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Molecular Organization in Nematic Polymers. 2. Evolution of the Mesophase

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ABSTRACT: We have probed the orientational dynamics of a nematic polymer melt in a magnetic field by broad-line proton NMR and its thermomechanical behavior upon solidification by torsion braid analysis. The objective of this work has been to understand the nature of the evolution of polymeric mesophases aging in the nematic phase. The experimental polymer was an aperiodic copolyester containing both aromatic and aliphatic structural units and having molecular weight in the range (0.4–1.6) × 10^4. Using a model for magnetic orientation we obtained values of a characteristic orientation time, τ, as a function of molecular weight and aging time in the nematic state. We found that τ, which is proportional to rotational viscosity, is proportional to molecular weight to a power that has a striking dependence on the age of the fluid. The exponent decreases approximately from 6 to 1 depending on isothermal age of the fluid in the range of several minutes to hours. Thermomechanical analysis of solid samples obtained from the nematic fluids revealed with aging a reduced tendency of the solid to order. This tendency is linked to the mesophase evolution to a more stable state which has longer range orientational order and aligns very rapidly in external magnetic fields relative to the unaged nematic state. Studies of orientation dynamics aimed at verifying physical theories must therefore define precisely the mesophase age and its texture.

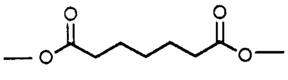
Introduction

In the previous paper of this series[1] we concluded that nematic polymers containing rigid and flexible structural units along the chain tolerate isotropic motion. This motion is possibly sustained by nematic–isotropic fluctuations with spatial and temporal periodicities which depend on temperature and molecular structure. Such departures from the classical image of a nematic phase should impact on the physicochemical properties of these self-ordering polymers. One interesting question is the impact of nematic–isotropic fluctuations on their solvent power for flexible polymers and small molecules. Technically this is important in our ability to formulate new materials on the basis of blends and for possibilities of using nematic polymers as matrices to create oriented structures.

We had previously reported on magnetic orientation dynamics of the nematogen studied here.[2,3] In our initial studies we analyzed the effects of molecular weight and temperature on orientation dynamics. The observed trends were expected but we were surprised to find that orientation dynamics were strongly time dependent. For example, isothermal aging of the mesophase for periods under one hour were found to reduce orientation time constants by 1 order of magnitude. We also found that in samples aged for a given time period this constant scaled with molecular weight to a power in the range of 3.1. One of the objectives of the present study has been to determine if and how this exponent changes with age of the mesophase. We felt this information would provide some insight on the evolution of the mesophase. We also probed for the same purpose the nature of motions in molecular segments of the polymer in solids obtained after the mesophase was aged for various periods of time. The study was carried out on polymers synthesized in our laboratory and the experimental techniques included broad-line proton NMR and torsion braid analysis (TBA).

Experimental Section

We described in earlier publications the synthesis and characterization of the liquid crystal polymer used in this work.[2] The polymer is a random copolyester containing pimeolate **1**, oxybenzoate **2**, and hydroquinone **3** structural units. The viscosity average molecular weight of the chemically aperiodic polymer varied within the range 4 300–16 700. Viscosities of the polymer samples were measured with a Ubbelohde type viscometer at 30 ± 0.01 °C using solutions of the polymers in tetrachloroethane. Flow times at four different concentrations were obtained with dilutions made directly in the viscometer bulb. Limiting viscosity at infinite dilution, [η], was taken as the average value of the least-squares intercept of η_{sp}/c vs c and ln (η_r/c) vs c curves. Samples for broad-line proton NMR were prepared in standard 5-mm-diameter tubes, each containing 0.4 g of the polymer. The tubes were filled in stages with five equal portions and heated to 200 °C for 2 min after each addition. A glass rod was used to lightly pack each of the portions in NMR tubes. Filled tubes were evacuated, purged with dry nitrogen gas, and heated to 200 °C for various periods of time. Proton NMR measurements were carried out at 185 °C with a Varian XL-200 instrument equipped with a variable-temperature probe. A spectral width of 80 kHz, pulse width of 1.0 μs (90° pulse width = 13 μs), and acquisition times of 100 ms were used for data collection. The Fourier transformation utilized 256 data points, and the magnetic field and radiation frequency were 4.7 T and 200 MHz, respectively.



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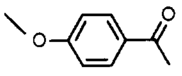

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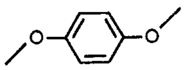

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The polymer used in TBA experiments had an estimated viscosity average molecular weight of 6.2 × 10^3 (inherent viscosity in tetrachloroethane at 30 °C of 0.441 dL/g). Clean glass braids were dipped several times into freshly prepared 4% by weight solutions of the polymer in tetrachloroethane. The polymer-coated braids were then dried for 24 h in a vacuum oven maintained at 50 ± 2 °C. We also dried some of the coated glass braids under the hood at room temperature for 48 h and obtained identical results. Approximately 2 mg of polymer were adsorbed on the glass braids after several dippings in the tetrachloroethane solution. Unless otherwise indicated, aged samples were stored at room temperature in a dry place for various periods of time after the first thermal cycle of TBA. The instrument used

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was a low frequency (<2 Hz) torsium pendulum from Macromolecular Associates, Inc., and the substrates were 5-cm-long glass braids obtained from Custom Scientific, Inc. Measurements of relative shear modulus, G_r, and logarithmic decrement, Δ, were obtained in the temperature range 40–220 °C. The heating rate used during TBA experiments was 1 °C/min and cooling was by natural convection. There was very good reproducibility of the TBA scans.

Results and Discussion

Recording the NMR spectrum of the polymer melt as a function of time we were able to follow the gradual macroscopic alignment of the molecules in an external magnetic field. The second moment of the broad-line spectrum yields the time dependence of the quantity $\langle S^2_{z'z'} \rangle$ where $S_{z'z'}$ is the macroscopic order parameter given by

$$S_{z'z'} = {}^3/_2 \cos^2 \theta_0 - {}^1/_2 \quad (1)$$

In eq 1 θ_0 is the angle between the mesophase director axis and the external magnetic field. These measurements are carried out at 185 °C, a temperature at which the melt is uniformly birefringent and isotropic fluid is not detected by the light microscope. The conversion of second moment data to $\langle S^2_{z'z'} \rangle$ is explained in a previous publication from our group.[3] At the time data collection begins the sample is unoriented and then gradually aligns in the external magnetic field. The data therefore measures the time dependence of the orientational distribution of local directors in the polydomain sample relative to the external field. We showed earlier that a simple model of the orientational process allows us to calculate $\langle S^2_{z'z'} \rangle$ by averaging a time dependent distribution function over the sphere of directions[3]

$$\langle S^2_{z'z'} \rangle = \frac{\int_0^\pi \rho(\theta_0,t_r)[{}^3/_2 \cos^2 \theta_0 - {}^1/_2]^2 \sin \theta_0 \, d\theta_0}{\int_0^\pi \rho(\theta_0,t_r) \sin \theta_0 \, d\theta_0} \quad (2)$$

where the distribution function is given by

$$\rho(\theta_0,t_r) = \left[\frac{\sin[\tan^{-1}(\exp(t_r)\tan\theta_0)]}{\sin\theta_0}\right] \times \left[\frac{\exp(t_r)}{\cos^2\theta_0 + \exp(2t_r)\sin^2\theta_0}\right] \quad (3)$$

t_r is equal to t/τ; and τ is a characteristic orientation time for the sample. We calculate values of τ by iteratively varying its value to obtain the best fit to experimental data. Reasonable fits to experimental data are normally obtained in the range of short reduced times, t_r.

Figure 1 shows four plots of τ as a function of intrinsic viscosity for samples which only differ in the period of time they were kept at 200 °C before exposure to the orienting field. The sensitivity of orientation dynamics to molecular weight is clearly dependent on isothermal aging time of the mesophase. In Figure 2 the orientation time constant has been plotted as a function of aging time for each of the four molecular weights. It is very clear from this graph that the greatest sensitivity of orientation dynamics to aging time occurs in systems of high average molecular weight. The ongoing molecular reorganization with time is apparently a process sensitive to chain length. A least-squares fit of data indicates that

$$\tau \sim M^n \quad (4)$$

where the exponent n decreases drastically with aging time.

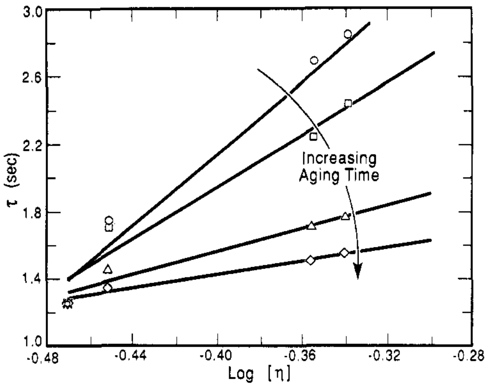

Figure 1. Orientation time at 185 °C for nematic melts in an external magnetic field as a function of the polymer's solution intrinsic viscosity. Each curve corresponds to a set of samples aged at 200 °C for a different period of time in the nematic state (in the absence of the magnetic field).

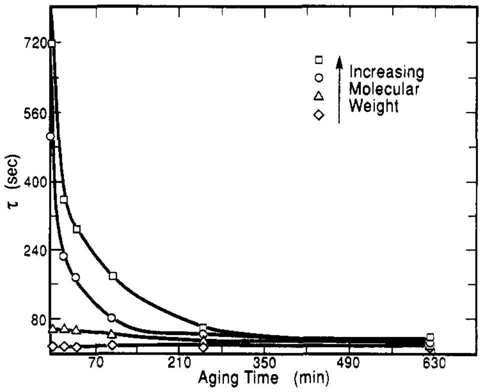

Figure 2. Orientation time in an external magnetic field at 185 °C as a function of aging time in the nematic state for four different samples varying in molecular weight: □, 16 700; ○, 14 000; △, 5 400; and ◇, 4 300.

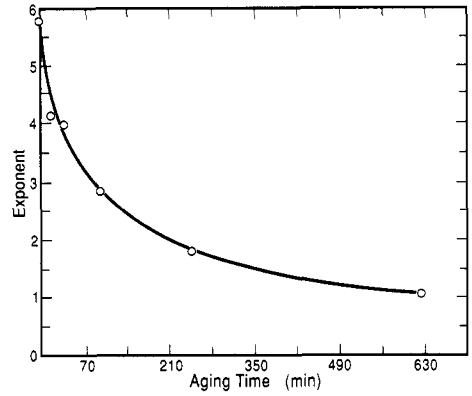

Figure 3. Value of the exponent n as a function of aging time in the expression $\gamma \sim M^n$ where γ is the rotational viscosity of the mesophase.

The plot in Figure 3 shows this exponent drops by nearly a factor of 6 as aging time increases. Our previously reported data[3] is consistent with this curve since n was found to be approximately equal to 3.1 after an aging time of 60 min.

We carried out measurements to determine the factors involved in the strong effect of aging time on macroscopic orientability of the system. Table I lists the measured viscosities for unaged samples and two samples subjected to aging times of 20 and 250 min. It is clear that molecular weight changes cannot explain the increased orientability of the system with aging time. Furthermore, we had established earlier that chemical changes are not detected in the samples as a function of aging time.[3] Specifically,

Table I
Effect of Aging Time on Intrinsic Viscosity

aging time, min	$[\eta]$, dL/g	τ, s
0	0.44 ± 0.01	720
20	0.45 ± 0.01	360
250	0.42 ± 0.01	60

we did not observe changes in structural unit composition or sequence structure at the diad level by high-resolution ^{13}C NMR. These observations are therefore supportive of the idea that changes in physical and not chemical structure lead to the observed changes in orientation dynamics.

The theoretical interpretation of the observed changes in exponent with age of the fluid will remain a challenge for sometime. However, it is interesting to consider in this context the exponent predicted for simpler systems. In the orientation model mentioned before the rotational viscosity of the system, γ_1, is directly proportional to τ:

$$\gamma_1 = \tau B^2 \Delta\chi \qquad (5)$$

where B is the magnetic field strength, and $\Delta\chi$ is the molecule's anisotropy in diamagnetic susceptibility. If the system could be microscopically described as an array of independent rod-like molecules[4] we would expect γ_1 to scale with molecular weight as M^2. In a hypothetical system consisting of entangled flexible chains caused to reptate in a biased direction by the external magnetic field, γ_1 would scale with molecular weight as M^3 according to the well-known model of de Gennes.[5] Such a system is of course hypothetical since polymeric mesogens are not flexible coils, and the orienting influence of the field on flexible diamagnetic chains would be negligible. It remains an open question what is the nature of the evolution experienced by the mesophase during aging that could explain the large changes in molecular weight exponent. The simplest explanation is that unaged fluids have complex textures with high defect densities and that these textures coarsen at rates that depend on molecular weight. In the unaged textures large internal surface areas of disclination boundaries would produce a very high rotational viscosity. This viscosity would then decrease rapidly as the defect density diminishes with aging time. If the coarsening rate is molecular weight dependent one may explain the large differences in exponent after different aging times. That is, after short aging times the low molar mass samples will have coarsened much more than high molar mass samples, producing the apparent high sensitivity of τ to molecular weight. The more basic question is how molar mass affects the time necessary to reach the apparent equilibrium organization where $\tau \sim M$. Is it simply a question of internal viscosity within domains as molecular weight increases or is this time controlled by the topological nature of interdomain boundaries (i.e., entanglements, anisotropic attractive forces among segments)? Furthermore, it is interesting that $\tau \sim M$ and not M^2 when the apparent equilibrium molecular organization is reached. A possible explanation is alignment cooperativity among domains which is very effective in achieving macroscopic orientation when domain sizes are large.

As discussed in the previous paper of this series[1] isotropic motion in the nematic phase is detected by NMR. The first paper linked the isotropic motion to nematic–isotropic fluctuations and not to a coexisting isotropic phase. We measured here the intensity of the isotropic signal as a function of aging time in samples differing in molecular weight and the data are shown in Figure 4. The general trend of greater isotropic motion with increasing molecular weight is clear and in agreement with our own previous data on the same system.[3] The intensity of isotropic motion does not change appreciably with aging time except perhaps in samples of intermediate molecular weight. The observed decrease with aging time in samples of intermediate molar mass is also consistent with data we reported previously.[3] In the highest molecular weight sample the intensity of isotropic motion does not decrease with aging time. However, it is clear from data discussed before that in this same sample magnetic orientation times decrease steadily with aging. One therefore infers that a decrease in the isotropic motion per se is not the necessary condition for more cooperative dynamics in the system. We do not know if the slight increase in isotropic motion with aging time in the sample of highest molar mass is a significant observation. It may be simply an artifact of greater macroscopic orientation which allows better resolution of the isotropic signal.

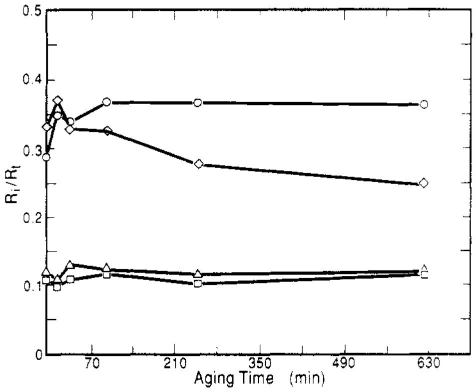

Figure 4. Fraction of isotropic resonance in the broad-line proton NMR spectrum of four polymers varying in molecular weight as a function of aging time in the nematic phase: □, 4 300; △, 5 400; ◇, 14 000; and ○, 16 700.

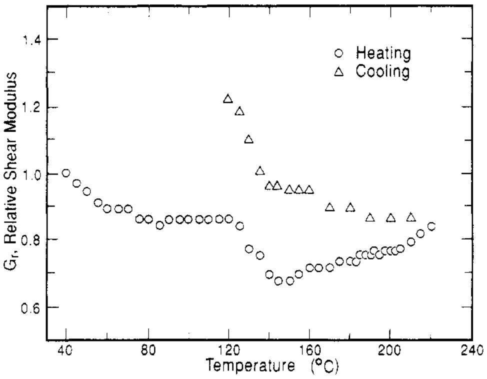

Figure 5. Plot of relative shear modulus as a function of temperature for a freshly prepared sample of the nematic polymer during the first heating and cooling cycles.

It is known that texture coarsening is part of the mesophase evolution;[6,7] however, it is important to gain further insight on its nature. With this objective we probed solid samples by torsion braid analysis[8] after the nematic fluid had been aged for the same periods of time used in magnetic orientation experiments. Figure 5 shows plots of G_r as a function of temperature for a fresh sample of the aperiodic LCP. G_r is defined as

$$G_r = (P_{40\,°\mathrm{C}}/P_T)^2 \qquad (6)$$

where $P_{40\,°\mathrm{C}}$ is the period of the braid's oscillation at 40 °C and P_T is the period of the braid's oscillation at temperature T. A plot showing the thermal dependence of the logarithmic decrement, Δ, of the same sample is presented

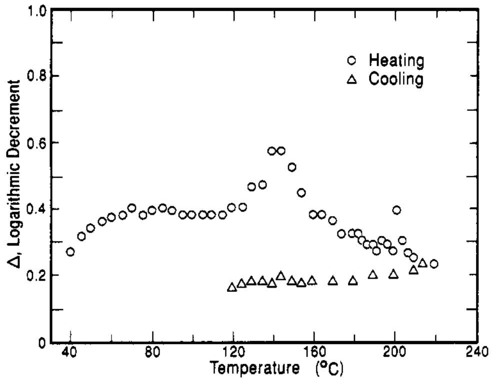

Figure 6. Plot of the logarithmic decrement as a function of temperature for a freshly prepared sample of the nematic polymer during the first heating and cooling cycles.

in Figure 6. Δ is defined as

$$\Delta = (1/n) \ln (A_m/A_{(m+n)}) \qquad (7)$$

where A_m and $A_{(m+n)}$ are the amplitudes of the mth and $(m + n)$th oscillations of the braid. Δ and tan δ are related by the expression

$$\Delta = \pi \tan \delta \qquad (8)$$

Δ peaks are observed in the TBA scan of samples in the range 60–80 °C and 145 °C. The low temperature peak is rather broad and coincides with the drop in G_r observed in the temperature range 40–80 °C. Both Δ and G_r remain approximately constant in the range 80–120 °C. The well defined Δ peak at 145 °C corresponds to the melting endotherm observed by DSC in the experimental polymer and previously reported by our group.[2] This peak is therefore associated with melting of the solid polymer into a liquid crystalline fluid. As expected, a drop in relative shear modulus is also observed in the temperature range of this melting transition. Unexpectedly, we observe a gradual increase in G_r as the temperature is raised to 200 °C. This increase may be explained by factors other than structural changes in the sample, for example, the loss of residual solvent above the melting point of crystalline regions of the microstructure. Another plausible explanation is the penetration of fluid polymer into the pores of the glass braid. It is difficult to assess at this point whether or not a structural reorganization contributes to the increase in G_r. The logarithmic decrement scan reveals a small peak near 200 °C while G_r continues to rise at a faster rate. The cooling portion of G_r scans reveals a slow increase in the range 220–145 °C, and a faster increase below 145 °C which we associate with solidification of the sample.

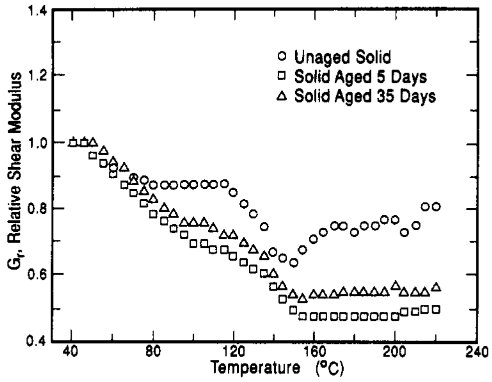

Figure 7. Plots of relative shear modulus as a function of temperature during the first heating cycle and two subsequent cycles, one taken 5 days after the solid sample was aged at room temperature and the second one after 35 days of aging.

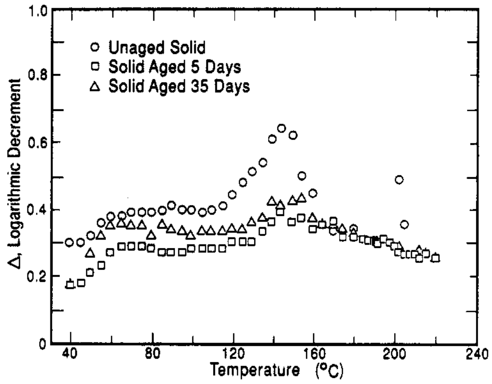

Figure 8. Plots of logarithmic decrement as a function of temperature during the first heating cycle of a freshly prepared sample and two subsequent cycles, one taken 5 days after the solid sample was aged at room temperature and the second one after 35 days of aging.

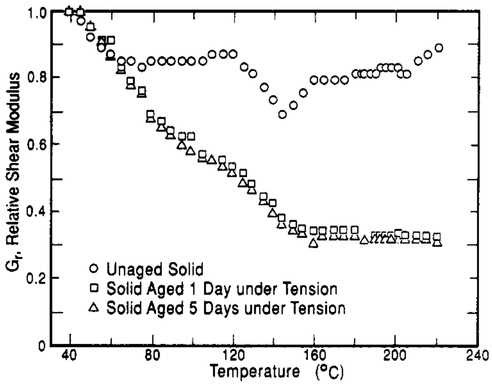

Figure 9. Plots of relative shear modulus as a function of temperature during the first heating cycle of a freshly prepared sample and two subsequent cycles, one taken after the solid sample was aged for 1 day at room temperature sustaining a tensile stress of 30 kg/cm² and the other taken after 5 days of similar aging of the solid sample.

Samples that are aged at room temperature for days after the first heating cycle have somewhat similar but not identical thermomechanical behavior relative to unheated samples. Second scans obtained after 5 or 35 days are shown in Figures 7 and 8. The low temperature relaxation is observed but one observes only partial reappearance of the Δ peak associated with the melting point. Our interpretation is that an ordering process among the chemically disordered chains occurs gradually during aging at room temperature. This ordering could involve the partial crystallization of a liquid crystalline glass formed when samples are cooled to room temperature after the first heating cycle. Interestingly, a different TBA scan is observed if samples are aged in the instrument's sample chamber for either one or five days sustaining a tensile stress of approximately 30 kg/cm². Figures 9 and 10 show the typical data obtained during a second heating scan along with that obtained during the first heating cycle for comparative purposes. Although more diffuse, the low temperature transition is still observed in the Δ scan within the range 60–80 °C. However, the peak associated with the melting transition is hardly detectable in the second heating cycle. G_r is observed to decrease steadily during the second cycle and what appeared as a "rubbery plateau" below the melting point in the first cycle is no longer well defined upon reheating. Our conclusion is that the applied tensile stress inhibits the ordering transformation of the liquid crystalline glass.

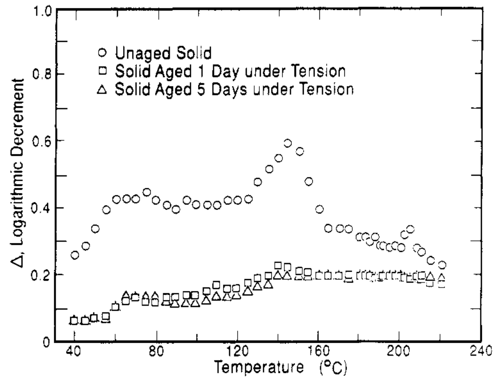

Figure 10. Plots of logarithmic decrement as a function of temperature during the first heating cycle of a freshly prepared sample and two subsequent cycles, one taken 5 days after the solid sample was aged at room temperature sustaining a tensile stress of 30 kg/cm^2 and the other taken after 5 days of similar aging of the solid sample.

Some samples after their initial preparation were heated to 200 °C and aged at this temperature for a given period of time. The aging of the liquid crystalline fluid was identical to that described previously in connection with measurements of magnetic orientation. As stated earlier aging gave rise to an increase in the macroscopic orientability of the nematic fluid. This was revealed as a significant reduction in the characteristic orientation time of samples as calculated from NMR data (this time is reduced by more than 1 order of magnitude). In this work we have measured the thermal dependence of G_r in samples that had been aged at 200 °C for various periods of time and then solidified by cooling to room temperature. The results are shown in Figure 11. The data indicate that aging of the fluid prior to solidification stabilizes the liquid crystalline glass. This is revealed by the near absence of the modulus plateau between the low-temperature relaxation and the melting point of the sample after the longest period of aging. From this observation we conclude that the reduced tendency of the system to order in the solid state is linked to the evolution of the mesophase during aging to a more stable state with longer range orientational order. In this sense there could be a connection between the inhibited ordering during aging under an external mechanical force and inhibited ordering after long term aging in the nematic state. Under both conditions long range orientational order is promoted.

Conclusions

The fluid mesophases formed by nematic polymers undergo an evolution to a more stable state which has a reduced tendency to order when solidification occurs. This more stable state has longer range orientational order and aligns very rapidly in external magnetic fields relative to the unaged nematic state. This evolution is very clearly revealed by a decrease in the molecular weight exponent of orientation time by a factor of 6 after samples are aged in the nematic state. Studies of orientation dynamics aimed at verifying physical theories must therefore define precisely the mesophase age and its texture.

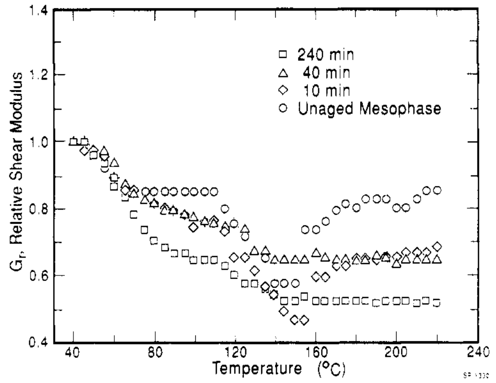

Figure 11. Plots of relative shear modulus as a function of temperature for solid samples which were previously aged in the nematic state at 200 °C for periods of 10, 40, or 240 min before solidification to begin the scan. The scan corresponding to an unaged sample is shown as well.

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