might be able to decide on the "best" model in describing lattice breakdown by matching predicted and observed entropy changes in several different polymeric solids. However, one can argue that the experimental values of ΔS are of sufficiently high uncertainty to negate this expectation. Variations in degree of crystallinity and crystalline homogeneity of the samples can lead to significant variation in experimental values of ΔS.

Both third- and fourth-order theories allow a given chain to interact with a variable number of neighboring chains. For polymethylene we found that each chain interacted with slightly more than two other chains in order to yield a realistic melt temperature.[11] The same is true for polytetrafluoroethylene. When the chain is set up energetically to interact with four chains instead of two chains, the melt temperature changes from 586 to 832 K for the third-order theory and from 571 to 823 K for the fourth-order theory. How this apparent interaction of a given chain with only two of its neighbors is produced in the actual melt process is not clear. It would suggest that polymethylene and polytetrafluoroethylene crystals melt out via similar if not identical mechanisms. It would also appear that while several chains maintain close contact in the crystalline states this proximity is not reflected in the energetics of the melt process.

At this point, a question can be raised concerning effects of the approximations made in going from the continuum model to the discrete two-level model. The answer tc this question is the goal of our current research. Solving the continuum model directly poses difficulties and computer-dependent numerical techniques need to be employed rather than analytic equations as is the case with the discrete two-level system. Once the initial work is done, the models presented here can be tested in the continuum case, and also other models will be tested to determine how one might better describe lattice breakdown.

Acknowledgments. A.J.H. is a Sloan Research Fellow. This work was supported by the National Science Foundation through a Materials Research Laboratory Grant to Case Western Reserve University.

References and Notes

(1) (a) Department of Physics; (b) Department of Macromolecular Science.
(2) (a) F. Boyle, P. L. Taylor, A. J. Hopfinger, and R. Simha, *J. Appl. Phys.*, **46,** 4218 (1975); (b) R. L. Humphries et al., *J. Chem. Soc., Faraday Trans. 2,* **68,** 1031 (1972).
(3) S. Marcělja, *Biochim. Biophys. Acta*, **367,** 165 (1974).
)4) B. Wunderlich, *J. Phys. Chem.*, **69,** 2078 (1965).
(5) C. A. Sperati and H. W. Starkweather, Jr., *Fortschr. Hochpolym. Forsch.*, **2,** S.465 (1961).
(6) P. Weiss, *J. Phys. Radium*, **4,** 661 (1907).
(7) A. J. Hopfinger, "Conformational Properties of Macromolecules", Academic Press, New York, N.Y., 1973.
(8) S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta*, **13,** 1 (1969).
(9) A. J. Hopfinger, *Macromolecules*, **4,** 731 (1971).
(10) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", 2d ed, Wiley, New York, N.Y., 1975.
(11) Figure 4 of our first paper[2a] is mislabeled; curve b is with two interacting chains, and curves c, d, and e are four, six, and eight interacting chains, respectively.

Brillouin Scattering from Poly(vinylidene fluoride)–Poly(methyl methacrylate) Mixtures

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ABSTRACT: Brillouin scattering has been observed from poly(vinylidene fluoride) (PVF_2)-poly(methyl methacrylate) (PMMA) mixtures in the temperature range 20–200 °C. The mixtures are shown to be homogeneous in the melt, and to quench to an amorphous film. A single glass–rubber relaxation region is observed for the quenched mixtures, indicating a compatible polymer mixture. The PVF_2 crystallizes from the mixture at temperatures between T_g and T_m. These measurements demonstrate the usefulness of Brillouin scattering in the study of melting in polymers.

The polymer blend of poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) has been the subject of several recent studies.[1–3] This mixture has been shown to be compatible above the melting point of PVF_2 (170 °C).[2] Below T_m the PVF_2 may crystallize from the melt if the mixture is well above the glass–rubber relaxation temperature T_g.[3] Conversely, amorphous films of PVF_2/PMMA mixtures may be formed by rapid quenching from the melt.[3] In the present work, Brillouin scattering is employed to study the thermal behavior of PVF_2/PMMA films.

Theory

Brillouin scattering from longitudinal acoustic phonons in a homogeneous amorphous phase results in fully polarized peaks shifted in frequency by

$$\pm \frac{\Delta\omega_l}{\omega_0} = 2\tilde{n}\,\frac{V_l}{C}\sin\theta/2 \qquad (1)$$

where ω_0 is the incident frequency, $\tilde{n}$ is the refractive index, V_l is the longitudinal phonon velocity, C is the speed of light in a vacuum, and θ is the scattering angle in the scattering plane. Typical Brillouin splittings for polymers are of the order of 10^{10} Hz, so that the phonon velocity may differ considerably from the low-frequency velocity of sound.

The phonon velocity V_l is given by

$$V_l = \sqrt{\frac{3K + 4\mu}{3\rho}} \qquad (2)$$

where K is the modulus of compression, μ is the modulus of rigidity, and ρ is the density.

In the region of the glass–rubber relaxation, the moduli reflect the change from equilibrium behavior above T_g to nonequilibrium behavior below T_g. Thus there is a change in slope in the plot of $\Delta\omega_l$ vs. T at T_g.[4–6] The modulus of rigidity shows an enormous change in the glass–rubber relaxation region at very low frequencies, but at hypersonic frequencies there is no discontinuity in either K or μ at T_g.

At a melting transition, μ changes considerably, even at high frequencies. Thus, the Brillouin splitting is expected to be a sensitive probe of crystallization and melting in polymers. Another notable effect of crystallization in polymers is that the material becomes locally birefringent. This leads to de-

Table I

	M_n	M_w	M_w/M_n
Kynar 821	2.1×10^5	4.0×10^5	1.9
Kynar 301	1.1×10^5	3.8×10^5	3.6
Acrylite B115	4.7×10^4	1.1×10^5	2.3

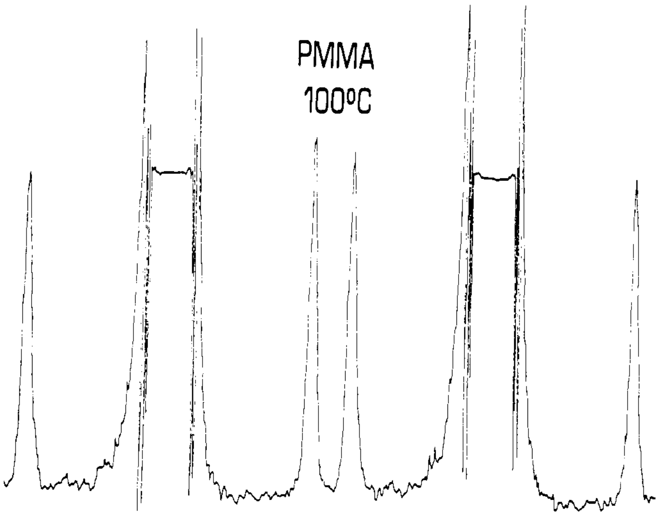

Figure 1. Brillouin spectrum of PMMA at 100 °C. Peaks 1 and 3 are the longitudinal Brillouin peaks associated with the first order and peaks 4 and 6 with the second order. The splitting $\Delta\omega_l$ is determined by measuring the distances between peaks 1 and 3 and between peaks 4 and 6 relative to the distances between peaks 1 and 4 and between 3 and 6. The latter distances correspond to the free spectral range of 0.525 cm^{-1}.

polarization of the longitudinal Brillouin peaks. One of the most sensitive tests for a fully amorphous sample is the degree of polarization of the longitudinal peaks.[6]

Experimental Section

Materials. PVF$_2$ resin (Kynar 821) and two PVF$_2$/PMMA mixtures 75/25 (Kynar RC 3335A) and 40/60 (Kynar RC 3335B) by weight were obtained from the Pennwalt Corp. These mixtures were compounded from Kynar 301 PVF$_2$ resin and Acrylite B115 resin, a PMMA supplied by American Cyanamid. The molecular weights and M_w/M_n ratios for Kynar 821, Kynar 301, and Acrylite B115 are contained in Table I. The pure PMMA sample was Acrylite H-12, also obtained from American Cyanamid. Its molecular weights were identical with the Acrylite B115 sample. The film samples were prepared by pressing the resin between two thin glass cover slips at 200 °C. The two mixtures were annealed at 200 °C and then quenched in liquid nitrogen to obtain the amorphous films.

Brillouin Spectra. The Brillouin splittings were obtained as described previously.[6-8] However, the samples described herein deserve special consideration. In most earlier work[4-7,9] the samples were either clear cast blocks or were contained in glass cuvettes, much larger than the scattering volume. The technique for examining Brillouin scattering from polymer films was, however, demonstrated in a recent report.[8] In order to study the films above T_g, and even above T_m, some method of supporting the films is necessary. A pair of thin glass cover slips have been used in the present study. The increase in elastic scattering due to the increase in the number of surfaces becomes easily tolerable with the use of the high contrast multipass interferometer.[5,7] However, the glass will also give a contribution to the scattering due to its own Brillouin scattering. This problem was usually overcome by using films that were much thicker than the glass and focussing the collimating lens carefully on the center of the films. Even when thinner films were used, it was found that the Brillouin intensity due to the glass was over an order of magnitude smaller than that due to the polymer. Thus, the extraneous scattering did not obscure the longitudinal Brillouin spectrum of the polymer and the splittings for the polymer were easily determined.

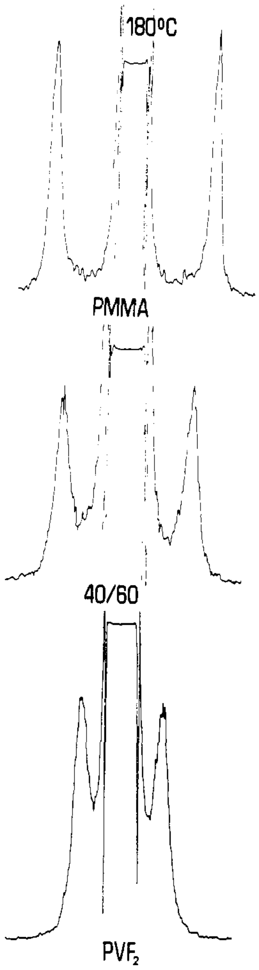

Figure 2. Brillouin spectra PVF$_2$, 40/60 mixture, and PMMA at 180 °C.

As before,[8] the true scattering angle in the polymer is given by

$$\theta = 2 \text{ arc sin } (0.707/\tilde{n}) \qquad (3)$$

Since the refractive index of PVF$_2$ is 1.42, and that of PMMA is 1.49, the scattering angle for the mixtures was between 60° (for PVF$_2$) and 56° (for PMMA). The Brillouin splitting also depends explicitly on the refractive index, so that some of the observed differences in $\Delta\omega_l$ are primarily a reflection of optical differences in the samples, rather than mechanical differences. However, the qualitative trends will not be affected by such considerations.

The free spectral range used in the present study was 0.525 cm^{-1}. The Brillouin splittings are determined from the spectra by measuring the fraction of the free spectral range spanned by the two Brillouin peaks.

The Brillouin splittings were determined at fixed temperatures from 20 to 200 °C at 20 °C intervals. The typical heating or cooling rates were 20 °C/h.

Results and Discussion

Two orders of the Brillouin spectrum of the PMMA film at 100 °C are shown in Figure 1. The longitudinal Brillouin peaks are sharp and fully polarized. This result is characteristic of an amorphous polymer near T_g.[5-7]

A qualitative comparison of the Brillouin spectra of PVF$_2$, the 40/60 mixture, and PMMA at 180 °C is shown in Figure 2. The pure PVF$_2$ is above its melting point and the Brillouin peaks are intense, broad, and fully polarized. This result is characteristic of a crystallizable polymer in the melt above T_m. The PMMA still displays a sharp spectrum at 180 °C. The 40/60 mixture shows a single pair of fully polarized Brillouin peaks with splitting intermediate between the pure PVF$_2$ and PMMA. Such a result is strong evidence of a single homogeneous phase.[6]

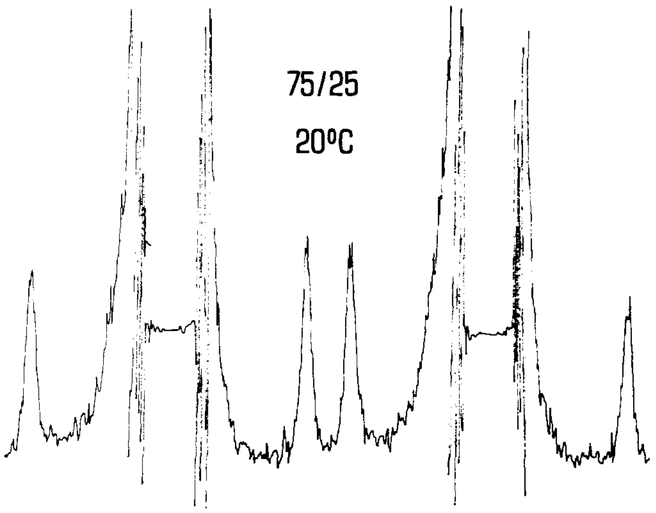

Figure 3. Brillouin spectrum of 75/25 mixture annealed at 200 °C, quenched in liquid N_2, and measured at 20 °C.

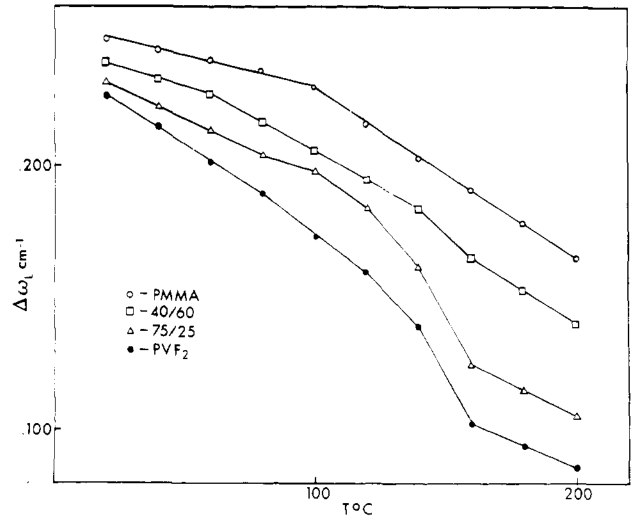

Figure 4. Brillouin splitting vs. temperature for PMMA (○), 40/60 mixture (□), 75/25 mixture (△), and PVF_2 (●).

Two orders of the spectrum of the quenched 75/25 mixture at 20 °C are shown in Figure 3. The single pair of fully polarized Brillouin peaks are evidence for a homogeneous amorphous phase. Thus, the mixtures are shown to be compatible in the melt and to quench to fully amorphous films.

The Brillouin splittings for the four samples are plotted vs. temperature in Figure 4. The pure PMMA exhibits only the glass–rubber relaxation at approximately 100 °C. As demonstrated in Figures 1 and 2, the longitudinal Brillouin spectrum of PMMA remains quite sharp over the entire temperature range.

The PVF_2 splittings were obtained by starting at 200 °C and decreasing in 20 °C decrements. The point at 160 °C was obtained with the supercooled melt. The magnitude of $\Delta\omega_l$ below 160 °C depends on the thermal history of the sample. However, several distinctive features can be noted. Since the amorphous regions of the PVF_2 are well above T_g (−50 °C)[3] there is a basic, strong, downward trend of $\Delta\omega_l$ with temperature. This trend is further enhanced by partial melting of the lower molecular weight species between 80 and 140 °C. At the main melting transition there is a sharp drop in $\Delta\omega_l$. A discontinuity in the Brillouin splitting is characteristic of a first-order phase transition. Because PVF_2 only partially crystallizes, the transition is smeared out over a large temperature range. The polydispersity also contributes significantly to the large range of crystallization behavior.

The quenched 40/60 mixture exhibits a single glass–rubber relaxation at approximately 60 °C. The slope of $\Delta\omega_l$ vs. T below T_g reflects the typical glassy behavior shown by the PMMA. Above T_g, $\Delta\omega_l$ for the 40/60 mixture changes more slowly with temperature than either the pure PMMA or PVF_2. This is evidence that the PVF_2 may be crystallizing from the melt above T_g. Such evidence is further supported by the drop in $\Delta\omega_l$ between 140 and 160 °C which suggests a first-order melting transition in this temperature range. Above 160 °C, the 40/60 mixture behaves as a homogeneous amorphous phase.

The glass–rubber relaxation of the quenched 75/25 mixture is below room temperature.[3] As with the 40/60 mixture, the slope of $\Delta\omega_l$ vs. temperature for the 75/25 mixture in the range 20 to 100 °C is lower than would be expected for an amorphous phase above T_g. In this sample the crystallization behavior is very obvious between 80 and 120 °C. From 120 to 160 °C there is a very sharp drop in $\Delta\omega_l$ due to the melting of the PVF_2. The point at 160 °C was obtained with the supercooled melt. From 160 to 200 °C, the 75/25 mixture behaves as a homogeneous amorphous phase.

The use of Brillouin scattering as a technique for studying the glass–rubber relaxation in amorphous polymers is now well established.[4–7,9,10] The present work demonstrates the utility of Brillouin scattering in the study of melting behavior in polymers. With the use of supported films, the thermal behavior of polymers can now be studied over any temperature range of interest.

References and Notes

(1) J. S. Noland, N. N.-C. Hsu, R. Saxon, and J. M. Schmitt, *Adv. Chem. Ser.*, **99,** 15 (1971).
(2) D. R. Paul and J. O. Altamirano, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15,** 409 (1974).
(3) T. Nishi and T. T. Wang, *Macromolecules*, **8,** 909 (1975).
(4) E. A. Friedman, A. J. Ritger, and R. D. Andrews, *J. Appl. Phys.*, **40,** 4243 (1969).
(5) E. M. Brody, C. J. Lubell, and C. L. Beatty, *J. Polym. Sci., Polym. Phys. Ed.*, **13,** 295 (1975).
(6) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **14,** 741 (1976).
(7) G. D. Patterson, *J. Polym. Sci., Polym. Lett. Ed.*, **13,** 415 (1975).
(8) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **14,** 143 (1976).
(9) G. D. Patterson, *J. Macromol. Sci.*, in press.
(10) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, in press.