Polymer Bulletin 19, 97–101 (1988)

Polymer Bulletin

Crystalline melting 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 through the crystalline melting range, using a five-pass Fabry-Perot interferometer. Discontinuities have been observed in the Brillouin shift and width and the Landau-Placzek ratio near the melting temperature. The results are discussed in terms of phenomena associated with the process of melting.

Introduction

Polyethylene is a semi-crystalline thermoplastic of great commercial importance. Upon the application of heat it undergoes a process of melting which destroys the crystalline nature of the polymer. Although most plastics melt over a range of temperatures, the melting point T_m is usually reported as a single temperature where melting is complete. The importance of determining the melting point of a thermoplastic is obvious since this temperature represents the minimum temperature for the processing of the plastic and also in most cases represents the upper use temperature for the plastic where structural integrity is required. Recently the technique of Brillouin light-scattering has been used to study the glass transition of polymers and has yielded interesting results (1 - 3). In particular for polyethylene, slope discontinuities of opposite directions have been observed in the Brillouin shift and width near the glass transition temperature (3). The purpose of the present work is to investigate what information may be gained about the crystalline melting of polyethylene using the same technique. To our knowledge investigations of this type have not been reported in the literature.

Experimental

The polyethylene used in this work was an injection-moulded test piece in a Resinkit supplied by K.G. Roberts Associates Inc., U.S.A. It is of low density, measured to be 0.919 g cm^{-3} at room temperature. A differential scanning calorimetry (DSC) measurement gave a peak melting point of 379 K and a degree of crystallinity of 26% (3). A sample of this

polyethylene was cut and polished to dimensions of 0.2 cm x 0.2 cm x 1.0 cm. It was of relatively good optical quality. The sample was enclosed within thin glass walls so that the same scattering geometry could be maintained when the sample melted. Scattering of laser light from the glass walls themselves was found to be negligibly small. The sample was first annealed in vacuum at $\sim$ 334 K for a day and its Brillouin spectra were then measured as a function of temperature which was increased from $\sim$ 334 K to $\sim$ 426 K. Steps of increment in temperature were $\sim$ 5 K, except when the temperature was near the melting range in which case the steps were $\sim$ 2 K. 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 in vacuum at a fixed temperature (± 0.1 K) and analysed using a Burleigh DAS-1 five-pass Fabry-Perot interferometer system operated with a spectral range of 20.01 GHz, as described previously (4). The measured spectrum was then deconvoluted to remove the effects of instrumental resolution and the Brillouin shift ν_B and true width Γ_B (f.w.h.m.) obtained by least-squares fitting to the resulting spectrum with a Lorentzian lineshape.

Results

The Brillouin shift ν_B for polyethylene is shown in fig. 1 as a function of temperature. In general, ν_B decreases roughly linearly with increasing temperature. The lines are

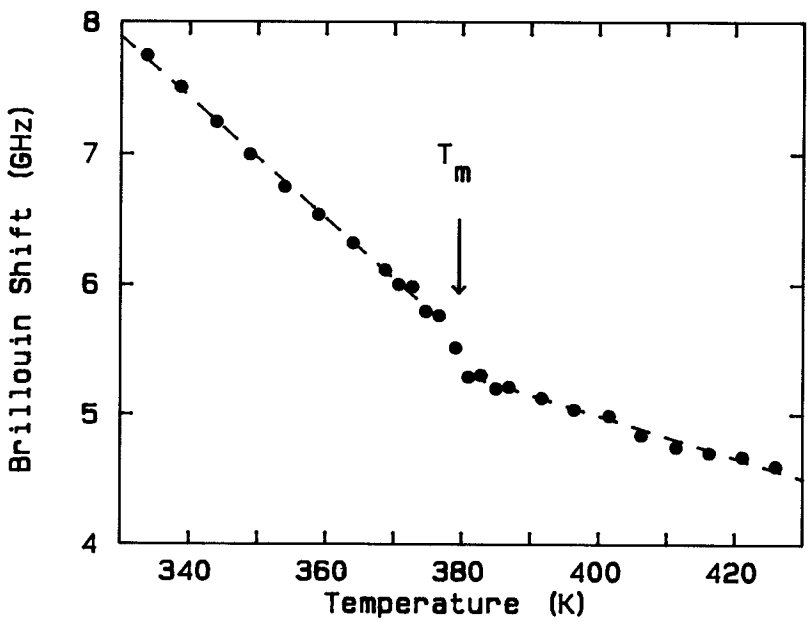

Fig. 1 The Brillouin shift of Polyethylene as a function of temperature. The lines are linear least-square fits. T_m is near the crystalline melting temperature.

linear regressive fits to two different portions of the data with $\nu_B = \nu_o + T(d\nu_B/dT)$. We obtain ν_o = 23.137 and 11.414 GHz for the upper and lower lines respectively, while $d\nu_B/dT$ = - 0.04620 and - 0.01606 GHz K^{-1}, respectively. Of particular interest is the discontinuous decrease of $\sim$ 0.44 GHz ($\sim$ 7.7%) over a region of width $\sim$ 4.3 K centred at 379.05 K where crystalline melting occurs.

The Brillouin width Γ_B as a function of temperature is shown in fig. 2. Similar to the behaviour of ν_B, Γ_B also decreases with temperature and exhibits an abrupt and conspicuous decrease of $\sim$ 0.33 GHz ($\sim$ 21.3%) over a range of $\sim$ 3.7 K centred at 380.93 K. The lines are again linear regressive fits given by $\Gamma_B = 3.3666 - 4.7418 \times 10^{-3}$ T and $\Gamma_B = 4.3578 - 8.1574 \times 10^{-3}$ T respectively.

The Landau-Placzek (LP) ratio, computed by dividing the integrated Rayleigh intensity by the integral of the deconvoluted Brillouin lineshape, is shown in fig. 3 as a function of temperature. The fact that our values of the LP ratio are much larger than expected from simple theories is typical of measurements on this quantity. Here, again, a drop in the LP ratio of about two orders of magnitude is apparent over a width of $\sim$ 12 K centred on 380.93 K. The abrupt changes in the LP ratio are due entirely to the corresponding decrease in the integrated Rayleigh intensity, reflecting the reduction observed in the elastic scattering when the polyethylene melts. It is to be noted that the nature of the log plot in fig. 3 tends to de-emphasize the abruptness of the decrease in the LP ratio and over-emphasize the width of the melting region.

The value of T_m obtained from the plots of ν_B, Γ_B and LP ratio agree very well with that obtained by the DSC measurement (3).

Discussion

Laser-Brillouin scattering from phonons in a system under study results in scattered light shifted in frequency by $\pm \nu_B = \pm 2\, n v \sin\frac{1}{2}\theta/\lambda$, where v is the phonon velocity, λ the wavelength in vacuum of the probe laser, n the refractive index of the system and θ the scattering angle. The phonon velocity is given by $v = \sqrt{(K + 4\mu/3)/\rho}$ where K is the modulus of compression, μ the modulus of rigidity and ρ the density of the scattering system. Since crystalline melting constitutes a first-order phase transition, a discontinuous decrease in ρ is expected (5). Moreover, μ also decreases considerably at the melting transition. Indeed, the sharp drop in ν_B observed near the melting transition is mainly a reflection of these changes and evidently the decrease in μ is the predominating influence in causing the decrease in ν_B.

The Brillouin width Γ_B is related to the phonon attenuation coefficient γ by $\Gamma_B = \gamma v/\pi$. The fact that Γ_B and ν_B both decrease abruptly over the melting range implies a percentage decrease in γ of $\sim$ 14.8% over the same transition range. As crystallinity disappears over the melting range, so also does the associated contribution to the sound scattering and this effect could account for the abrupt drop in γ.

The sample of polyethylene is optically slightly hazy in

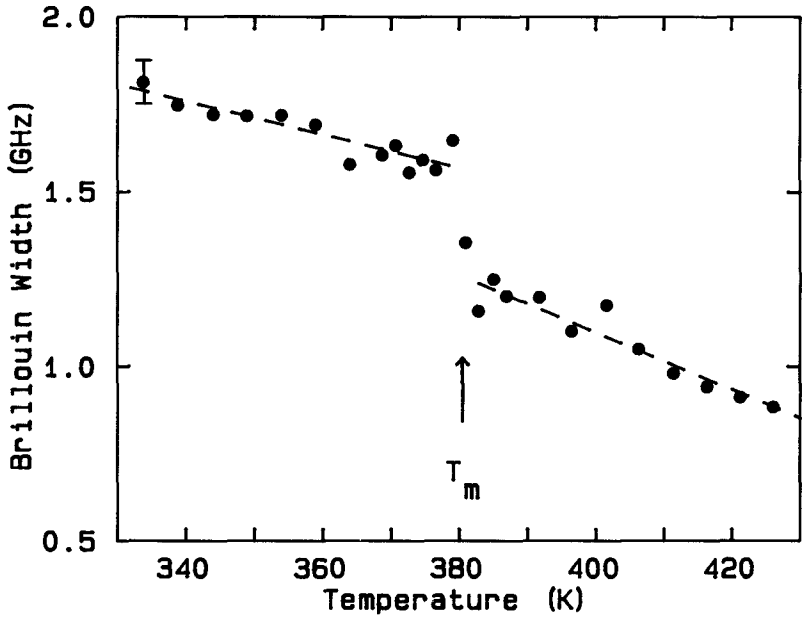

Fig. 2 The Brillouin width of Polyethylene as a function of temperature. The lines are linear least-square fits. T_m is near the cyrstalline melting temperature.

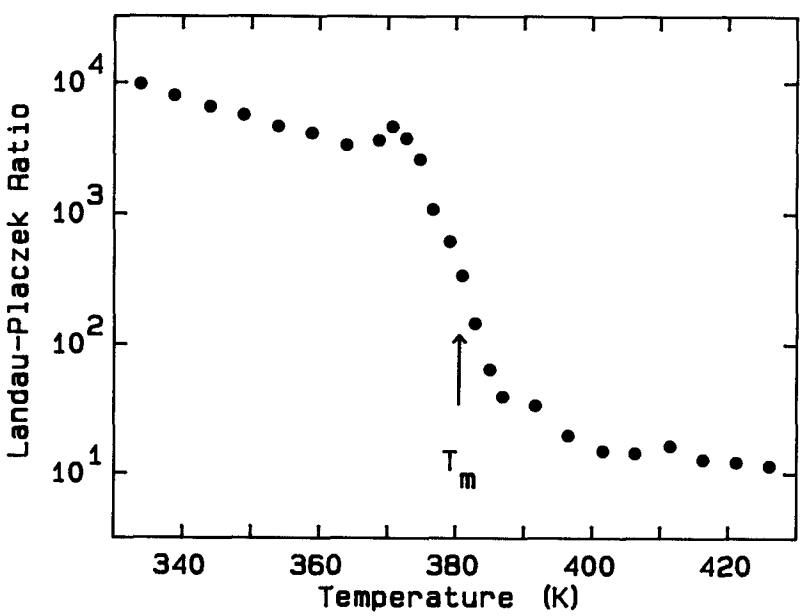

Fig. 3 The Landau-Placzek ratio of Polyethylene as a function of temperature. T_m is near the crystalline melting temperature.

the semi-crystalline state because of differences in the refractive index between amorphous and crystalline portions. On melting the sample becomes clear. The decrease in the LP ratio observed between the semi-crystalline and molten states is due to the same effect.

The crystalline melting of thermoplastics may be observed by several experimental techniques (6). The sample becomes liquid and flows, although this behaviour may not immediately be apparent because of the high viscosity of the polymer. The disappearance of crystallinity may also be observed in a polarizing microscope with crossed polarizers. The sharp X-ray pattern characteristics of crystalline materials give way to diffuse halos at the melting temperature. Since melting is a first-order phase transition, a discontinuous change in specific volume is expected. The melting temperature and percent crystallinity may be determined from a DSC scan on the sample. While each of the above methods monitors essentially the changes of one physical property near the transition region, Brillouin spectroscopy measures three quantities ν_B, Γ_B and the LP ratio simultaneously. These quantities are related to a large number of physical properties such as n, v, K, μ, ρ, γ, etc. Thus Brillouin scattering measurements of melting systems have the potential to reveal considerably more information than conventional techniques.

The results discussed above have clearly demonstrated the usefulness of Brillouin spectroscopy in the study of crystalline melting in thermoplastics such as polyethylene.

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Accepted November 19, 1987 S