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Rheological Properties of a Homogeneous Thermotropic Liquid-Crystalline Polyester: Dynamic Viscoelastic and Interrupted-Flow Measurements

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ABSTRACT: Dynamic viscoelastic and shear stress properties at various shear rates with intermediate rest periods of varying length were measured for a thermotropic nematic liquid-crystalline polyester of homogeneous backbone structure, with a long flexible spacer. Data obtained in the liquid-crystalline and isotropic states were found to independently superimpose when shifted along the ω axis. In the low-frequency region of the liquid-crystalline state, data exhibit log G' and log G'' values ≤ 1 when plotted vs log ω. Properties for the isotropic state correspond to other wide molecular weight distribution melts except here, and in the liquid-crystalline state, $\eta(\dot{\gamma}) < |\eta^*(\omega)|$. While interrupted-flow (I-F) results in the isotropic state were similar to other isotropic materials, in the liquid-crystalline state at 145 °C and similarly at 160 °C, previously unsheared samples sheared at $\omega = 0.1\ \mathrm{s}^{-1}$ showed a stress maximum, accompanied by a transient negative first normal stress difference peak and later by a positive N_1 peak. At 160 °C, $\omega = 0.5\ \mathrm{s}^{-1}$, a second stress overshoot appeared, as did another positive N_1 peak. When compared with optical micrographs of sheared samples, the first peak may be related to initial domain structure deformation, not reappearing in subsequent shear events after short rest periods. The second stress overshoot that appears with higher shear rates appears to correspond to the complete breakdown of these domains, producing a birefringent yet featureless appearance. Structure reappears with longer rest periods but differs from initial texture. If sheared, this structure is capable of producing an initial stress overshoot.

Introduction

Recent advances in the understanding of the structure necessary to produce the liquid-crystalline state are beginning to lead to thermotropic liquid-crystalline polymers of less complicated physical properties than their so-called "random" copolyester predecessors. In certain cases, this results not only in lower thermal transitions but also in materials that are not prone to supercooling. Combined with the fact that these materials are chemically homogeneous along the chain, this leads to polymers that are more conducive to rheological study, for example, how molecular structure capable of forming liquid crystals affects flow properties. The opportunity now exists to study what could be not only a different kind of isotropic state but also the fundamental rheological properties of another molten state (the liquid-crystalline phase), as well as the transition between. This work begins to look into some of these areas.

In the initial report on this polymer, temperature sweeps of viscoelastic properties revealed an intermediate temperature minimum that was not subject to hysteresis behavior on cooling. This method proved to be a more sensitive indication than optical microscopy of the change from the liquid crystalline to the isotropic state and vice versa.[1] Additional evidence of this phase transition was provided by differential scanning calorimetry (DSC).

In a further work on a significantly lower molecular weight version of the same material,[2] two interesting differences were observed. First, the temperature of the transition from the nematic to the isotropic state was found to decrease significantly with lowered molecular weight. Also an accompanying decrease in the "intensity" of the viscoelastic transition suggested that the exponent that scales molecular weight to viscosity may vary significantly between the two states.

In the high polymer range,[2] as compared to molecular weights leading up to that range,[3] where the opposite effect has been observed, a consequence of lowering molecular weight may be that the apparent width of the biphasic region may decrease, at least as measured by viscoelastic temperature sweeps, although molecular weight distribution plays a role as well. Difficulties in preparing these samples in various molecular weights[2] unfortunately limit us at this time to these general statements. It is hoped that studies of thermotropic liquid-crystalline (hydroxypropyl)cellulose (HPC) derivatives of different molecular weight will provide further answers in this area, yet these systems, whose side chains are formed by reaction with alkyl chlorides, are believed to be initially cholesteric before shear.[4]

For this paper the higher molecular weight nematic thermotropic liquid-crystalline polymer, with its more well-defined phase transition, was selected in an attempt to further understand the rheological differences between the isotropic and the liquid-crystalline phase and the transition state between them. The rheology, particularly the phase transition associated with the nematic to isotropic transition, has been studied at high shear rates by Wunder et al.[5] for three thermotropic liquid-crystalline polyesters, one of which was a homopolymer. Here dynamic viscoelastic frequency dispersion and steady viscosity and interrupted-flow (I-F) measurements performed at constant temperature in the isotropic and liquid-crystalline states are emphasized. Also optical microscopy results are used to supplement the steady shear and I-F results in the liquid-crystalline state.

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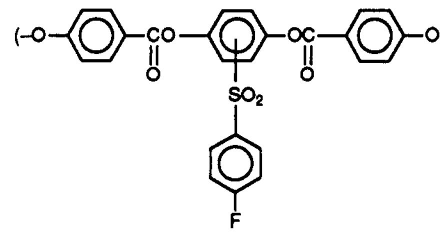
Experimental Section

The polymer used in this study was PFSPDB [poly[[(*p*-fluorophenylene)sulfonyl]-*p*-phenylene 1,10-decamethylene bis(4-oxybenzoate)]]. It was prepared by melt polymerization, the



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details of which can be found in a preceding publication.[1] This material was found to have an inherent viscosity of 0.99 dL/g in tetrachloromethane at 0.5 g/dL and 40 °C.[2] Gel permeation chromatography (GPC) results showed this material to have a weight-average molecular weight of 80 000 when compared with polystyrene standards and a suprisingly wide molecular weight distribution (MWD) of 4.1 when this value was estimated from the shape of the GPC curve.[1] Actual molecular weight values are probably significantly lower due to the use of much more flexible polystyrene as a standard.

A Model 605 Rheometrics mechanical spectrometer (RMS) was employed to measure the rheological behavior of samples. Sample preparation for the RMS consisted of initial drying of the polymer under vacuum at 105 °C for at least 6 h. Then compression molding of the sample was performed at 200 °C. Dynamic viscoelastic frequency sweeps and I-F, as well as steady shear, measurements were conducted with a cone and plate fixture, both of a diameter of 25 mm and a cone angle of 0.055 rad. Gaps employed were approximately 150 μm in all cases. All measurements were carried out in an extremely dry air environment. Steady-shear viscosity experiments were carried out separately from interrupted-flow experiments. In the I-F experiment, virgin (unsheared) samples were employed at each temperature and shear rate. Measurements were made with rest periods of increasing duration, separated by periods of flow and accompanying rheological measurements.

Preceding frequency dispersion measurements, strain dependence of the polymer was measured at constant temperature in the isotropic and liquid-crystalline states. Approximate temperatures for measurement were determined from DSC results.[1] As is usual for isotropic melts, no effect of strain amplitude was observed at low strain amplitudes, in this case at $T = 195$ °C and $\omega = 100\ \mathrm{s}^{-1}$ for $7 < \gamma_0 < 21\%$. For two measurements in the liquid-crystalline state, results at 145 and 160 °C can be seen in Figure 1. In both cases strain amplitude had no effect for $1 < \gamma_0 < 15\%$ at $\omega = 1\ \mathrm{s}^{-1}$. Accordingly, maximum strain amplitudes employed in dynamic measurements were carried out within the linear range, varying from $\gamma_0 = 8$ to 20%.

One of the factors complicating thermotropic LCP isotropic state–property measurements in the past has been these materials' lack of high-temperature thermal stability. To determine the stability of the present material, three sets of single-frequency measurements were performed at each of three frequencies (ω = 0.1, 1, and 10 s^{-1}), with one set at each of following temperatures, in the order listed: 195, 180, 160, 145, 130, 145, 160, 180, and 195 °C. Employing this thermal history, "before and after" comparisons of the absolute levels of viscoelastic properties at each temperature were made. To set the gap at 210 °C required 45 min, with the 130 °C measurement being concluded approximately 3 h after the sample was placed in the rheometer. Nearly 6 h had elapsed by the time the final measurements at 195 °C were concluded. Excluding the before and after results at 195 °C, which showed a significant decrease in levels (as much as a 50% drop at the end of an experimental elasped time of nearly 6 h), all results were at least as good as those at 180 °C, which showed a decrease of only 7–10% between the first and second sets of frequency measurements at each respective temperature. It is felt that this decrease in viscosity may indicate thermal degradation, resulting in a decrease in molecular weight. Measurements at constant temperatures at and below 160 °C were virtually identical, except for slight increases exhibited at 160 °C. Consequently this material should be suitable for rheological measurements as long as excessively long, high-temperature measurements are avoided.

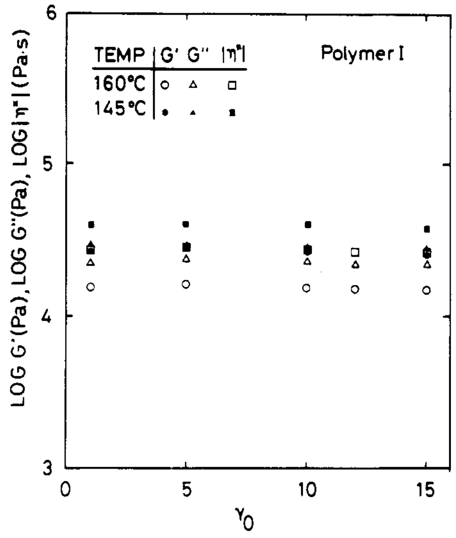

Figure 1. Effect of strain amplitude on viscoelastic properties in the liquid-crystalline state. Cone and plate geometry was used for this and all other measurements with a diameter of 25 mm and a cone angle of 0.055 rad.

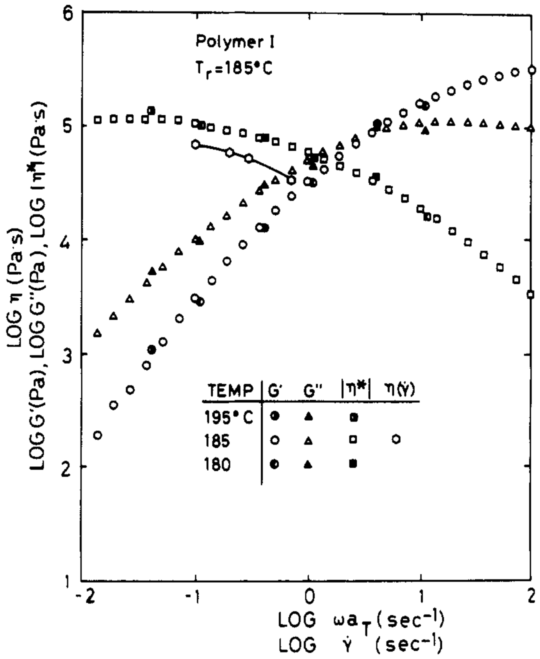

Figure 2. Isotropic-region dynamic viscoelastic property results, with data reduced to 185 °C. Steady-state viscosity results are also shown.

Results and Discussion

I. Dynamic Viscoelastic Results. (A) Isotropic State. Viscoelastic property measurement frequency sweeps in the isotropic state performed at $\gamma_0 = 20\%$ at 180, 185, and 195 °C superimposed well when shifted along the time axis for G' (shear storage modulus) and G'' (shear loss modulus) and shifted equally along both axes in the case of $|\eta^*| = (G'^2 + G''^2)^{1/2}/\omega$, the absolute value of the complex viscosity. The results are shown in Figure 2. From the shift factor required to superimpose the G' and G'' curves, an activation energy of flow could be estimated for this system from a plot of log a_T vs $1/T$ and was found to

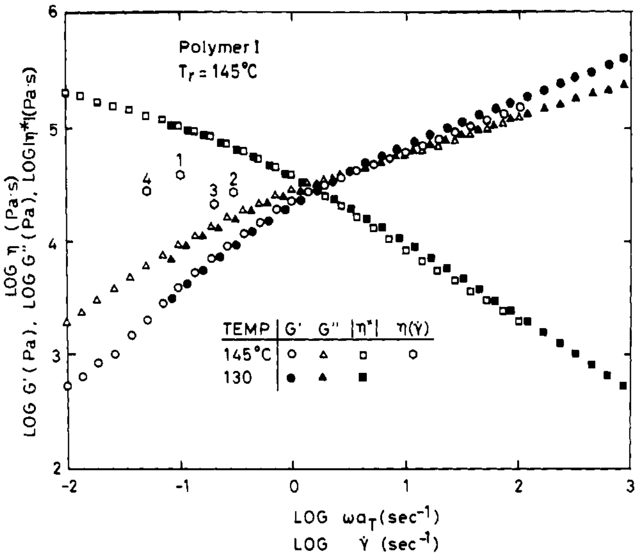

Figure 3. Liquid-crystalline region dynamic viscoelastic property results, with data reduced to 145 °C. Steady-state viscosity results are also shown. Numbers indicate order in which the data were collected.

be ΔH = 49.2 kcal/mol. As is typical for most viscoelastic systems in the limit of small log ω, the slope of the log G'' plot was found to be 1.0.

On the other hand, in the limit of small ω, logarithmic values of G' were found to be proportional to a value somewhat less than 2.0, the typical value for monodisperse viscoelastic materials; exponential values less than 2 are often an indication of a wider molecular weight distribution.[6] A thermotropic liquid-crystalline HPC derivative of unknown molecular weight distribution had been previously reported to have a slope value equal to approximately 1.8.[4] Here, the elasticity coefficient, A_G, was estimated by the relation $A_G = \lim_{\omega \to 0} G'/\omega^2$ and was found to be 1.05×10^6 Pa·s^2. The composite $|\eta^*|$ curve shows very Newtonian shear behavior, especially at lower shear rates. A calculated value for η_0 ($= \lim_{\omega \to 0} G''/\omega = \lim_{\omega \to 0} |\eta^*| = 1.14 \times 10^5$ Pa·s) corresponds to the observed value obtained by extrapolating to low shear rates. The recoverable compliance, J_e^0, was estimated as being 8.08×10^{-5} Pa^{-1} from the relation $J_e^0 = A_G/\eta_0^2$. For example, this compares to a value of $J_e^0 = 1.5 \times 10^{-5}$ Pa^{-1} reported for monodisperse polystyrenes.[6]

(B) Liquid-Crystalline State. Results that have been reduced to 145 °C are seen in Figure 3. Measurements at 130 and 145 °C were made at 8% strain applitude, well within the linear viscoelastic region. Previous thermal history involved initial gap setting and sample shaping in the isotropic state at 210 °C for about 45 min and then cooling to 130 °C, which required about 20 min. During the cooling from 210 to 130 °C the gap was adjusted as was necessary to keep normal force values within the range of the transducer. After measurements at 130 °C were completed, measurements at 145 °C followed directly. As was the case with the HPC derivative,[4] liquid-crystalline data were found to superimpose, suggesting, at least in this strain range, that the standard time–temperature superposition may also be applicable to the flow properties of nematic liquid-crystalline polymers,[7] as well as those of cholesteric liquid-crystalline polymers, although much more data are necessary to draw definite conclusions. The superposition in the current liquid-crystalline system also suggests that, regardless of thermal history, samples in the liquid-crystalline state can come quickly to an equilibrium condition and that, at least at small strains, the character of this liquid-crystalline behavior is not fundamentally altered over a wide range of temperatures.

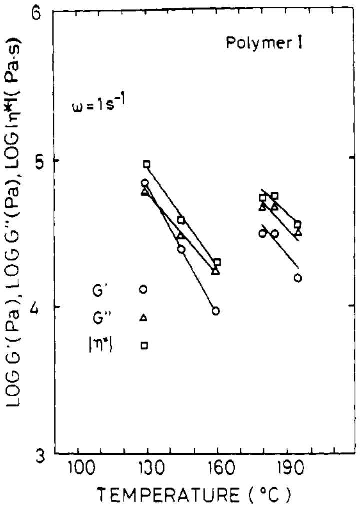

Figure 4. Temperature dependence of dynamic viscoelastic functions constructed from dynamic data presented thus far, at ω = 1.0 s^{-1}. Data suggest an intermediate temperature–viscoelastic property minimum.

A further similarity observed with the HPC derivatives was the values of the slopes of log–log plots of G' and G'' vs ω at low frequencies. Both systems showed liquid-crystalline G' values to be proportional to $\omega^{1.0}$ in the terminal flow region, while G'' was proportional to $\omega^{0.7}$ for this PSFPDB. Values ranged from $\omega^{0.8}$ to $\omega^{1.0}$ for the liquid-crystalline HPC derivative.[4] In this case ΔH was determined to be 44.5 kcal/mol, compared with values as high as 120 kcal/mol, for a random copolymer 60 mol % PHB/PET [p-hydroxybenzoic acid/poly(ethylene terephthalate)] sample[8] in which there was crystallinity in the nematic melt, to values as low as approximately 17 kcal/mol, for liquid-crystalline melts of cholosteric HPC derivatives.[4]

(C) Temperature Dependence of Viscoelastic Functions. When data collected in the dynamic measurements presented thus far are used, a plot representative of the behavior of viscoelastic properties vs temperature for this material at ω = 1 s^{-1} is presented in Figure 4. The characteristic behavior of an intermediate temperature minimum in the properties is readily evident. Comparing this data to that presented previously,[1] 160 °C should lie near the viscoelastic property minimum, consequently on the edge of the 100% liquid crystalline–partially isotropic region, i.e., the biphasic region where a sudden increase in viscoelastic properties began. Optical microscopy results presented in the same paper show little visible evidence of the change to isotropic material, namely, a disappearance of birefringence, until well into what would be expected to be the biphasic region from viscoelastic and optical light transmission[2] results. The effect of higher strains on material near the transition region, as well as into the liquid-crystalline and isotropic states, will be considered in the following section.

II. Shearing Flow Behavior. In this section, interrupted-flow shear stress, σ, and accompanying first normal stress difference, N_1, results will be presented in the isotropic state at 185 °C, and in the liquid-crystalline state at 145 and 160 °C. Particular attention is paid to the apparent breakdown of structure with initial shear, as well as the effect of rest periods of varying length on subsequent rheology. Optical micrographs at 165 °C are presented on unsheared and sheared samples in an attempt to understand how varying amounts of deformation affect structure

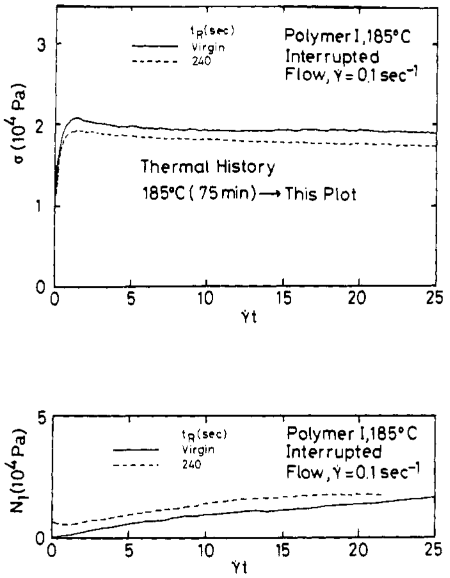

Figure 5. Isotropic–state interrupted flow, shear stress and first normal stress difference values at 185 °C. Curve labeled "240" represents data obtained after resting the initially sheared (virgin) sample for 240 s (t_R = rest period).

and what effect rest after deformation has on texture. Also shear rate dependent steady-state viscosity in the isotropic and liquid-crystalline states (after the initial structure has been broken down) is compared to $|\eta^*|$ values from the dynamic tests.

(A) Isotropic State. I-F results for the polymer are seen in Figure 5, for 185 °C $\dot{\gamma}$ = 0.1 s^{-1}. A rest period (t_R) of the noted duration was utilized. Although they differ in relative values, qualitatively the curves are of the same shape, regardless of strain history. As is typical for isotropic materials, when shear rate is sufficient, a maximum (overshoot), in this case quite small, is observed in the vicinity of $\dot{\gamma}t$ (=γ) = 1–2, as has been seen for solutions of typical isotropic melt forming polymers.[9] The difference in the absolute level of stress is thought to be caused by the slight, unavoidable flow of the sample from between the platens during rest periods of increasing duration. Here in the isotropic state, no residual stress was observed, even with only a short rest period.

Steady-state viscosity data collected at 185 °C in the isotropic state can be found in Figure 2. Although qualitatively of the same shape as dynamic isotropic data, it differs, being somewhat lower in absolute levels of viscosity, especially at high shear rates. This is difficult to explain at this time. Nevertheless, enough data do not exist to say that the so-called Cox–Merz relationship ($\eta(\dot{\gamma}) = |\eta^*(\omega)|$) must hold for isotropic melts of polymer liquid crystals. Also, the values of these two viscosities differ the most in the high shear rate region, suggesting the possibility of a "flow-induced liquid crystallinity" as has been observed for lyotropic liquid-crystalline systems.[10]

(B) Liquid-Crystalline State. As a complementary method to I-F tests in the liquid-crystalline state that follow, in order to gain information about how shear affects the texture (for example, if shear hastens the material's entry into the biphasic region, i.e., induces the formation of isotropic material), a hot-stage-equipped cross-polarized optical microscope was utilized at 165 °C. A simple sample shearing operation was performed by hand (the sample had been prepared by raising it to a temperature well into the isotropic state while placed between two glass microscope slides) while the sample was still in the hot stage. Photomicrographs were made on the sample before and after shear and then again several times during a long period without shear. Sample thickness was about 50 μm. (In all cases photomicrographs were recorded with the sample rotated 45° to the cross polars.)

The original texture of the sample is shown in Figure 6a. The field appears to be largely if not completely birefringent, so a predominantly liquid-crystalline structure was assumed. This result agrees with the previous result, which showed almost complete birefringent behavior well into the biphasic region.[1]

Immediately after a slight shear of the "virgin" (previously unsheared) sample (Figure 6a), the photograph shown in Figure 6b was taken. A slight elongation of the domains can be seen in the direction of the shear. This level of shear is considered to be insufficient to break down the domains.

Further shear leads to the complete breakdown of texture: a completely white, but nonetheless still birefringent, appearance under crossed polars (except for one unexplained high melting impurity, which appears in Figure 6c). For this more subtantial shear, a rough estimate of the shear rate yielded a value of about $\dot{\gamma}$ = 20 s^{-1}. Subsequently, it was necessary to wait 8 min before Figure 6c was taken because of an initial lack of contrast after shear. By this time enough texture had appeared so that a photograph could be taken. Photographs followed at the same magnification at 44 (Figure 6d) and 113 min (Figure 6e) and finally at $^1/_4$ the magnification at 116 min (Figure 6f).

These results are noteable because they do not show any evidence of the formation of bands perpendicular to the direction of shear, as have results for various liquid-crystalline systems including PBLG solutions[11] and thermotropic "random" copolymers[12-16] and homopolymers.[16,17] Several potential explanations exist. The simplest would be sample thickness. Zachariades, Navard, and Logan[14] noted that for both 60 and 80 mol % PHB/PET systems that thick samples did not exhibit "ordered band structures". Another possibility could be unique behavior of this experiment's PFSPDB type polymers because of long flexible –(CH_2)– spacers in the repeat unit. Both Alderman and Mackley[16] and Kleman, Liebert, and Strzelecki[17] found that line defects, present in optical micrographs of two different thermotropic liquid-crystalline homopolymers with short flexible spacers, disappeared as the number of –(CH_2)– units in the spacer increased to approximately 10. The present study's optical micrographs are consistent with those findings. Evidence that optical properties of thermotropic liquid-crystalline homopolymers with long flexible spacers such as PFSPDB differ from those with shorter spacers or that lack spacers may set this work's polymer apart from the results such as those of Kiss and Porter,[11] whose experiments showed banded structures appearing during and/or after shearing for homogeneous chain PBLG solutions. While in the current work it was impractical to monitor optically during the shearing process because of the method used, Kiss and Porter showed for a high molecular weight polymer that banded structures perpendicular to the shear direction occurred during the shearing as shear rate increased to 3.3 s^{-1} and that visible texture was completely destroyed at shear rates above approximately 40 s^{-1}. For a lower molecular weight PBLG solution it was also found that, for shear rates sufficient to create a banded structure, that structure began to disappear within 5 min of cession of shear. These results seem to indicate a somewhat different process in the evolution of postshear structure for these homogeneous

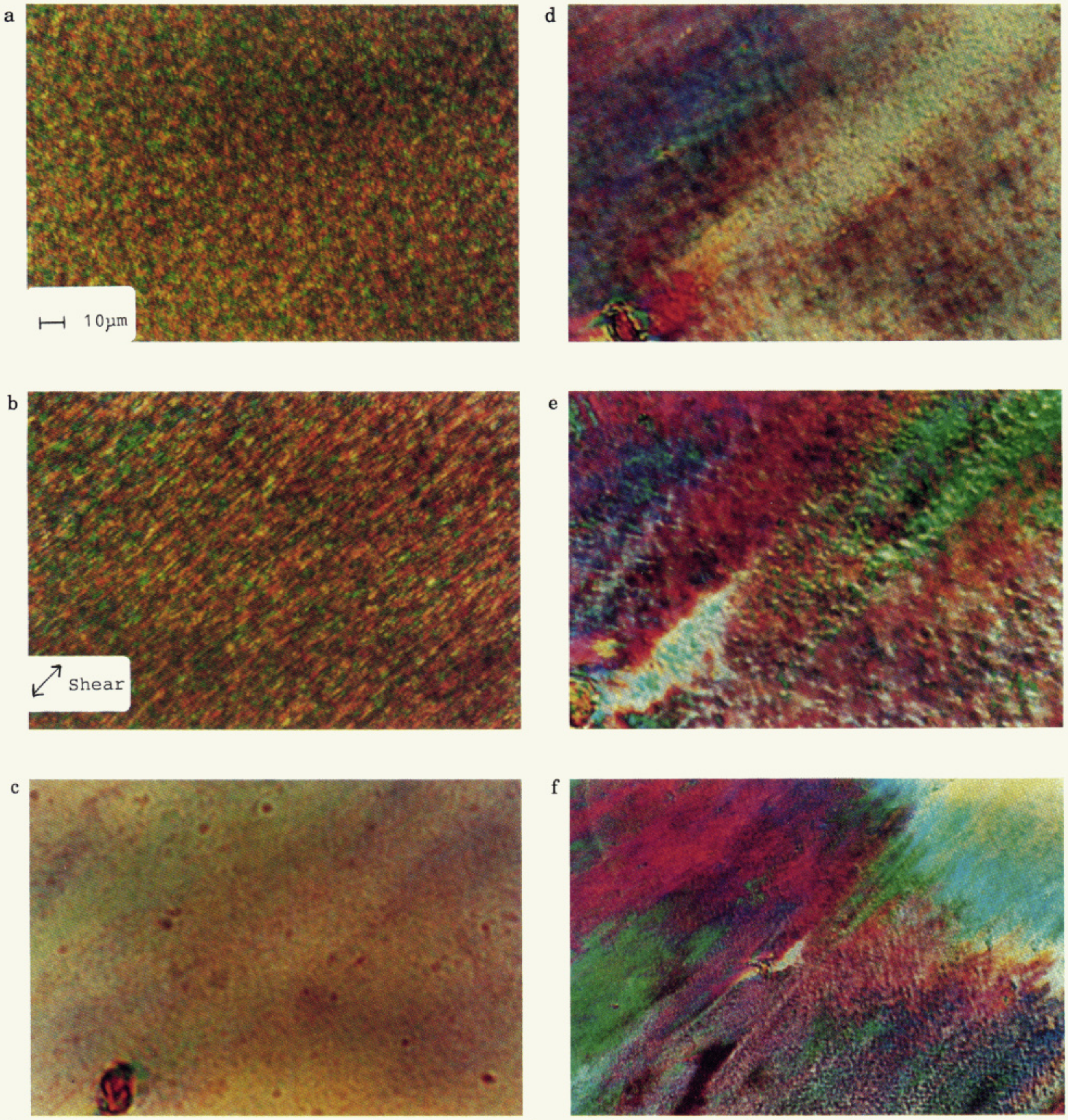

Figure 6. Polarized optical micrographs at 165 °C: (a) unsheared sample, (b) sample after slight shear, (c) sample 8 min after large shear, (d) 44 min after, (e) 113 min after, and (f) 116 min after. All photos are 400X except (f) which is 100X.

chain materials that lack flexible spacers, compared with the very qualitative optical microscopy results of the current study. In the Kiss and Porter study it was also noted that perpendicular striations were not found in liquid-crystalline solutions that did not exhibit "negative normal stress". There "negative normal stress", it seems safe to assume, refers to the long-time equilibrium type, which is the kind reported in that work[11] and elsewhere on those and similar polymer systems.[10,18] The current study's rheological results showed only temporary negative normal stress soon after start up in the liquid-crystalline state in all shear rates tested.

Results of interrupted-flow measurements performed at 145 °C, well within the liquid-crystalline range, are seen in Figure 7. The sample was brought directly from 185 °C into the liquid-crystalline state, and measurements were made at $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$. Shear stress showed a maximum at approximately 2–3 strain units ($\dot{\gamma}t = \gamma$). This amount of strain corresponds almost exactly to a minimum value in the first normal stress difference. A temporary negative N_1 response has been seen in 60 mol % PHB/PET systems by Fujiwara et al.[19] In addition, in steady shear in certain shear rate ranges, long-time equilibrium negative normal stresses have been reported for lyotropic polymers such as poly(benzyl L-glutamate), PBLG (for example, see refs 10 and 18), and have more recently been observed in several thermotropic systems (80 mol % PHB/PET) by Gotis and Baird[20] and an HPC derivative[21]). Although not shown in this plot, N_1 eventually reached a positive maximum value in the vicinity of $\dot{\gamma}t = 40$, at which point readings were terminated. Subsequently, rest periods of steadily increasing duration, each followed by deformation, were

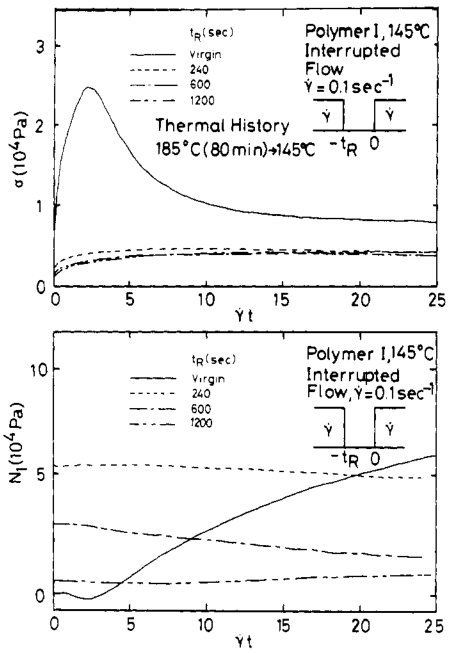

Figure 7. Liquid-crystalline-state interrupted-flow data at 145 °C. Rest periods of t_R between subsequent measurements are of the duration listed.

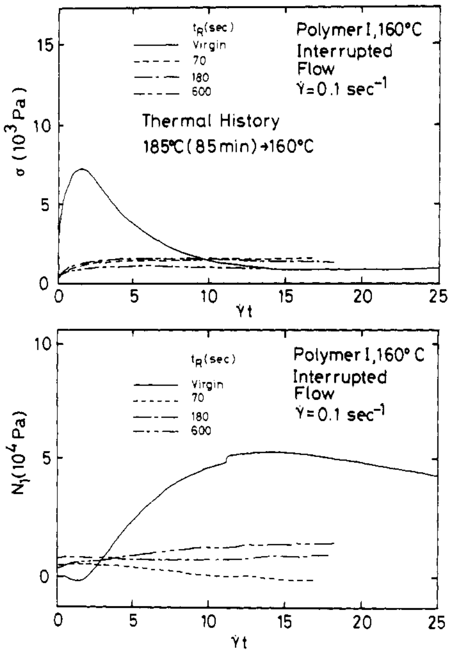

Figure 8. Liquid-crystalline-state interrupted-flow data at 160 °C. Shear rate was γ = 0.1 s^{-1}. Rest periods are as indicated.

employed as is shown in the figure. After the initial rest period of 240 s, while shear stress values had returned to nearly their initial value, N_1 had decreased little from its value at the termination of deformation. On the other hand, shear stress showed no overshoot behavior on this or subsequent runs, behavior similar to isotropic melts that have been strained with rates insufficient to produce an overshoot. N_1 values, almost independent of deformation, seem to show steadily decreasing values to almost zero until a slight increase during the final deformation.

At 160 °C measurements were again performed at ω = 0.1 s^{-1}; results are shown in Figure 8. Again a single stress overshoot was observed, the peak value of which corresponded to the minimum negative value of N_1. A positive N_1 peak was subsequently observed at about $\dot{\gamma}t$ = 15. As might be expected from Figure 4 (vs T), lower viscoelastic property values translate into much lower stress and normal force values. A maximum value and the relaxation of N_1 occurred much faster at this temperature, with values of zero being approached after rest periods of only 70 s. Subsequent deformation once again did not produce overshoot, although equilibrium stress values here were quite similar to those observed at the termination of the initial deformation, unlike measurements at 145 °C.

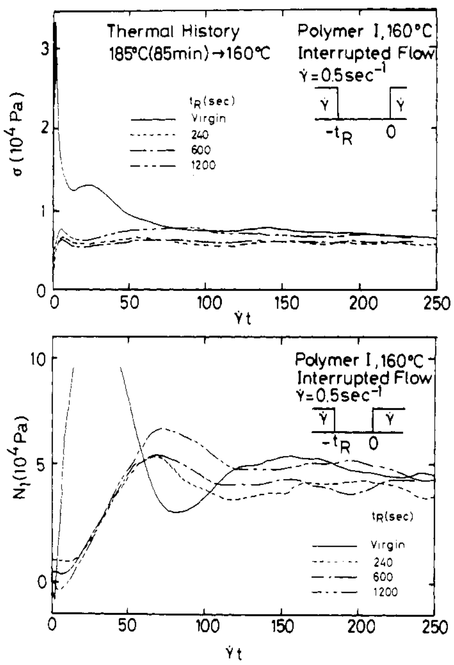

Figure 9. Liquid-crystalline-state interrupted-flow data at 160 °C. Shear rate was γ = 0.5 s^{-1}. Rest periods are as indicated.

Significantly lower stress values at 160 °C compared to 145 °C suggested that shear rates could be increased, in order to observe the effect on initial and subsequent deformation events. Figure 9 shows results on a new sample at $\dot{\gamma}$ = 0.5 s^{-1} at 160 °C. It should be noted that a higher level of shear rate allowed collection of data to higher levels of strain; namely, the γt axis scale has been expanded by a factor of 10. In this case the now familiar initial stress overshoot accompanied by negative N_1 was followed by a second stress overshoot. The first stress overshoot it is felt corresponds to the first maximum in N_1, of an unidentified value. The validity of a second stress overshoot was brought into question because of the correspondence of a normal force transducer overload (which is represented by the break in the curve) and the relative location of the second overshoot (along the γt axis). Nevertheless, this peak seems to be real because less pronounced but similar N_1 behavior is evident on subsequent runs after rest periods of all measured lengths. The longer rest periods corresponding to those used in Figure 7 were again used to allow stress and normal forces to decay to near zero values before starting the next deformation.

Combining I-F and optical results, it is possible to make some general observations. Although slightly high at 165 °C and by viscoelastic measurements close, if not into the biphasic region, it is felt that these photographs are still representative of liquid-crystalline behavior and not that of a biphasic system. Although there has been past evidence of optical microscopy being initially insensitive to the transition to isotropic state,[1] shear has been suggested to maintain liquid-crystalline behavior to higher temperature, although at shear rates hundreds of times higher than explored here.[5] On the other hand, shear has been found to induce the isotropic to liquid-crystalline transition in lyotropic systems,[10] as was mentioned earlier.

Comparing I-F results on initial shear, virgin samples at all temperatures and shear rates showed a stress overshoot accompanied by a corresponding negative N_1 value. This initial stress overshoot is believed to correspond to the deformation of the initial domain structure seen in Figure 6a, which is shown after being slightly deformed in Figure 6b. The domain structure is then finally completely broken down preceding Figure 6c. This final breaking down of structure is believed to correspond to the second stress overshoot peak. Here this appears at 160 °C, $\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$ (see Figure 9), other versions of which have been observed for solutions in chlorinated biphenyls of two monodisperse polystyrenes[22] and for liquid-crystalline 60 mol % PHB/PET copolyesters,[19] in the latter case after an initial shearing. The I-F rheological properties of this type of once-sheared sample, still birefringent according to optical microscopy results and therefore a kind of domainless "oriented liquid-crystalline material", are much different optically and rheologically than those of the virgin sample, even after long periods of rest.

For lower shear rates on subsequent deformation no overshoot behavior is seen at $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$ at either 145 or 160 °C when short rest periods are used. Residual positive N_1 levels at 145 °C may be an indication of a slow relaxation of the deformed liquid-crystalline domains, which leads to lower equilibrium stress values in all strain events, compared to the final levels when shear was terminated after the first shear event. If it is valid to refer to Figure 6b when discussing the $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$ case, at higher temperature such as 160 °C, N_1 force decays toward zero faster than at 145 °C, and this apparently corresponds to subsequent shear event shear levels also approaching zero more quickly, so N_1 decay toward zero values must be a prerequisite to, but not necessarily an indication of, domains regaining their initial shape.

At higher shear rates when rest periods are increased, as shown in Figure 9, qualitatively similar overshoot behavior to the virgin sample, although delayed along the $\dot{\gamma}t$ axis, is observed. Rest periods of 240 s at this temperature allow structure, although not readily visible with optical microscopy until 8 min at 165 °C (Figure 6c), to be characterized with flow measurement. With increasing time, flow curves, especially those for normal forces, show increasingly similiar behavior to that seen originally on shear of the virgin sample, including initial negative N_1 values, even with this sample having been sheared several times. Still, optical microscopy suggests that the same initial texture will not be recovered, even for rest periods of several hours. It is felt that an excursion into the isotropic state for at least a certain minimum period of time may be a requirement for this.

In the liquid-crystalline state at 145 °C, steady viscosity behavior can been seen in Figure 3. All steady-shear data points fall below the $|\eta^*(\omega)|$ curve. These data are then consistent with the observation that the so-called Cox–Merz relation $\eta(\dot{\gamma}) = |\eta^*(\omega)|$ usually does not hold for liquid-crystalline polymers, and as has been found for most liquid-crystalline materials, $\eta(\dot{\gamma}) < |\eta^*(\omega)|$.[23] Here at 145 °C I-F tests preceded $\eta(\dot{\gamma})$ tests, so initial structure associated with overshoot behavior seen in the previous section should have been eliminated and was not expected to return with the short rest periods used between measurements. Lower viscosity levels compared to $|\eta^*|$ may be associated with lower viscosity levels seen in subsequent shear events in I-F tests and elimination of structure seen in Figure 6c. In addition, returning to lower shear rates from higher values (the numbers listed indicate the order of data collection), steady viscosity exhibits further decreases in the absolute level. This effect is believed to be associated with the long relaxation time of the molecules, causing lower apparent viscosities on return to lower shear rates, because of residual orientation. Nevertheless, experimental difficulties should not be discounted. Measurements were made difficult here because of the high viscosity of the liquid-crystalline state in this temperature range, which, coupled with high shear rates caused by some beading of the sample on edge of the platens, reduced the effective diameter of the sample and hence to some extent lowered the measured viscosity. In the interest of maintaining the (liquid-crystalline) thermal history of the sample, no measures were taken to repair the sample's edge.

Conclusions

For a high molecular weight nematic liquid-crystalline polymer with well-defined thermal transitions and homogeneous chemical structure along the chain, dynamic frequency sweep data were found to be superimposible, although not mutually so, in the isotropic and liquid-crystalline state.

Interrupted-flow measurements for all cases investigated in the liquid-crystalline state show overshoot behavior upon startup of shear accompanied by a temporary negative first normal stress difference, which soon became a positive N_1 peak. At sufficiently high shear rates, a second stress overshoot appeared, this time accompanied by a positive N_1 peak. Optical micrograph results show a visible domain structure that deforms and then breaks down at sufficient shear rate levels. Consequently, the first set of stress overshoot peaks appears to be related to the deformation of this structure, while the second is felt to signify, when shear rate is sufficient to produce domainless, "oriented liquid-crystalline polymer". It is also notable that this material with a long flexible spacer did not at any time during observation exhibit band formation perpendicular to the flow direction, as discussed in the text. Although optical micrographs show an apparently different texture eventually will return to this oriented liquid-crystalline polymeric material after significant deformation, interrupted-flow results show a qualitatively similar stress overshoot and N_1 behavior returning to the sample with time, with only peak height, which appears to be approaching initial values with time, and the relative location of the peaks being different. On the contrary, in the isotropic range, none of the above-mentioned anamolies were observed in interrupted flow.

Comparing complex viscosity to steady-shear values, it was found that the Cox–Merz rule does not apply in either of these states with $|\eta^*(\omega)| > \eta(\dot{\gamma})$. This is not particularly unusual behavior in the liquid-crystalline state but possibly a new observation for a homogeneous backbone melt of a nematic liquid-crystalline polymer.

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