were prepared by first dissolving PSHQ10 in dichloromethane in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent at room temperature for a week. The cast films with the thickness of 1 mm were further dried in a vacuum oven at room temperature for at least 3 weeks and at 90 °C for 48 h to remove any residual solvent. Specimens for optical microscopy and light scattering experiments were prepared by casting from a 1 wt % solution of 1,1,2,2-tetrachloroethane on a slide glass to make a thin film of about 2–3 μm in thickness.

Rheological Measurement. A Model R16 Weissenberg rheogoniometer (Sangamo Control, Inc.) in the cone-and-plate (25 mm diameter plate and 4° cone angle) configuration was used to measure, in the oscillatory shear mode, the dynamic storage modulus (G') and dynamic loss modulus (G''). From the measurements of G' and G'', the absolute values of complex viscosity $|\eta^*(\omega)|$ were calculated using the relationship: $|\eta^*(\omega)| = [(G'(\omega)/\omega)^2 + (G''(\omega)/\omega)^2]^{1/2}$. Strain amplitude was varied from 0.01 to 0.06, which was well within the linear viscoelastic range of the materials investigated. This, together with data acquisition during measurement, was accomplished with the aid of a microcomputer interfaced with the rheometer. All experiments were conducted in the presence of nitrogen in order to preclude oxidative degradation of the specimen. Oscillatory shear measurements were made at various temperatures in the range from 130 to 190 °C. Temperature control was satisfactory to within ±1 °C. For oscillatory shear measurements during isothermal annealing, an angular frequency, ω = 0.237 rad/s, was chosen, which lasted about 50 s. The interval between two consecutive measurements varied from 5 min to 48 h, depending upon the measurement temperatures chosen.

Differential Scanning Calorimetry. Thermal transition temperatures of the PSHQ10 synthesized were determined by differential scanning calorimetry (DSC) (Perkins-Elmer DSC-7). All DSC runs were made under a nitrogen atmosphere with heating and cooling rates of 20 °C/min, and the thermal histories of the specimens were chosen, so as to simulate the conditions used for rheological measurements.

Light Scattering. A He–Ne (λ = 632.8 nm) light scattering apparatus constructed in our laboratory was used to monitor the intensity of scattered light from PSHQ10 specimens during isothermal annealing. The light scattering apparatus was attached to a programmable temperature controller; the temperature control was satisfactory to within ±1 °C.

Optical Microscopy. A hot-stage, polarized microscope (Nippon Kogaku) with a camera, a programmable temperature controller, and photomicrographic attachment was used to take pictures of the film samples placed on a glass slide under cross-polarized condition.

Results and Discussion

Below we present and discuss experimental results, describing the effects of thermal history on the oscillatory shear flow properties of PSHQ10 during isothermal annealing in the nematic region. In order to help interpret the variations of the rheological properties of PSHQ10 observed during isothermal annealing, we shall also present (a) the results of DSC measurements taken with the specimens which experienced the same thermal histories as those used for rheological measurements, (b) the coarsening process of domain texture, as determined by light scattering, of PSHQ10 specimens which were subjected to various thermal histories, and (c) micrographs, taken from a polarized optical microscope, describing the evolution of domain texture of PSHQ10 during isothermal annealing. We employed the specimens that were subjected to various thermal histories, namely, (a) as cast from a solvent, (b) as-cast specimens that were annealed for a predetermined period at a temperature between T_m and T_{NI}, and (c) as-cast specimens that were heated to a temperature above T_{NI}, held there for a fixed period, and finally cooled slowly down to a temperature between T_{NI} and T_m (hereafter referred to as "thermally treated specimens").

Effect of Isothermal Annealing on the Oscillatory Shear Flow Properties of PSHQ10 in the Nematic Region. Figure 1 describes variations of $|\eta^*|$, with annealing time up to 6 h at a fixed angular frequency ω = 0.237 rad/s for as-cast specimens at various annealing temperatures, 130, 135, 140, and 145 °C. Note that each measurement lasted about 50 s, and a fresh specimen was used for each test. It should be mentioned that in obtaining the results summarized in Figure 1, an as-cast specimen was first placed in the cone-and-plate fixture, which had been heated to a predetermined temperature. Oscillatory shear flow was resumed at a predetermined time interval, which depended on the measurement temperature. For instance, at 130 °C rheological measurements were taken at an interval of 5 min initially, whereas at 145 °C rheological measurements were taken initially at an interval of 30 min but, as will be described below, after about 8 h from the beginning of the experiment, rheological measurements were taken every 24 h and the entire test lasted for about 3 weeks.

It can be seen in Figure 1 that for an annealing period up to 6 h, $|\eta^*|$ at 130, 135, and 140 °C, respectively, increases with annealing time, the rate of increase being faster as the anealing temperature is decreased from 140 to 130 °C, whereas $|\eta^*|$ at 145 °C decreases initially and then remains

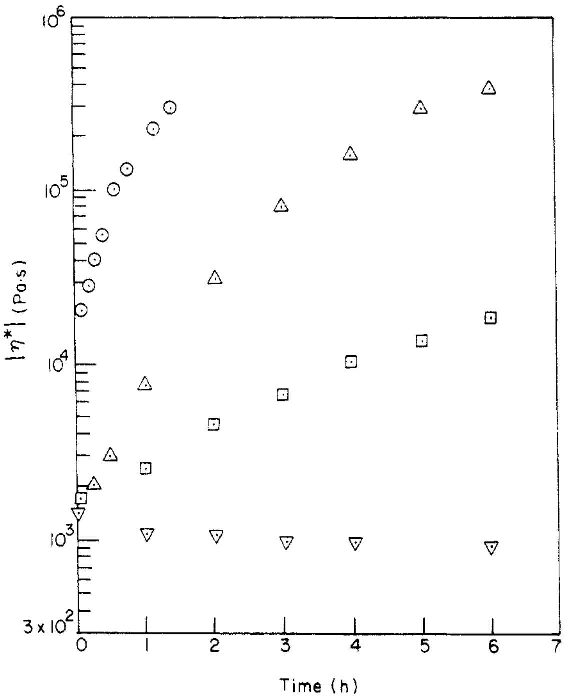


Figure 1. Variations of $|\eta^*|$ with annealing time up to 6 h for as-cast PSHQ10 specimens at various temperatures: (⊙) 130 °C; (▲) 135 °C; (⊡) 140 °C; (▼) 145 °C. Measurements were taken at an angular frequency ω of 0.237 rad/s.

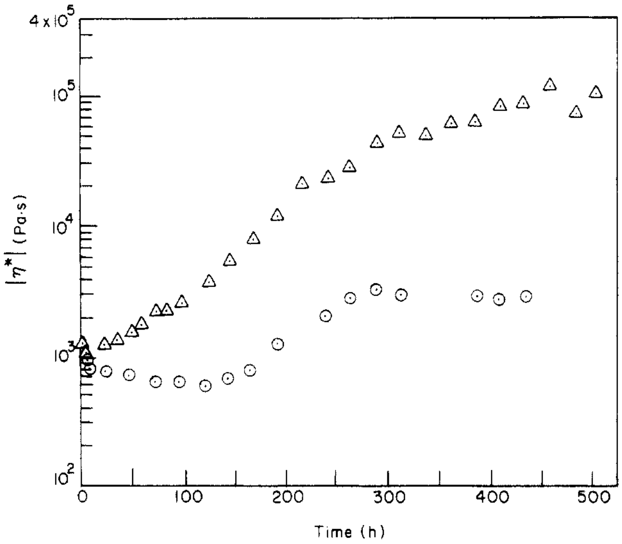


Figure 2. Variations of $|\eta^*|$ with annealing time up to 500 h for as-cast PSHQ10 specimens at various temperatures: (⊙) 145 °C; (▲) 150 °C. Measurements were taken at ω = 0.237 rad/s.

more or less constant as annealing progresses. However, as the annealing time is extended to about 500 h, as can be seen in Figure 2, $|\eta^*|$ at 145 °C starts to increase with annealing time after about 10 h from the beginning of the test and then tends to level off after 500 h (ca. 3 weeks!), and $|\eta^*|$ at 150 °C starts to increase with annealing time after about 125 h from the beginning of the test and then tends to level off after about 430 h (ca. 2.5 weeks!).

For illustration, DSC traces for as-cast PSHQ10 specimens are given in Figure 3, which were annealed for 4 h at various temperatures, as indicated on the figure. It should be remembered that $|\eta^*|$ increased 2 orders of magnitude after the sample had been annealed for 4 h at 135 °C (see Figure 1). The following observations are worth noting in Figure 3: (a) At annealing temperatures between 95 and 110 °C, a single endothermic peak appears, the peak temperature being shifted from 121 to 135 °C. (b) At the annealing temperature of 115 °C, a second endothermic peak appears on a higher temperature side of the first endothermic peak. (c) At the annealing temperature of 130 °C, the height of the peak at 170 °C becomes greater than that of the peak at 150.8 °C, and a third, small endothermic peak at 104.2 °C appears. (d) As the annealing temperature is increased to 140 °C and higher, the first endothermic peak disappears completely and only two distinct endothermic peaks persist, one at about 110 °C, which is regarded as the T_m and the other at about 174 °C, which is regarded as the T_{NI}. (e) At the annealing temperature of 125 °C, a small transition appears in the vicinity of 75 °C, which is then shifted to 81 °C when the annealing temperature is increased to 150 °C. The temperature 81 °C is regarded as the glass transition temperature of the polymer. The above observations suggest that a "crystal-like phase"[41] is formed at annealing temperatures between ca. 95 and ca. 140 °C. Similar observations were reported earlier[42-46] for thermotropic copolyesters. Later in this paper we shall elaborate on the similarities and differences in thermal transition behavior observed between the present study and previous studies.[42-46]

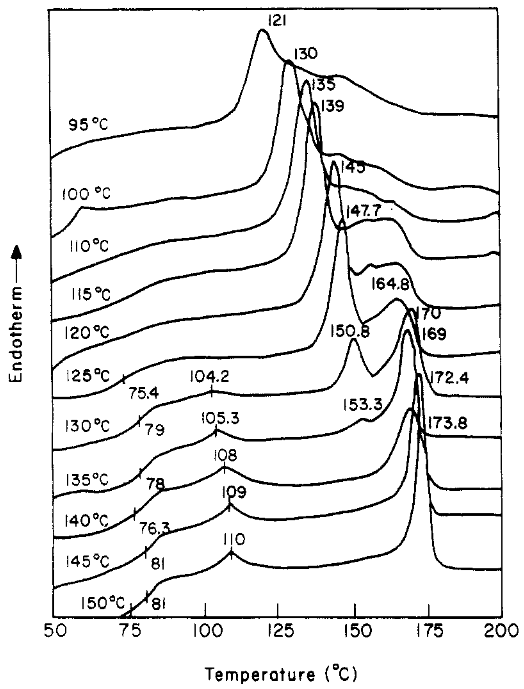


Figure 3. DSC traces for as-cast PSHQ10 specimens annealed for 4 h at different temperatures, as indicated on the plot. The heating rate used was 20 °C/min.

In order to have a better understanding of the effect of annealing temperature on the appearance of the two major endothermic peaks in the heating cycle of DSC runs shown in Figure 3, let us compare the DSC trace during the heating cycle (curve 1) with that during the subsequent cooling cycle (curve 2), given in Figure 4, for an as-cast specimen, which was annealed at 130 °C for 4 h. Notice in Figure 4 that there is only one exothermic peak on curve 2, whereas there are two endothermic peaks on curve 1, indicating that the endothermic peak B present on curve 1 was suppressed, owing to supercooling during the cooling cycle from the isotropic region. Because of the overlap of the two endothermic peaks, A and B, on curve 1 of Figure 4, the area under the endothermic peaks could not be calculated without peak deconvolution. However, we observe in Figure 5 that when DSC runs were made for an as-cast specimen which was annealed at 160 °C for 20 h, only one endothermic peak appears during the heating

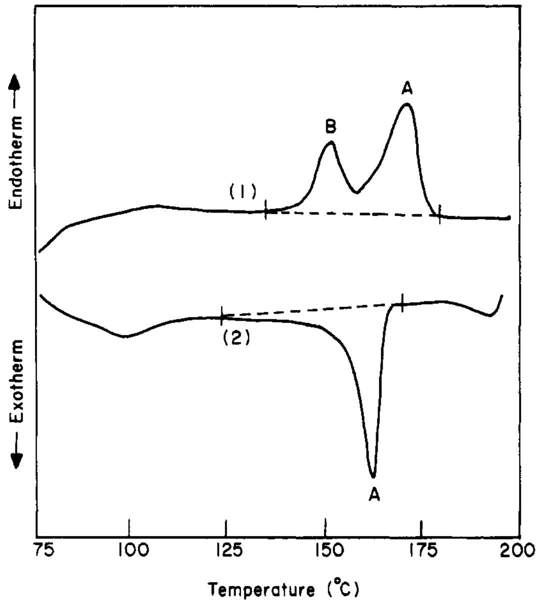


Figure 4. DSC traces for an as-cast PSHQ10 specimen annealed at 130 °C for 4 h, where curve 1 represents the heating cycle at 20 °C/min and curve 2 represents the cooling cycle at 20 °C/min. The sum of the areas under peaks A and B on curve 1 has ΔH = 9.95 J/g, which is larger than that, ΔH = 8.145 J/g, obtained from the area under peak A on curve 2.

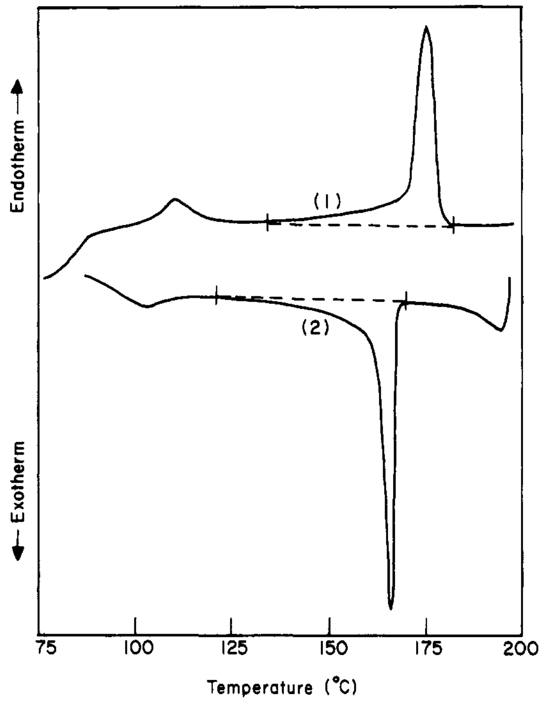


Figure 5. DSC traces for an as-cast PSHQ10 specimen annealed at 160 °C for 20 h, where curve 1 represents the heating cycle at 20 °C/min and curve 2 represents the cooling cycle at 20 °C/min. The area under the peak on curve 1 has ΔH = 8.07 J/g, which is virtually the same as that, ΔH = 8.19 J/g, obtained from the area under peak on curve 2.

cycle (curve 1) and the area under the peak is estimated to be 8.07 J/g, which is virtually the same as the area (8.19 J/g) under the exothermic peak appearing during the cooling cycle (curve 2). Notice further that the area (8.15 J/g) under the exothermic peak during the cooling cycle given in Figure 4 is virtually the same as the area (8.19 J/g) under the exothermic peak during the cooling cycle given in Figure 5. Thus, in reference to Figure 4, we calculated the area under the endothermic peak B on curve 1 to be 1.805 J/g, by substracting the area (8.145 J/g) under an exothermic peak A in the cooling cycle (curve 2) from the total area (9.95 J/g) for both peaks, A and B, in the heating cycle (curve 1).

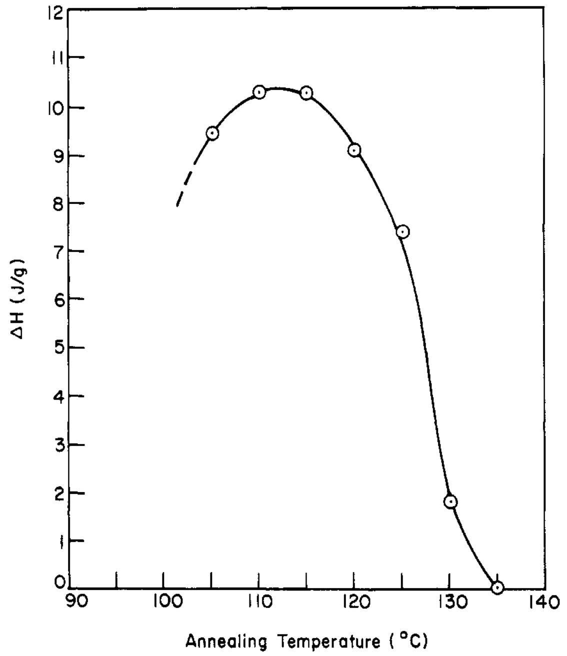


Figure 6. Plots of endothermic enthalpy ΔH, representing the area under the peak of DSC trace, versus annealing temperature for as-cast PSHQ10 specimens.

Similar calculations were performed by making DSC runs at annealing temperatures 105, 110, 115, 120, 125, and 135 °C, and the results are summarized in Figure 6, where ΔH denotes the enthalpy associated with the formation of a crystal-like phase which appears only in the heating cycle of DSC runs at annealing temperatures below about 140 °C (see Figure 3). It is of interest to observe that the "bell-shaped" curve in Figure 6 is very similar to that reported previously by others,[47-49] who investigated the crystallization of flexible semicrystalline homopolymers. Those investigators used such a curve to interpret the dependence of the rate of crystallization on temperature. In other words, we find a similarity between the plot of ΔH versus annealing temperature for PSHQ, given in Figure 6, and the plot of the rate of crystallization versus temperature, which has been reported previously[47-49] for semicrystalline homopolymers. However, at present we have no direct information on whether a crystal-like phase, which apparently forms at temperatures below about 140 °C during isothermal annealing of PSHQ10 (see Figures 3 and 4), can be attributed to a solid–solid transition or a liquid–liquid transition. Nevertheless, below we shall use Figure 6 to interpret the seemingly complicated dependence of the rheological behavior of PSHQ10 on annealing temperature, presented in Figures 1 and 2.

Notice in Figure 6 that ΔH goes through a maximum at 113 °C, from which we can conclude that the rate of the formation of a crystal-like phase in PSHQ10 will increase (or decrease) with increasing (or decreasing) annealing temperature if the annealing temperature is below 113 °C, whereas the rate of the formation of a crystal-like phase in PSHQ10 will decrease (or increase) with increasing (or decreasing) annealing temperature if the annealing temperature is above 113 °C. Based on this premise, we can now explain the seemingly complicated dependence of $|\eta^*|$ on thermal history, observed in Figure 1; that is, the observed increase in the rate of growth of $|\eta^*|$ with decreasing annealing temperature from 140 to 130 °C may be attributable to the concomitant increase in the rate of

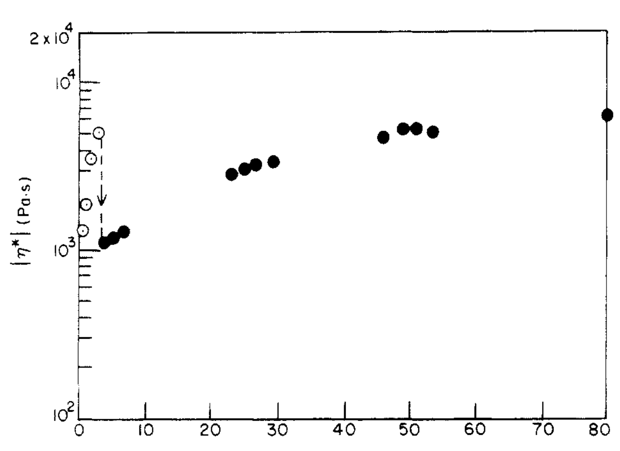


Figure 7. Variations of $|\eta^*|$ with annealing time for an as-cast PSHQ10 specimen, which was first annealed at 140 °C for 3 h (open symbol) and then heated to 150 °C and annealed there for 77 h (closed symbol). Measurements were taken under isothermal conditions at ω = 0.237 rad/s.

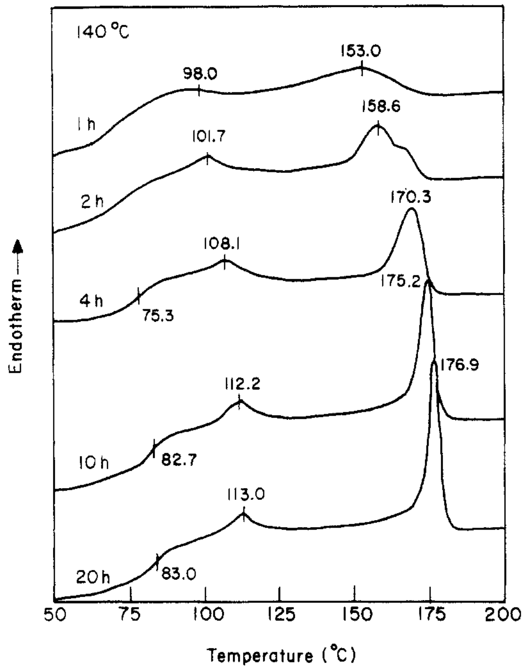


Figure 8. DSC traces for as-cast PSHQ10 specimens annealed at 140 °C for different periods, as indicated on the plot. A fresh specimen was used for each run and the heating rate was 20 °C/min.

the formation of a crystal-like phase in PSHQ10.

Figure 7 describes variations of $|\eta^*|$ with time for an as-cast specimen, which had the following thermal history: (a) annealed first at 140 °C for 3 h (denoted by open circle) and (b) subsequently heated to 150 °C and annealed there for 77 h (denoted by closed circle). It can be seen in Figure 7 that the rate of increase in $|\eta^*|$ slowed down considerably when the specimen was subjected to annealing at 150 °C, as compared to that at 140 °C, suggesting that the rate of the formation of a crystal-like phase is much slower at 150 °C than at 140 °C. DSC traces for as-cast specimens, which were annealed at 140 °C for different periods up to 20 h, given in Figure 8, show only two distinct endothermic peaks, one representing T_m and the other representing T_{NI}, and give *no* clue as to why $|\eta^*|$ increases with annealing time (see Figure 7). This seems to suggest that rheological measurements are far more sensitive than DSC to a variation in the morphological state of the PSHQ10 specimen during isothermal annealing. This observation is based on the stipulation that there ought to be *no* variation in $|\eta^*|$ if there had been no change in the morphological state of the specimen as annealing progressed.

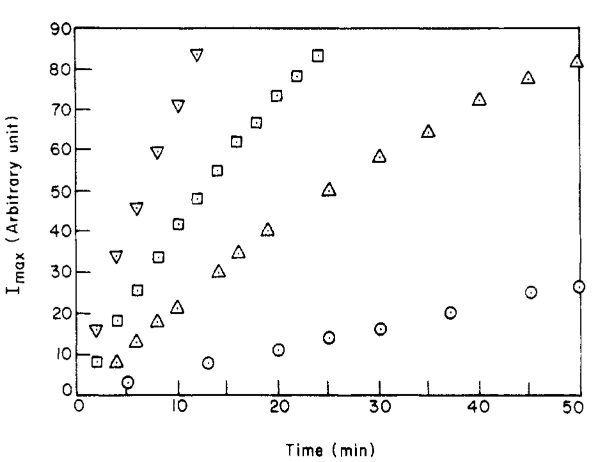


Figure 9. Variations of I_{max} with time for as-cast PSHQ10 specimens during isothermal annealing at various temperatures: (⊙) 130 °C; (▲) 140 °C; (⊡) 150 °C; (▼) 160 °C. A fresh specimen was used for each run.

Earlier, using small-angle light scattering Rojstaczer and Stein[50] reported that the domain texture of PSHQ10 coarsens as annealng progresses. In the present study, we performed similar experiments with the hope that the results of such an experiment will enable us to explain the effect of thermal history on the oscillatory shear flow properties presented above.

Figure 9 describes how, within the first 50 min after annealing began, the maximum intensity of scattered light (I_{max}) without polarizer varied with time for as-cast specimens under isothermal conditions. Note that a fresh specimen was used for each annealing temperature. It can be seen in Figure 9 that at a fixed annealing temperature I_{max} increased with time, the rate of which increased as the annealing temperature increased. It should be noted that domain sizes smaller than about 2.5 μm could not be detected with the laser light source employed in the scattering experiment. There are two factors that might have contributed to the increasing trend of I_{max} given in Figure 9. They are (a) an increase in the number of "domains" with sizes greater than about 2.5 μm and (b) the growth of domain textures having sizes greater than 2.5 μm. It seems reasonable to speculate that during isothermal annealing the PSHQ10 specimen in the nematic region forms polydomains by coalescence of small domains, the rate of which would depend, among many factors, on annealing temperature, which in turn controls the viscosity of the specimen.

Figure 10 gives distributions of scattered light intensity during isothermal annealing of an as-cast specimen at 140 °C, where θ is the scattering angle and q is the magnitude of the wave vector. Notice in Figure 10 that the maximum intensity in the distribution curve increases and the peak position (θ_{max} or q_{max}) in the distribution curve moves toward the left as the annealing progresses. Earlier, Rojstaczer and Stein[50] reported similar results. According to Hashimoto and co-workers,[51] the magnitude of the scattering vector q_{max} corresponding to θ_{max} is related to the domain growth $\xi_d(t)$

$$\xi_d(t) \simeq 2\pi/q_{max}(t) \qquad (1)$$

$$q_{max}(t) = (4\pi/\lambda)\sin(\theta_{max}(t)/2) \qquad (2)$$

where λ is the wavelength of the incident light and θ_{max} is the scattering angle of the maximum intensity. It can

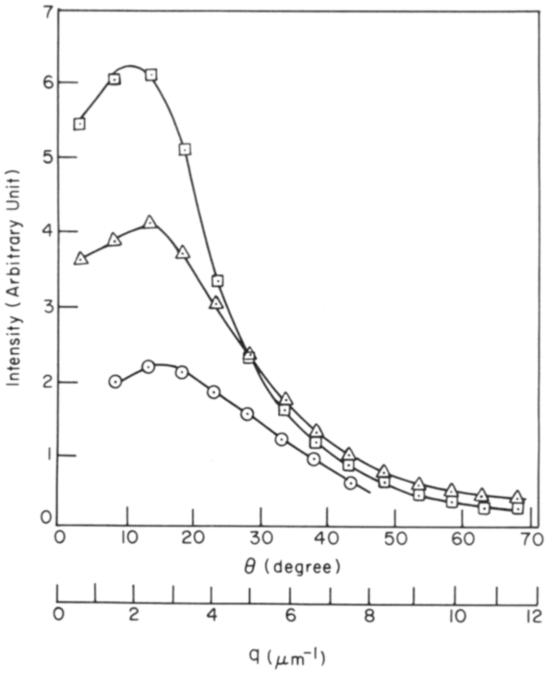


Figure 10. Distribution of scattered light intensity for as-cast PSHQ10 specimens after annealing at 140 °C for different periods: (⊙) 8 min; (▲) 14 min; and (⊡) 22 min. Scattered light intensity was measured from specimens, which were quenched after annealing for a predetermined period. A fresh specimen was used for each run.

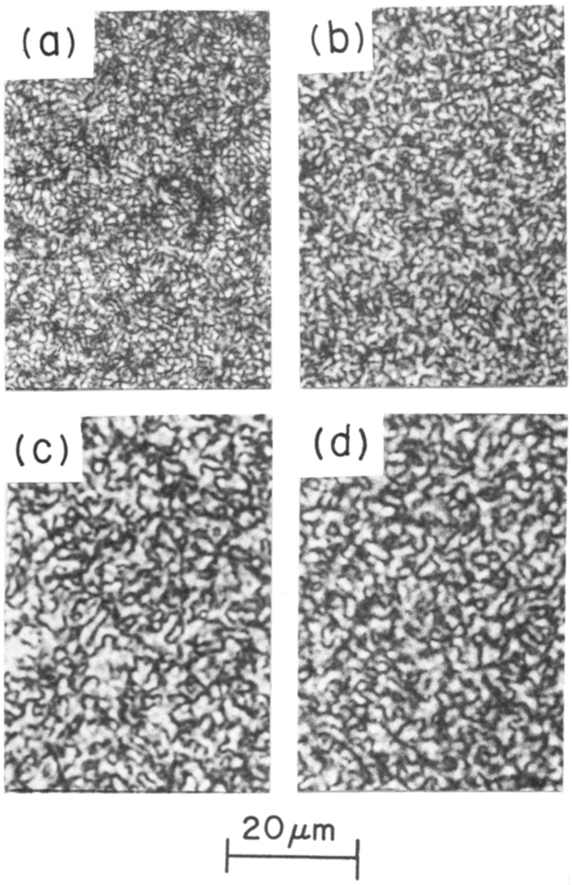


Figure 11. Cross-polarized optical micrographs of as-cast PSHQ10 specimens, which were annealed for 2 h at different temperatures: (a) 120 °C; (b) 140 °C; (c) 150 °C; (d) 160 °C. A fresh specimen was used for each run.

be seen in eqs 1 and 2 that the shift of θ_{max} or q_{max} is a consequence of the growth of $\xi_d(t)$. Indeed, Rojstaczer and Stein reported that at a fixed temperature the value of q_{max}^{-1} increased with increasing annealing time and the slope of q_{max}^{-1} versus time curve increased with increasing annealing temperature, implying that the growth rate of domain textures increased with increasing annealing temperature. Our results in Figures 9 and 10 agree with the observations made earlier by Rojstaczer and Stein.[50]

Optical microscopy was also employed to observe the evolution of domain textures during isothermal annealing of as-cast specimens having different thermal histories. Cross-polarized optical micrographs of as-cast specimens, which were annealed for 2 h at different temperatures (120, 140, 150, and 160 °C) are given in Figure 11 and show that domain textures grew faster as the annealing temperature increased from 120 to 160 °C, in support of the conclusions drawn from the light scattering experiments presented above (see Figure 9). Cross-polarized optical micrographs of as-cast specimens, which were annealed at 160 °C for different periods (20 min, 1 h, 2 h, 5 h, 17 h, and 65 h) are given in Figure 12, from which we observe that domain textures ceased to grow after the first 1–2 h of annealing.

Figure 13 describes variations of $|\eta^*|$ with time for an as-cast specimen, which had the following thermal history: (a) annealed first at 160 °C for 3 h (denoted by open circle) and (b) subsequently cooled slowly down to 130 °C and annealed there for 90 h (denoted by closed circle). Figure 14 gives DSC traces for as-cast specimens, which were annealed at 160 °C for different periods up to 20 h. Notice that the basic features of the DSC traces given in Figure 14 are virtually identical to those given in Figure 8. It is of interest to observe in Figure 13 that $|\eta^*|$ of PSHQ10 *decreased* with time during the isothermal annealing at 160 °C. It should be remembered that $|\eta^*|$ *increased* with time when a PSHQ10 specimen was annealed under isothermal conditions at a temperature of 130, 135, and 140 °C, respectively (see Figures 1 and 7). We already offered above an explanation for the increase in $|\eta^*|$ observed when a PSHQ10 specimen was annealed at a temperature below about 140 °C. We believe that the decrease in $|\eta^*|$ of PSHQ10 with time, observed during isothermal annealing at 160 °C (see Figure 13), is attributable to the domain growth or coarsening of the schlieren texture of PSHQ10.

Notice further in Figure 13 that when the annealing temperature was lowered from 160 to 130 °C $|\eta^*|$ remained more or less constant for the first 50 h and then increased rapidly with time. We attribute the small variations in $|\eta^*|$ observed in Figure 13 to the lack (or absence) of disclinations (or defects) in the PSHQ10 specimen, because while the specimen was annealed at 160 °C for 3 h, much, if not all, of the defects in the as-cast PSHQ10 specimen must have been annihilated. Therefore, when the specimen was cooled slowly from 160 to 130 °C, it would have required a long induction time, in the absence of defects in the specimen, for the nucleation of a crystal-like phase. We believe that this is the reason why in Figure 13 we begin to observe an increase in $|\eta^*|$ only after about 50 h of annealing at 130 °C.

Earlier, a similar observation was reported by Lin and Winter,[42] who used a 73/27 HBA/HNA copolyester, where 73/23 refers to mole percent of HBA and HNA. Specifically, they did not observe any significant variations of G' and G'' with time when the 73/27 HBA/HNA copolyester specimen had been preheated to 320 °C followed by a cooling to 290 °C and an isothermal annealing there, while there was a rapid increase in G' and G'' when the 73/27 HBA/HNA specimen was annealed at 290 °C without being preheated at a higher temperature. Also, similar to

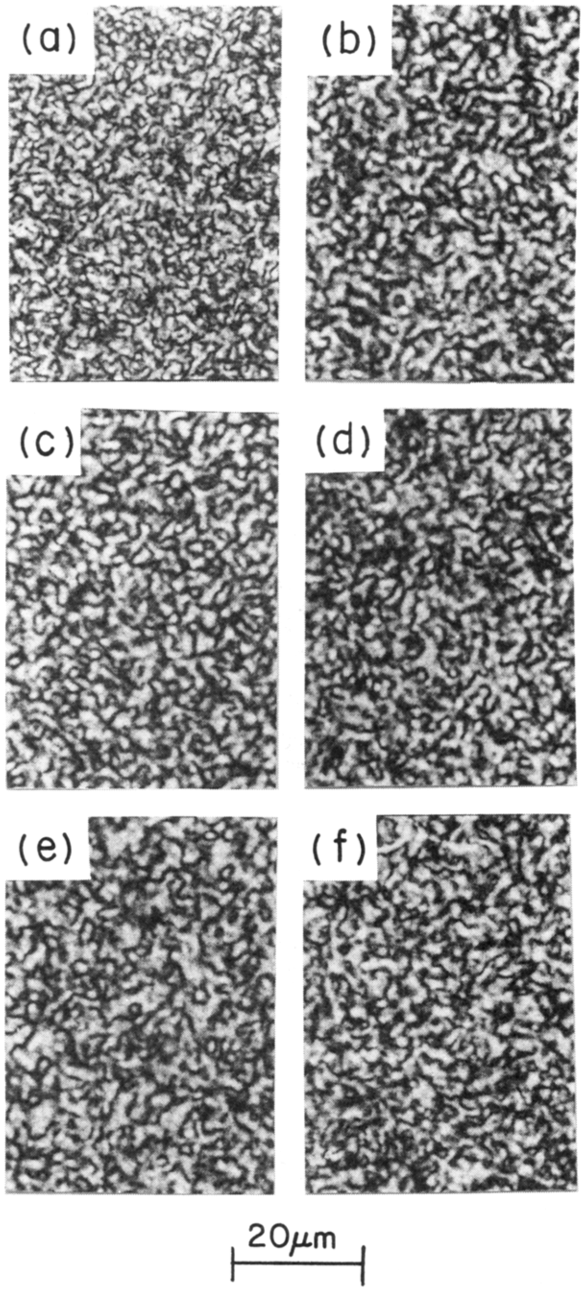


Figure 12. Cross-polarized optical micrographs of as-cast PSHQ10 specimens, which were annealed at 160 °C for different periods: (a) 20 min; (b) 1 h; (c) 2 h; (d) 5 h; (e) 17 h; (f) 65 h. A fresh specimen was used for each run.

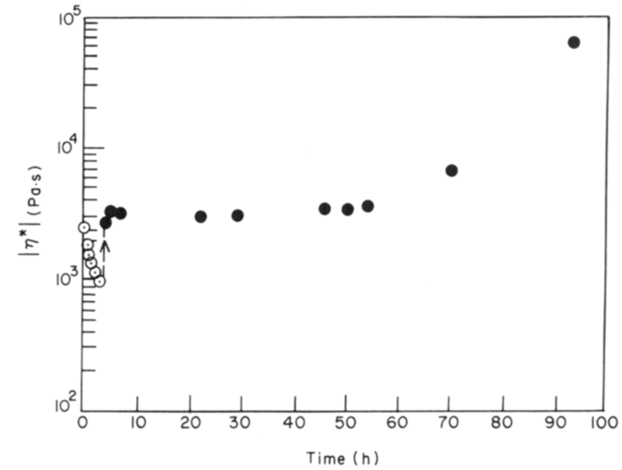


Figure 13. Variations of $|\eta^*|$ with annealing time for an as-cast PSHQ10 specimen, which was first heated at 160 °C for 3 h (open symbol) and then cooled slowly to 130 °C and annealed there for 95 h (closed symbol). Measurements were taken under isothermal conditions at ω = 0.237 rad/s.

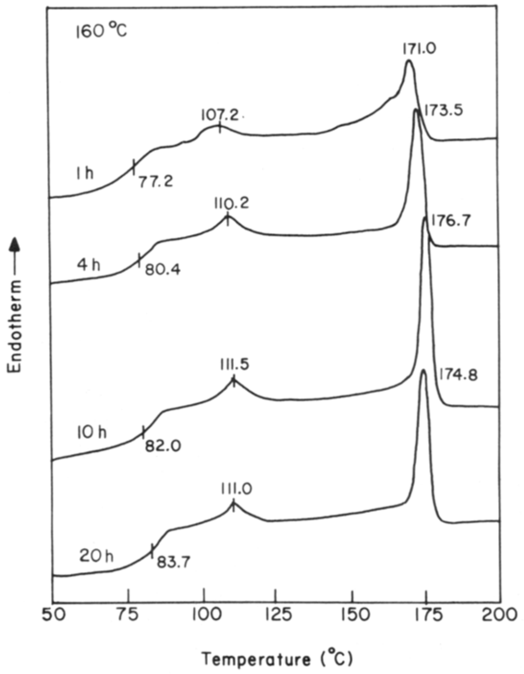


Figure 14. DSC traces for as-cast PSHQ10 specimens annealed at 160 °C for different periods, as indicated on the plot. A fresh specimen was used for each run and the heating rate was 20 °C/min.

our DSC thermograms given in Figure 14, Lin and Winter did not observe a high-temperature endothermic peak at about 315 °C for the 73/27 HBA/HNA copolyester specimen when it was preheated at 320 °C. They attributed the appearance of a high-temperature endothermic peak for the copolyester to the presence of a crystalline solid which was formed during isothermal annealing at temperatures below 315 °C.

Effect of Thermal Treatment at the Isotropic State on Subsequent Oscillatory Shear Flow of PSHQ10 in the Nematic Region. We now discuss how the rheological properties of a PSHQ10 specimen in the nematic region vary with annealing time after having been subjected to thermal treatment, with or without shear, at the isotropic state. Figure 15 describes variations of $|\eta^*|$ with annealing time at 130 °C for three as-cast specimens having the following thermal and shear histories: (1) an as-cast specimen (circle); (2) a specimen placed in the cone-and-plate fixture at 190 °C, held there for 30 min, and then cooled slowly down to 130 °C (triangle); and (3) a specimen placed in the cone-and-plate fixture at 190 °C, sheared at $\dot{\gamma}$ = 0.085 s^{-1} for 5 min, and then cooled slowly down to 130 °C (square). Note that a fresh specimen was used for each run. It can be seen in Figure 15 that (a) the $|\eta^*|$ of the as-cast specimen without any thermal treatment increased rapidly during annealing at 130 °C, (b) the $|\eta^*|$ of the specimen, which received thermal treatment under *quiescent* conditions for 30 min at 190 °C, remained more or less constant initially and then began to increase rapidly ca. 20 h after annealing had started, and (c) the $|\eta^*|$ of the specimen, which had been subjected to *steady shear flow* at a rate of 0.085 s^{-1} for 5 min at 190 °C, remained more or less constant for ca. 50 h. The above observations indicate that thermal treatment of PSHQ10 at 190 °C under *quiescent* conditions for 30 min was not sufficiently long enough to erase completely the thermal history, which

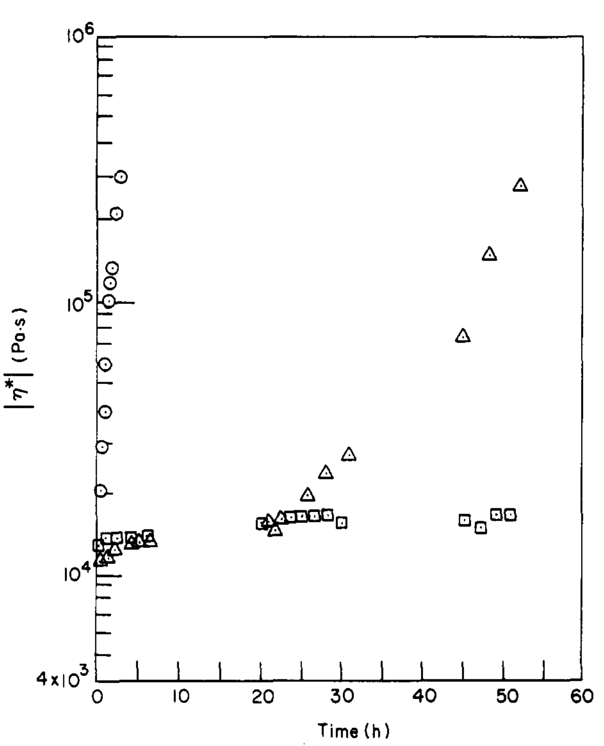


Figure 15. Variations of $|\eta^*|$ with annealing time during annealing at 130 °C for three as-cast PSHQ10 specimens having the following thermal histories: (⊙) an as-cast specimen; (▲) a specimen placed in the cone-and-plate fixture at 190 °C (i.e., in the isotropic region), kept there for 30 min under quiescent conditions, and then cooled slowly down to 130 °C; (⊡) a specimen placed in the cone-and-plate fixture at 190 °C, subjected to steady shear flow at $\dot{\gamma}$ = 0.085 s^{-1} for 5 min at 190 °C, and then cooled slowly down to 130 °C. Measurements were taken under isothermal conditions at ω = 0.238 rad/s.

was associated with sample preparation. This seems to point out that in order to erase completely any thermal history of polymers having semiflexible chains, such as PSHQ10, a very long thermal treatment in the isotropic region or thermal treatment under shear flow would be required.

The observations made above prompted us to investigate thermal transitions, via DSC, of the PSHQ10 specimens, which had the same thermal histories as those used in the rheological measurements given in Figure 15. We shall now present the results of DSC to interpret the seemingly complicated rheological responses presented above. Figure 16 gives DSC traces for as-cast specimens which were annealed at 130 °C for different periods. Note that a fresh specimen was used for each DSC run. It can be seen in Figure 16 that the specimen annealed for 30 min shows two endothermic peaks, one at 94.9 °C and the other at 146.0 °C, but as the annealing period increased to 2 h, an additional endothermic peak appears at 165.4 °C, giving rise to three endothermic peaks. Notice in Figure 16 that the three peak temperatures increase slowly with increasing annealing period and that for the specimen annealed for 20 h, the height of the intermediate endothermic peak at 151.9 °C has become greater than that of the high-temperature peak at 173.9 °C.

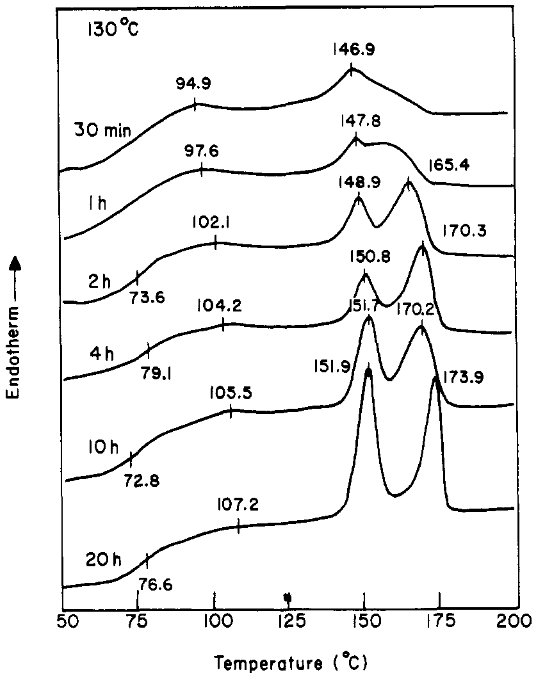


Figure 16. DSC traces for as-cast PSHQ10 specimens annealed at 130 °C for different time periods, as indicated on the plot. A fresh specimen was used for each run and the heating rate was 20 °C/min.

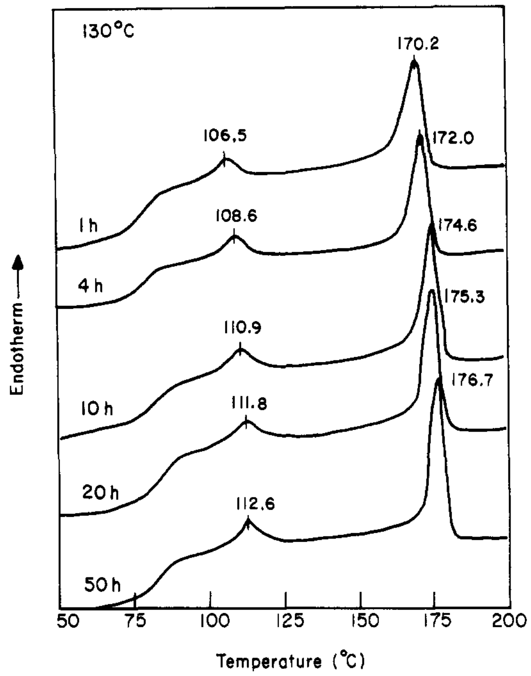


Figure 17. DSC traces for as-cast PSHQ10 specimens annealed at 130 °C for different periods, as indicated on the plot, having the following thermal histories: an as-cast specimen was first annealed at 130 °C for 30 min, then heated to 190 °C and held there for 30 min, and then finally cooled down slowly to 130 °C for further annealing. A fresh specimen was used for each run and the heating rate was 20 °C/min.

However, when an as-cast specimen was first subjected to thermal treatment at 190 °C for 30 min, then cooled slowly down to 130 °C and annealed there for different periods of time, as can be seen in Figure 17, the intermediate endothermic peak which was observed in Figure 16 has disappeared, leaving only two peaks, one at 106–112 °C and the other at 170–176 °C. We conclude from Figure 17 that the low-temperature endothermic peak at about 110 °C represents the T_m and the high-temperature endothermic peak at about 175 °C represents the T_{NI}. What is of great interest in Figure 17 is that when an as-cast specimen had received thermal treatment at a temperature above T_{NI}, even after isothermal annealing at 130 °C for 50 h the specimen did not exhibit an intermediate endothermic peak. The observations made above in reference to Figures 16 and 17 seem to suggest that a rapid increase in $|\eta^*|$ with annealing time for an as-cast specimen, displayed in Figure 15, is attributable

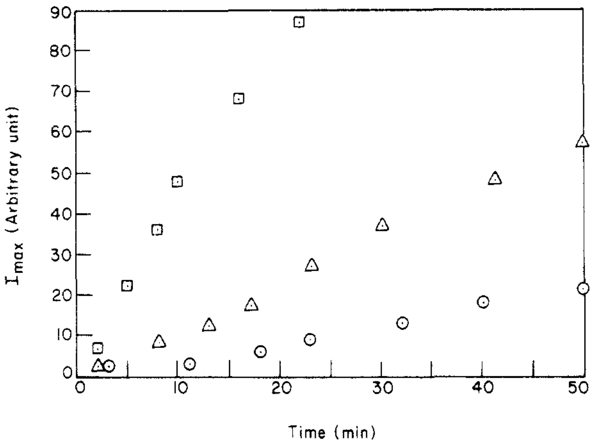


Figure 18. Variations of $I_{\max}$ with time during isothermal annealing for as-cast PSHQ10 specimens, which were heated to 190 °C, held there for 5 min, and then cooled down slowly to a predetermined temperature: (⊙) 140 °C; (▲) 150 °C; (⊡) 160 °C. A fresh specimen was used for each run.

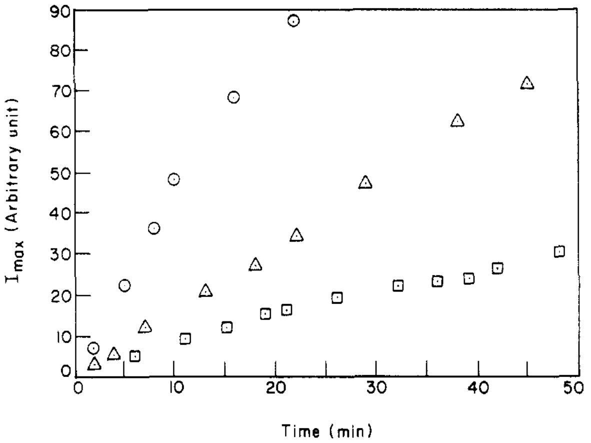


Figure 19. Variations of $I_{\max}$ with time during isothermal annealing at 160 °C for as-cast PSHQ10 specimens, which were heated to 190 °C and held there for different periods: (⊙) 5 min; (▲) 10 min; (⊡) 20 min. A fresh specimen was used for each run.

to the existence of an intermediate endothermic peak at about 150 °C in the DSC run, i.e., to the presence of a crystal-like phase which melts at about 140 °C. Once an as-cast specimen is subjected to a temperature above the T_{NI} (ca. 175 °C) of PSHQ10 and subsequently cooled slowly down to a temperature in the nematic region (say, 130 °C), the formation of a crystal-like phase is delayed (i.e., a longer induction time is required for the formation of the crystal-like phase). We hasten to add, in reference to Figure 17, that we would expect to observe the appearance of an intermediate endothermic peak in the DSC if we had extended the annealing period much longer than 50 h.

At present we have no explanation as to why in Figure 15 the $|\eta^*|$ of the thermally-treated specimen under quiescent conditions increases with annealing time (triangle), while in the DSC traces given in Figure 17 there is no intermediate endothermic peak. It is possible that within the annealing period employed in our experiment the crystallinity of the crystal-like phase was so low or the crystalline structure was so imperfect that the DSC could not detect its existence in the specimen. This will be a subject of future investigation.

In this study we also investigated how, within the first 50 min after annealing began, thermal treatment in the isotropic region might affect the growth rate of domain textures of PSHQ10, by conducting light scattering experiments with as-cast specimens, which were heated to 190 °C, held there for 5 min, and then cooled down to 140, 150, and 160 °C, respectively. Again, a fresh specimen was used for each experiment. Figure 18 describes how $I_{\max}$ varied with time for thermally treated specimens during isothermal annealing at different temperatures in the nematic region. It can be seen in Figure 18 that $I_{\max}$ increased more rapidly with time as the annealing temperature increased, similar to that observed in Figure 9. However, a comparison of Figure 18 with Figure 9 reveals that the rate of increase in $I_{\max}$ is much less for the specimen which received thermal treatment than for the specimen which did not. Having observed that thermal treatment had a profound influence on the *initial* rate of increase in $I_{\max}$, we next investigated whether or not the duration of thermal treatment might influence the *initial* rate of increase in $I_{\max}$, and the results of light scattering measurements at 160 °C are summarized in Figure 19. It can be seen in Figure 19 that the duration of thermal treatment at 190 °C had a profound influence on the *initial* rate of increase in $I_{\max}$.

Concluding Remarks

In this paper we have synthesized a thermotropic liquid-crystalline polyester (PSHQ10) and investigated the effects of thermal history on its oscillatory shear flow properties (G', G'', and $|\eta^*|$). We have found that there are two different mechanisms which govern the rheological behavior of PSHQ10, depending on the temperature to which an as-cast specimen was subjected. Specifically, during isothermal annealing, at temperatures between ca. 110 and 140 °C, the presence of a high-temperature endothermic peak, as observed by DSC, is believed to give rise to an increase in G', G'', and $|\eta^*|$, whereas at temperatures between ca. 140 and 160 °C the growth of a fine schlieren structure is believed to give rise to a decrease in G', G'', and $|\eta^*|$. We have also found that thermal treatment of PSHQ10 at a temperature above its T_{NI} (i.e., in the isotropic region) has a profound influence on its rheological behavior in the nematic region. Such experiment was made possible owing to the fact that (a) the PSHQ10 synthesized in this study has a relatively low value of T_{NI} (175 °C) and (b) the range of temperatures between the T_m and the T_{NI} is broad, about 60 °C. Such experiment could not have been performed using TLCPs having a very high T_{NI}, e.g., HBA/PET and HBA/HNA copolyesters. When using such copolyesters, it would not be possible to erase the thermal history built in the as-polymerized specimens. However, in the present study, using PSHQ10 it was possible for us to erase the thermal histories, which might be induced by isothermal annealing in the nematic region and/or built in the as-polymerized specimens, by heating the specimen to a temperature(s) above its T_{NI} and holding there for an extended time period. There is evidence indicating that the variations observed in $|\eta^*|$ are not attributable to changes in the chemical structure (e.g., transesterification) but to the formation of a crystal-like phase at a temperature between ca. 110 and 140 °C. We have confirmed via GPC that no discernible change in average molecular weight occurred after a specimen had been subjected to isothermal annealing in the nematic region for a prolonged period.

At this juncture it is appropriate to first summarize, in light of previous studies,[42–46] the observations made in this study of two endothermic peaks at temperatures below the T_{NI} of PSHQ10 and then speculate on a possible mechanism(s) which may explain the existence of two (slow and fast) transition processes (or dual transitions). Earlier, dual endothermic transitions at temperatures below T_{NI} were observed by Lin and Winter[42,43] on the 73/27 HBA/HNA copolyester, by Butzbach and co-workers[46] on the 58/42 HBA/HNA copolyester, by Cheng and co-workers[44] on a thermotropic copolyester consisting of *p*-benzenedicarboxylic acid, phenylhydroquinone, and (1-phenylethyl)hydroquinone, and by Kyu and co-workers[45] on a thermotropic copolyester consisting of Bisphenol E diacetate, isophthalic acid, and 2,6-naphthalenedicarboxylic acid. In order to facilitate our discussion here, let T_{m1} denote the endothermic peak temperature in a slow process and let T_{m2} denote the endothermic peak temperature in a fast process.

The seemingly complicated dual endothermic transitions for the TLCPs with vastly different chemical structures have the following similarities: (1) a fast process occurs even for a sample which was quenched from a temperature which is higher than T_{m1} and T_{m2}; (2) a slow process occurs during a long-period isothermal annealing; (3) during isothermal annealing the value of T_{m1} increases rapidly with increasing annealing time, whereas the value of T_{m2} remains more or less constant; (4) after a sufficiently long annealing time, the transition enthalpy for a slow process is much greater than that for a fast process; (5) after a sufficiently long annealing time, the peak height of DSC thermogram for a fast process is suppressed and it is not easily discernible (with an exception of the observation made by Kyu and coworkers[45]). These similarities lead us to conclude that the underlying mechanism(s), which is responsible for the existence of dual transitions, may be independent of the chemical structures of the TLCPs and may be an intrinsic nature of TLCP.

However, there are important differences among these studies in two aspects: one is the locations of T_{m1} and T_{m2}, and the other is the kinetics of the slow process. Let us first analyze the locations of T_{m1} and T_{m2}. Using the 73/27 HBA/HNA copolyester Lin and Winter[42,43] reported that T_{m1} was higher than T_{m2} in the range of annealing temperatures employed, whereas using the 58/42 HBA/HNA copolyester Butzbach and co-workers[46] observed that at low annealing temperatures, T_{m1} was lower than T_{m2}, but the value of T_{m1} increased rapidly with increasing annealing temperature and eventually exceeded the value of T_{m2}, yielding a cross-over. By examining the results reported in a paper by Kyu and co-workers[45] (refer to Figure 1 in ref 45), we have noted that a cross-over between T_{m1} and T_{m2} also occurred in their TLCP. A cross-over between T_{m1} and T_{m2} seems to suggest that the location of T_{m1}, regardless of whether it is a high-temperature melting peak or low-temperature melting peak, depends on annealing conditions. Insofar as the locations of T_{m1} and T_{m2} are concerned, the observation made in this study for PSHQ10 is similar to that for the 73/27 HBA/HNA copolyester investigated by Lin and Winter.[42,43]

Let us now analyze the kinetics of the slow process. It should be remembered that the kinetics of the slow process occurring in PSHQ10 was explained with the aid of the plot of transition enthalpy ΔH versus annealing temperature, given in Figure 6. We observe that the rate of phase transition associated with the slow process for the 73/27 HBA/HNA copolyester investigated by Lin and Winter[42] decreases with increasing annealing temperature, suggesting that the range of the annealing temperatures employed lies on the right-hand side of the bell-shaped curve given in Figure 6. We observe, on the other hand, that the rate of phase transition associatied with the slow process for the copolyesters investigated by Cheng and co-workers[44] and Kyu and co-workers[45] increases with increasing annealing temperature, suggesting that the range of the annealing temperatures employed lies on the left-hand side of the bell-shaped curve given in Figure 6. It is of interest to point out that in all experimental results discussed above, T_{m2} coincides closely with the temperature at which ΔH has a maximum in Figure 6. Specifically, T_{m2} for PSHQ10 is about 110 °C at which point the plot of ΔH versus annealing temperature has a maximum.

The similarities and differences observed above regarding the dual-transition behavior of TLCPs lead us to conclude that (1) dual endothermic transitions may be an intrinsic nature of TLCP, (2) the slow transition for different materials may have the same physical origin(s), and (3) the mechanism(s) for dual transition processes may not be independent of each other.

Now a question remains to be answered regarding a possible molecular mechanism(s) for the dual endothermic transition which occurs at a temperature below the T_{NI} of a TLCP. Based on the results from wide-angle X-ray diffraction (WAXD) Lin and Winter[42] attributed the existence of the slow process to high-temperature recrystallization, and Kyu and co-workers[45] attributed it to melting and recrystallization. On the other hand, Cheng and co-workers[44] attributed the existence of the slow process to a solid-solid transformation. We are of the opinion that an analysis of WAXD patterns alone, without having further information on chain conformation, cannot give us a definitive answer to the question posed to us.

According to Rojstaczer and Stein[50] and Hashimoto and co-workers,[51] the mechanism of texture coarsening in typical fine schlieren structures involves the annihilation of disclinations (defects). It should be noted that as-cast PSHQ10 specimens are believed to have considerable amounts of disclinations, which were generated during the evaporation of the solvent (dichloromethane in this study) from solution, and that evaporation of solvent may be regarded as a form of very rapid quenching. This observation then leads us to speculate that during the isothermal annealing at 160 °C much of the disclinations in PSHQ10 might have been annihilated, resulting in domain growth, and thus, when the specimen was cooled slowly down to 130 °C, both the domain growth and the formation of a crystal-like phase were very slow due to an insufficient amount of disclinations present, resulting in very little change in viscosity during the subsequent annealing at 130 °C.

In the investigation of the transient rheological behavior of a TLCP, one needs to control the initial conditions, i.e., the initial morphology of the specimen. In this regard, PSHQ10 offers a very unique opportunity for one to control its initial morphology, by first heating the specimen to the isotropic region, then applying a steady shear flow, thereby annihilating all the defects in the specimen, and finally cooling slowly down to a desired temperature in the nematic region. In Figure 15 we showed that indeed such procedures can be used very effectively to control the initial morphology of PSHQ10 in the nematic region. Such a possibility does not exist in other TLCPs, such as HBA/PET copolyesters and HBA/HNA copolyesters, because the T_{NI}s of these copolyesters are very close to or above their thermal degradation temperatures (say, above 400 °C).

The results of future study which provides the transient rheological responses of a TLCP having a well-controlled initial morphology would be very valuable to compare with theoretical predictions or to provide insight for the development a molecular theory for the dynamic behavior of TLCPs. Having learned in this study how to control the morphology of PSHQ10 in the nematic region, in the future we shall investigate the transient rheological behavior of PSHQ10.

References and Notes

(1) Jackson, W. J.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(2) Calundann, G. W. U.S. Patent 4067852, 1978; 4130545, 1978; 4161470, 1979; 4184996, 1980.
(3) Wissbrun, K. F. *Br. Polym. J.* **1980**, *13*, 163.
(4) Jerman, R. E.; Baird, D. G. *J. Rheol.* **1981**, *25*, 275.
(5) Gotsis, A. D.; Baird, D. G. *J. Rheol.* **1985**, *29*, 539.
(6) Viola, G. G.; Baird, D. G. *J. Rheol.* **1986**, *30*, 601.
(7) Done, D.; Baird, D. G. *Polym. Eng. Sci.* **1987**, *27*, 816.
(8) Sun, T.; Lin, Y. G.; Winter, H. H.; Porter, R. S. *Polymer* **1989**, *30*, 1257.
(9) Kalika, D. S.; Giles, D. W.; Denn, M. M. *J. Rheol.* **1990**, *34*, 139.
(10) Masuda, T.; Fujiwara, K.; Takahashi, M. *Int. Polym. Process.* **1991**, *6*, 225.
(11) Wissbrun, K. F.; Kiss, G.; Cogswell, F. N. *Chem. Eng. Commun.* **1987**, *53*, 149.
(12) Cocchini, F.; Nobile, M. R.; Acierno, D. *J. Rheol.* **1991**, *35*, 1171.
(13) Guskey, S. M.; Winter, H. H. *J. Rheol.* **1991**, *35*, 1191.
(14) Prasadarao, M.; Pearce, E. M.; Han, C. D. *J. Appl. Polym. Sci.* **1982**, *27*, 1343.
(15) Wissbrun, K. F.; Griffin, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1835.
(16) Simoff, D. A.; Porter, R. S. *Mol. Cryst. Liq. Cryst.* **1984**, *110*, 1.
(17) Blumstein, A.; Thomas, O.; Kumar, S. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 27.
(18) Wunder, S. L.; Ramachandran, S.; Cochanour, C. R.; Weinberg, M. *Macromolecules* **1986**, *19*, 1696.
(19) Kiss, G. *J. Rheol.* **1986**, *30*, 585.
(20) Zhou, Z.; Wu, X.; Wang, M. *Polym. Eng. Sci.* **1988**, *28*, 136.
(21) Irwin, R. S.; Sweeny, W.; Gardner, K. H.; Gochanour, C. R.; Weinberg, M. *Macromolecules* **1989**, *22*, 1065.
(22) Gonzalez, J. M.; Minoz, M. E.; Cortazar, M.; Santamaria, A.; Pena, J. J. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1533.
(23) Schneider, H. A.; Stocker, W.; Korn, M.; Krischeldorf, H. R.; Percec, V. *Mol. Cryst. Liq. Cryst.* **1991**, *196*, 57.
(24) Ober, C. K.; Jin, J. I.; Zhou, Q.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
(25) Sirigu, A. In *Liquid Crystallinity in Polymers*; Ciferri, A. Ed.; VCH Publishers: New York, 1991; Chapter 7.
(26) Marcelja, S. *J. Chem. Phys.* **1974**, *60*, 3599.
(27) Dowell, F.; Martire, D. E. *J. Chem. Phys.* **1978**, *68*, 1094.
(28) Ronca, G.; Yoon, D. Y. *J. Chem. Phys.* **1982**, *76*, 3295; **1984**, *80*, 925, 930.
(29) Yoon, D. Y.; Bruckner, S. *Macromolecules* **1985**, *18*, 651.
(30) Abe, A. *Macromolecules* **1984**, *17*, 2280.
(31) Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Macromolecules* **1984**, *17*, 2270.
(32) Antoun, S.; Lenz, R. W.; Jin, J. I. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1901.
(33) Blumstein, A.; Maret, G.; Vilasagar, S. *Macromolecules* **1981**, *14*, 1543.
(34) Roviello, A.; Sirigu, A. *Makromol. Chem.* **1982**, *183*, 895.
(35) Blumstein, A.; Thomas, O. *Macromolecules* **1982**, *15*, 1264.
(36) Zhou, Q.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3313.
(37) Furukawa, A.; Lenz, R. W. *Macromol. Chem., Macromol. Symp.* **1986**, *2*, 3.
(38) 10 at the end of PSHQ10 refers to the number of methylene units present, which in this case is decamethylene, $(CH_2)_{10}$. This convention is chosen in order to distinguish PSHQs with varying methylene units as flexible spacers. In a future study we intend to synthesize PSHQs with varying lengths of the flexible spacers, e.g., PSHQ8 having $(CH_2)_8$ and PSHQ12 having $(CH_2)_{12}$.
(39) Kim, S. S.; Han, C. D. *Polymer*, in press.
(40) The molecular weight of PSHQ10 employed in this study is different from that employed in our previous study (ref 39), because we had to synthesize them at two different occasions.
(41) At present we have no direct information on whether the formation of a new phase, which is associated with the appearance of a high-temperature endothermic peak on the DSC thermogram, is a liquid–solid, liquid–liquid, or solid–solid transition. Therefore, in this paper this new phase is referred to as a crystal-like phase.
(42) Lin, Y. G.; Winter, H. H. *Macromolecules* **1988**, *21*, 2439.
(43) Lin, T. G.; Winter, H. H. *Macromolecules* **1991**, *24*, 2877.
(44) Cheng, S. Z. D.; Zhang, A.; Johnson, R. L.; Wu, Z.; Wu, H. H. *Macromolecules* **1990**, *23*, 1196.
(45) Nam, J.; Fukai, T.; Kyu, T. *Macromolecules* **1991**, *24*, 6250.
(46) Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* **1986**, *27*, 1337.
(47) Wood, L. A.; Bekkedahl, N. *J. Appl. Phys.* **1946**, *17*, 362.
(48) MaGill, J. H. *J. Appl. Phys.* **1964**, *35*, 3246.
(49) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964; Chapter 8.
(50) Rojstaczer, S. R.; Stein, R. S. *Macromolecules* **1990**, *23*, 4863.
(51) Shiwaku, T.; Nakai, A.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1990**, *23*, 1590.