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Glass transition of polyethylene as studied by Brillouin spectroscopy

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Summary

The Brillouin spectrum of polyethylene has been measured as a function of temperature. Slope discontinuities of opposite directions have been observed in the Brillouin shift and width near the glass transition temperature. The former is attributed to a corresponding discontinuity in the temperature coefficient of specific volume, while the latter to the onset of long-range coordinated molecular motion near the transition region.

Introduction

The glass transition temperature, T_g, of polyethylene has been a controversial subject of much discussion (1). In fact a rather wide span of temperature ranging from 140 to 340 K has been reported as T_g in the literature by different investigators using various standard methods (2). The most frequent reported T_g however centers around 150, 200 and 250 K. According to Boyer (1), semi-crystalline polyethylene appears to possess two glass transition temperatures : a lower one, ~200K, which refers to completely amorphous state and an upper value, ~250K, which occurs in the semi-crystalline material. The transition at ~150K is believed to be related to the Schatzki crankshaft motion. Brillouin light-scattering has already been used to study the glass transition in many polymers mostly through studies of the temperature dependence of the Landau-Placzek ratio and Brillouin shift (3,4) and recently through that of the Brillouin width (5,6). The purpose of the present work is to investigate what information may be obtained about the glass transition of polyethylene using the technique of Brillouin light-scattering. To our knowledge such a study has not been reported in the literature.

Experimental

The polyethylene used in this study was an injection molded low density polyethylene test piece in a Resinkit supplied by K.G. Roberts Associates Inc., U.S.A. The density of the sample was 0.919 g cm^{-3}. Differential scanning calorimetry (DSC) measurement showed a melting peak at 379K with a heat of fusion of 73.6 Jg^{-1} corresponding to a degree of crystallinity of 26%. A sample of the polyethylene of 0.2 cm x 0.2 cm x 2 cm was cut and polished. It was of relatively good optical quality. High density polyethylene is opaque due to its high crystallinity and therefore is not suitable for Brillouin scattering study. The sample was first quenched from room temperature to about 90K and its Brillouin spectra were then measured as a function of temperature which was increased in steps of ~10K from ~95K to ~260K. At each temperature the sample was held for an equilibration time of typically 30 min. Laser light at 514.5 nm was scattered through 90° from the sample held at a fixed temperature (±0.1K) and analysed using a Burleigh DAS-1 five-pass Fabry-Perot interferometer system operated with a spectral range of 41.5 GHz as described previously (7). The measured spectrum was then deconvolated and the Brillouin shift ν_B and truth width Γ_B (f.w.h.m.) obtained by least-squares fitting of a Lorentzian lineshape.

Results

The Brilluoin shift ν_B for polyethylene is shown in fig. 1 as a function of temperature. A change in slope is apparent at the arrow sign. This feature, a slope discontinuity in ν_B, is by now well known and has been used to identify T_g by workers who have examined polymers by Brillouin scattering (3-5). A special linear least-squares-fitting procedure described in ref (7) was used to fit the data and determine T_g. The results are shown by lines in fig. 1 and the T_g obtained is 204 ± 5K.

The Brillouin width Γ_B as a function of temperature is shown in fig. 2. A change in slope of opposite sign to that of ν_B, is also obvious at about the same temperature. In fact, the slope discontinuity in Γ_B appears even more pronounced than that in ν_B. We believe this is the first observation of its kind. The lines in fig. 2 are again linear least-squares fits and the resulting T_g is 201 ± 2K.

We have also computed the Landau-Placzek (LP) ratio by dividing the integrated Rayleigh intensity by the integral of the deconvoluted Brillouin lineshape. The results show that the LP ratio decreases monotonously with increasing temperature indicating no obvious change near T_g. Abrupt changes in the LP ratio near T_g were reported by earlier workers and were believed to be due to the relaxation of internal strains above T_g (3). Our results suggest we have a strain-free specimen.

Discussion

The Brillouin shift ν_B is related to the velocity of sound v in the light-scattering system by $\nu_B = 2nv\sin\frac{1}{2}\theta/\lambda$ where λ is the wavelength of light in vacuum, n the refractive index of the system and θ the scattering angle. The observed discontinuity in the temperature coefficient of ν_B (and therefore v) near T_g has been explained as a consequence of the well known corresponding discontinuity in the temperature coefficient of the specific volume (thermal expansion coefficient) (3).

The Brillouin width Γ_B is given by $\Gamma_B = \gamma v/\pi$, where γ is the sound absorption coefficient. The fact that the slope discontinuity in Γ_B and ν_B near T_g are in opposite direction

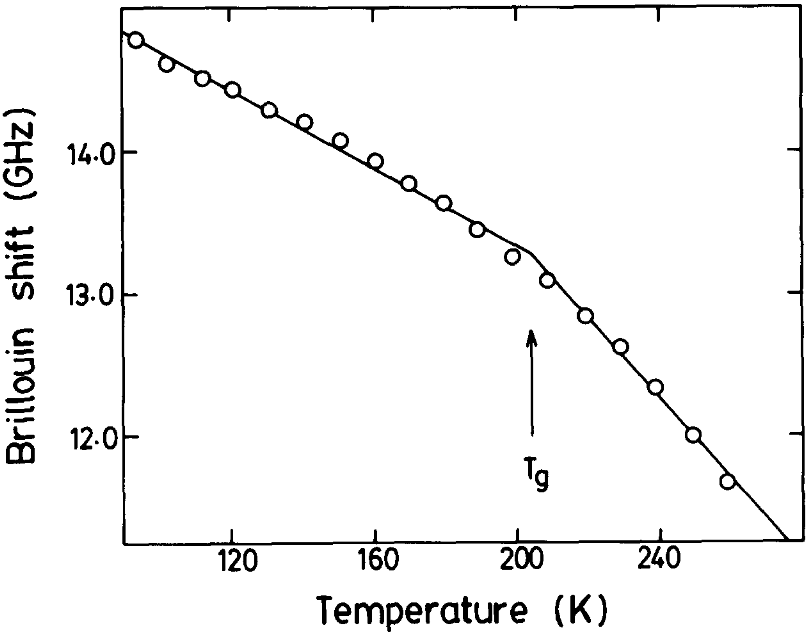

Fig. 1 The Brillouin shift of Polyethylene as a function of temperature. The lines are linear least-squares fits. T_g is the glass transition temperature.

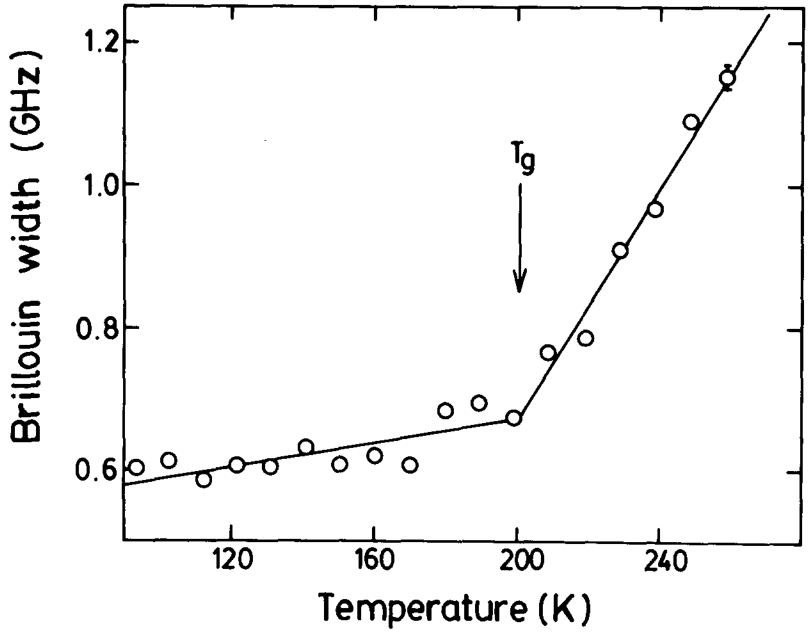

Fig. 2 The Brillouin width of Polyethylene as a function of temperature. The lines are linear least-squares fits. T_g is the glass transition temperature.

implies that the temperature dependence of γ is not only similar to, but also stronger than that of Γ_B. The slope discontinuity observed in Γ_B (γ) may be interpreted as follows. Glass transition region can be considered as the onset of long-range coordinated molecular motion. While only very few chain atoms are involved in motion below T_g, more and more chain atoms attain sufficient thermal energy to move in a coordinated manner above T_g. The slope discontinuity in Γ_B (γ) near T_g may be attributed to the increase in sound scattering due to this long-range coordinated molecular motion above T_g.

Standard techniques such as measurements of thermal expansion, heat capacity, refractive index, mechanical damping etc, which can be used to identify glass transition in a wholly amorphous polymer may yield less clear results in a partially crystalline polymer like polyethylene. This is because large contribution is made by crystalline order to these measured physical properties. For example, the specific volume-temperature curves may not exhibit a distinct discontinuity in slope. This brings in an element of judgement and subjectivity into the determination of T_g by these curves. In Brillouin light-scattering measurement, T_g is determined from both results of ν_B and Γ_B. Determination of T_g by ν_B alone offers no advantage over that by specific volume, as the former is a reflection of the latter. However, since the slope discontinuity near T_g in Γ_B is more pronounced, the resulting T_g is more reliable. The fact that both values of T_g, 204 ± 5K and 201 ± 2K, obtained for polyethylene are so close and agree with the value, ~200K, which refers to the completely amorphous state (1), suggests that Brillouin spectroscopy may provide a more objective identification of T_g for a semi-crystalline polymer such as polyethylene.

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