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Transient flow of thermotropic liquid crystalline polymers in step strain experiments

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Synopsis

The transient response of two thermotropic liquid crystalline polymers (a copolyester of 60 mol % *p*-hydroxybenzoic acid, PHB, and 40 mol % poly(ethylene terephthalate), PET, and a copolyester of PHB and 2-hydroxy-6-naphthoic acid, following step strains up to 20 strain units was measured. The relaxation curves typically show an initially rapid decay followed by a long relaxation tail. The lower the temperature, the more remarkable is the length of the long relaxation tail. This behavior makes the LCP uniquely different from most flexible chain polymers such as PET and polystyrene, which show a relaxation modulus which decreases continuously having no discontinuity in the slope. This behavior is probably due to unmelted solid phase which exists in the melt up to quite high temperatures. When the LCP's are heated to temperatures well above their melting points as determined by DSC, then the long relaxation tails are eliminated. Furthermore, on cooling the sample rapidly down from a temperature well above the melting point the relaxation modulus resembles that at the higher temperature as a result of the supercooling effect. The relaxation modulus was also determined for samples subjected to lubricated squeezing flow. Whereas for polystyrene the relaxation modulus determined in lubricated squeezing flow was equal to that determined in step shear strain experiments, this was not the case for the LCP's. It is not known whether the behavior reported here is common to nematic LCP's or to the multiphase structure (crystallites, nematic phase, isotropic phase) which might be present.

INTRODUCTION

Thermotropic liquid crystalline polymers (LCP's) have been of considerable interest in the last few years because they can be processed to form high modulus materials. For example, the flexural modulus of

injection molded plaques can exceed that found for fiber reinforced materials.[1] Furthermore, the modulus of fibers processed from thermotropic LCP's is similar to that reported for steel.[2] The exceptional properties are related to the high degree of molecular orientation generated during melt processing. Hence, it is apparent that polymer systems with liquid crystalline order (LCO) can be oriented much more readily than isotropic polymer systems.

It is suggested by theories such as those of Leslie and Ericksen[3,4] and Doi[5] that the change in transient rheological properties is due to changes in the orientation of the rod-like molecules. Although under some conditions it is predicted by Ericksen's theory that the rod-like molecules will tumble, in general it is predicted that the molecules will orient in both shear and extensional flow. In studies by Viola and Baird[6] it was found for a thermotropic copolyester that in isothermal shear flow there was no evidence of molecular orientation after cessation of shear flow. However, if the flow was carried out nonisothermally so that the fluid was cooled while it was sheared, then considerable orientation was observed.[6] The conclusion of this work was that the transient behavior was not due to changes in molecular orientation, but to changes in the domain structure.

In another study by Baird and co-workers[7] stress growth behavior was reported for thermotropic copolyesters of PHB and PET. In particular it was observed that for 60 mol % PHB/PET the shear stress exhibited two types of behavior. For temperatures less than or equal to 250 °C there was just one overshoot peak in the shear stress vs time curve. However, for temperatures above 250 °C, two peaks were evident. Furthermore, the primary normal stress difference exhibited negative values at low shear rates $\dot{\gamma}$ below 250 °C but positive values for all $\dot{\gamma}$ above 250 °C. Similar behavior was reported for 80 mol % PHB/PET but the transition temperature was 328 °C.[8] The point of the above work is that the stress growth behavior of thermotropic LCP's is highly dependent on the temperature at which the measurements are made.

The purpose of this work is to investigate further the transient behavior of thermotropic LCP's. In particular, we would like to know whether there is anything unique about the rheology of fluids composed of rigid chain molecules. Furthermore, we would like to know if the transient response of thermotropic LCP's following step strains is similar to flexible chain polymers. To investigate these topics the following experiments are reported here. Results for shear step strain experiments are reported for two LCP's and two flexible chain polymers. For flexible chain polymers, the stress relaxation modulus $G(t,\gamma)$ can usually be

separated into two components: a linear relaxation modulus $G^0(t)$ and a strain dependent function $h(\gamma)$.[9] $h(\gamma)$ is called the damping function and describes the nonlinear rheological response of polymer melts. Since liquid crystalline polymers exhibit a domain structure which is quite different from the random coil structure of flexible chain polymers, it is possible that LCP's will relax differently following a step strain. The thermal history is another important factor investigated here because the presence of high melting crystallites can lead to behavior which might be attributed to liquid crystalline order. Another objective of this work is to determine the transient response of LCP's in shear-free flow. To accomplish this step strain experiments using lubricated squeezing flow were carried out. As reported by Winter and co-workers,[10,11] lubricated squeezing flow can be used to generate equal biaxial extensional flow at least at low strain levels. Lin and Winter[12] have studied the morphology of a LCP deformed in lubricated squeezing flow and found no significant orientation. As this flow represents a different deformation history relative to shear deformation, the relaxation moduli obtained in the two step strain experiments are compared.

EXPERIMENTAL

Materials

Two liquid crystalline polymers were used in this research. The first was a copolyester of 60 mol % *p*-hydroxybenzoic acid (PHB) and 40 mol % poly(ethylene terephthalate) (PET), 60/40 PHB/PET, supplied by Tennessee Eastman. The detailed synthetic method was described by Jackson *et al.*[13] and the melting temperature was around 250 °C. The second polymer consisted of *p*-hydroxybenzoic acid (PHB) and 2-hydroxy-6-naphthoic acid (HNA), with a commercial description of LCP2000, and was obtained from Hoechst-Celanese. The melting point is reported to be 283 °C.[14] The basic synthetic procedure was given by Calundann and Jaffe.[14] PET was also supplied by Tennessee Eastman and polystyrene, STYRON 678, was bought from Dow. All samples but polystyrene were dried in a vacuum oven at 110 °C for 72 h in order to remove any moisture.

Rheological measurements

The shear step strain experiments were carried out on a RMS-800 using a cone and plate geometry with cone angles of 0.025 and 0.1 rad and 25 mm in diameter. The maximum angular displacement was 0.5 rad. The strain range used was from 0.1 to 20. Pellets were loaded

directly on to the bottom plate and heated to the test temperature. The cone was then loaded into position and the excess polymer removed. Fresh samples were used for each test. At each strain level, two repeat tests were run but there was less than 2% difference in the runs.

The main variable studied was the temperature history. 60 mol % PHB/PET was studied initially at 250, 260, and 275 °C. The melting point as determined by means of DSC has been reported to be 250 °C.[15,16] Furthermore, 250 °C seems to be the temperature where a distinct change in the stress growth behavior occurs as discussed in the introduction. At 260 and 275 °C no differences in the rheological properties were observed, including the magnitude of the properties.[17] Furthermore, it has been observed that on heating 60/40 PHB/PET above 250 °C (e.g., to 275 °C) and then cooling the sample down to temperatures below 250 °C, that the polymer supercools.[17] Hence, experiments were also carried out in which samples were subjected to temperatures of 275 °C, cooled to 250 °C in about 30 s, and then $G(t,\gamma)$ was recorded.

For LCP2000, the melting point was recorded to be 283 °C[16] which was in agreement with that reported by others.[14] Isothermal tests were run at 300, 320, 330, and 350 °C. Samples were also heated up to 350 °C and then cooled in about 1 min back down to 300 °C where the jump strain test was performed immediately. Further discussion of the importance of these tests will be presented in the next section.

Two factors which could affect the accuracy of the measurements are a dependence of measurements on the cone angle and the thermal stability of the melt. There was no observed dependence of the results on the cone angle. However, in the case of the parallel plate device Gotsis and Baird[8] have reported experiments in which the steady state normal stresses were gap dependent for a certain temperature range. As long as the samples are properly dried, they were thermally stable for periods up to 45 min.[16] Hence, for the temperature range used in these experiments we can expect the results to be devoid of any problems associated with geometry, transesterfication, or degradation.

RESULTS AND DISCUSSION

Shear step strain

The relaxation modulus $G(t,\gamma)$ for 60/40 PHB/PET was first measured at 275 °C in strain ranges from 0.1 to 10. It is seen in Fig. 1 that for strains less than 1.0, $G(t,\gamma)$ is independent of strain. The trace of $G(t,\gamma)$ becomes too small and scattered for accurate measurements after 0.2 s. This is due to the low viscosity of the melt at 275 °C which lead

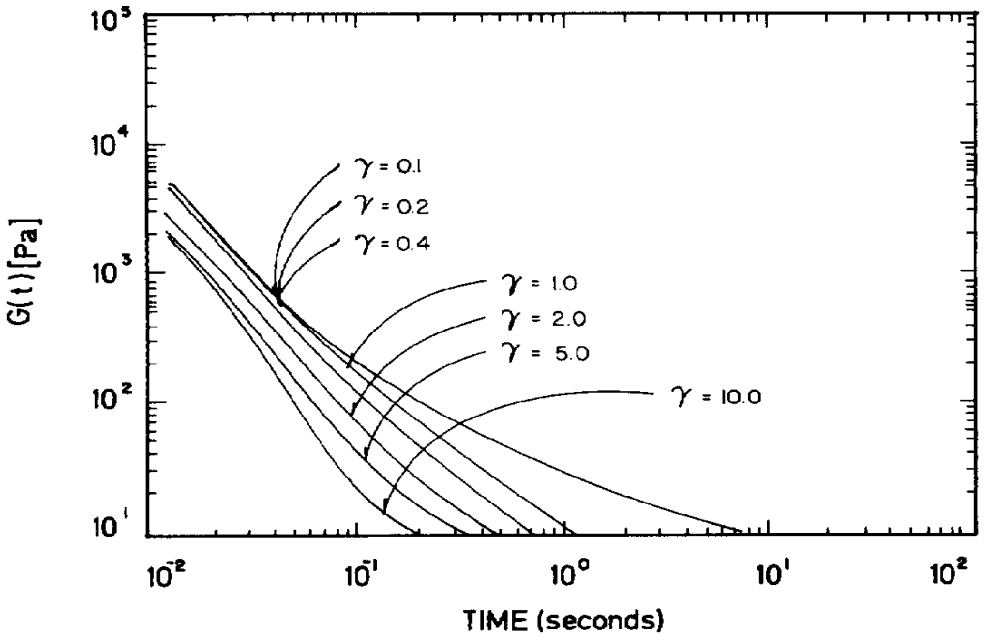

FIG. 1. Stress relaxation following a step shear strain for 60/40 PHB/PET at 275 °C.

to values of torque less than 2×10^{-4} N m, which is below the lower limit of the transducer. Therefore, reliable data for this polymer are only measured from 0.01 to 0.2 s. For strains higher than 1, $G(t,\gamma)$ becomes smaller as the strain increases. There is no parallel relationship between these curves and the shape depends on γ. The sample was observed to be expelled from the gap at strains greater than 10. Hence, data reported for strains above a strain of 10 are not reported. For the most part the relaxation modulus goes to zero at this temperature in very short times.

Similar behavior is exhibited by 60/40 PHB/PET at 260 °C as shown in Fig. 2. Scattered $G(t,\gamma)$ traces are also observed beyond 0.2 s for lower γ. Again, these relaxation curves are not parallel to each other and indicate that $G(t,\gamma)$ can not be separated into time and strain factors. The higher the strain, the faster the stress relaxes. The main difference in $G(t,\gamma)$ at these two temperatures is the presence of a longer tail in the $G(t,\gamma)$ curves at 260 °C as compared with those measured at 275 °C. This could be due to the existence of some structure in the melt or solid phase which remains unmelted. Confirmation of the presence of

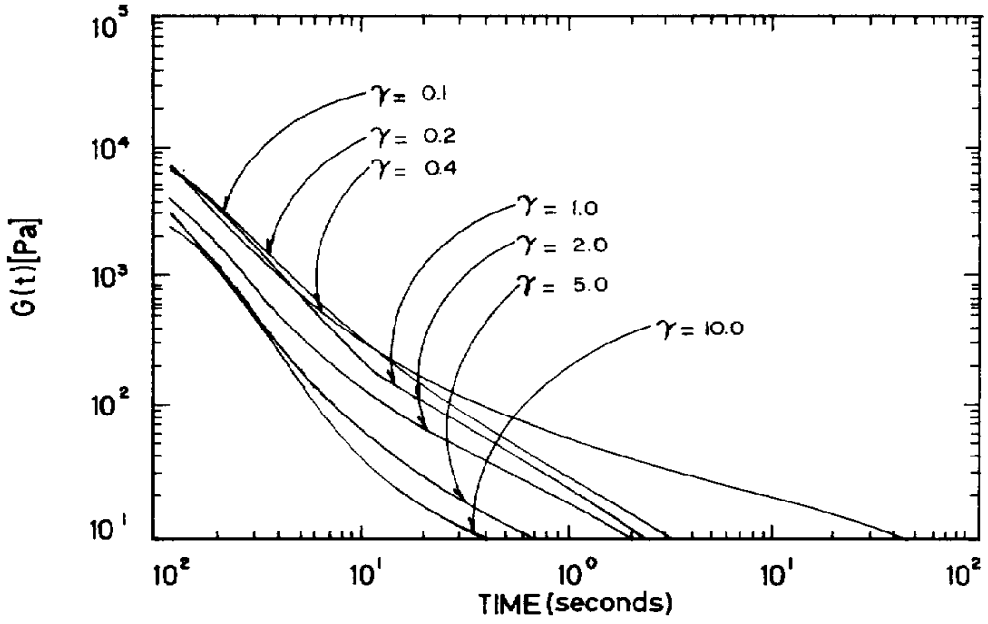

FIG. 2. Stress relaxation following a step shear strain for 60/40 PHB/PET at 260 °C.

unmelted material is given by Mühlebach and co-workers.[19] This behavior is certainly different than for flexible chain polymers where the shape of $G(t,\gamma)$ curves remains unchanged as the temperature is changed.

To further investigate the possibility of unmelted solid, $G(t,\gamma)$ was measured at 250 °C. In Fig. 3 even longer tails in $G(t,\gamma)$ curves are observed. The temperature of 250 °C is just at the melting temperature for 60/40 PHB/PET and there may be some solid phase which remains unmelted.[18,19]

For 60/40 PHB/PET at all three temperatures, the rate of relaxation increased slightly with an increase in strain. Therefore, the relaxation curves are nonparallel and one cannot separate $G(t,\gamma)$ into the product of $G^0(t)$ and $h(\gamma)$. This is one indication of the difference between this liquid crystalline polymer and flexible chain polymers. However, it is not clear if the difference is due to liquid crystalline order or some other structure.

In addition, to determine $G(t,\gamma)$ at constant temperatures, it is interesting to investigate the effect of thermal history on $G(t,\gamma)$. The rheology of 60/40 PHB/PET has been reported to be highly thermal

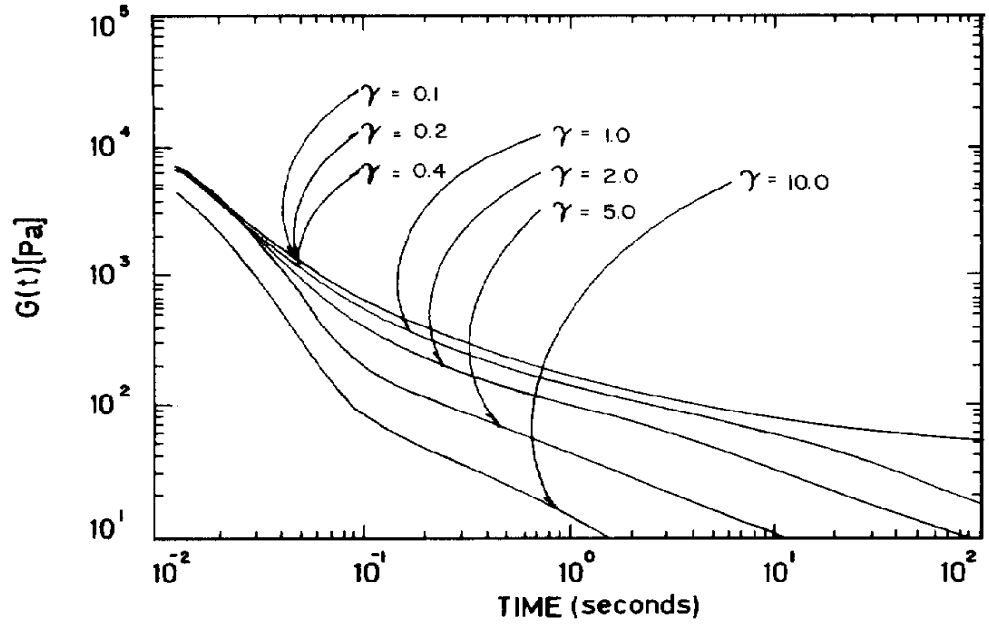

FIG. 3. Stress relaxation following a step shear strain for 60/40 PHB/PET at 250 °C.

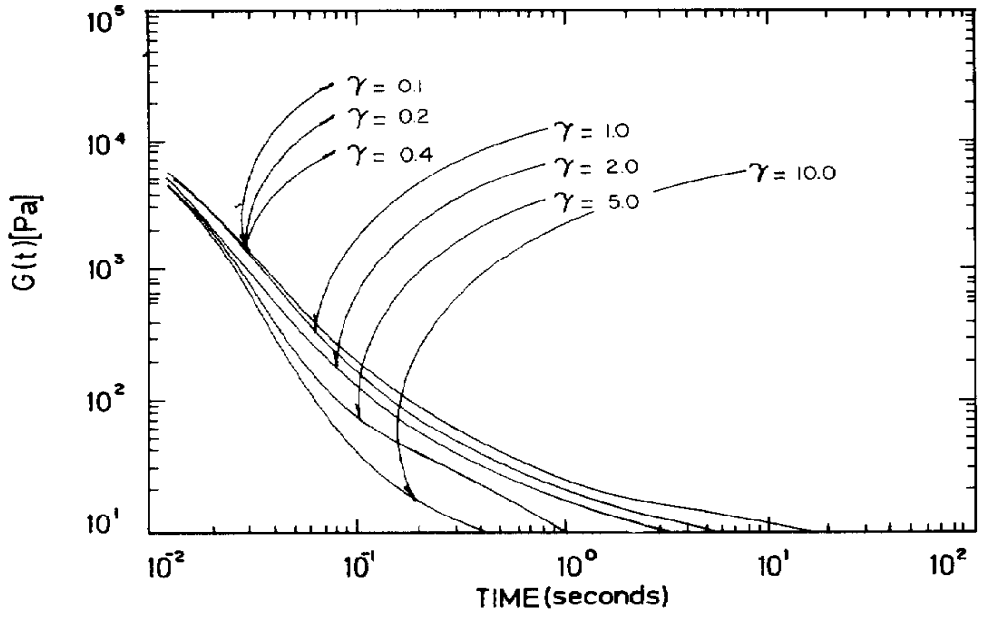

FIG. 4. Stress relaxation following a step shear strain for 60/40 PHB/PET at 250 °C after being cooled from 275 °C.

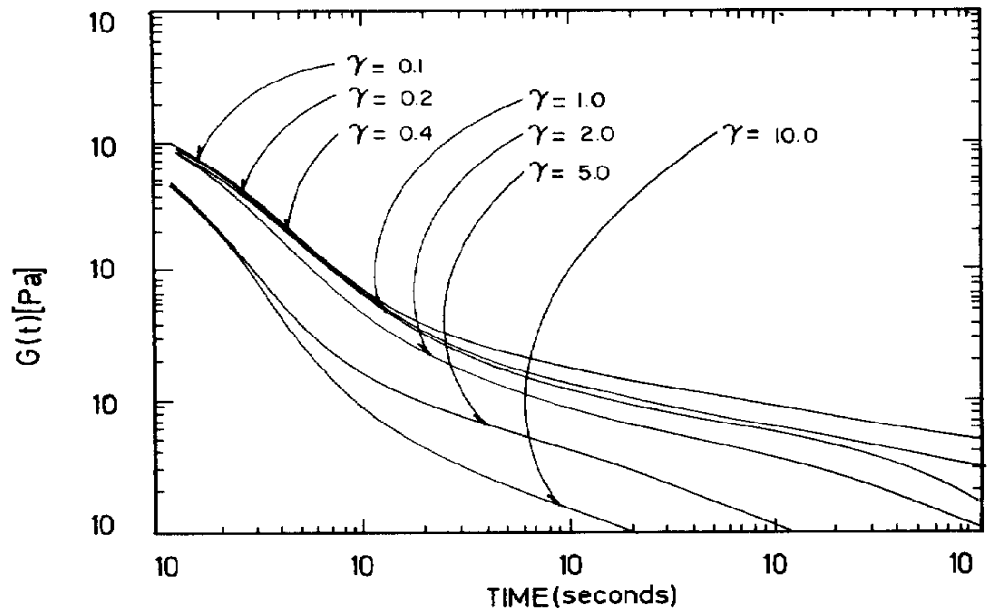

FIG. 5. Stress relaxation following a step shear strain for LCP2000 at 350 °C.

history dependent.[17] Therefore, the sample was preheated to 275 °C and held for 3 min, then cooled to 250 °C (in about 30 s) and a step strain experiment was performed. In Fig. 4 it is shown that there is no long tail present in the $G(t,\gamma)$ curves as compared with those measured at 250 °C with no preheating. This may indicate that once the residual solid phase is melted out at 275 °C and then the sample cooled to 250 °C, the melt behaves as if it were still at 275 °C. This is in agreement with the observation of a significant degree of supercooling reported by Done and Baird.[17,18]

It is necessary to know whether the relaxation behavior observed for 60/40 PHB/PET is unique or common to that of other thermotropic liquid crystalline polymers. Therefore, the shear step strain experiment was carried out on LCP2000. These two systems have different chemical structures but both of them exhibit nematic textures once melted. In Fig. 5 is plotted $G(t,\gamma)$ vs time for LCP2000 at 350 °C. $G(t,\gamma)$ behaves similarly to that of the 60/40 PHB/PET system at 250 °C showing a long relaxation tail. However, this behavior is in contrast to that of PHB/PET at 260 and 275 °C. This again may indicate that some structure still exists in the melt even at temperatures as high as 350 °C. Again

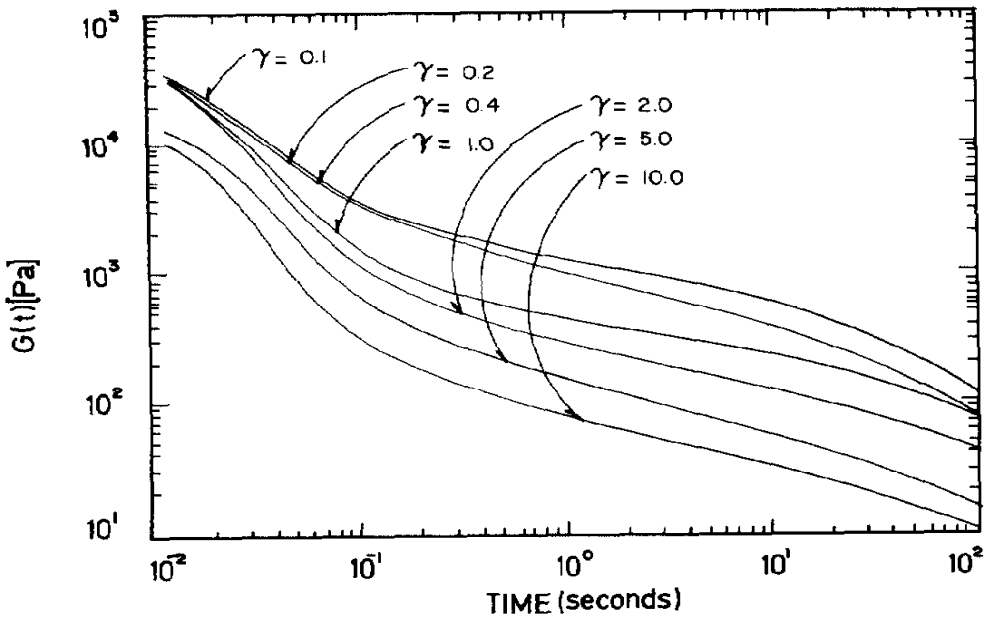

FIG. 6. Stress relaxation following a step shear strain for LCP2000 at 300 °C.

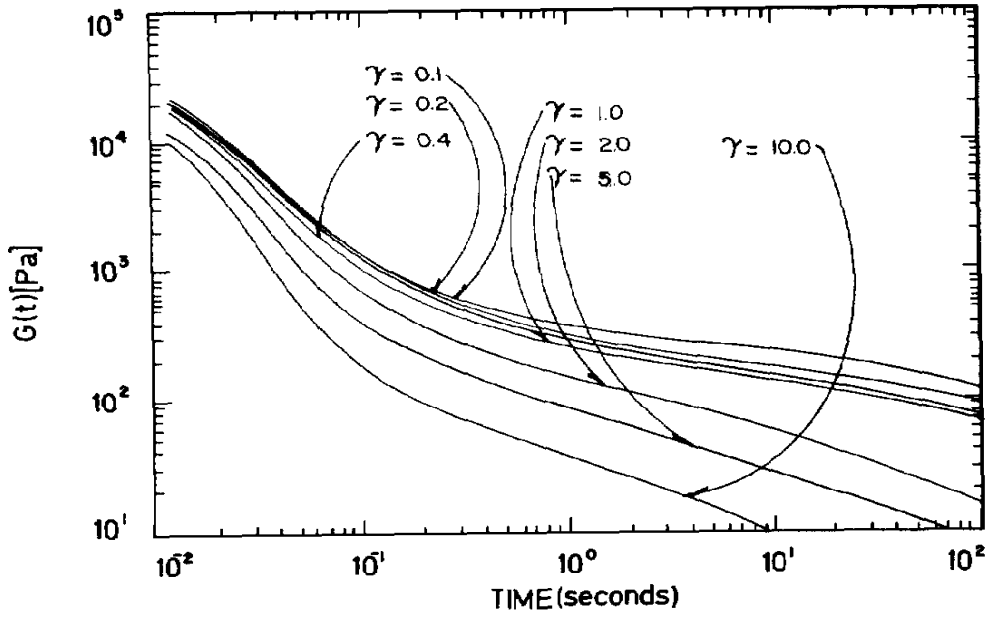

FIG. 7. Stress relaxation following a step shear strain for LCP2000 at 300 °C after being cooled from 350 °C.

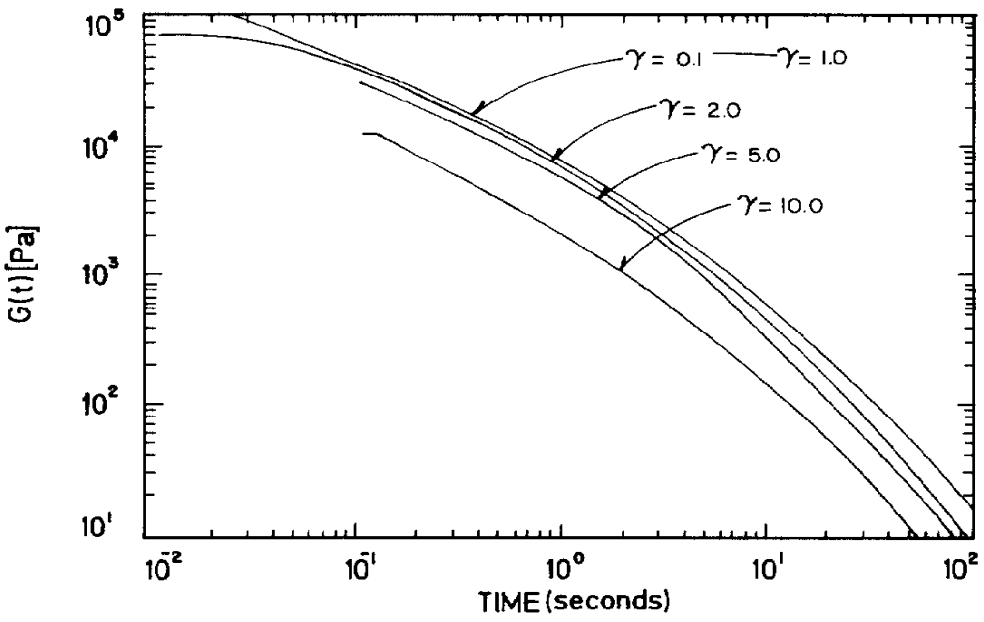

FIG. 8. Stress relaxation following a step shear strain for polystyrene at 190 °C.

nonparallel relaxation curves are observed. Similar $G(t,\gamma)$ curves are observed at temperatures of 330, 320, and 300 °C, but only results at 300 °C are shown in Fig. 6. A slower relaxation rate and longer tails are observed as the temperature is lowered. From the relaxation curves of 60/40 PHB/PET and LCP2000, it is concluded that thermotropic liquid crystalline polymers show long relaxation times at certain temperatures which may be caused by the unmelted solid phase or structure existing in the melt. In other words, the samples may contain several phases even at higher temperatures.

The effect of thermal history on the step relaxation behavior for LCP2000 was also studied. The melt at 300 °C, after being preheated at 350 °C for 3 min, shows $G(t,\gamma)$ curves which relax faster than those measured at 300 °C without preheating, as illustrated in Fig. 7 (note it took about 1.0 min to cool the sample from 350 to 300 °C). This indicates that it may be necessary to heat LCP2000 to temperatures higher than 350 °C in order to melt out any crystallites. This conclusion is based on the fact that the shape of the $G(t,\gamma)$ curves at 350 °C are still similar to those at 300 °C.

It is interesting to compare the relaxation modulus of liquid crystalline polymers with that of flexible chain polymers. Two flexible chain

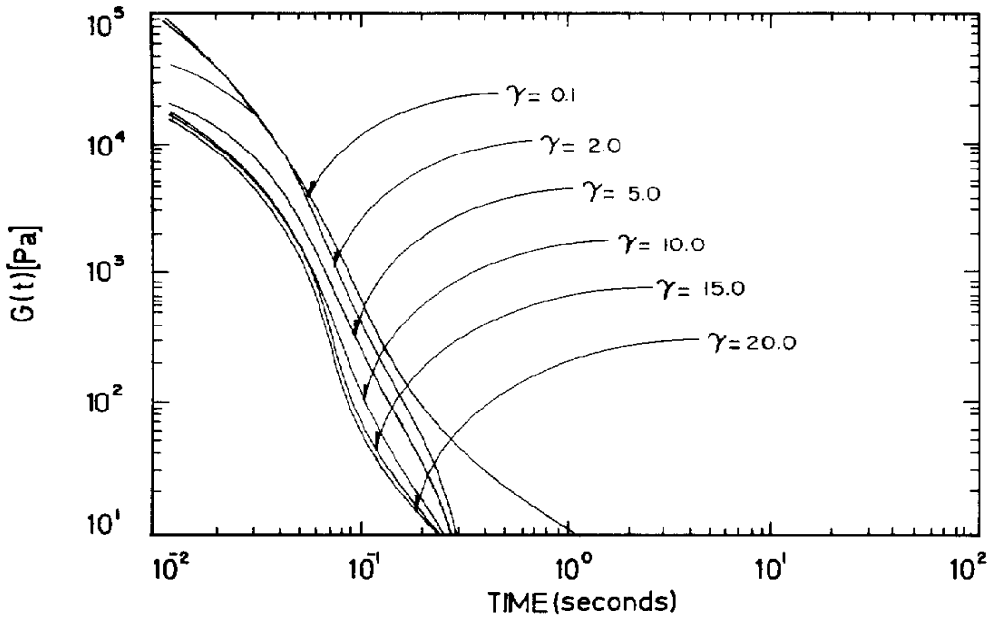

FIG. 9. Stress relaxation following a step shear strain for PET at 260 °C.

polymers were chosen: polystrene, PS, and polyethylene terephthalate, PET. The former shows a typical shear thinning behavior while the latter exhibits Newtonian behavior over a wide shear rate range. $G(t,\gamma)$ for PS at 190 °C is shown in Fig. 8. All curves are concave downward and parallel to each other before the stress level becomes too small to be measured accurately. $G^0(t)$ is observed at strains less than 2. For PET at 260 °C, $G(t)$ relaxes very fast and shows no change in slope as shown in Fig. 9. The difference in the shape of the curves is partly due to the short time scale for relaxation and the plotting of the data in the case of PET. PS and PET do not show the long relaxation tails as are observed for the liquid crystalline polymers. Hence, flexible chains and liquid crystalline ploymers behave differently in the step shear strain experiment, but the difference may not be due totally to liquid crystalline order but to the presence of crystallites. However, it is difficult to confirm the presence of crystallites using other techniques because of the low level of these structures. Similar problems are observed for polymer such as polyvinylchloride.

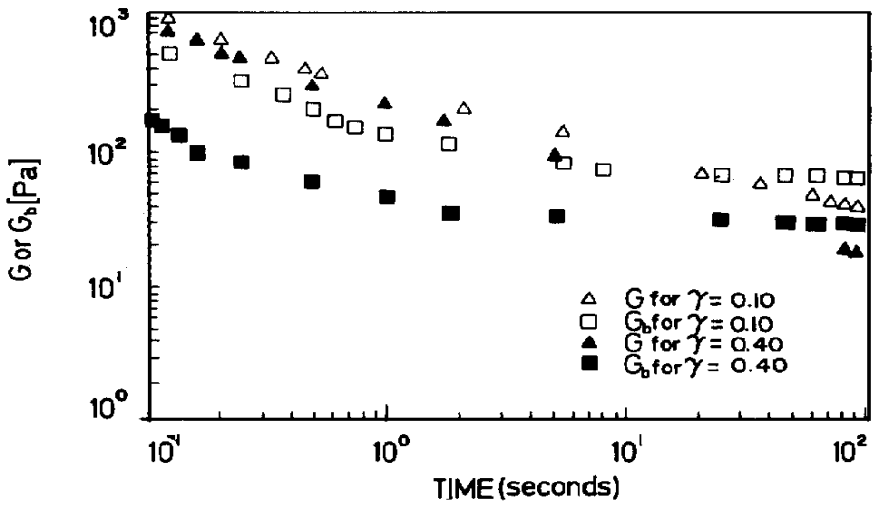

FIG. 10. Comparison between G and G_b for 60/40 PHB/PET at 250 °C.

Squeezing step strain

The operation of the apparatus and quality of the measurements are discussed elsewhere.[16] Measurements of $G_b(t,\gamma)$ agreed well with those obtained in step shear for polystyrene. Even though the viscosity of the lubricant was about 0.001 that of the polymer as recommended by Soskey and Winter,[9] loss of the lubricant seemed to occur at values of ϵ_b of about 0.4. Hence, it is believed that the squeezing flow device gave acceptable results up to about 0.4 stain units.

The relaxation moduli following step shear and squeezing flow are compared for both LCP's in Figs. 10 and 11. Results for 60/40 PHB/PET obtained at 250 °C are shown in Fig. 10 while those for LCP 2000 at 330 °C are shown in Fig. 11. For both polymers it is observed that G_b is always less than G and that the difference increases as the strain is increased from 0.1 to 0.4. One can only guess at the origin of the difference at this point without data pertaining to any structural changes. As shear is a stronger flow than biaxial extensional flow, one might expect G to be more strain dependent than G_b. Obviously this is not the case. However, G_b does take longer to relax than does G which is in-line with the idea that less structural changes occur in biaxial extensional flow.

CONCLUSIONS

Step strain experiments have been carried out for two thermotropic liquid crystalline ploymers, 60/40 PHB/PET and LCP2000. Both of

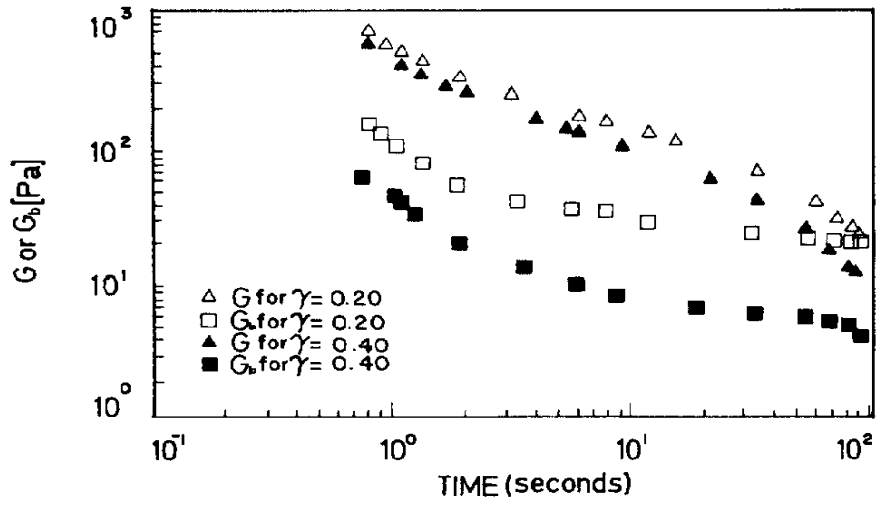

FIG. 11. Comparison between G and G_b for LCP2000 at 330 °C.

them showed a fast initial stress relaxation period followed by a slower relaxation period, and a tail in the relaxation curve was observed. The rate of relaxation was strain dependent as the higher the strain level the faster the relaxation of stress. It is suspected that some structure or unmelted solid phase in the melt may be responsible for this unique relaxation behavior as compared with the flexible chain polymers, such as PET and polystryrene. The above assumption was supported by the reduction of the long tail as the temperature was increased. The agreement between G and G_b (obtained in lubricated squeezing flow) was poor for both LCP's. Unfortunately, the highest strain achieved was only 0.4 which was due to the loss of lubricant for higher strains. In order to actually observe how the structure rearrangement takes place during relaxation, it is recommended that the same experiments be performed using a cone and plate constructed from quartz in order to use small angle light scattering for obtaining structural changes.

ACKNOWLEDGMENTS

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