

Dynamic Birefringence and Dynamic Mechanical Studies on Acrylonitrile Copolymers

SATISH KUMAR,* W. T. MEAD, and R. S. STEIN, *Polymer Research Institute and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

Dynamic birefringence and dynamic mechanical studies have been done on (i) acrylonitrile/methyl acrylate copolymer and (ii) rubber-modified copolymer, in the frequency range of 0.06–5.55 Hz (acrylonitrile/methyl acrylate copolymer only at 0.92 Hz) and temperature range of –85 to +85°C. These studies were made on a computerized dynamic birefringence apparatus. A comparison of the dynamic birefringence and dynamic mechanical properties in the rubber-modified copolymer reveals a rubber glass transition peak, which is much more pronounced in dynamic birefringence data than in dynamic mechanical data. In addition to the glass transition of the rubber part in the rubber modified copolymer, there is a main transition of the copolymer in the vicinity of 80°C. Before the main transition there is a shoulder in the mechanical and optical loss curves. The reasons for the occurrence of the shoulder are discussed.

INTRODUCTION

It has been demonstrated by several authors that dynamic birefringence is a useful technique to study the molecular motion in polymers.^{1–19} The technique has been applied to amorphous as well as to semicrystalline polymers, and the mechanisms of molecular motion are identified in them. Among the amorphous polymers studied are (i) atactic polypropylene,³ (ii) polyacetaldehyde,⁷ (iii) poly(methyl acrylate),⁸ and (iv) poly(methyl methacrylate).⁹ Among the crystalline polymers most of the dynamic birefringence studies have been made on low, medium, and high density polyethylene,^{4,13–17} and limited work on (i) isotactic polypropylene,^{3,4,16} (ii) polybutene-1,^{3,19} (iii) nylon 6,⁴ (iv) nylon 11,¹⁸ and (v) nylon 12.¹⁸ It was concluded³ that the temperature dependence of birefringence and stress is similar in amorphous and crystalline polypropylene. From the dynamic birefringence tests it was possible to demonstrate that, in the case of poly(methyl acrylate) and polyacetaldehyde, overlapping distortional and orientational mechanisms were involved in the relaxation region associated with the rubber–glass transformation.^{7,8} In the case of poly(methyl methacrylate),⁹ a single wide distribution of secondary mechanical relaxation process β is broken down into two narrower relaxations when viewed with respect to birefringence–strain and birefringence–stress. This suggests the association of two types of molecular motions with this

*Author to whom correspondence should be addressed: University of Dayton Research Institute, Dayton, Ohio 45469.

secondary relaxation process rather than one. From the dynamic birefringence data on semicrystalline polymers in combination with dynamic X-ray data, it was possible to conclude whether a particular dispersion is associated with (i) lamellar detwisting, (ii) lamellar shearing, (iii) lamellar bending, (iv) spherulitic deformation, or (v) crystalline reorientation, or a combination of more than one of these processes.^{14,20,21} In this paper we report the dynamic studies done on acrylonitrile/methacrylate copolymer and on rubber (acrylonitrile butadiene) modified copolymer to see if one can get more information about the molecular motion than obtainable from the mechanical tests.

EXPERIMENTAL

The dynamic birefringence experiments were done on the following two systems: (i) Acrylonitrile/methyl acrylate (AN/MA) copolymer, 75% acrylonitrile and 25% methyl acrylate by weight. The AN/MA base resin was prepared by emulsion polymerization. (ii) Rubber-modified copolymer (Barex 210* resin): AN/MA copolymer grafted onto 10% butadiene/acrylonitrile (BD/AN) rubber. The BD/AN rubber was prepared by emulsion polymerization of approximately 30% acrylonitrile and 70% butadiene. Grafting was done by copolymerizing AN and MA monomer in the presence of BD/AN latex. For both samples approximately 0.038 cm thick sheets were obtained by compression molding the resin between aluminum plates at 200°C. From these sheets samples of 2.5 cm in length and 0.5 cm in width were cut.

Details of the dynamic birefringence apparatus and that of the data analysis are given elsewhere.²² A sinusoidal strain, $\epsilon = \epsilon_0 \sin \omega t$, was superimposed over a static strain of 3%. Peak to peak amplitude of the dynamic strain is $2\epsilon_0$. The value of this dynamic strain was 0.6%. All the samples were allowed to vibrate at these strains for at least 30 min before the measurements were taken. Samples were cooled with liquid nitrogen to about -85°C. Measurements were made with increasing temperature up to about +85°C, and the static strain was adjusted for thermal expansion. AN/MA copolymer was studied at 0.92 Hz, and rubber-modified copolymer at 0.06, 0.33, 0.92, 1.95, and 5.55 Hz. In the case of these two materials, contribution of low angle dynamic light scattering and the contribution from the attenuation factor was negligible and therefore ignored.

RESULTS AND DISCUSSION

Storage modulus and mechanical loss tangents for the rubber modified copolymer are given as a function of temperature at 0.06, 0.92, and 5.55 Hz in Figure 1. Strain optical coefficient and $\tan \alpha$ for the copolymer are plotted in Figure 2. From these figures the following points are noted: (i) the strain optical coefficient for this copolymer is positive within the whole temperature range studied, (ii) the strain optical coefficient decreases with a decrease in frequency, and (iii) $\tan \alpha$ is positive, which means birefringence leads the macroscopic strain. Moduli (E' and E'') and mechanical loss tangents for (AN/MA) copolymer and for the rubber modified copolymer are given in Figure 3 as a function of temperature at 0.92 Hz. Strain optical coefficient and

*Barex 210 is a registered trademark of Standard Oil Co., Ohio.

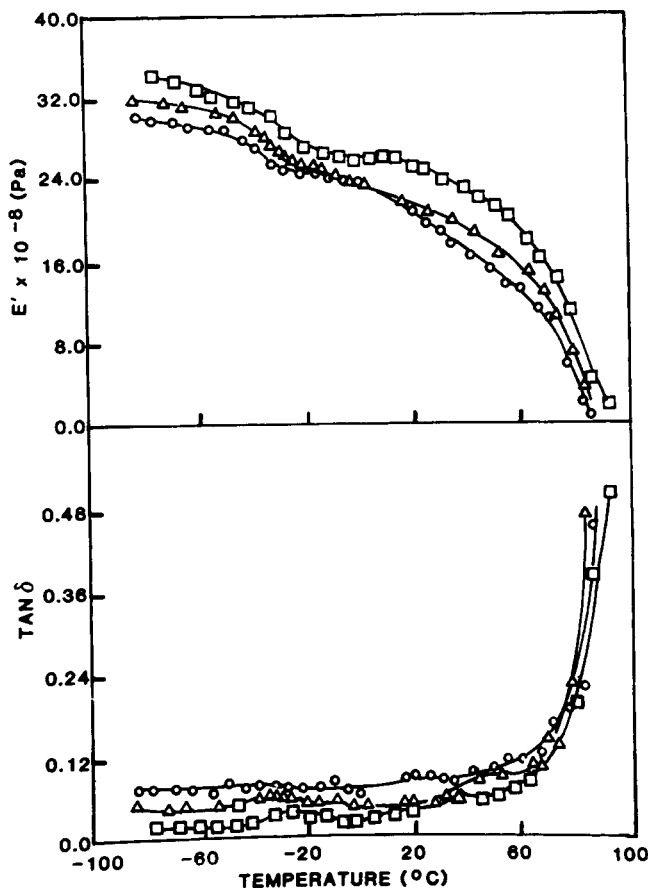


Fig. 1. Storage modulus and mechanical loss tangent as a function of temperature in rubber-modified copolymer at: (□) 5.55 Hz; (Δ) 0.92 Hz; (○) 0.06 Hz.

$\tan \alpha$ for the two copolymers are given in Figure 4, and stress optical coefficient and $\tan(\alpha - \delta)$ in Figure 5. From Figures 3–5 the following points are noted: (i) modulus of AN/MA copolymer is higher as compared to the modulus of the rubber modified copolymer; (ii) in the spectrum of $\tan \delta$, $\tan \alpha$, and $\tan(\alpha - \delta)$ (Figs. 3–5) there is an occurrence of a shoulder just before the main transition of the copolymer; (iii) rubber-modified copolymer exhibits an additional transition in the vicinity of -30°C , which is the glass transition of the rubber (AN/BD); this transition is observed predominantly in the optical data as compared to a weak transition observed mechanically; (iv) strain optical coefficient for (AN/MA) copolymer is also positive (same is the case for rubber modified copolymer) within the temperature range studied; (v) the stress optical coefficient (C') is higher for the rubber-modified copolymer as compared to the stress optical coefficient of AN/MA copolymer; (vi) stress optical coefficient (C') decreases with an increase in temperature except in a small region where stress optical coefficient increases with temperature.

First let us discuss the occurrence of positive strain optical coefficient in the two copolymers. In a separate study²³ on these two copolymers, birefringence

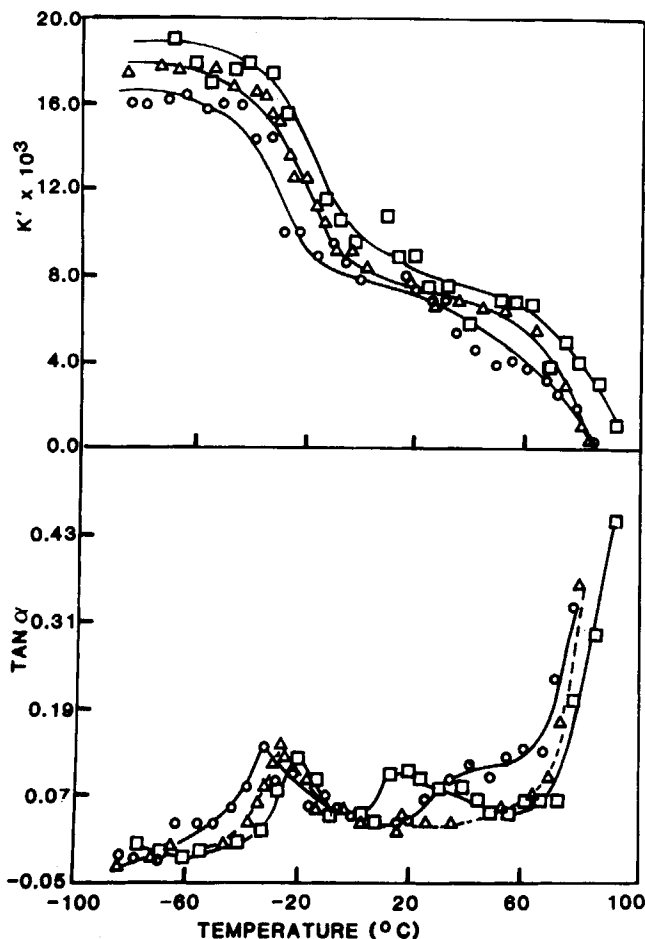


Fig. 2. Real part of strain optical coefficient and $\tan \alpha$ as a function of temperature in rubber-modified copolymer at: (\square) 5.55 Hz; (Δ) 0.92 Hz; (\circ) 0.06 Hz.

was measured (after complete relaxation) as a function of strain. This relaxed birefringence increases in the negative direction for the two copolymers with increasing strain, while, in the dynamic birefringence test, birefringence measured at a finite frequency is not completely relaxed. First we consider the case of AN/MA copolymer. It was estimated²³ that $\Delta n_{\max}(\text{AN}) = -0.009$ and $\Delta n_{\max}(\text{MA}) = 0.0030$. When stretching below the glass transition, if simple molecular orientation was taking place, then total birefringence would increase in the negative direction as predicted by the following equation of the additivity of birefringence:

$$\Delta n = [V_{\text{AN}} \cdot \Delta n_{\max}(\text{AN}) + V_{\text{MA}} \cdot \Delta n_{\max}(\text{MA})] f \quad (1)$$

where V_{AN} and V_{MA} are the volume fractions of acrylonitrile and methyl acrylate copolymers, respectively, and f is the orientation factor of the

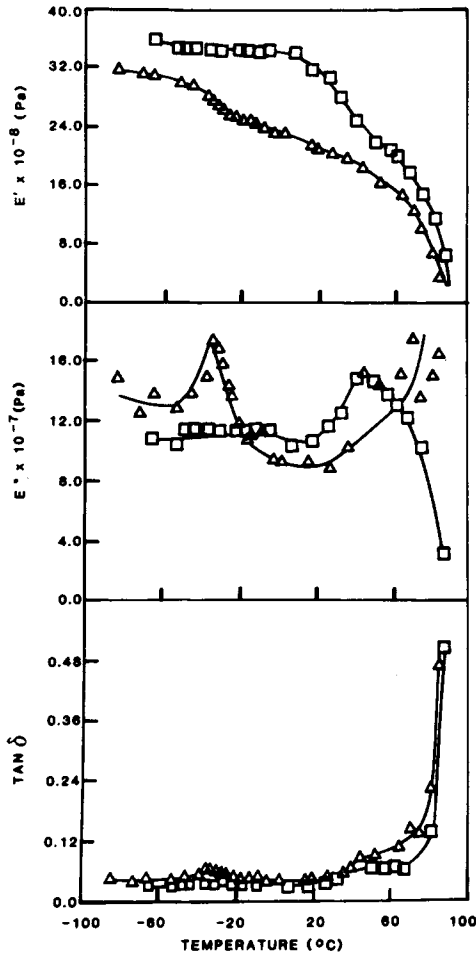


Fig. 3. Storage modulus, loss modulus, and $\tan \alpha$ of (\square) AN/MA copolymer and of (Δ) rubber-modified copolymer as a function of temperature at 0.92 Hz.

molecular chains. A more general form of eq. (1) is

$$\Delta n = \left[\frac{V_{AN} \Delta n_{\max}(AN) L_{AN}^2 f_{AN} + V_{MA} \Delta n_{\max}(MA) L_{MA}^2 f_{MA}}{V_{AN} L_{AN}^2 + V_{MA} L_{MA}^2} \right] \quad (2)$$

where L_{AN} and L_{MA} are the Kuhn segment lengths^{24,25} and f_{AN} and f_{MA} are the chain orientation functions of the AN and MA components, respectively. Equation (1) is a special case of eq. (2) if $L_{AN} = L_{MA}$ and $f_{AN} = f_{MA}$. When the birefringence increases in the negative direction with increasing strain, strain optical coefficient is negative. Below the glass transition temperature, it is conceivable that the distortion of some side groups such as CN and COOCH₃ is associated with the orientation of the main chain. That is to say the angles which CN and COOCH₃ groups make with the main chain axis may reduce after stretching below the glass transition because of bond

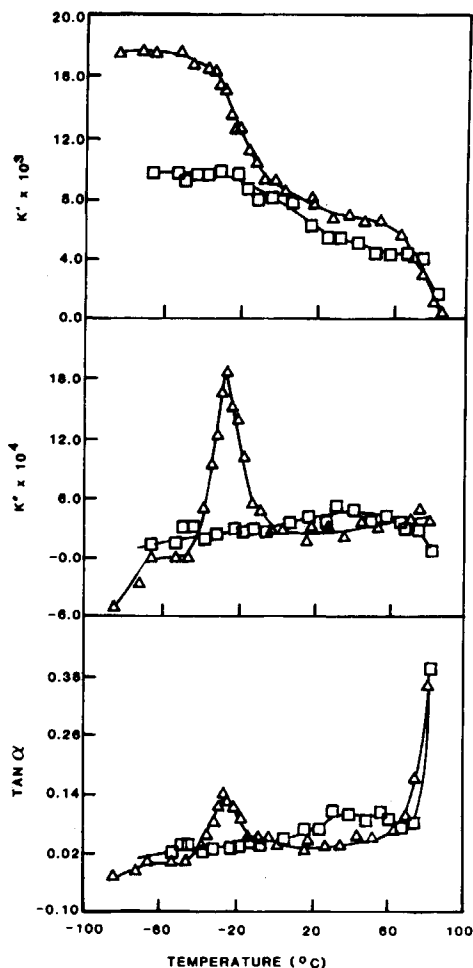


Fig. 4. K' , K'' , and $\tan \alpha$ of (\square) AN/MA copolymer and of (Δ) rubber-modified copolymer.

bending. When the distortion of these side groups is along the main chain axis (i.e., angle between side groups and main chain axis reduces), then change in birefringence will be positive and will result in a positive strain optical coefficient. However, if this stretched sample is allowed to relax, then the distorted side groups of CN and COOCH₃ will relax and thus increase the overall birefringence in the negative direction. Such a reasoning is in agreement with the earlier work on PMA,⁸ where it was suggested that the distortions of the side group COOCH₃ along the stretching direction and the release of such distortions at glass transition temperature is responsible for the positive strain optical coefficient below glass transition temperature and negative strain optical coefficient above it. Such distortion was not contemplated in PMMA because of CH₃ group (in place of H in PMA) in the main chain. This contemplation was experimentally verified—as suggested by the negative strain optical coefficient for PMMA⁹ below and above the glass transition temperature.

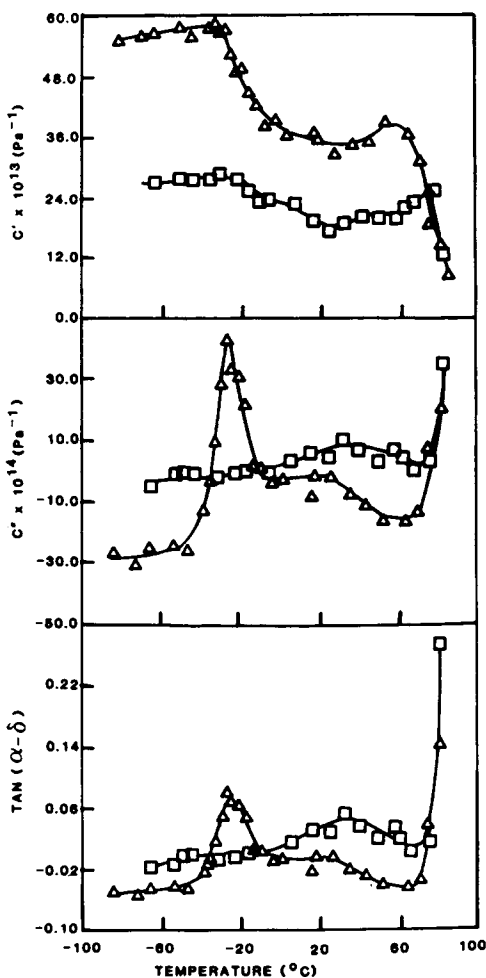


Fig. 5. C' , C'' , and $\tan(\alpha - \delta)$ of (\square) AN/MA copolymer and of (Δ) rubber-modified copolymer.

In the case of rubber modified copolymer at low temperatures (Fig. 4), strain optical coefficient is almost double that of the AN/MA copolymer. However, it is only marginally greater above about -20°C (the region of glass transition of acrylonitrile/butadiene rubber). In the rubber-modified copolymer below the glass transition of AN/BD rubber, in addition to the reasons discussed above, two other factors are important: (i) a positive birefringence contribution from butadiene²³ and (ii) distortion of CN group in that part of acrylonitrile which is in AN/BD rubber. These reasons will explain the exceptionally high strain optical coefficient at low temperatures. Above glass transition temperature of AN/BD rubber, two processes are likely to take place: (i) acrylonitrile of the AN/BD rubber will not be distorted and hence will give the negative birefringence, and (ii) orientation/distortion of the glass part AN/MA will be more than that of the

AN/BD rubber. Both these factors combined reduce the strain optical coefficient, which make its value comparable to that of the AN/MA copolymer.

There is evidence in the literature that in different polymers birefringence can lead or lag the macroscopic strain or may lead for a part of the temperature scale and lag for the other part.^{3,4,7,9,13} In AN/MA copolymer throughout the temperature range studied $\tan \alpha$ is positive, suggesting that birefringence leads the macroscopic strain, while in the case of rubber-modified copolymer $\tan \alpha$ is negative below about -50°C and positive above this temperature, suggesting that birefringence lags the macroscopic strain below -50°C and leads above it.

In addition to the main transition of the copolymers around 80°C and a transition in the rubber modified copolymer in the vicinity of -30°C , there is an occurrence of shoulder in both the copolymers as seen from optical as well as from mechanical data (Figs. 3-5) in the temperature range of 20 - 70°C . Such a secondary relaxation is also observed in the dynamic birefringence study on PMMA⁹ and in the dielectric study of PAN²⁶ (data at 10^2 Hz in Ref. 26). It is suggested that this is due to the motion of the side groups such as CN and COOCH_3 . The motion of these side groups is very well resolved in the $\tan(\alpha - \delta)$ and in the C'' curve (Fig. 5). The motion of these side groups is seen to be very pronounced in the E'' curve in AN/MA copolymer but is suppressed in rubber-modified copolymer.

The behavior of the real part of the stress optical coefficient can be divided into four regions. In the case of rubber-modified copolymer C' increases with an increase in temperature, in the temperature range of -80 to -40°C and 20 - 60°C . In the vicinity of the glass transition of rubber AN/BD and at the glass transition of the copolymer itself, C' decrease with an increase in

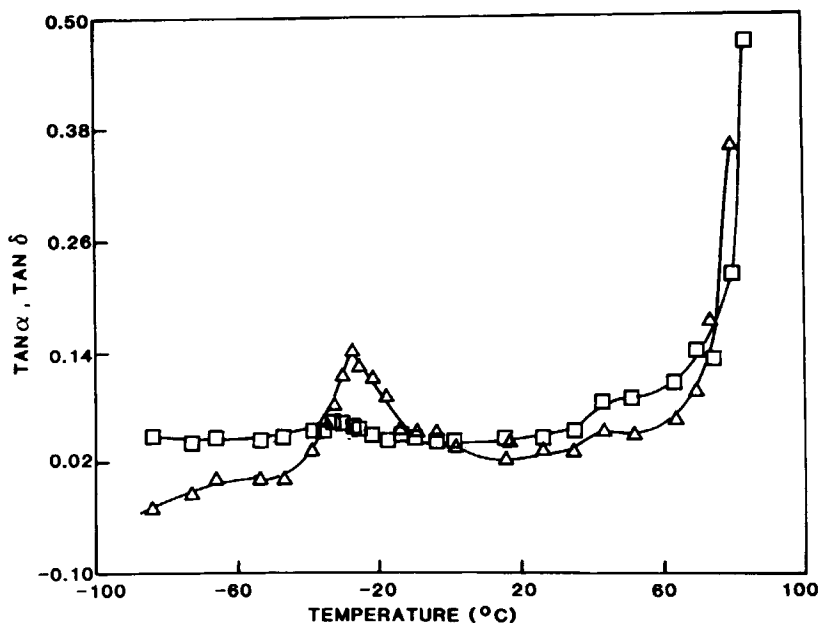


Fig. 6. (Δ) $\tan \alpha$ and (\square) $\tan \delta$ as a function of temperature in rubber-modified copolymer.

temperature. In these regions decrease in birefringence is faster than the decrease in stress. The behavior of C' for AN/MA copolymer is almost similar in nature to that of the rubber-modified copolymer except that the first region when C' increases with temperature extends up to 0°C in the absence of rubber.

The data presented in Figure 5 suggest that, in these two copolymers, birefringence may lead or lag the stress. For rubber-modified copolymer $\tan(\alpha - \delta)$ is negative on the whole temperature spectrum except in the vicinity of glass transition of rubber AN/BD and in the vicinity of the glass transition of the copolymer itself. In these regions large orientational changes take place with little change in stress (as contemplated from the C' data). Yamada and Stein⁴ have observed for linear polyethylene, polypropylene, and nylon that $\tan \alpha$ can be greater than, equal to, or less than $\tan \delta$. This implies that $\tan(\alpha - \delta)$ can be negative or positive, i.e., stress can lead or lag the birefringence. This observation of Yamada and Stein⁴ and the data presented in this paper (Fig. 5) contradicts the contention of Kyu et al.²¹ that stress always leads orientation.

The $\tan \alpha$ and $\tan \delta$ curves for the rubber modified copolymer are compared in Figure 6. A 7°C shift has been observed between the peak positions of $\tan \alpha$ (-27°C) and $\tan \delta$ (-34°C) for the glass transition peak of AN/BD rubber. Shift between $\tan \alpha$ and $\tan \delta$ was also observed⁴ for polypropylene and nylon 6 by Yamada and Stein and remains to be understood.

SUMMARY

The current dynamic birefringence work on AN/MA copolymer and on rubber-modified copolymer gives a strong optical ($\tan \alpha$) peak in the rubber-modified copolymer. This indicates that the dynamic birefringence test will be sensitive to the presence of much smaller levels of rubber which may not be detected by mechanical tests. This is because the motions of the certain groups may influence the overall chain polarizability more than the overall stress. This work and the previously published work on other polymers strongly indicates that much more can be learned about the motions of the polymeric chains when dynamic mechanical tests are complemented with dynamic birefringence tests. The use of dynamic birefringence tests perhaps has been limited in part because of the unavailability of commercial apparatus.

The writers acknowledge the support of the Standard Oil Co. (Ohio), the National Science Foundation, the Army Research Office (Durham), and the Materials Research Laboratory of the University of Massachusetts.

References

1. R.S. Stein, S. Onogi, and D. A. Keedy, *J. Polym. Sci.*, **57**, 801 (1962).
2. R. S. Stein, S. Onogi, K. Sasaguri, and D. A. Keedy, *J. Appl. Phys.*, **34**(1), 80 (1963).
3. K. Sasaguri and R. S. Stein, *J. Polym. Sci.*, **C5**, 139 (1963).
4. R. Yamada and R. S. Stein, *J. Appl. Phys.*, **36**(10), 3005 (1965).
5. A. Takeuchi and R. S. Stein, *J. Polym. Sci.*, *Part A-2*, **5**, 1079 (1967).
6. B. E. Read, *Techniques of Polymer Science*, SCI Monographs No. 17, Society of the Chemical Industry, London, 1963, p. 198.

7. B. E. Read, *J. Polym. Sci.*, **C5**, 87 (1964).
8. B. E. Read, *Polymer*, **1**, 5 (1964).
9. B. E. Read, *J. Polym. Sci.*, **C16**, 1887 (1967).
10. D. E. LeGrand and P. F. Erhardt, *Trans. Soc. Rheol.*, **6**, 301 (1962).
11. D. G. LeGrand, *J. Polym. Sci., Part A*, **2**, 931 (1964).
12. J. F. Rudd, *J. Polym. Sci., Polym. Lett. Ed.*, **3**, 345 (1965).
13. T. Kyu, N. Yasuda, S. Suehiro, S. Nomura, and H. Kawai, *Polym., J.*, **8**(6) 565 (1976).
14. T. Kyu, N. Yasuda, S. Suehiro, T. Hashimoto, and H. Kawai, *Polymer*, **21**, 1205 (1980).
15. T. Kyu, N. Yasuda, M. Tabushi, S. Nomura, and H. Kawai, *Polym. J.*, **7**(11), 108 (1975).
16. S. Onogi, Y. Fukui, T. Asada, and Y. Naganuma, *Proc. Int. Congr. Rheol. 5th*, 1968 (pub. 1970), Vol. 4, pp. 87-100.
17. A. Tanaka, K. Tanai, and S. Onogi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **55**(2), 177 (1977).
18. S. Onogi, T. Asada, Y. Fukui, and I. Tachinaka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**(2), 463 (1974).
19. A. Todo, T. Hashimoto, Y. Tsukahara, and H. Kawai, *Polymer*, **20**, 943 (1979).
20. A. Tanaka, E. P. Chang, B. Delf, I. Kimura, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1891 (1973).
21. Thein Kyu, S. Suehiro, S. Nomura, and H. Kawai, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 951 (1980).
22. S. Kumar and R. S. Stein, *J. Appl. Polym. Sci.*, **34**, 1693 (1987).
23. S. Kumar and R. S. Stein, *J. Appl. Polym. Sci.*, **27**, 3407 (1982).
24. W. Kuhn and F. Gr \ddot{u} n, *Kolloid-Z.*, **101**, 248 (1942).
25. Y. Shindo, B. E. Read, and R. S. Stein, *Makromol. Chem.*, **118**, 272 (1968).
26. A. K. Gupta and N. Chand, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1125 (1980).

Received December 5, 1986

Accepted January 27, 1987