

Dynamic and Transient Flow Behavior of Thermotropic Homopolyester with Nonamethylene Flexible Unit

Young Jun LEE and Sung Chul KIM*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong, Yusong, Taejon 305-701, Korea

(Received August 30, 1993)

ABSTRACT: Rheological properties of a semiflexible polyester having nonamethylene flexible spacer were investigated by small amplitude oscillatory shear flow and intermittent forward flow both in liquid crystalline state and in isotropic state. In dynamic measurements, it was found that the slope of the modulus *versus* frequency in terminal region was uniquely determined by the intrinsic nature of each phase and the slope was higher in isotropic state than in liquid crystalline state. The viscoelastic data measured in the isotropic state at different temperatures can be drawn on a master curve, which reflects the homogeneous nature of the phase. The complex viscosity showed Arrhenius type decrease with increasing temperature in isotropic phase. In transient experiments, the large stress overshoot and negative N_1 undershoot were observed upon start-up of shear flow in the liquid crystalline state. The negative N_1 undershoot was significantly affected by the shear history and did not reappear under subsequent flow even after long rest. The stress relaxed almost instantly after cessation of shear for all shear rates, implying that high structural distortion was introduced by shear flow. The large stress overshoot was not observed in isotropic state due to homogeneous structure.

KEY WORDS Rheological Properties / Thermotropic Polyester / Transient Flow / Stress Overshoot / Texture /

It is well known that the unusual rheological properties of the liquid crystalline polymers are caused by the characteristic domain structure, so called, texture.¹⁻⁵ The unusual rheological properties include large stress overshoot under weak shear, transient and/or steady negative N_1 , large strain recovery with the magnitude independent of applied shear rates and shear thinning viscosity at low shear rates.⁶⁻¹² The structure tends to be changed by both deformation and thermal treatment so that the precise identification and complete control of the structure is a prerequisite to the study on the rheological properties.^{13,14} It should be mentioned that the disclinations, which mean the discontinuities in director orientation, are usually present in liquid crystal structure and the resulting distortion of director profile

around them produced elastic stress, called Frank or Ericksen stress.¹⁵ The influence of the elastic stress can be critical in low shear regime where the viscous stress is small.

In past five years, several researchers developed molecular models for the dynamics of lyotropic liquid crystalline polymers based on Leslie-Ericksen model or Doi's rigid rod model (Marrucci and Maffettone,^{16,17} Larson,¹⁸ Larson and Doi¹⁹). In the weak shear and linear regime, the confined geometry version of Leslie Ericksen model (Burghardt and Fuller²⁰), 2-dimensional version of Doi model (Marrucci and Maffettone¹⁷), and mesoscopic domain theory (Larson and Doi¹⁹) were developed and the models predicted the oscillatory stress response and director tumbling. Two dimension model of Marrucci and

* To whom all correspondence should be addressed.

Maffetone has produced many noteworthy predictions including the presence of wagging region between tumbling and flow aligning and the intermediate shear range where negative N_1 is found. Whether the director will tumble or not is determined by 1) the sign of α_3 among the six phenomenological constants in Leslie-Ericksen model or 2) the magnitude of anisotropy of equilibrium distribution function of rigid rod molecules which is proportional to the intensity of molecular interaction potential in Marrucci and Maffetone model.

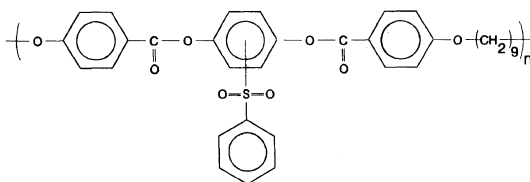
The tumbling at low shear rates has been experimentally confirmed at least in two lyotropic systems, polybenzylglutamate¹² and phenylenebenzobisthiazole (PBT),²¹ while any report on tumbling in thermotropic system, to our knowledge, has not been published up to now. For the rheological properties are thought to be determined by the intrinsic liquid crystalline structure regardless of the origin of liquid crystallinity, we believe that the general concept as mentioned for lyotropic system can be applied to thermotropic polymers for qualitative understanding of the rheological behavior. However, compared to many works done on the rheological properties of lyotropic polymers, most of the experimental studies on the thermotropic polyesters have been limited to few materials such as poly(hydroxybenzoate) (PHB)/poly(ethylene terephthalate) (PET) copolyester^{7,8,22} and hydroxybenzoic acid (HBA)/hydroxynaphthoic acid (HNA) copolyester^{9,23,24} but the copolyesters have relatively high transition temperatures so that the underlying previous thermal and deformation history can not be removed by isotropic state treatment. In isotropic state treatment, the liquid crystalline polymer is heated above the isotropization temperature, kept for some time to remove the built-in deformation and thermal history and then lowered to the desired temperature.^{25,26} It should be noted that the uncertainty in virgin structures of the polymer often led to the discrepancy between two studies conducted on the same material.^{9,24} In

this context, the preparation of thermotropic polymers with low transition temperature, which make the isotropic state treatment possible, is very valuable to the study of thermotropic liquid crystalline polymers.

For this study, we have prepared a semi-flexible homopolyester with a low transition temperature.

EXPERIMENTAL

The polymer used in this study was poly-[[phenylsulfonyl)-*p*-phenylene 1,9-nonamethylene bis(4-oxybenzoate)], designated hereafter as NP9, and prepared *via* solution polymerization. Recently, the effect of thermal history on the phase transition of the polyesters with low transition temperature, including this one, was studied.^{27,28} The phase transition of the polyesters was found to be strongly affected by thermal history. The weight average molecular weight of the polyester determined by GPC was 22700 with the polydispersity index of 1.68. Thermal transition temperature of NP9 was determined by Du Pont thermal analyzer 2000. The melting temperature and isotropization temperature were 105 and 145°C, respectively. In liquid crystalline region, the worm-like texture which contains numerous disclinations was observed on polarizing optical microscope.



NP9

The rheological behavior of NP9 polymer was investigated both in the liquid crystal state and the isotropic state on Rheometrics Mechanical Spectrometer (RMS800). Dynamic and steady shear experiments as well as transient shear experiments were conducted.

To ensure a homogeneous flow field, cone and plate with diameter of 25 mm and 0.1 rad cone angle was used. The test samples were molded at 180°C, well above the isotropization temperature and then dried at 60°C for 1 day before use. To eliminate the influence of the previous thermal and shear history and produce virtually identical liquid crystalline structure for all samples, every fresh specimen was heated to 180°C in RMS fixture, maintained for *ca.* 10 min and then slowly cooled to the desired temperature. For dynamic test, the applied strain amplitude was in the range of 3–10%, well within linear viscoelastic range. For transient experiments, intermittent forward flow scheme was employed and the stress as well as the first normal stress difference, N_1 was measured as a function of time. As noted elsewhere, the normal force transducer of the RMS 800 is automatically set to zero at the beginning of the shear even if the normal force still has non-zero value.^{29,30} In this experiment, all samples, though the built-in residual stress was already removed by the isotropic state treatment, were kept on fixture for 10 min without shear to completely relax the normal force. The gap size was kept constant (50 μm) for all measurements.

RESULTS AND DISCUSSION

Small Amplitude Oscillatory Shear Flow

Figure 1 shows plots of log complex viscosity *versus* log frequency. The temperature sweep encompasses both the liquid crystalline and the isotropic state. As can be seen in this figure, the shear thinning at low frequency was observed in the liquid crystalline state and this characteristics has been known to reflect the polydomain structure deformation under shear field. When temperature was raised above 140°C, the shear thinning regime virtually disappeared and the Newtonian regime was found, which indicates the absence of the heterogeneous domain structure.

The frequency dependence of modulus at

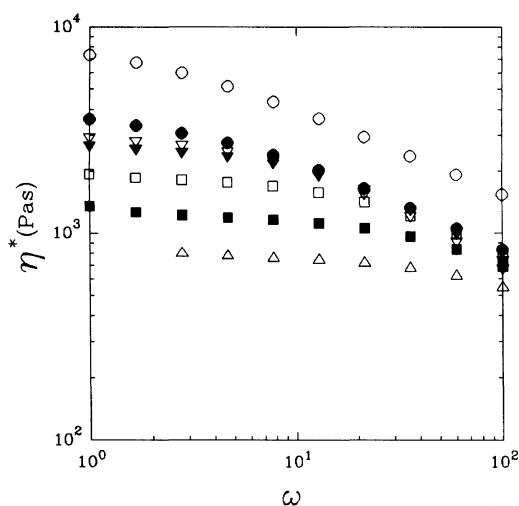
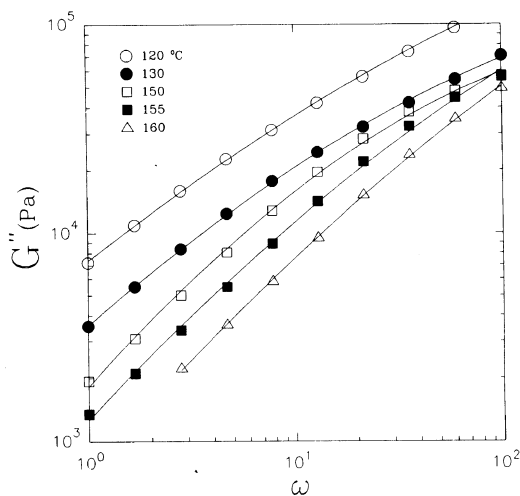


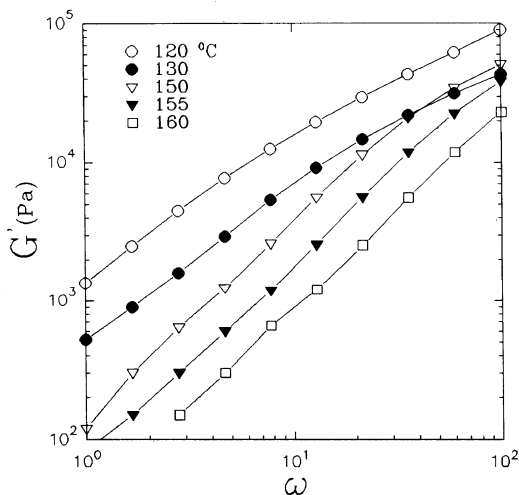
Figure 1. Complex viscosity *versus* frequency at different temperature for NP9. ○, 120°C; ●, 130°C; ▽, 140°C; ▾, 145°C; □, 150°C; ■, 155°C; △, 160°C.

various temperatures is shown in Figure 2. It is well established that for the linear flexible polymer melt, G' and G'' are proportional to ω^2 and ω respectively in the terminal zone, where the viscoelastic properties are dominated by the long range motions of molecules.³¹ Note in this figure that both the liquid crystalline state and the isotropic state have characteristic slope of log modulus *versus* log frequency in the limit of low frequency and the temperature variation induces little decrease in the slope within each phase. In other words, the slope of log modulus *versus* log frequency is phase-related. In the isotropic state, the slope of log G'' *versus* log ω is just unity while the slope of log G' has a value of *ca.* 1.6. In liquid crystalline state, the corresponding values were *ca.* 0.8 and 1.2, respectively. Similar behavior was found in other thermotropic polyester.²⁵

The viscoelastic data measured at various temperatures in the isotropic state can be drawn on a master curve as shown in Figure 3, which indicates the homogeneous nature of the isotropic phase. The reduced moduli and viscosity are defined by $G'_r(\omega, T_0) = G'(\omega, T)T_0\rho_0/T\rho$, $G''_r(\omega, T_0) = G''(\omega, T)T_0\rho_0/T\rho$, $\eta_r^*(\omega, T_0) =$



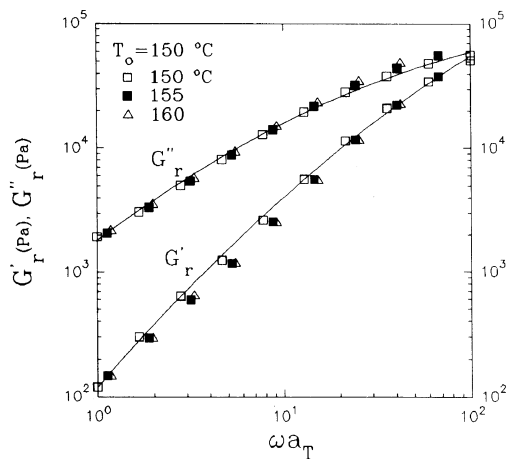
(a)



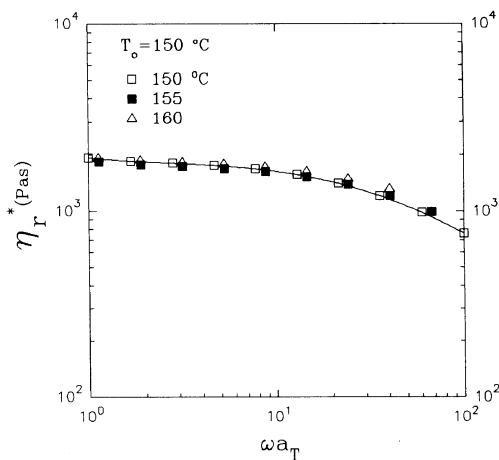
(b)

Figure 2. Storage modulus (G') and loss modulus (G'') versus frequency for NP9. (a) G'' ; (b) G' .

$\eta^*(\omega, T)T_0/a_T T$. The reference temperature is noted as T_0 . Figure 4 shows the temperature dependence of the complex viscosity measured at a fixed frequency, $\omega = 5 \text{ rad s}^{-1}$. The viscosity was measured after waiting for 5 min at each temperature. The temperature was lowered to the set temperature from higher one manually. The viscosity decrease accompanying the liquid crystal structure formation was not found but rather the viscosity continuously



(a)



(b)

Figure 3. Master curve of dynamic viscoelasticity. (a) modulus; (b) viscosity.

increased with decreasing temperature. The Arrhenius type of complex viscosity change was noted in isotropic state and the activation energy of viscous flow was calculated to be 32.1 kJ mol^{-1} .

Transient/Steady Shear Flow

The transient shear stress response of the liquid crystalline structure at 130°C was shown in Figure 5. The initial large stress overshoot was always observed over all shear rates and

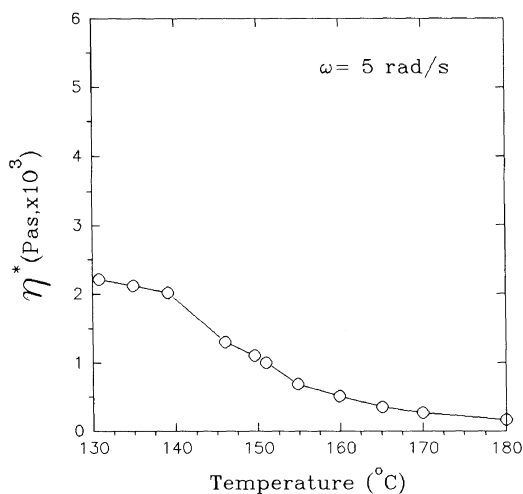


Figure 4. Temperature dependence of the complex viscosity for NP9.

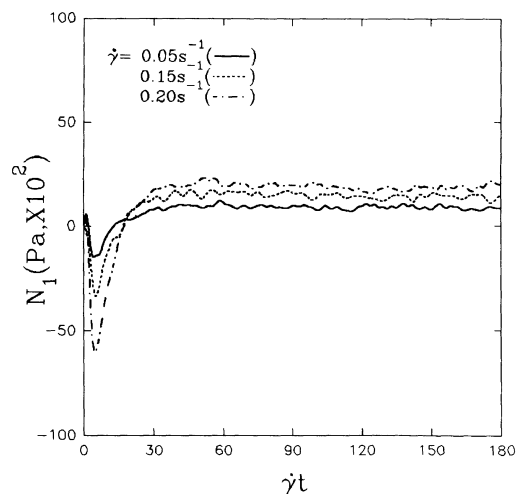


Figure 6. Transient response of N_1 under various shear rates at 130°C.

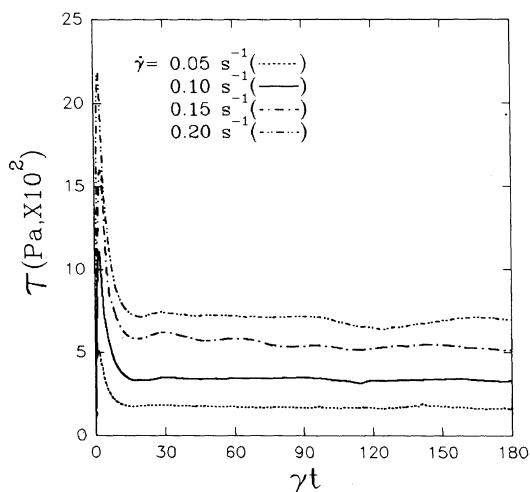


Figure 5. Transient response of shear stress of NP9 under various shear rates at 130°C.

the small second overshoot following the undershoot also appeared above $\dot{\gamma} = 0.10 \text{ s}^{-1}$. The first overshoot peak appeared in the strain range of 1.1–2.0. The total strain at which the initial stress peak was located slightly increased with increasing shear rates. For $\dot{\gamma} = 0.2 \text{ s}^{-1}$, the broad undershoot appeared at about 125 strain units. According to the monodomain theory of Burghardt and Fuller,²⁰ the multiple overshoot is due to the transient realignment of director

toward steady orientation. It should be also noted that even for linear flexible polymer. If shear rate is higher than some threshold value, the stress overshoot appears and the maximum occurs approximately at the same strain, usually 2–3 strain units.³² However, in flexible polymers, the stress overshoot is associated with the entanglement network which restricts the motion of chains, while in the liquid crystalline system, the peak is related with the deformation of polydomain structure and director orientation.

The transient first normal stress difference profile is shown in Figure 6. Summarizing the results, 1) the position of transient negative N_1 is about 5 strain for all shear rates, 2) the characteristic strain required to reach steady N_1 value was almost the same, about 30 strain for all shear rates, and 3) the steady N_1 values increased with increasing shear rate. Baird and his co-workers³³ observed the negative N_1 in (PHB/PET, 0.8/0.2) copolyester. Though there exists a controversy on the validity of the measured N_1 value,^{29,30} Guskey and Winter⁹ also reported the negative N_1 for (HBA/HNA, 0.73/0.27) copolyester. In their study, N_1 was found to be always positive at small strain, reaching a maximum at *ca.* 2 strain units.

However, at shear rates lower than 0.5 s^{-1} , the N_1 values stabilized to negative steady value while for shear rates greater than 0.5 s^{-1} , the initial peak was followed by an undershoot which may be negative, and then stabilized at a steady positive value. The effect of the shear on the first stress overshoot is quite similar both in HBA/HNA copolyester and in NP9 homopolyester: as shear rate increases, the amplitude of the overshoot increases and the

characteristic strain of the overshoot is, though not the same in strict sense for NP9, approximately the same. However, the effect of shear on the N_1 is markedly different in two cases. For (HBA/HNA), the positive N_1 peak was located at low strain and intensified toward higher positive value as shear rate increases, while in NP9, the N_1 value showed negative undershoot at low strain and the undershoot intensified toward negative value as shear rates increase.

To investigate the effect of the rest time on the structural recovery of the liquid crystalline structure, intermittent forward flow scheme was introduced. Figure 7 shows the shear stress and first normal stress response observed in this scheme at $\dot{\gamma} = 0.2 \text{ s}^{-1}$. The stress value was scaled by its terminal or steady value. The initial overshoot reappeared independent of the rest period and the relative height of the overshoot to the terminal or steady value increased as rest time increased. The first undershoot originally found right after the initial overshoot around 20 strain units (see Figure 5) was missing after $t_R = 60 \text{ s}$ but undershoot appeared after $t_R = 1200 \text{ s}$. Moldenaers and co-workers⁵ studied the flow induced liquid crystalline structure deformation and its recovery using 25% poly(benzyl D-glutamate) (PBDG) solution. In the intermittent forward flow experiment, they found that the initial sharp overshoot did not appear again under subsequent shear unless the rest time is longer than 400 s at $\dot{\gamma} = 0.4 \text{ s}^{-1}$. It could be said that the structural change of the PBDG solution which causes the first stress overshoot requires longer time than 400 s to recover its pre-shear state. Figure 7b shows the transient N_1 response measured after various rest periods. The N_1 values are more or less fluctuating and the relative height of the first overshoot to steady value is again an increasing function of rest time. The most striking feature in the response of N_1 is the absence of transient negative undershoot, which implies that during the rest time, the deformed liquid crystalline structure

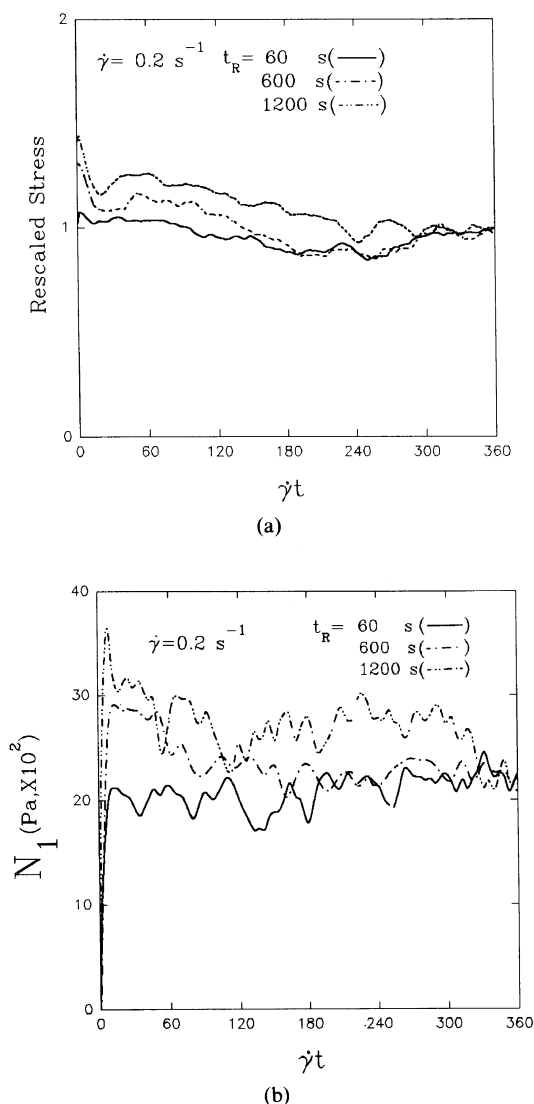
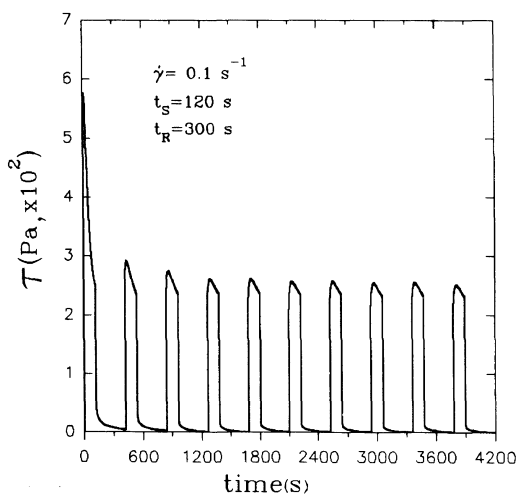


Figure 7. Transient response of NP9 after various rest times at 130°C. (a) stress response; (b) N_1 response.

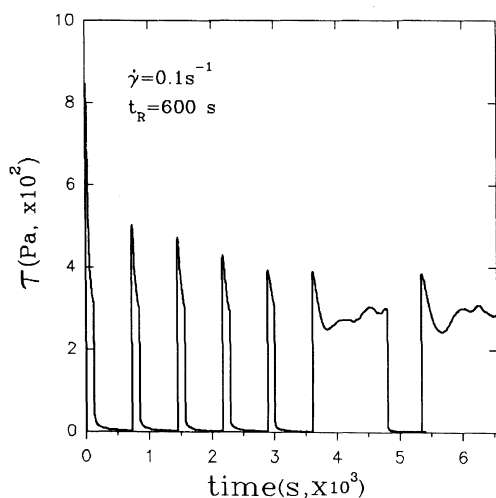
did not recover its original state.

To assess the memory of the deformed structure of its previous cumulative shear history, shear flow with constant shearing time, t_S and rest duration, t_R was repeatedly applied (Figure 8). The effect of different rest durations on the stress response was also studied. The shear stress obtained under $t_S=120$ s and $t_R=300$ s reached steady stress height within 1200 s while the stress profile with the same t_S

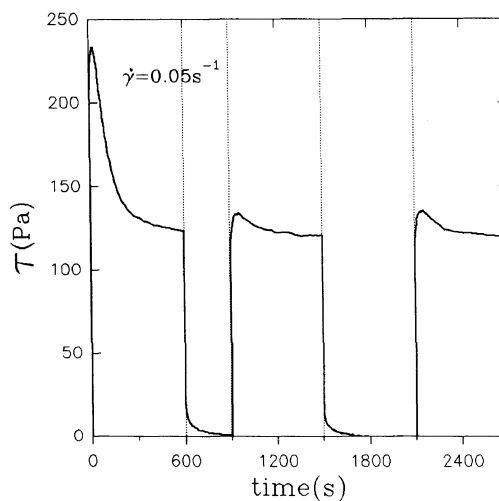
and more longer rest time, $t_R=600$ s did not reach the steady stress height even after 3000 s. These results indicated that as more time was permitted for the structural recovery, the time to reach the steady profile also increased. When long time (1200 s) shear was applied after repeated short time shear, the oscillatory shear profile appeared with notable undershoot following the first overshoot as shown in Figure 8b. Whether we interpret the damped oscillation



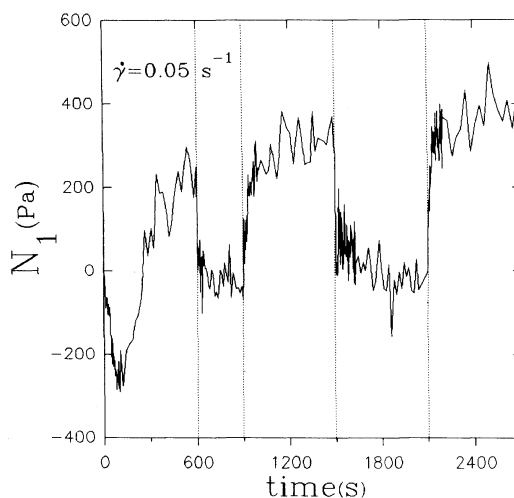
(a)



(b)



(a)



(b)

Figure 8. Transient response of shear stress of NP9 at 130°C to the repeated shear with (a) short duration, $t_R=300$ s; (b) long duration, $t_R=600$ s.

Figure 9. The transient response of NP9 ($\dot{\gamma}=0.05$ s $^{-1}$) at 130°C under intermittent shear flow. (a) stress response; (b) N_1 response.

tory stress response as originating from the successive break-up to polydomain structure of liquid crystal or the director reorientation toward steady direction, the oscillatory response at later period indicates that the liquid crystalline phase did not yet reach the equilibrium structure corresponding to the applied shear due to the partial relaxation during the intervening rest time. Figure 9 shows the typical shear stress and N_1 profile in the intermittent forward flow under shear rate of 0.05 s^{-1} . Of particular interest is the stress relaxation pattern after removal of shear flow: The sudden discontinuous drop in early period and slow continuous relaxation at later stage. This type of relaxation pattern has been observed in other polymers such as (HBA/HNA, 0.73/0.27) copolyester,²³ (PHB/PET, 0.6/0.4) copolyester²³ and 20 wt% racemic PBG solution in *m*-cresol.¹⁰ It seems that the first sudden drop is associated with molecular viscoelasticity, while the later slower relaxation is coupled with the domain structure including both director profile relaxation, as predicted by Burghardt and Fuller's monodomain calculation and structural relaxation involving the change in number density of disclinations. It

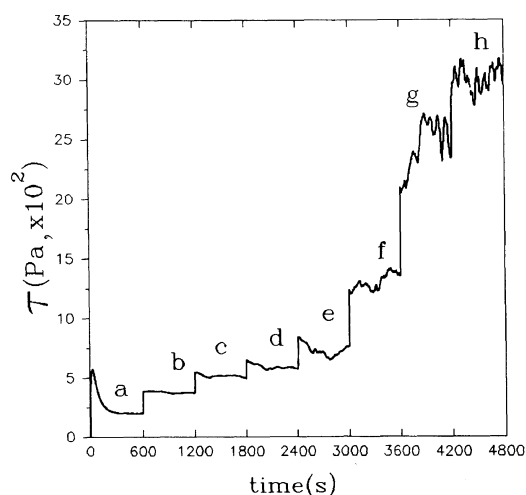


Figure 10. Stress response of NP9 to the continuous step-up shear increase at 130°C . $\dot{\gamma} =$ (a) 0.05 s^{-1} , (b) 0.1 s^{-1} , (c) 0.15 s^{-1} , (d) 0.2 s^{-1} , (e) 0.3 s^{-1} , (f) 0.5 s^{-1} , (g) 0.8 s^{-1} , (h) 1.0 s^{-1} .

is well established that the structural changes occur over much longer time scale than stress relaxation or strain recovery. The transient negative N_1 undershoot observed at initial shear application, once deformed, did not reappear under the subsequent shear even though the stress relaxed completely during rest time.

Figure 10 shows the stress profile measured under successive stepwise shear application from 0.05 s^{-1} to 1.0 s^{-1} with constant shearing time. It can be seen in the figure that 1) the characteristic initial overshoot was observed at early time under first shear ($\dot{\gamma} = 0.05 \text{ s}^{-1}$) and 2) at $0.10 \leq \dot{\gamma} \leq 0.3 \text{ s}^{-1}$, the amplitude of the stress overshoot grew as shear rate was increased and the undershoot also appeared, becoming more pronounced with increasing shear. 3) At $0.5 \leq \dot{\gamma} \leq 1.0 \text{ s}^{-1}$, though the stress became more oscillatory, the initial sharp overshoot observed at relatively early time was reduced in amplitude 4) At $\dot{\gamma} \geq 0.8 \text{ s}^{-1}$. The pronounced stress oscillation continued. The stress response to the stepwise shear increase was also studied in the isotropic state (Figure 11). The initial stress overshoot which was always found in liquid crystalline state was missing and the time to reach the steady state

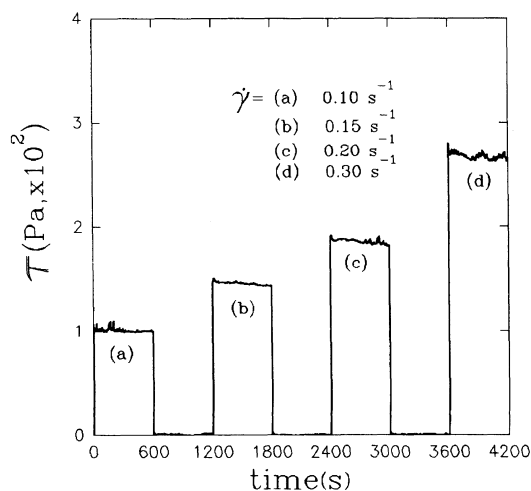


Figure 11. Transient shear stress response of NP9 polyester to the intermittent shear at 170°C (isotropic state).

was very short compared to the liquid crystal state (see Figure 9). Another noteworthy characteristic is the stress relaxation pattern. The stress relaxation completed almost instantly upon cessation of shear, indicating that there did not exist any structural change contributing long term stress relaxation found in the liquid crystalline state.

CONCLUSION

From the study on the rheological properties of the semiflexible liquid crystalline polyester, the following observations were made.

The viscosity drop in the liquid crystalline state when cooled from the isotropic state was not found in this polymer. It may be due to the low value of order parameter in the liquid crystal state for this semiflexible polyester which has odd-number flexible methylene unit.

In transient shear flow experiments, the stress overshoot and negative first normal stress undershoot reflecting the domain structure deformation and the rotation of the director to the steady alignment were found at initial shear application for all shear rates. However, compared to the stress overshoot which appeared again under reinitiated shear flow, the transient negative N_1 undershoot did not reappear under subsequent shear even though rest time up to 1200 s was allowed and rather the overshoot replaced the undershoot. Independent of shear conditions, the large stress overshoot was not observed in isotropic state, which reflected the domainless structure or homogeneous state. The stress relaxation profile of liquid crystal state could be divided by two distinct periods: the sudden discontinuous drop in early period and slow relaxation at later period which was related with structure and director profile relaxation.

Acknowledgment. The authors are grateful to Korea Research Foundation for the financial support of this work.

REFERENCES

1. S. Onogi and T. Asada, "Rheology," Vol. 1, G. Astarita, G. Marrucci, and L. Nicolais, Ed., Plenum New York, N.Y., 1980.
2. K. F. Wissbrun, *J. Rheol.*, **25**, 619 (1981).
3. P. Moldenaers, G. Fullers, and J. Mewis, *Macromolecules*, **22**, 960 (1989).
4. P. Moldenaers and J. Mewis, *J. Non Newtonian Fluid Mech.*, **34**, 359 (1990).
5. P. Moldenaers, H. Yanase, and J. Mewis, *J. Rheol.*, **35**, 1681 (1991).
6. G. Kiss and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 361 (1980).
7. A. D. Gotsis and D. G. Baird, *J. Rheol.*, **29**, 539 (1985).
8. G. G. Viola and D. G. Baird, *J. Rheol.*, **30**, 601 (1986).
9. S. M. Guskey and H. H. Winter, *J. Rheol.*, **35**, 1191 (1991).
10. W. R. Burghardt and G. G. Fuller, *Macromolecules*, **24**, 2546 (1991).
11. K. Hongladarom, W. R. Burghardt, S. G. Baek, S. Cementwala, and J. J. Magda, *Macromolecules*, **26**, 772 (1993).
12. K. Hongladarom and W. R. Burghardt, *Macromolecules*, **26**, 785 (1993).
13. Y. G. Lin and H. H. Winter, *Macromolecules*, **21**, 2439 (1988).
14. T. Shiwaku, A. Nakai, H. Hasegawa, and T. Hashimoto, *Macromolecules*, **23**, 1590 (1990).
15. P. G. de Gennes, "The Physics of Liquid Crystals," Oxford, London, 1976.
16. G. Marrucci and P. L. Maffettone, *J. Rheol.*, **34**, 1217 (1990a).
17. G. Marrucci and P. L. Maffettone, *J. Rheol.*, **34**, 1231 (1990b).
18. R. G. Larson, *Macromolecules*, **23**, 3983 (1990).
19. R. G. Larson and M. Doi, *J. Rheol.*, **35**, 539 (1991).
20. W. R. Burghardt and G. G. Fuller, *J. Rheol.*, **34**, 959 (1990).
21. M. Srinivasarao and G. C. Berry, *J. Rheol.*, **35**, 379 (1991).
22. D. G. Kalika, D. W. Giles, and M. M. Denn, *J. Rheol.*, **34**, 139 (1990).
23. D. Done and D. G. Baird, *J. Rheol.*, **34**, 749 (1990).
24. F. Cocchini, M. R. Nobile, and D. Acireno, *J. Rheol.*, **35**, 1171 (1991).
25. P. Driscoll and T. Masuda, *Macromolecules*, **24**, 1567 (1991).
26. S. R. Rojstaczer and R. S. Stein, *Macromolecules*, **23**, 4863 (1990).
27. Y. J. Lee and S. C. Kim, *Polymers for Advanced Technology*, in press.
28. S. S. Kim and C. D. Han, *Macromolecules*, **26**, 3176 (1993).
29. F. Cocchini, M. R. Nobile, and D. Acireno, *J. Rheol.*, **36**, 1307 (1992).

Rheological Behavior of Thermotropic Polyester

30. H. H. Winter and W. Wedler, *J. Rheol.*, **37**, 409 (1993).
31. J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley and Sons, New York, N.Y., 1970.
32. R. B. Bird, R. C. Armstrong, and O. Hassager, "Dynamics of Polymeric Liquids," Vol. 1, Wiley, New York, N.Y., 1987.
33. D. G. Baird, A. Gotsis, and G. Viola, "Polymeric Liquid Crystals," Plenum Press, New York, N.Y., 1985.