The triplet state $Hg-Li_2$ is likely formed to some extent, but it would be electrically inactive.

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INTENSITY RATIO OF RAYLEIGH TO BRILLOUIN SCATTERING AT THE GLASS TRANSITION IN POLYETHYL METHACRYLATE

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Light scattering has recently been used to study second-order transitions in solids. In the ferroelectric crystal rochelle salt, De Martini[1] observed a discontinuity in the threshold for stimulated Brillouin scattering; in triglycine sulfate, also a ferroelectric crystal, Gammon and Cummins[2] observed an anomalous change in the frequencies of the longitudinal and transverse Brillouin components. In this Letter we report on studies of the light-scattering spectrum of an amorphous solid, polyethyl methacrylate, in the region of the "glass transition." At the glass-transition temperature, T_g, the material undergoes a change from a viscous (or rubbery) liquid to a brittle glass, but the detailed nature of this transition is not well understood.[3,4] Our measurements reveal a sharp discontinuity in the intensity ratio of Rayleigh to Brillouin scattering at T_g which may be interpreted as evidence of a second-order transition.

It is well known that amorphous polymers, inorganic glasses, and strongly associated liquids undergo a glass transition during which changes in the temperature coefficients of various physical properties associated with the free volume occur. However, there is no large change in volume as the material passes through the glass transition, no latent heat, nor abrupt changes in the thermodynamic quantities such as occur in first-order transitions. Consider-

able interest has developed as to the possible thermodynamic origin of the glass transition.[5,6] Some authors[7,8] have interpreted the glass transition as involving an Ehrenfest second-order transition; that is, one with a discontinuity in the specific heat, but with no latent heat. Others[4] have suggested that it is caused by relaxational effects associated with the volume change.

For our light-scattering experiments, the polymer polyethyl methacrylate was chosen because its glass temperature is in a convenient range, $T_g \approx 63°C$, and because its optical properties are excellent. The sample of polyethyl methacrylate was made from highly purified monomer to which 0.1% azobisbutyronitrile had been added as an initiator. To eliminate dust, this liquid was passed through a filter of $0.01-\mu$ pore size. The monomer was then polymerized in an evacuated glass cell at about 40°C and annealed at 100°C for 24 h. For this experiment the sample was prepared in the shape of a cylinder (2 in. in diameter and 2 in. in length) and was surrounded by a thermostatted metal jacket.

The light-scattering apparatus was essentially that described by Chiao and Stoicheff.[9] The He-Ne laser emitted 20 mW of radiant power at 6328 Å. A 1-cm spacer was used in the pressure-scanned Fabry-Perot interferometer and the resultant instrumental linewidth was 750

Mc/sec. The photomultiplier detector was followed by a linear amplifier, pulse-height analyzer, and ratemeter.

The frequency spectrum of light scattered at 70° to the incident beam was recorded at various temperatures in the range 20 to 85°C. At each temperature approximately 30 min was allowed for the sample to reach thermal equilibrium. A series of measurements were taken with temperature increasing up to 85°C and a second series with temperature decreasing down to 20°C. Typical spectra below and above the glass transition are shown in Fig. 1. The salient features in these spectra are (a) the very high intensity of the central or Rayleigh component in comparison with the shifted or Brillouin components and (b) the increase in intensity in both the Rayleigh and Brillouin components immediately above T_g; the Rayleigh peak changes by approximately 5% and the Brillouin peaks by approximately 20%.

The intensity ratio of Rayleigh to Brillouin components, $I_c/2I_B$, commonly called the Landau-Placzek ratio, is shown as a function of temperature in Fig. 2. This ratio decreases markedly with increasing temperature. Moreover it exhibits a sharp discontinuity at 61.4 ± 0.5°C, well within the normal range of T_g. No discontinuity was found in the frequency shifts of the Brillouin components to 0.5%; thus there is no corresponding discontinuity in the velocity of the hypersonic thermal waves although a smoothly decreasing velocity with

increasing temperature was observed. (Unfortunately, our experimental resolution was not sufficient to detect the true width of the Brillouin lines nor changes in this width, resulting from possible changes in the temporal absorption coefficient.) Finally, the very large magnitude of the Landau-Placzek ratio shown in Fig. 2 should be noted. This is to be compared with values of less than 1 in many liquids[10,11] and values of up to 8 in very viscous liquids.[12]

The Landau-Placzek ratio for liquids is given in its simplest form by[11,13]

$$\frac{I_c}{2I_B} = \frac{[\beta_T - \beta_S]_{st}}{[\beta_S]_{hs}} = \frac{[C_p - C_v]_{st}}{[C_v]_{hs}}, \tag{1}$$

where β_T and β_S are the adiabatic and isothermal compressibilities, C_p and C_v are the heat capacity at constant pressure and volume, respectively. In the numerator, the static values (st) are used since the Rayleigh component is due to scattering from slowly damped entro-
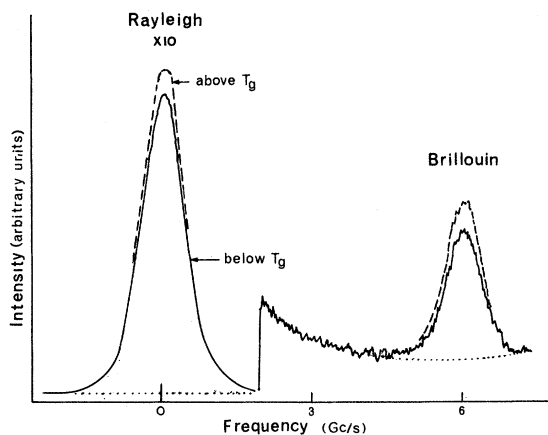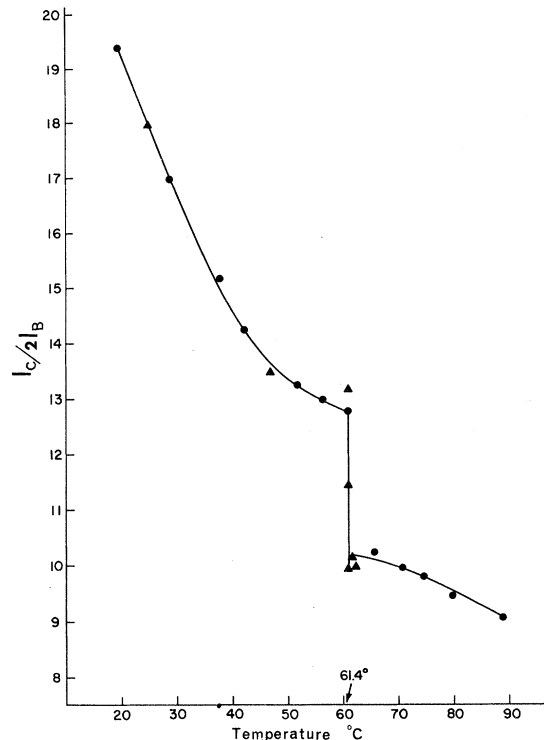

FIG. 1. Light-scattering spectra of polyethyl methacrylate recorded immediately below the glass transition temperature T_g (solid line) and immediately above T_g (dashed line). The Rayleigh component is reduced by 10, and only the Stokes Brillouin component is shown. The dotted lines indicate zero intensity.

FIG. 2. Graph of the intensity ratio of Rayleigh to Brillouin scattering, $I_c/2I_B$, plotted against temperature of specimen. Measurements with temperature increasing are indicated by triangles, and with temperature decreasing by circles.

py fluctuations which do not propagate in normal liquids. In the denominator, the hypersonic (hs) values are used because the Brillouin components arise from propagating pressure fluctuations oscillating at hypersonic frequencies.

According to Eq. (1) the observed magnitude of $I_c/2I_B$, its change with temperature, and the sharp discontinuity in the region of T_g find a ready explanation in a large ratio of the heat capacities $[C_p - C_v]_{st}/[C_v]_{hs} = [\beta_T - \beta_S]_{st}/[\beta_S]_{hs}$, a decrease in this ratio with increasing temperature, and a discontinuity in this ratio at or near T_g. This behavior seems plausible for amorphous polymers. It is reasonable to assume that the density of low-frequency molecular degrees of freedom will be proportionately higher in polymers than in low molecular-weight liquids. This would result in a larger value of $[C_p - C_v]_{st}/[C_v]_{hs} = [\beta_T - \beta_S]_{st}/[\beta_S]_{hs}$ and in a larger ratio of $I_c/2I_B$ for polymers than for normal liquids (although we cannot rule out completely the possibility that parasitic scattering or scattering from crystallites is contributing to the large Rayleigh intensity observed). As the temperature of the polymer is increased and the polymer approaches the rubber state it acquires new degrees of freedom at both low and high frequencies as shown by the slow increase in both the Rayleigh and Brillouin peaks. At T_g there is a discontinuity in the ratio $[C_p - C_v]_{st}/[C_v]_{hs}$ and a marked increase in both low- and high-frequency degrees of freedom as shown by the large increase in the intensities of both the Rayleigh and Brillouin components. Moreover, although the fractional change in the intensity of the Rayleigh line (5%) is smaller than that of the Brillouin lines (~20%), the absolute change is much larger (~3:1) and therefore at T_g the absolute change in $[C_p - C_v]_{st}$ is larger than that in $[C_v]_{hs}$. This is in keeping with the usual definition. of the glass transition in polymers as that temperature below which the main chain configurations (associated with low-frequency motions) are "frozen in." The observed discontinuity in $I_c/2I_B$ and increase in Rayleigh scat-

tering at T_g in polyethyl methacrylate are thus manifestations of a structural change at T_g, with a sudden onset of low-frequency motions above T_g and a sudden freezing in of these motions below T_g.

The present investigation has shown that the ratio of Rayleigh to Brillouin scattering is a very sensitive probe for observing structural transitions in amorphous polymers. Moreover such investigations will be of general interest in the study of phase transitions in solids and will complement studies using other experimental techniques. Finally, the very sharp change in $I_c/2I_B$, which is in marked contrast to the changes in expansion coefficient and mechanical properties known to occur within a 2-3°C range of T_g, may serve as a more definite measure of the glass transition.

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