A Thermotropic Main-Chain Random Copolyester Containing Flexible Spacers of Differing Lengths. 2. Rheological Behavior

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ABSTRACT: The rheological behavior of a thermotropic main-chain random copolyester containing flexible spacers of 6 and 12 methylene groups (PSHQ6-12) was investigated. This copolyester undergoes only two thermal transitions: (i) glass transition at ca. 92 °C and (ii) nematic−isotropic transition at ca. 192 °C. Such a very broad range of temperatures between the glass transition temperature and the nematic−isotropic transition temperature allowed us to take rheological measurements in the transient/steady-state shear flow mode or in the oscillatory shear flow mode over a wide range of temperatures in the nematic region. The initial conditions (i.e., the initial morphology) for transient shear flow were controlled by first heating an as-cast specimen to the isotropic region, shearing there at a rate of 0.1 s^{-1} for ca. 10 min, and then cooling slowly down to a preset temperature (140, 150, 160, 170, or 180 °C) in the nematic region. A fresh specimen was used for each transient shear flow experiment, and the shear stress growth ($\sigma^+(t,\dot{\gamma})$) and first normal stress difference growth ($N_1^+(t,\dot{\gamma})$) were recorded as functions of time (t) for various shear rates ($\dot{\gamma}$) and temperatures. In the nematic region, PSHQ6-12 exhibited a single overshoot in $\sigma^+(t,\dot{\gamma})$, but multiple overshoots in $N_1^+(t,\dot{\gamma})$ with its peak value greater than that of $\sigma^+(t,\dot{\gamma})$. In the isotropic region, however, PSHQ6-12 exhibited Newtonian behavior with negligible overshoot in both $\sigma^+(t,\dot{\gamma})$ and $N_1^+(t,\dot{\gamma})$. Only *positive* values of the steady-state first normal stress difference (N_1) were observed in PSHQ6-12 for all temperatures and shear rates investigated. Also conducted were intermittent shear flow experiments after cessation of start-up shear flow, showing evidence of structural recovery in PSHQ6-12 as determined by the overshoot in $N_1^+(t,\dot{\gamma})$. The steady-state shear viscosity of PSHQ6-12 exhibited three regions at 140 and 150 °C: (i) a shear-thinning region at very low $\dot{\gamma}$, (ii) a Newtonian region at an intermediate range of $\dot{\gamma}$, and (iii) another shear-thinning region at higher $\dot{\gamma}$. But PSHQ6-12 exhibited a very mild shear-thinning behavior as the temperature was increased to 180 °C, approaching the isotropic region. Logarithmic plots of N_1 vs shear stress (σ) for PSHQ6-12 were found to vary with temperature in the nematic region but to be independent of temperature in the isotropic region. A similar temperature dependence was also observed in logarithmic plots of the dynamic storage modulus (G') vs dynamic loss modulus (G''). We conclude that plots of log N_1 vs log σ or plots of log G' vs log G'' may be used to determine the isotropization temperature of thermotropic liquid-crystalline polymers.

Introduction

During the past decade, numerous investigators[1−16] reported on the rheological behavior of thermotropic liquid-crystalline polymers (TLCPs). One unique feature which distinguishes the rheological behavior of TLCPs from that of homopolymers lies in the fact that the rheological behavior of the former depends very much on thermal and deformation histories.[1,5,11−14] Therefore, a comparison of the rheological properties of a TLCP reported by one research group with those reported by another research group is not necessarily warranted and can lead to controversy unless the thermal and deformation histories of the specimens are identical. It should be mentioned that the thermal and deformation histories of a TLCP specimen may greatly influence its morphological state as well as its orientational order, which in turn influences its rheological behavior. This then suggests that the thermal history of a TLCP specimen, before being subjected to rheological measurements, be controlled very carefully.

Further, one often observes a continuous change in the rheological properties of a TLCP specimen during experiment, thus making it very difficult, if not impossible, to obtain reproducible rheological data.[5,11] Such situations are encountered when the morphology of a TLCP specimen keeps changing during rheological measurements. Changes in the morphology of a TLCP specimen during rheological measurements may come from, among many factors which depend on the chemical structure of the LCPs and experimental temperature, (i) the growth of liquid crystals, (ii) the formation, via recrystallization, of high-temperature melting crystals, (iii) rearrangements or interchanges of certain chain segments in the specimen, and/or (iv) postpolymerization. To suppress, if not eliminate them completely, changes in the morphology of a TLCP specimen during rheological measurements, earlier Han and coworkers[12−14] suggested that a TLCP specimen be first heated to the isotropic region, thereby erasing its thermal history associated with the polymerization and subsequent sample preparation procedure, and then cooled slowly down to a preset temperature in the nematic region. Such a suggestion is not of practical use for a TLCP which has the clearing temperature (T_{NI}) higher than the thermal degradation temperature.

In part 1 of this series,[17] we reported on the synthesis of a thermotropic main-chain copolyester (PSHQ6-12) with chemical structure

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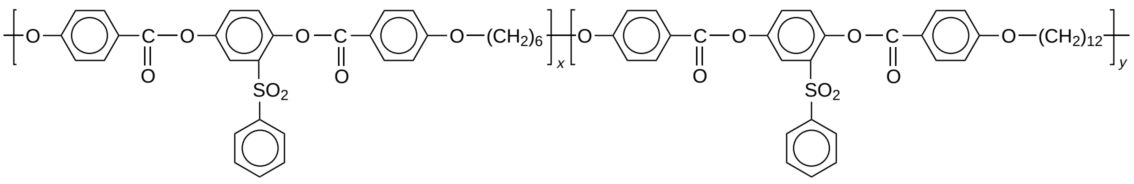

PSHQ6–12

having random distributions of flexible spacers of two different lengths, 6 and 12 methylene (CH_2) groups in the main chain. We observed that PSHQ6-12 has only a glassy nematic phase as determined by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD).

Another important issue in the rheological behavior of TLCPs, which has been discussed rather extensively in the recent literature[9,10,13−15,18] and appears to have not been settled completely among researchers, is the sign of the first normal stress difference (N_1) in steady-state shear flow. In their recent paper,[14] Han et al. have pointed out that the *negative* values of N_1 reported by Guskey and Winter,[9] who employed a commercial TLCP (Vectra A900, Hoechst-Celanese Co.), arose from an erroneous interpretation of their experimental results. Specifically, Guskey and Winter were not aware of the fact that a considerable amount of *unrelaxed* normal stress existed in the Vectra A900 specimen just before a start-up shear flow was applied; i.e., apparently they thought that the specimen was at zero level of normal stress before a start-up shear flow was applied. Han et al.[14] have shown that the values of N_1 in the experiments of Guskey and Winter would have turned out to be *positive* if nonzero initial values of normal stress in the Vectra A900 specimen had been recognized just before a start-up shear flow was applied. Using main-chain TLCPs, Kim and Han[13] and Baek et al.[15] obtained only *positive* values of N_1 in the nematic region.

Very recently, we conducted a comprehensive experimental study on the rheological behavior of copolyester PSHQ6-12, placing emphasis on controlling the initial conditions for the specimen in investigating (1) transient shear flow behavior, (2) steady-state shear flow behavior, and (3) oscillatory shear flow behavior. Independent of the rheological measurements performed, we investigated the morphology of specimens using an optical microscope under cross-polarized light, by duplicating the thermal histories (without shear flow) experienced by the specimens during rheological measurements. In this paper, we report the highlights of our findings.

Experimental Section

Materials and Sample Preparation. The synthesis procedure and characterization of copolyester PSHQ6-12 employed in this study are described in our previous papers.[17,20] Specimens for rheological measurements were prepared by dissolving in dichloromethane in the presence of an antioxidant, and the solvent was evaporated slowly first at room temperature for a week and then in a vacuum oven at 90 °C for 3 days. Just prior to the rheological measurement, the specimen was further dried at 110 °C under vacuum for 2 h to remove any residual solvent and moisture.

Rheological Measurement. A Rheometrics mechanical spectrometer (RMS Model 800) with a cone-and-plate (8-mm-diameter plate, 0.1 rad cone angle) fixture was used to measure (1), in the transient shear mode, the shear stress growth ($\sigma^+(t,\dot{\gamma})$) and first normal stress difference growth ($N_1{}^+(t,\dot{\gamma})$) as functions of time (t) for various shear rates ($\dot{\gamma}$) and temperatures and (2), in the steady-state shear mode, the shear viscosity (η) and first normal stress difference (N_1) as functions of shear rate ($\dot{\gamma}$) and temperature. Also, the dynamic storage and loss moduli (G' and G'') were measured as functions of the angular frequency (ω). Strain amplitude was varied from 0.01 to 0.06, which was well within the linear viscoelastic range of the materials investigated. All experiments were conducted under a nitrogen atmosphere in order to preclude oxidative degradation of the specimen. The temperature control was satisfactory to within ±1 °C.

Polarized Optical Microscopy (POM). It would have been ideal to simultaneously take rheological measurements and observe the morphology while a specimen was under shear flow. Lacking of such experimental capabilities in our laboratory, we conducted separate experiments to observe the morphology of PSHQ6-12 specimens under static conditions, by duplicating the thermal histories of the specimens employed for the rheological measurements. The primary purpose of the POM was to identify the initial conditions for rheological measurements, especially for transient shear flow. A hot-stage (TH-600 type, Linkham Scientific Co.), microscope (Nikon, Model Optiphoto polXTP-11) with a camera and a programmable temperature controller, and photomicrographic attachment were used to take pictures, under cross-polarized light, of as-cast films which were placed between two glass plates which were sealed by silicone adhesive.

Wide-Angle X-ray Diffraction (WAXD). WAXD experiments were conducted at room temperature, using a General Electric X-ray generator (Model XRD-6) operating at 30 kV and 30 mA (Ni filtered Cu Kα radiation), on an as-cast PSHQ6-12 specimen (i) right after being squeezed from ca. 1.5 mm to 50 μm within the cone-and-plate fixture of the rheometer and (ii) also after being subjected to an oscillatory shear flow at ω = 1 rad/s for a predetermined period (2.7 h) under isothermal conditions. The specimen was cut along the radial direction, which was the major flow direction during squeeze flow, with a width of ca. 1 mm. The purpose of the WAXD experiments performed was to investigate how the squeezing applied to a specimen might have affected the orientation patterns of the polymer chains during the rheological measurement of the specimen. The flat plate diffraction patterns were recorded. The exposure time for each measurement was ca. 4 h.

Results and Discussion

Procedures Employed for Controlling the Initial Conditions for Rheological Measurements of the PSHQ6-12 Specimens in the Nematic Region. As mentioned in the Introduction, it is extremely important for one to establish procedures for controlling the initial conditions for rheological measurements of TLCPs in the nematic region. In a previous paper,[17] we have reported from DSC traces that PSHQ6-12 is glassy below 92 °C and undergoes a nematic−isotropic transition at 192 °C; i.e., it has only a nematic phase at temperatures between 92 and 192 °C.

Figure 1 describes the variations of G' and G'' with time for as-cast PSHQ6-12 specimens, which were placed in the cone-and-plate fixture of the rheometer at 140, 160, and 180 °C, respectively, in the nematic region and then subjected to an oscillatory shear flow at ω = 1 rad/s. Note that a fresh specimen was employed for each experimental run. The following observations are noteworthy in Figure 1: (1) at a fixed experimental temperature, the values of G'' are greater than those of G'; (2) both G' and G'' decrease as the temperature is increased from 140 to 180 °C; (3) at 140

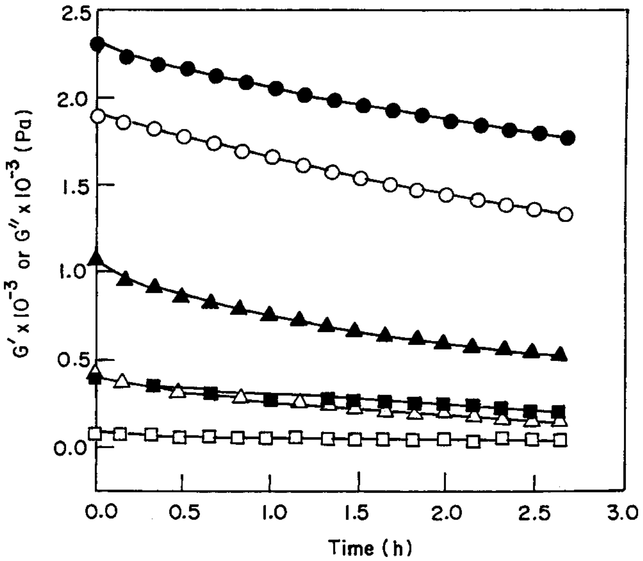

Figure 1. Variations of G' (open symbols) and G'' (filled symbols) with time at $\omega = 1$ rad/s for as-cast PSHQ6-12 specimens at various temperatures: (○, ●) 140 °C; (△, ▲) 160 °C; (□, ■) 180 °C.

°C, both G' and G'' monotonically decrease with time during the entire period of experiment which lasted for ca. 2.7 h; (4) at 160 °C, the rate of decrease in G' is much slower than that in G''; and (5) at 180 °C, G'' decreases very slowly with time, while G' remains more or less constant for the entire period of experiment, which lasted for ca. 2.7 h.

In order to determine a factor(s) which might have contributed to the steady decrease of G' and G'' with time observed in Figure 1, we monitored the time evolution of morphology of a PSHQ6-12 specimen, using an optical microscope under cross-polarized light. The experimental procedures employed are as follows: (i) a thin film was first cast from a solution on a glass plate, and then the film was dried in a vacuum oven to remove the solvent; (ii) the thin film was covered with another glass plate, and the edges of the two glass plates were sealed with an adhesive in order to avoid any contact between the specimen and air during subsequent experiment; and (iii) the glass plates containing a specimen were placed on a cross-polarized optical microscope stage which was heated at a preset temperature (140, 160, or 180 °C), and then pictures were taken at intervals during the period of ca. 3 h. Figure 2 gives micrographs for PSHQ6-12 specimens having the following thermal histories: (i) upon being placed on the microscope at 140 °C and after subsequent annealing for 3 h, (ii) upon being placed on the microscope at 160 °C and after subsequent annealing for 3 h, and (iii) upon being placed on the microscope at 180 °C and after subsequent annealing for 3 h. In Figure 2, we observe that (1) PSHQ6-12 has Schlieren textures at all three temperatures (140, 160, and 180 °C) investigated and (2) Schlieren texture grows with time, the rate of which is faster with increasing temperature from 140 to 180 °C.

Since an as-cast PSHQ6-12 specimen had to be squeezed from ca. 1.5 mm to 50 μm within the cone-and-plate fixture of the rheometer before rheological measurements began, we were interested in knowing how much the squeezing applied to the specimen might have affected its subsequent rheological behavior. For this, WAXD measurements were taken of as-cast PSHQ6-12 specimens before and after being squeezed in the cone-and-plate fixture and, also, after being annealed for a predetermined period in the cone-and-plate fixture. WAXD patterns of an as-cast PSHQ6-12 specimen, which had been dried in a vacuum oven at 90 °C for 3 days before rheological measurement, indicated that the specimen had uniform diffraction patterns. However, as can be seen in Figure 3a, when an as-cast PSHQ6-12 specimen was loaded into the cone-and-plate fixture at 140 °C in the nematic region and then squeezed from ca. 1.5 mm to 50 μm, it exhibits evidence of orientation introduced by squeezing. Figure 3b shows that the orientation in the specimen introduced by squeezing persisted even after annealing at 140 °C for 2.7 h under an oscillatory shear flow at $\omega = 1$ rad/s. This may be due to the fact that the moduli (G' and G'') of the specimen were too large to undergo discernible relaxation during annealing at 140 °C for 2.7 h. It is of interest to observe in parts c and d of Figure 3, however, that when an as-cast PSHQ6-12 specimen was loaded into the cone-and-plate fixture at 160 °C in the nematic region and then squeezed from ca. 1.5 mm to 50 μm, the extent of orientation introduced to the specimen by squeezing decreased considerably during the subsequent annealing at 160 °C for 2.7 h. Notice in Figure 1 that the values of G' at 160 °C are much smaller than those at 140 °C. Therefore, it seems reasonable to speculate that the orientation introduced to the specimen by squeezing at 160 °C underwent considerable relaxation during subsequent annealing under an isothermal condition.

We can now conclude from the above observations that the variations of G' and G'' with time shown in Figure 1 are attributable to (1) the growth of Schlieren textures with time during rheological measurements and (2) the orientational change in domain texture which was caused by the squeeze flow introduced during sample loading. It should be mentioned that the squeeze flow applied to the specimen in the nematic region might have disrupted the initial domain texture (the boundaries of the polydomains) of the as-cast PSHQ6-12 specimen and consequently contributed significantly to a change in domain texture.

Figure 4a gives the temperature protocol employed, and Figure 4b gives variations of G' with time after a PSHQ6-12 specimen was placed in the cone-and-plate fixture of the rheometer and then subjected, in accordance with the prescribed temperature protocol, to an oscillatory shear flow at $\omega = 1$ rad/s. In Figure 4b, we observe that the repeated measurement at 160 °C in the nematic region, after an excursion to 140 °C (step 2), is not reproduced (compare curve 1 with curve 3). This observation indicates to us that the morphology of the specimen at step 1, after being cooled to 140 °C, was not reproduced at step 3. What is of great interest in Figure 4b is that during the oscillatory shear flow at $\omega = 1$ rad/s for ca. 2.7 h, the values of G' at steps 1 and 3 decrease steadily with time, while the value of G' at step 4 (curve 4) stays more or less constant at ca. 5000 Pa, which is about 5 times greater than the value of G' at step 3 (curve 3) at the end of annealing for 2.7 h. Note that curve 4 in Figure 4b was obtained after the specimen was heated to 205 °C in the isotropic region and then cooled slowly down to 160 °C. The above observations suggest to us that three different thermal histories, steps 1, 3, and 4, give rise to different specimen morphologies and, consequently, different rheological responses. Which of the three thermal histories (steps 1, 3, or 4) might give rise to the most

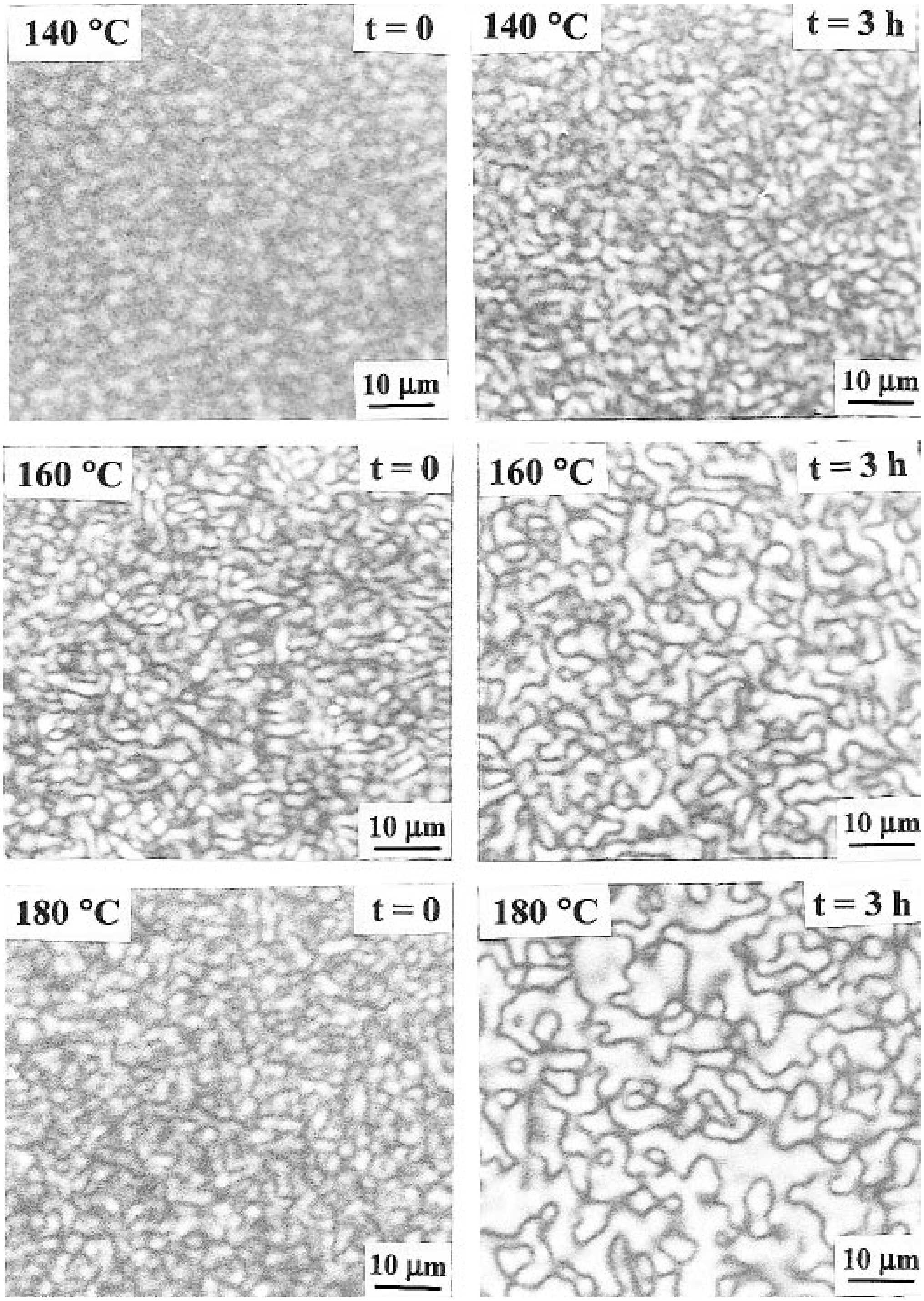

Figure 2. Cross-polarized optical micrographs for as-cast PSHQ6-12 specimens annealed at temperatures indicated for different periods: (a) in the beginning of annealing at 140 °C; (b) after annealing for 3 h at 140 °C; (c) in the beginning of annealing at 160 °C; (d) after annealing for 3 h at 160 °C; (e) in the beginning of annealing at 180 °C; (b) after annealing for 3 h at 180 °C.

reproducible rheological responses was investigated by the procedures described below.

Figure 5a gives the temperature protocol employed and Figure 5b gives the frequency dependence of G' for a PSHQ6-12 specimen at 205 °C in the isotropic region and at 160 °C in the nematic region. The arrow placed on the left side of Figure 5a indicates the time at which rheological measurements commenced, i.e., 20 min after a specimen was loaded in the rheometer at 205 °C. In Figure 5b, we observe that the rheological measurements taken at 160 °C at steps 2 and 4 are reproduced, in contrast to the results given in Figure 4b (steps 1 and 3). This observation indicates to us that the thermal treatment given to a PSHQ6-12 specimen at 205 °C in the isotropic region was very effective to obtain reproducible rheological measurements in the nematic region. Note that the value of G' at $\omega = 1$ rad/s at steps 2 and 4 in Figure 5b agrees well with the value of G' at step 4 in Figure 4b.

We observed that the specimen which was first heated to 205 °C in the isotropic state followed by squeezing and then cooled slowly down to 160 °C in the nematic region exhibits *uniform* WAXD patterns, indicating *little* evidence of radial orientation introduced to the specimen by squeezing. This observation is quite different from that made in reference to Figure 3, showing strong radial orientation introduced to an as-cast PSHQ6-12 specimen which was loaded into the cone-and-plate

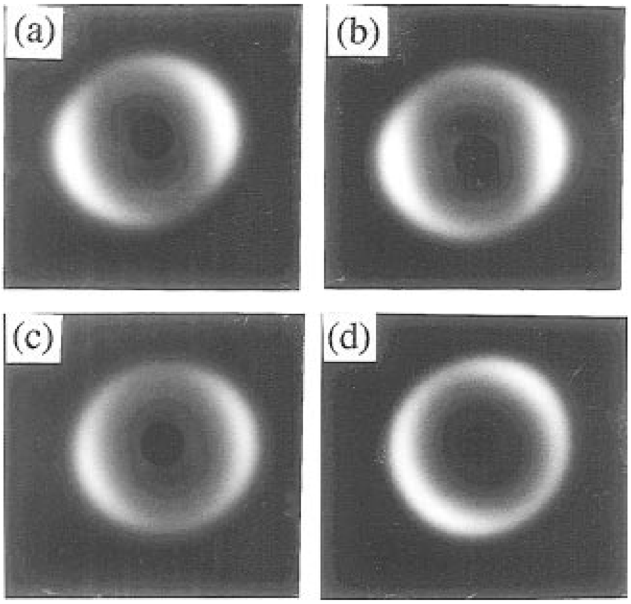

Figure 3. WAXD patterns of as-cast PSHQ6-12 specimens: (a) right after being squeezed in the cone-and-plate fixture at 140 °C; (b) after being annealed for 2.7 h at 140 °C under an oscillatory shear flow at $\omega = 1$ rad/s; (c) right after being squeezed in the cone-and-plate fixture at 160 °C; (d) after being annealed for 2.7 h at 160 °C under an oscillatory shear flow at $\omega = 1$ rad/s.

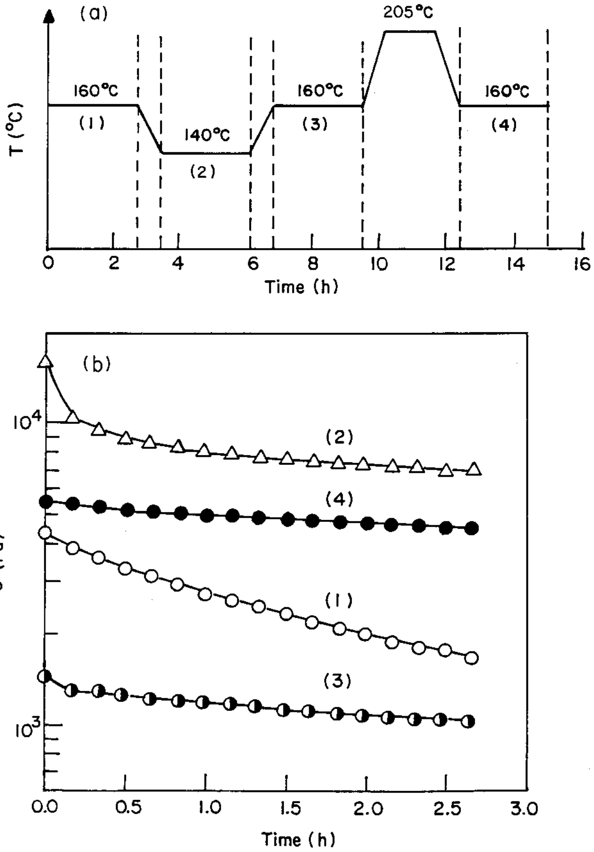

Figure 4. (a) Temperature protocols employed and (b) variations of G' with time for an as-cast PSHQ6-12 specimen having the thermal histories as indicated in the temperature protocols, namely, curve 1 for the temperature protocol 1, curve 2 for the temperature protocol 2, curve 3 for the temperature protocol 3, and curve 4 for the temperature protocol 4.

fixture at 160 °C in the nematic region, without receiving thermal treatment in the isotropic region, followed by squeezing. Therefore, in all subsequent rheological measurements, the results of which are presented below, as-cast PSHQ6-12 specimens were first heated to the isotropic region and then cooled slowly down to a preset temperature in the nematic region. Note that in this procedure, a specimen was squeezed at 205 °C in the isotropic region.

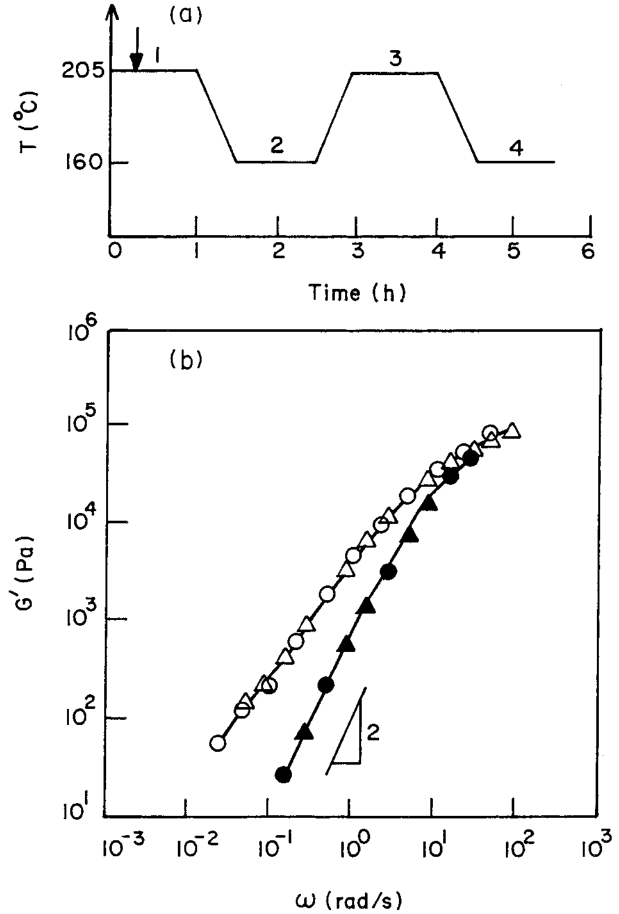

Figure 5. (a) Temperature protocols employed where the arrow indicates the time at which rheological measurements commenced and (b) plots of log G' vs log ω for an as-cast PSHQ6-12 specimen having the thermal histories as indicated in the temperature protocols: (●) temperature protocol 1; (○) temperature protocol 2; (▲) temperature protocol 3; (△) temperature protocol 4.

Transient Shear Flow Behavior of the PSHQ6-12 Specimens. Figure 6 gives plots of $\sigma^+(t,\dot\gamma)$ vs shear strain ($\dot\gamma t$), and Figure 7 gives plots of $N_1{}^+(t,\dot\gamma)$ vs $\dot\gamma t$, at $\dot\gamma = 0.1$ s^{-1} for PSHQ6-12 specimens at 205 °C in the isotropic region and at 189, 180, 170, 160, and 150 °C in the nematic region. Note that a fresh specimen was used for each temperature to obtain the transient shear flow responses given in Figures 6 and 7. In obtaining Figure 7 and all other results for the $N_1{}^+(t,\dot\gamma)$ presented below, we ascertained that initially (i.e., at $t = 0$) the normal stress was zero. This was made possible by first loading a specimen in the cone-and-plate fixture, which was preheated at a temperature in the isotropic region, and then cooling the specimen very slowly (at a rate of 1 °C/min) to a preset temperature in the nematic region. During cooling, the gap was adjusted to compensate for thermal shrinkage of the plates.

In Figure 6, we observe, upon start-up of shear flow, an overshoot for 189, 180, 170, 160, and 150 °C, respectively, in a very short time, but not for 205 °C. The overshoot in $\sigma^+(t,\dot\gamma)$ observed in Figure 6 signifies the presence of polydomains in the specimen.[13] The

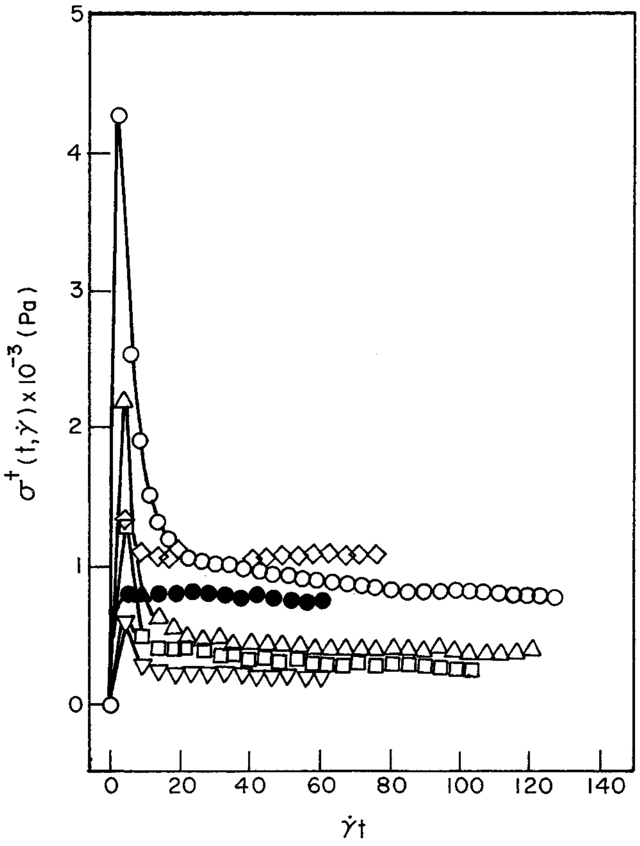

Figure 6. Plots of $\sigma^+(t,\dot{\gamma})$ vs $\dot{\gamma}t$ for PSHQ6-12 specimens at $\dot{\gamma} = 0.1$ s^{-1} for various temperatures: (○) 150 °C; (△) 160 °C; (□) 170 °C; (▽) 180 °C; (◇) 189 °C; (●) 205 °C. A fresh specimen was used for each temperature. Except for the data taken at 205 °C, each specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

peak values (σ_{max}) in Figure 6 at various temperatures have the following ordering: $\sigma_{max,150°C} > \sigma_{max,160°C} > \sigma_{max,189°C} > \sigma_{max,170°C} > \sigma_{max,180°C}$, whereas the steady-state shear stresses (σ) at various temperatures have the following ordering: $\sigma_{189°C} > \sigma_{150°C} > \sigma_{160°C} > \sigma_{170°C} > \sigma_{180°C}$. What seems most appropriate here is to use the σ_{max}/σ ratio to assess the effect of temperature on $\sigma^+(t,\dot{\gamma})$.[13] We have the following ordering: $(\sigma_{max}/\sigma)_{150°C} > (\sigma_{max}/\sigma)_{160°C} > (\sigma_{max}/\sigma)_{170°C} > (\sigma_{max}/\sigma)_{180°C} > (\sigma_{max}/\sigma)_{189°C}$. This ordering makes sense because the σ_{max}/σ ratio decreases as the temperature approaches the T_{NI} (ca. 192 °C) of the specimen. Notice in Figure 6 that the σ_{max}/σ ratio is zero at 205 °C in the isotropic region.

In Figure 7, we make the following observations. (1) $N_1^+(t,\dot{\gamma})$ is virtually zero at 205 °C in the isotropic region. (2) A very large overshoot is seen at 150, 160, and 170 °C but a relatively small overshoot at 180 and 189 °C, indicating that the peak value ($N_{1,max}$) increases as the temperature moves farther away from its T_{NI}. An overshoot in $N_1^+(t,\dot{\gamma})$ also signifies the presence of polydomains in the specimen.[13] (3) The values of $N_{1,max}$ at various temperatures have the following ordering: $N_{1,max150°C} > N_{1,max160°C} > N_{1,max170°C} > N_{1,max180°C} \approx N_{1,max189°C}$, and the same ordering holds for the steady-state values (N_1). (4) Multiple overshoots in $N_1^+(t,\dot{\gamma})$ are seen at 150 and 160 °C.

Effect of Preshearing on the Transient Shear Flow Behavior of PSHQ6-12. Figure 8 gives plots of $\sigma^+(t,\dot{\gamma})$ vs $\dot{\gamma}t$, and Figure 9 gives plots of $N_1^+(t,\dot{\gamma})$ vs $\dot{\gamma}t$, at $\dot{\gamma} = 0.1$ s^{-1} for a PSHQ6-12 specimen, which was subjected to start-up shear flow by decreasing the temperature stepwise from 207 to 151 °C. In obtaining Figures 8 and 9, a single specimen was employed.

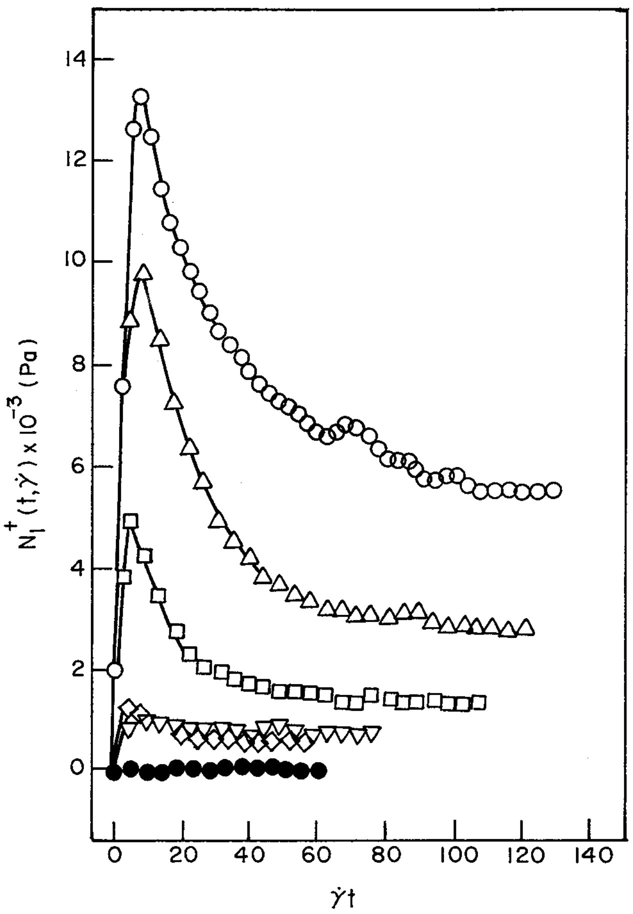

Figure 7. Plots of $N_1^+(t,\dot{\gamma})$ vs $\dot{\gamma}t$ for PSHQ6-12 specimens at $\dot{\gamma} = 0.1$ s^{-1} for various temperatures: (○) 150 °C; (△) 160 °C; (□) 170 °C; (▽) 180 °C; (◇) 189 °C; (●) 205 °C. A fresh specimen was used for each temperature. Except for the data taken at 205 °C, each specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

The following observations are noteworthy in Figure 8. (1) $\sigma^+(t,\dot{\gamma})$ is increased, without an overshoot, as the temperature is decreased from 207 to 196 °C in the isotropic region. (2) However, at 191 °C, very close to the T_{NI} (192 °C) of PSHQ6-12, a small overshoot in $\sigma^+(t,\dot{\gamma})$ occurs and its steady-state value (σ) is considerably larger than that at other temperatures investigated. (3) As the temperature is decreased to 186 °C (ca. 6 °C below T_{NI}), a very large overshoot in $\sigma^+(t,\dot{\gamma})$ occurs and its steady-state value is smaller than that at 207 °C (ca. 15 °C above T_{NI}). The large overshoot at 186 °C signifies that a large shear stress is needed to disrupt the polydomains in the specimen under the influence of shear flow. (4) As the temperature is decreased from 186 to 181, 176, 171, and 166 °C, the values of both σ_{max} and σ are decreased steadily, in spite of the fact that the temperature of the specimen is driven farther away from its T_{NI}. (5) As the temperature is decreased further to 161 and to 151 °C, the values of σ_{max} and σ are increased, after going through a minimum at 166 °C, and a very large overshoot is seen at 151 °C, which is attributable to an increased orientation and, also, an increased intermolecular friction of the nematic phase in the specimen.

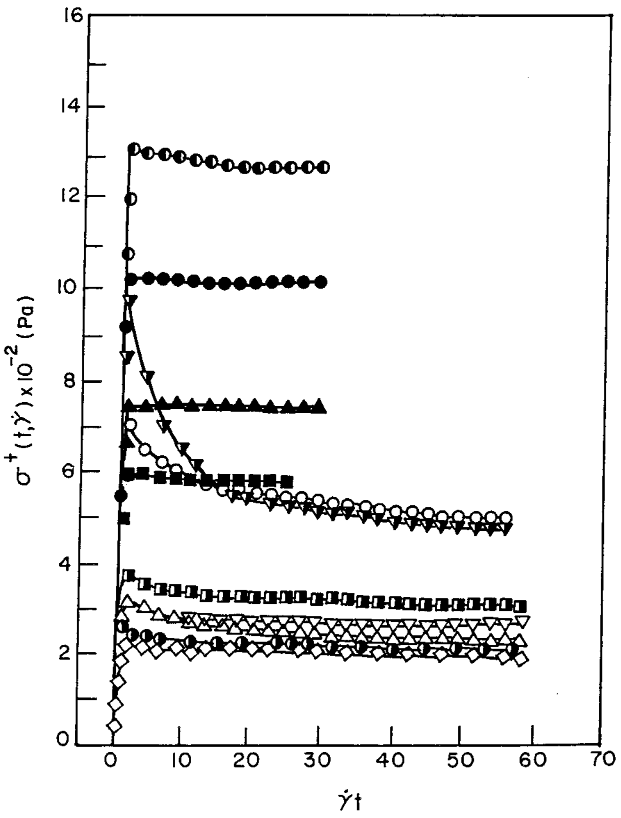

Figure 8. Plots of $\sigma^+(t,\dot\gamma)$ vs $\dot\gamma t$ for a PSHQ6-12 specimen at $\dot\gamma = 0.1$ s^{-1} for various temperatures: (■) 207 °C; (▲) 202 °C; (●) 196 °C; (◐) 191 °C; (▼) 186 °C; (◨) 181 °C; (▽) 176 °C; (◑) 171 °C; (◇) 166 °C; (△) 161 °C; (○)151 °C. A single specimen was used for all temperatures investigated. The specimen was first heated to 207 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, cooled stepwise to a preset temperature, and finally subjected to start-up shear flow.

A comparison of Figure 8 with Figure 6 indicates that the values of $\sigma_{\max}$ and, also, the $\sigma_{\max}/\sigma$ ratio, are much smaller for presheared specimens (Figure 8) than for fresh specimens (Figure 6). This observation can be explained by an argument that, upon start-up of shear flow, the grain boundaries of polydomains in a fresh specimen are disrupted, giving rise to domain textures closer to monodomains in which all directors tend to align more or less in the same direction. This suggests that preshearing has a profound influence on subsequent transient shear flow responses.

The following observations are noteworthy in Figure 9. (1) In the isotropic region, there is virtually no overshoot in $N_1^+(t,\dot\gamma)$ and negligibly small values of N_1 appear, indicative of Newtonian behavior. (2) In the nematic region, however, we observe multiple peaks of $N_1^+(t,\dot\gamma)$ at 151, 161, 166, and 171 °C, the magnitude of which becomes greater as the temperature decreased from 171 to 151 °C (i.e., farther away from T_{NI}). Notice that the strain $\dot\gamma t$ required for $N_1^+(t,\dot\gamma)$ to attain steady state is increased as the temperature is decreased from 171 to 151 °C. Earlier, similar observations were also reported for other types of TLCP.[12,13] The multiple peaks observed are believed to be characteristic of TLCP in general, which is predicted by Marrucci and Maffettone.[21] (3) Over the entire range of temperatures investigated in the nematic region, we only observe *positive* values of $N_1^+(t,\dot\gamma)$, in agreement with previous studies[10,13–15] on other types of TLCP. We wish to point out once again that in the present study, the normal force was zero before transient shear flow began. Again, the values of $N_{1,\max}$ are much smaller for presheared specimens (Figure 9) than for fresh specimens (Figure 7).

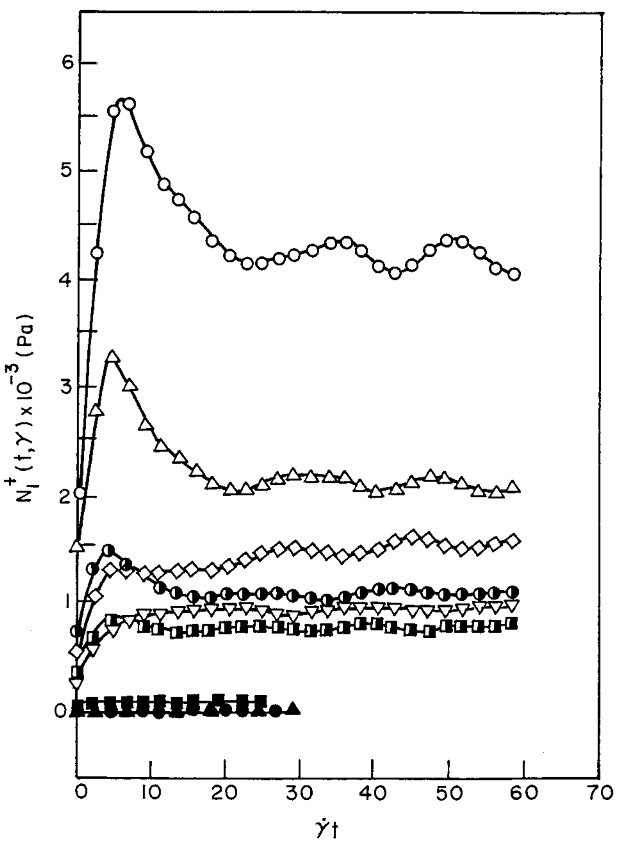

Figure 9. Plots of $N_1^+(t,\dot\gamma)$ vs $\dot\gamma t$ for a PSHQ6-12 specimen at $\dot\gamma = 0.1$ s^{-1} for various temperatures: (■) 207 °C; (▲) 202 °C; (●) 196 °C; (◨) 181 °C; (▽) 176 °C; (◑) 171 °C; (◇) 166 °C; (△) 161 °C; (○)151 °C. For clarity, the data points for 186 and 191 °C are not shown. A single specimen was used for all temperatures investigated. The specimen was first heated to 207 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, cooled stepwise to a preset temperature, and finally subjected to start-up shear flow.

Let us now discuss the initial morphology of PSHQ6-12 specimens just before being subjected to a start-up shear flow. It would have been ideal if we could have observed the domain textures of specimens while being sheared in the cone-and-plate fixture of the rheometer. However, such an endeavor would have required a specially designed apparatus (i.e., transparent cone-and-plate fixture constructed of quartz). In the absence of such an apparatus, in the present study, we employed an optical microscope, under cross-polarized light, to observe the domain textures of PSHQ6-12 specimens, by duplicating the thermal histories of the specimens employed in separate rheological measurements.

Figure 10 gives polarized optical micrographs for a PSHQ6-12 specimen, which was cooled in an optical microscope at 1 °C/min: (i) upon reaching 195 °C, (ii) upon reaching 181 °C, (iii) upon reaching 180 °C, (iv) 1 min after reaching 180 °C, (v) 30 min after reaching 180 °C, and (vi) 1 h after reaching 180 °C. In reference to Figure 10, with the magnification 1200×, during cooling we could first observe domain textures of the specimen at ca. 181 °C, very close to the isotropic–nematic transition temperature as determined by DSC during cooling (not shown here). It can be seen in Figure 10 that once nucleation began, domain textures grew very fast initially and then slowed down.

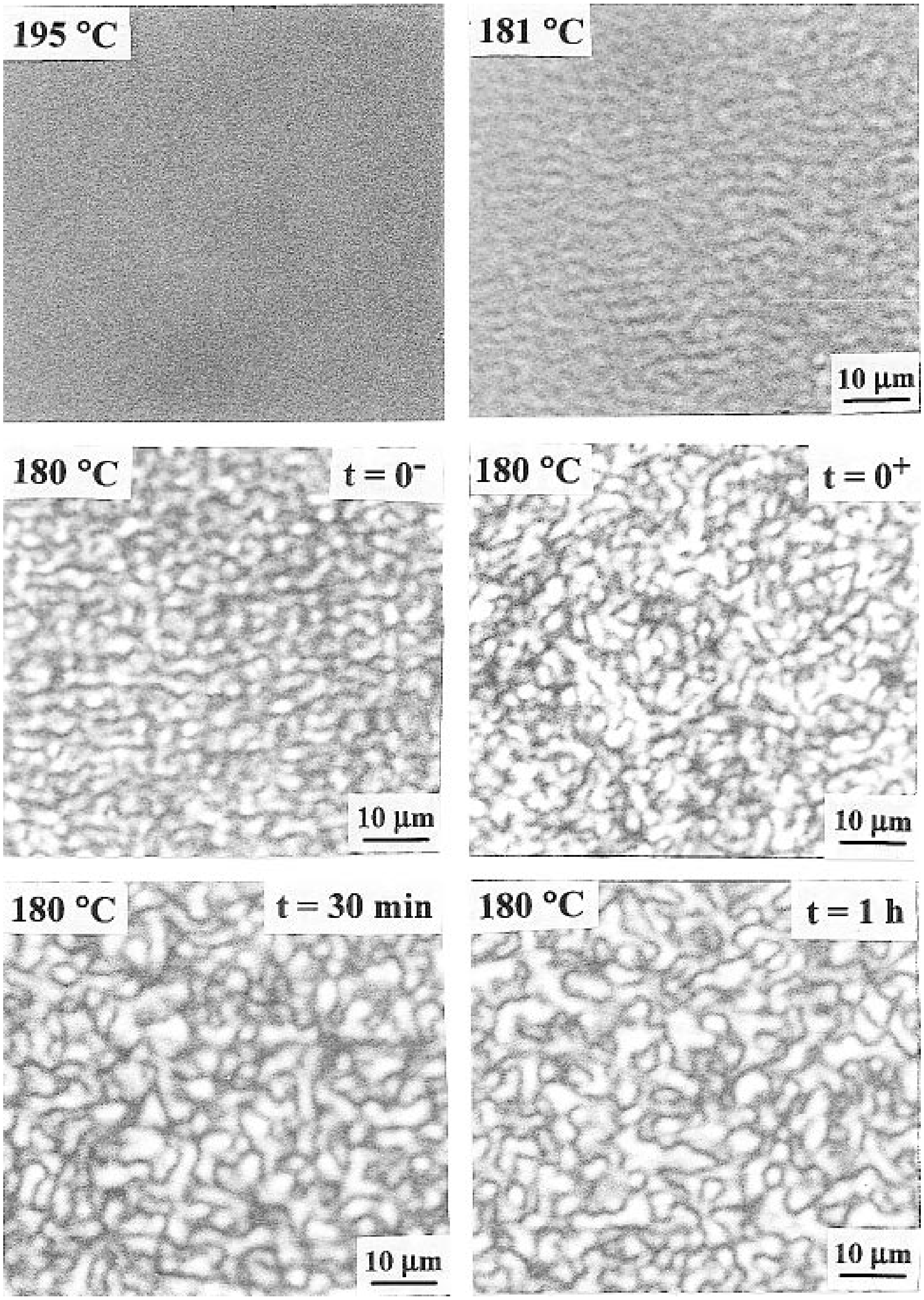

Figure 10. Cross-polarized optical micrographs taken of a PSHQ6-12 specimen during cooling from 195 °C in the isotropic region to 180 °C in the nematic region.

Effect of Shear Rate on Transient Shear Flow Behavior of PSHQ6-12. Figures 11 and 12 describe the effect of $\dot{\gamma}$ on the transient shear responses of PSHQ6-12 at 170 °C, where a fresh specimen was employed for each $\dot{\gamma}$. We detected an onset of flow instability at $\dot{\gamma}$ higher than ca. 0.3 s^{-1}. Figures 11 and 12 show that the peak values, $\sigma_{\max}$ and $N_{1,\max}$, and also the corresponding steady-state values, σ and N_1, are increased as $\dot{\gamma}$ is increased from 0.03 to 0.3 s^{-1}. A close look at Figures 11 and 12 shows that as $\dot{\gamma}$ is increased, the value of $\dot{\gamma}t$ at which the peak of $\sigma^+(t,\dot{\gamma})$ appears remains *virtually* constant, while the value of $\dot{\gamma}t$ at which the peak of $N_1{}^+(t,\dot{\gamma})$ appears is increased.

Intermittent Shear Flow of PSHQ6-12 and Structural Recovery after Cessation of Start-Up Shear Flow. A series of transient shear flows were applied intermittently to a fresh specimen after first receiving a thermal treatment at 205 °C in the isotropic region. Figures 13 and 14 describe $\sigma^+(t,\dot{\gamma})$ and $N_1{}^+(t,\dot{\gamma})$, respectively, at $\dot{\gamma} = 0.1$ s^{-1} in start-up shear flow and two intermittent shear flows for a PSHQ6-12 specimen at 160 °C. The following observations are made in Figures 13 and 14: (i) during the start-up shear flow (i.e., for fresh specimen) (○), both $\sigma^+(t,\dot{\gamma})$ and $N_1{}^+(t,\dot{\gamma})$ go through a large overshoot, (ii) during the first intermittent shear flow (◑), which took place after resting for 3 min upon cessation of the first start-up shear flow, there are virtually no overshoots in both $\sigma^+(t,\dot{\gamma})$ and $N_1{}^+(t,\dot{\gamma})$; (iii) during the second intermittent shear flow (△), which took place after resting for 3 h upon cessation of the

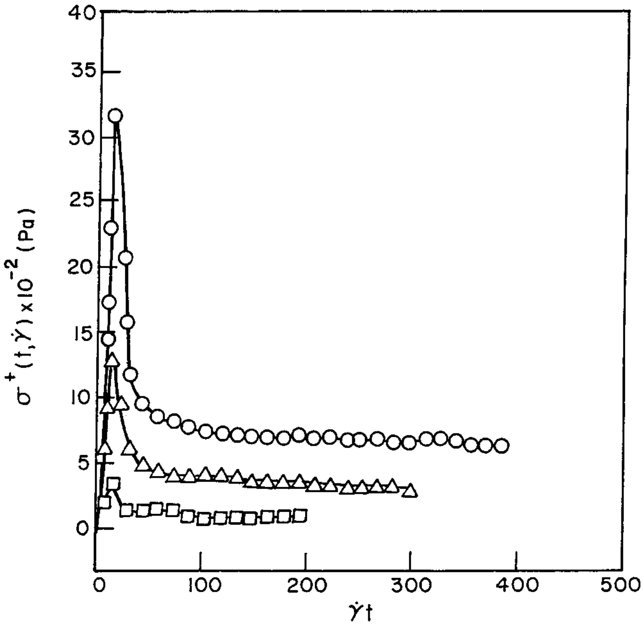

Figure 11. Plots of $\sigma^+(t,\dot\gamma)$ vs $\dot\gamma t$ for PSHQ6-12 specimens at 170 °C for different values of $\dot\gamma$: (○) 0.3 s^{-1}; (△) 0.1 s^{-1}; (□) 0.03 s^{-1}. A fresh specimen was used for each temperature. Each specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to 170 °C in the nematic region.

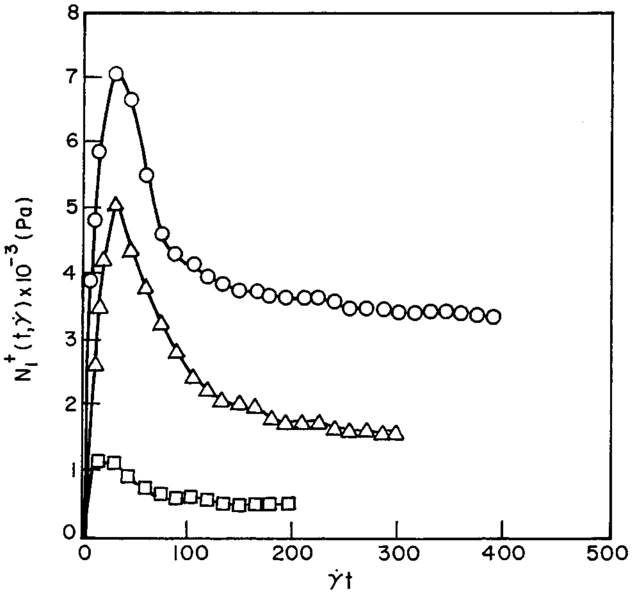

Figure 12. Plots of $N_1^+(t,\dot\gamma)$ vs $\dot\gamma t$ for PSHQ6-12 specimens at 170 °C for different values of $\dot\gamma$: (○) 0.3 s^{-1}; (△) 0.1 s^{-1}; (□) 0.03 s^{-1}. A fresh specimen was used for each temperature. Each specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to 170 °C in the nematic region.

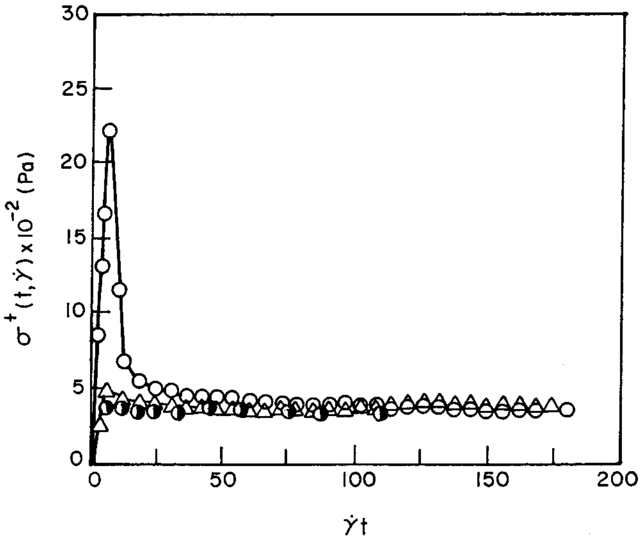

Figure 13. Plots of $\sigma^+(t,\dot\gamma)$ vs $\dot\gamma t$ for a PSHQ6-12 specimen at 160 °C and $\dot\gamma = 0.1$ s^{-1}: (○) the initial start-up shear flow; (◑) intermittent shear flow after resting for 3 min upon cessation of the initial start-up shear flow; (△) intermittent shear flow after resting for 3 h upon cessation of the initial start-up shear flow. A fresh specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to 160 °C in the nematic region.

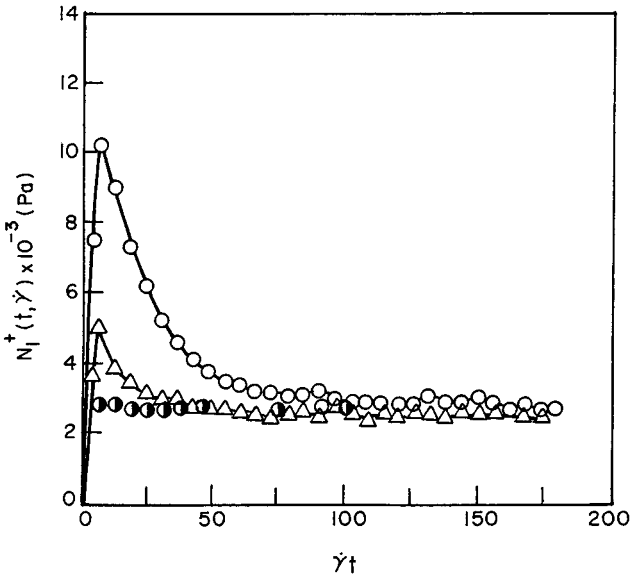

Figure 14. Plots of $N_1^+(t,\dot\gamma)$ vs $\dot\gamma t$ for a PSHQ6-12 specimen at 160 °C and $\dot\gamma = 0.1$ s^{-1}: (○) the initial start-up shear flow; (◑) intermittent shear flow after resting for 3 min upon cessation of the initial start-up shear flow; (△) intermittent shear flow after resting for 3 h upon cessation of the initial start-up shear flow. A fresh specimen, before being subjected to start-up shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to 160 °C in the nematic region.

first start-up shear flow, an appreciable overshoot in $N_1^+(t,\dot\gamma)$, but a very small overshoot in $\sigma^+(t,\dot\gamma)$, is seen. On the basis of the interpretation offered above to the origin of an overshoot in $N_1^+(t,\dot\gamma)$, we can conclude from Figure 14 that structural recovery has taken place in the specimen while resting for 3 h upon cessation of the first start-up shear flow, i.e., the grain boundaries in the polydomains, which had been disrupted during the start-up shear flow, were re-formed during rest for 3 h. The above observation suggests that $N_1^+(t,\dot\gamma)$ is much more sensitive to structural recovery taking place in PSHQ6-12 than $\sigma^+(t,\dot\gamma)$. Earlier, similar observations were reported for other types of TLCP.[22]

Steady-State Shear Flow Behavior of PSHQ6-12. Returning to Figure 8, the steady-state shear viscosity (η) has the following ordering: $\eta_{191°C} > \eta_{196°C} > \eta_{202°C} > \eta_{207°C} > \eta_{151°C} > \eta_{186°C} > \eta_{181°C} > \eta_{176°C} > \eta_{161°C} > \eta_{171°C} > \eta_{166°C}$. This behavior is summarized in Figure 15, showing how the η of PSHQ6-12 at $\dot\gamma = 0.1$ s^{-1} varies with temperature. We observe in Figure 15 that (i) η decreases steadily, going through a minimum, with

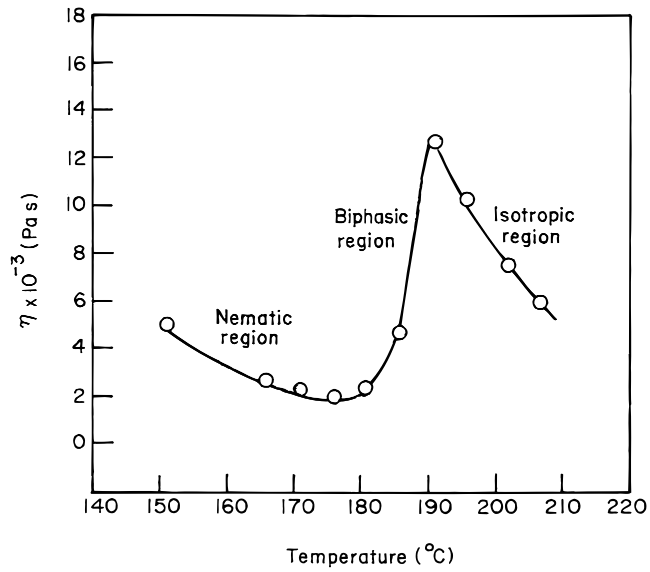

Figure 15. Dependence of η on temperature for a PSHQ6-12 specimens at $\dot{\gamma} = 0.1$ s^{-1}, where the data were taken from the steady-state value of transient shear flow experiments.

increasing temperature from 150 to ca. 175 °C, (ii) then η increases rapidly, going through a maximum, as the temperature approaches the T_{NI} (ca. 192 °C) of PSHQ6-12, and (iii) η decreases again as the temperature increases further in the isotropic region. The decreasing trend of η with increasing temperature in the isotropic region can be explained from the point of view of the Arrhenius relationship, while the decreasing trend of η with increasing temperature in the nematic region is attributable (i) to an increase in orientation of the nematic phase and (ii) to a lesser amount of polydomain textures under an applied shear flow. The rapid increase of η as the temperature is increased from ca. 175 °C toward the T_{NI} (ca. 192 °C) is attributable to the formation of a biphasic region. This phase transition can best be demonstrated by Figure 16, where the micrograph on the left side describes the domain texture at 170 °C and the micrograph on the right side describes the domain texture at 190 °C. Figure 16 shows clearly that much of the Schlieren texture that existed at 170 °C is lost as the specimen was heated to 190 °C, ca. 2 °C below the T_{NI} of PSHQ6-12. The physical origin of the formation of the biphasic region lies in the polydispersity (ca. 2.02) of the PSHQ6-12 specimen. There is experimental evidence, showing that the lower the molecular weight of a TLCP, the lower its T_{NI}.[12] Earlier, complex temperature dependence of η was also reported for other types of TLCP.[3,4,23]

We also measured η and N_1 of PSHQ6-12 as functions of $\dot{\gamma}$ in both the nematic and isotropic regions, using a fresh specimen at each temperature. As in transient shear flow experiments, the data in the nematic region were taken with fresh specimens which had first been heated to 205 °C in the isotropic region, sheared there at $\dot{\gamma} = 0.1$ s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region. Plots of log η vs log $\dot{\gamma}$ for PSHQ6-12 at various temperatures are given in Figure 17, where we observe at 140 and 150 °C (i) a "yield" behavior at very low shear rates, $\dot{\gamma} < 0.01$ s^{-1} (region I), (ii) Newtonian behavior at an intermediate range of $\dot{\gamma}$ (region II), and (iii) a shear-thinning behavior at $\dot{\gamma} \geq$ ca. 0.8 s^{-1} (region III). That is, at 140 and 150 °C, we observe the so-called three-region viscosity curve[24] for PSHQ6-12. But at 180 °C (i.e., as the temperature approaches the T_{NI} of the specimen), we observe only regions II and III in the viscosity curve. This observation seems to indicate that the three-region viscosity curve in a TLCP may be observed when the specimen stays far away from its T_{NI}. It should be mentioned at this juncture that preshearing of a TLCP can eliminate region I in the viscosity curve.[25] In view of the fact that fresh specimens were used to obtain the viscosity curves in Figure 17 and a proper preshearing can disrupt the grain boundary that existed in a fresh specimen, we are led to conclude that region I in the viscosity curve is related to the presence of polydomains in the specimen. In Figure 17, we observe that the viscosities at 195 and 205 °C in the isotropic region are higher than those at 150, 160, and 180 °C in the nematic region. This observation is consistent with that made in reference to Figure 15.

Figure 18 gives plots of log N_1 vs log $\dot{\gamma}$ for PSHQ6-12 at various temperatures in both nematic and isotropic regions. Over the entire range of $\dot{\gamma}$, from 0.001 to 1 s^{-1}, investigated, only *positive* values of N_1 are observed. When values of N_1 are plotted against σ on logarithmic coordinates, we observe in Figure 19 that such plots show temperature dependence at 140, 150, 160, and 180 °C in the nematic region but become independent of temperature at 195 and 205 °C in the isotropic region. There is ample experimental evidence[26−28] demonstrating that log N_1 vs log σ plots are independent of temperature for homopolymers and random copolymers, and a theoretical interpretation of such experimental observations is available.[28] One should then not be surprised to observe in Figure 19 the temperature dependence of log N_1 vs log σ plots for PSHQ6-12 at 140, 150, 160, and 180 °C in the nematic region. The rheological significance of Figure 19 lies in the fact that log N_1 vs log σ plots can be used to determine the T_{NI} of TLCP.

Oscillatory Shear Flow Behavior of PSHQ6-12. Figure 20 describes the frequency dependence of G' and G'' for PSHQ6-12 at 140, 160, 180, 195, and 205 °C. In Figure 20, we observe that (1) at low ω, the slope of log G' vs log ω plots is much less than 2 at 140, 160, and 180 °C in the terminal region, while it is 2 at 195 and 205 °C in the isotropic region, and (2) at high ω, both log G' vs log ω and log G'' vs log ω plots at 195 and 205 °C in the isotropic region cross over those at 140, 160, and 180 °C in the nematic region. Further, it is very difficult, if not impossible, to describe, using Figure 20, the effect of temperature on the dynamic moduli, G' and G'', of PSHQ6-12.

However, when using the log G' vs log G'' plots given in Figure 21, which were prepared from Figure 20, we observe that (1) at 195 and 205 °C in the isotropic region, such plots lie on a single line, independent of temperature, and have a slope of 2 over the entire range of G'' investigated and (2) log G' vs log G'' plots at 140, 160, and 180 °C in the nematic region are dependent upon temperature with a slope of less than 2 in the terminal region and the extent of deviation from the slope of 2 becomes greater as the temperature moves farther away from T_{NI} (192 °C). Notice that log G' vs log G'' plots (see Figure 21) have the same temperature dependence as log N_1 vs log σ plots (see Figure 19), because both G' and N_1 describe the energy stored, while both G'' and σ describe the energy dissipated, per unit volume of fluid. It should be mentioned at this juncture that Han and co-workers[29,30] have used log G' vs log G'' plots very successfully to determine the order−disorder transition temperature of microphase-separated block

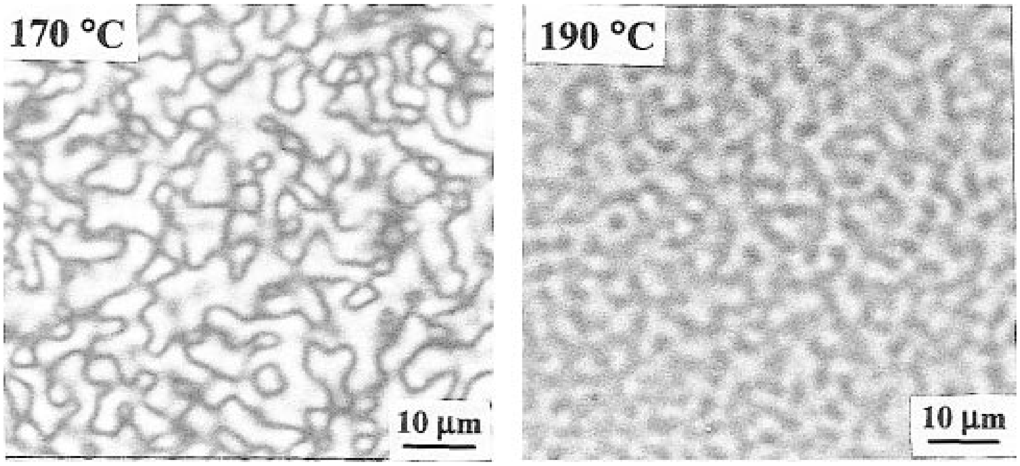

Figure 16. Cross-polarized optical micrographs of a PSHQ6-12 specimen: (a) annealed at 170 °C for 3 h after first being heated to an isotropic state at 195 °C and (b) heated to 190 °C after being annealed at 170 °C for 3 h. The micrograph taken at 190 °C shows clear evidence of a biphasic region.

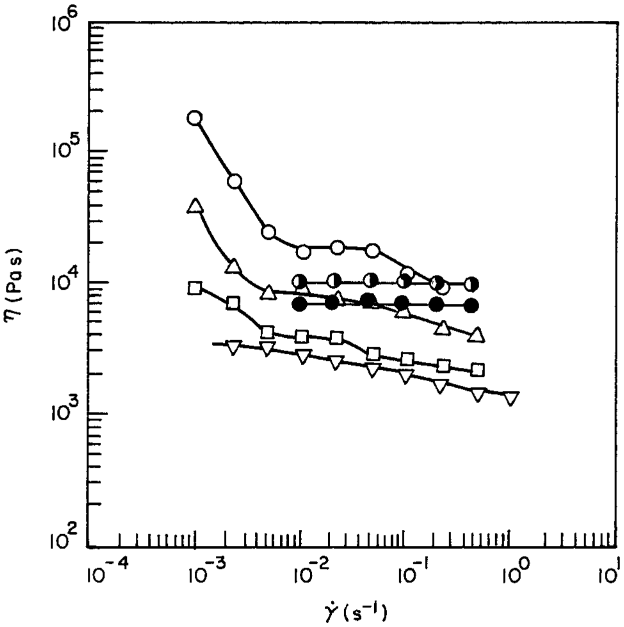

Figure 17. Plots of log η vs log $\dot{\gamma}$ for PSHQ6-12 specimens at various temperatures: (○) 140 °C; (△) 150 °C; (□) 160 °C; (▽) 180 °C; (◑) 195 °C; (●) 205 °C. A fresh specimen was used for each temperature. Each specimen, before being subjected to shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

copolymers. We conclude that log G' vs log G'' plots may also be used to determine the isotropization temperature of TLCPs.

Concluding Remarks

In this paper, we have presented the transient, steady-state, and oscillatory shear flow behaviors of a thermotropic main-chain random copolyester PSHQ6-12, which has only a glassy nematic phase between T_g (92 °C) and T_{NI} (192 °C).[17] Because this copolyester is thermally very stable in the presence of an antioxidant at temperatures below ca. 350 °C, we were able to take rheological measurements over a very wide range of temperatures in both the nematic and isotropic regions.

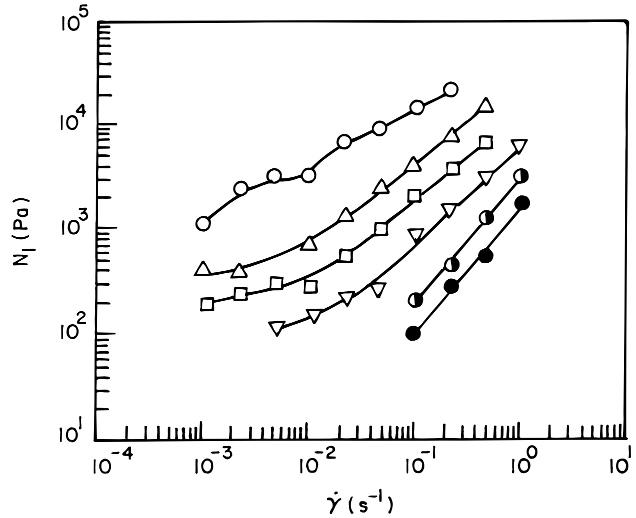

Figure 18. Plots of log $N_1^+(t,\dot{\gamma})$ vs log $\dot{\gamma}$ for PSHQ6-12 specimens at various temperatures: (○) 140 °C; (△) 150 °C; (□) 160 °C; (▽) 180 °C; (◑) 195 °C; (●) 205 °C. A fresh specimen was used for each temperature. The specimen, before being subjected to shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

One of the difficulties with taking rheological measurements of TLCPs lies in that their morphological state may change during the rheological measurements. Using such TLCPs, it is very difficult, if not impossible, to obtain reproducible rheological measurements unless the initial conditions (i.e., the initial morphology) can be controlled. As pointed out previously,[14] any rheological measurements of TLCPs would be of *no* physical significance if the value of N_1 in a specimen is nonzero before a step shear flow is applied. It has been shown[10,14] that when using certain TLCPs, such as Vectra A900, considerable amounts of residual force, which were generated from the initial squeezing of the specimen in the cone-and-plate fixture of the rheometer, remain in the specimen and it would require a very long time to have the residual force to relax completely. The morphological state and thus rheological responses of the specimen keep changing while the residual force relaxes. The most effective way of circumventing such a difficulty is to heat a specimen to a temperature in the isotropic region and then cool it very slowly to a preset temperature in the nematic region. This approach can be realized only when a specimen has a T_{NI} much lower than its thermal degradation temperature. It turns out that Vectra A900, for example, has a T_{NI}

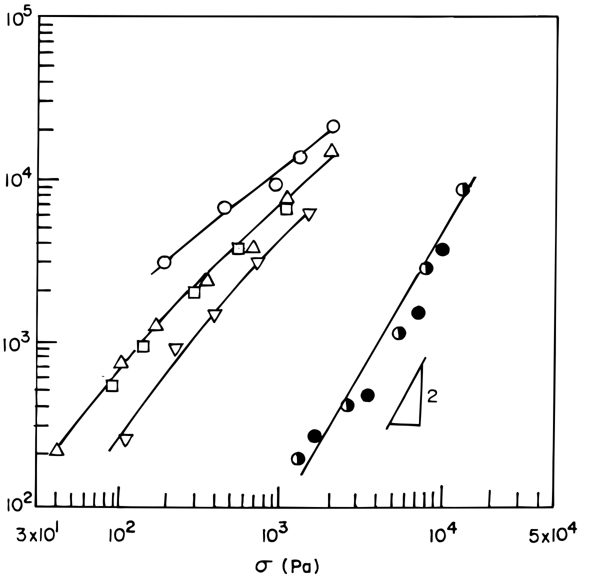

Figure 19. Plots of log $N_1^+(t,\dot{\gamma})$ vs log σ for PSHQ6-12 specimens at various temperatures: (○) 140 °C; (△) 150 °C; (□) 160 °C; (▽) 180 °C; (◑) 195 °C; (●) 205 °C. A fresh specimen was used for each temperature. The specimen, before being subjected to shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

very close to or higher than its thermal degradation temperature, and thus, it would not be possible to give thermal treatment to a specimen at a temperature above its T_{NI}. Under such circumstances, measurements of N_1 for Vectra A900 are of little rheological significance!

In a recent paper,[18] Langelaan and Gotsis, who used Vectra A900 and could not eliminate the residual force in the specimen after being squeezed in the cone-and-plate fixture of the rheometer, suggested that the nonzero value of N_1 be accepted as the initial condition for shear flow measurements. Such a suggestion should not be considered to be serious, because there would be no reference frame to compare the values of N_1 obtained during shear flow measurements if the initial value of N_1 is nonzero. Nonzero values of N_1 would depend, among many factors, on experimental temperature and the period during which a specimen was put to rest after the initial squeezing. Therefore, it would be virtually impossible for one to obtain zero values of N_1 (i.e., controlled initial condition for transient shear flow) for such polymers, as Vectra A900. It is appropriate to mention at this juncture that earlier, using Vectra A900, Guskey and Winter[9] reported *negative* values of N_1 with an erroneous thought that the specimen had *no* unrelaxed normal force after initial squeezing. It was Cocchini et al.[10] and Han et al.[17] who clarified the origin of the erroneous interpretations made by Guskey and Winter.[9] In the present study, we only obtained *positive* values of N_1 in both transient and steady-state shear flows of PSHQ6-12.

As a means of obtaining a zero value of N_1 before a step shear flow is applied to the Vectra A900, Cocchini et al.[10] suggested that a specimen be presheared. As shown in this paper (see Figures 13 and 14) and in a previous paper by Han and Kim,[22] preshearing may have a profound influence on the morphological state of a TLCP. Since the morphological state of TLCP affects very much its rheological behavior, one must not neglect the effect of preshearing on the rheological behavior of TLCP. Moreover, an attainment of a zero value of N_1 before a step shear flow is applied to a TLCP specimen is *not* sufficient for one to state that the initial condition of the specimen is well controlled. This assertion can best be illustrated with the following experimental results obtained in the present study.

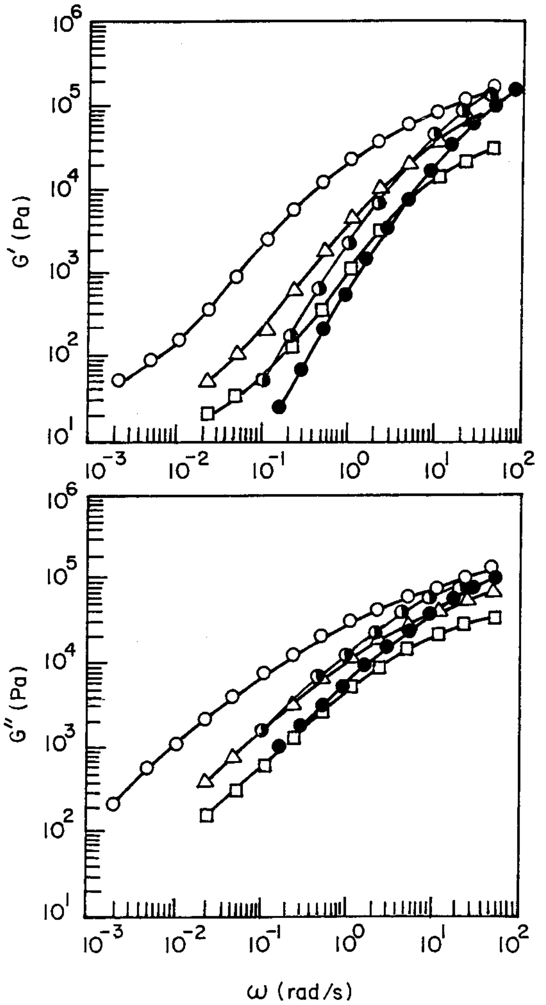

Figure 20. Plots of log G' vs log ω and log G'' vs log ω for PSHQ6-12 specimens at various temperatures: (○) 140 °C; (△) 160 °C; (□) 180 °C; (◑) 195 °C; (●) 205 °C. A fresh specimen was used for each temperature. The specimen, before being subjected to shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

Figure 22a describes how the N_1 of an as-cast PSHQ6-12 specimen at rest, which was loaded on the rheometer preheated at 150 °C, varies with time for a period of 1900 s, and Figure 23a describes how the N_1 of an as-cast PSHQ6-12 specimen at rest, which was first heated to 205 °C in the isotropic region followed by slow cooling down to 150 °C in the nematic region, varies with time for a period of 3300 s. In Figures 22a and 23a, we observe that the N_1 of the specimens attained a zero value in both situations. However, when a step shear flow at $\dot{\gamma}$ = 0.1 s^{-1} was applied to the respective specimens, the transient response in $N_1^+(t,\dot{\gamma})$ is quite different in the two situations; namely, in Figure 22b, the $N_1^+(t,\dot{\gamma})$ of the specimen increased steadily until attaining a steady-state value, whereas in Figure 23b the $N_1^+(t,\dot{\gamma})$ of the specimen exhibited a very large overshoot followed by smaller overshoots until attaining a steady-state value. The large difference in $N_1^+(t,\dot{\gamma})$ observed between the two situations may be explained

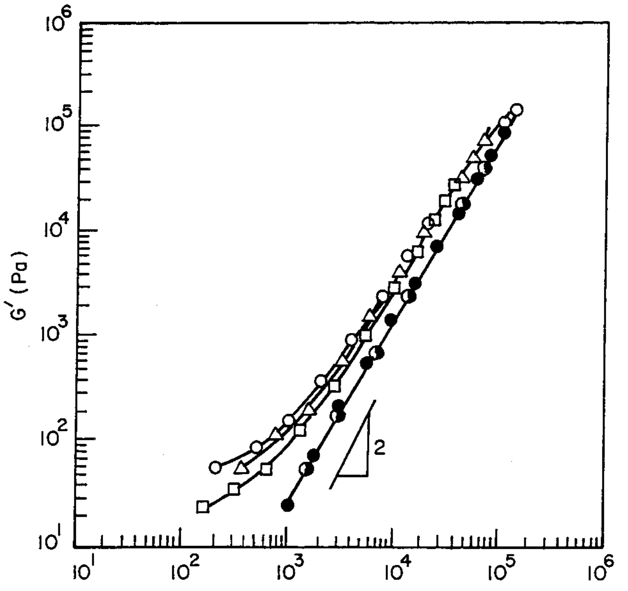

Figure 21. Plots of log G' vs log G'' for PSHQ6-12 specimens at various temperatures: (○) 140 °C; (△) 160 °C; (□) 180 °C; (◑) 195 °C; (●) 205 °C. A fresh specimen was used for each temperature. The specimen, before being subjected to shear flow, was heated to 205 °C in the isotropic region followed by squeezing, sheared there at 0.1 s^{-1} for 10 min, and then cooled slowly down to a preset temperature in the nematic region.

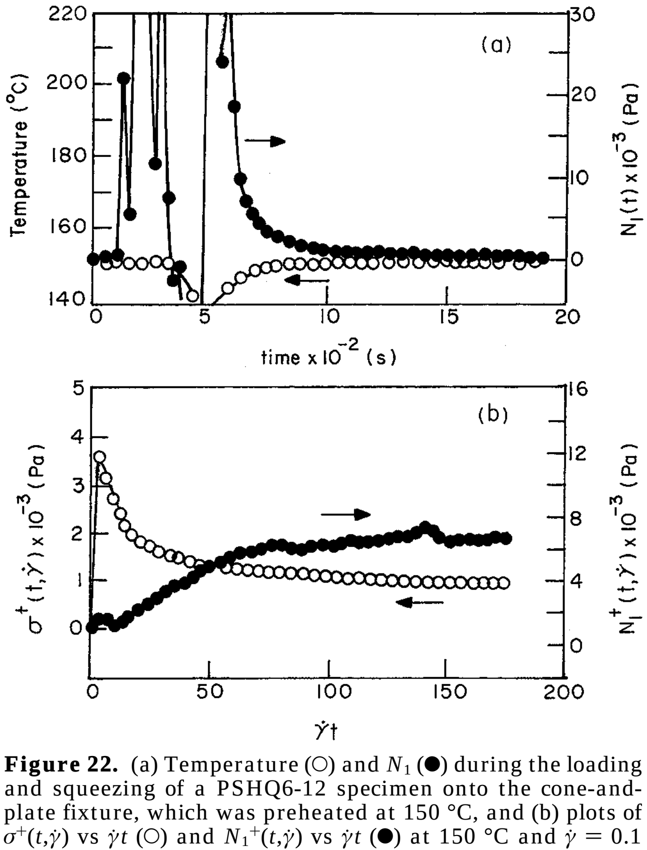

Figure 22. (a) Temperature (○) and N_1 (●) during the loading and squeezing of a PSHQ6-12 specimen onto the cone-and-plate fixture, which was preheated at 150 °C, and (b) plots of $\sigma^+(t,\dot\gamma)$ vs $\dot\gamma t$ (○) and $N_1^+(t,\dot\gamma)$ vs $\dot\gamma t$ (●) at 150 °C and $\dot\gamma = 0.1$ s^{-1} after temperature equilibration at 150 °C.

by the fact that the squeeze flow applied to an as-cast PSHQ6-12 specimen at 150 °C (Figure 22) disrupted the boundaries of the domain texture and also introduced texture orientations as evidenced by WAXD patterns (see Figure 3), whereas the specimen, which received thermal treatment at 205 °C in the isotropic region followed by slow cooling down to 150 °C in the nematic region, had *little or no* texture orientation, the WAXD patterns of which are not shown here. We thus conclude that the initial conditions (i.e., initial morphology) must have been different for the transient shear flow, applied to two different specimens: one without and the other with thermal treatment in the isotropic region.

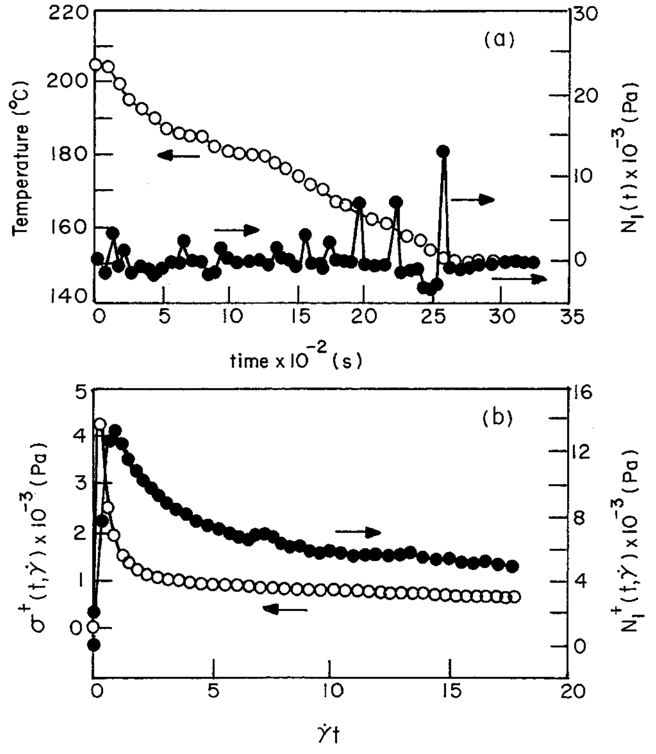

Figure 23. (a) Temperature (○) and N_1 (●) during the cooling from 205 to 150 °C after a PSHQ6-12 specimen was loaded and squeezed onto the cone-and-plate fixture at 205 °C (i.e., the specimen received thermal treatment at 205 °C in the isotropic region followed by squeezing and then was sheared at $\dot\gamma = 0.1$ s^{-1} for 10 min before being cooled down to 150 °C in the nematic region) and (b) plots of $\sigma^+(t,\dot\gamma)$ vs $\dot\gamma t$ (○) and $N_1^+(t,\dot\gamma)$ vs $\dot\gamma t$ (●) at 150 °C and $\dot\gamma = 0.1$ s^{-1} after temperature equilibration at 150 °C.

We have demonstrated above that PSHQ6-12 specimens having different thermal histories, although they both had zero values of N_1 before a step shear flow was applied, exhibit drastically different rheological responses in $N_1^+(t,\dot\gamma)$. Thus, we conclude that an attainment of a zero value of N_1 in TLCP is necessary but not sufficient for one to claim that the initial conditions for transient shear flow are controlled. It is of interest to observe in Figures 22b and 23b that the transient response in $\sigma^+(t,\dot\gamma)$, after a step shear flow was applied, is not so sensitive to the differences in the initial morphology of the respective specimens; namely, in both situations, $\sigma^+(t,\dot\gamma)$ of the specimen exhibits an overshoot and then levels off at a constant value.

In this paper, we have demonstrated that in order to control the initial conditions for transient, steady-state, or oscillatory shear flow measurements of TLCPs in the nematic region, it is essential for one to apply thermal treatment to a specimen at a temperature in the isotropic region and then cool slowly down to a preset temperature in the nematic region. Such a thermal treatment of a TLCP specimen would erase previous thermal and deformation histories associated with polymerization and sample preparation, thus offering a chance for controlling the initial condition (i.e., generating reproducible initial morphology) before commencing rheological measurements in the nematic region. This approach can be used only for thermally stable TLCPs whose T_{NI}'s lie much below the thermal degradation temperature.

In this study, we conducted rheological experiments under shear flow and optical experiments under static conditions, using a thermotropic copolyester PSHQ6-12. The main purpose of the optical experiments was to record the initial morphology of the specimens before being subjected to shear flow measurement. We have no way of knowing how the morphology of the specimen actually changed while it was under shear flow. After all, the rheological behavior and the morphology of PSHQ6-12 specimen (most likely for other TLCPs as well) during shear flow are interrelated, and therefore, they are inseparable insofar as correctly interpreting rheological measurements. What is most desirable is to conduct a rheooptical investigation of TLCP, which will enable one to make simultaneous measurements of rheological properties and phase morphology under shear flow. This subject is open for future investigation.

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