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Brillouin Spectroscopy at the Melt Transition of Poly-4-methyl-pentene-1: Discontinuous Melting of Superstructures?

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Summary:

The elastic properties of Poly-4-methylpentene-1 around the melt transition have been studied by Brillouin spectroscopy. A discontinuous change of the sound velocity is observed in the melting region of 10 K indicating a rather discontinuous melting and formation of spherulites with sharp boundaries. Another result is that practically the final elastic properties of the spherulites appear already during their formation.

Introduction:

Poly-4-methylpentene-1 (P4MP1) has its equilibrium melting point T_m at about 245°C (Griffith). Below T_m P4MP1 is partially crystalline with the crystallites belonging to the tetragonal space group $P\bar{4}b2$ (Kusanagi). Between T_m and a further transition temperature T_u within the melt, P4MP1 seems to be of local mesomorphic order (Krüger 1980, Krüger 1981). During the crystallization process sheaflike spherulites are developping in the melt, which can be observed by light microscopy (Inoue, Saunders). Besides these optical investigations dilatometric (Griffith) and calorimetric measurements (Karasz) were performed at the melt transition. The effect of pressure on the melting of P4MP1 was studied too (Jain).

Only little is known about the elastic properties at the melt transition of polymers. Concerning ultrasonic techniques this is a consequence of the enormous ultrasonic attenuation at elevated temperatures. For P4MP1, ultrasonic data exist only up to 65°C where the absorption amounts to 10 dB/cm for the longitudinal mode and about 28 dB/cm for the shear mode (Hartmann). The existing Brillouin data (Krüger 1980, Krüger 1981) do not cover the complete melt transition. In this paper we present the first high resolution Brillouin investigations on the melt transition (crystallization) of a polymer. It is worth noting that such investigations are interesting because the hypersonic wavelength involved (~364 nm) has at most the same order of magnitude as the diameter of the spherulites.

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Results and Discussion:

Thin industrial P4MP1 films[+] of 20 µm thickness were used as samples. The samples were dried and degassed at about 280°C for 5 hours. One sample was then investigated several times by DSC around the melt transition. The crystallization peak and the melt peak looked differently: Whereas the melt peak was just a single peak centered at about 230°C the peak of crystallization was splitted into two partially overlapping parts. This splitting of the crystallization peak which persists even in the third DSC run was not been explained yet. From DSC measurements the degree of crystallinity of our samples was determined as a function of temperature (fig. 1). The maximum of crystallinity was $W_c^{max}=0.55$.

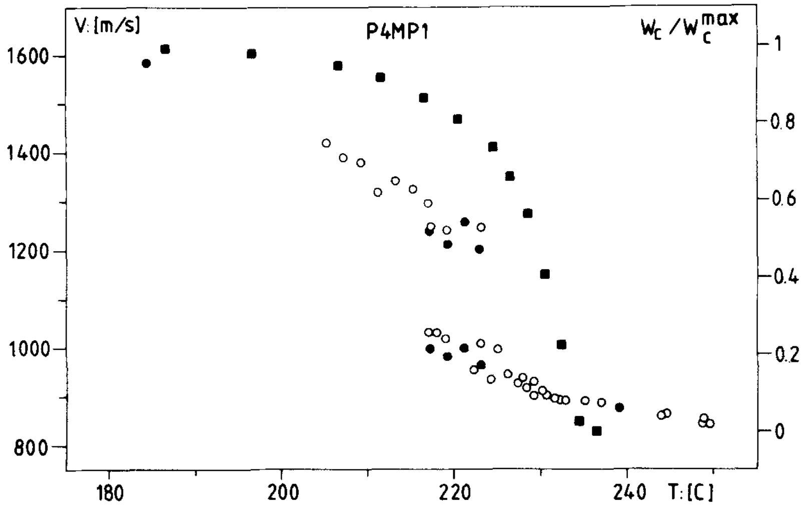

fig. 1: Sound velocity (o cooling; ● heating) and relative degree of crystallinity (■) of P4MP1 versus temperature T.

The Brillouin spectrometer used has been described elsewhere (Krüger 1978). All Brillouin measurements were performed in the so-called 90A scattering geometry (Krüger 1978, Krüger, Sailer 1978). It should be emphasized that for an elastical and optical isotropic sample the hypersonic wavelength Λ depends only on the outer scattering angle θ_o and on the vacuum laser wavelength λ and does therefore not change with respect to temperature. All these experiments are subject to: $\theta_o = 90°$, $\lambda = 514.5$nm and $\Lambda = 363.8$ nm.

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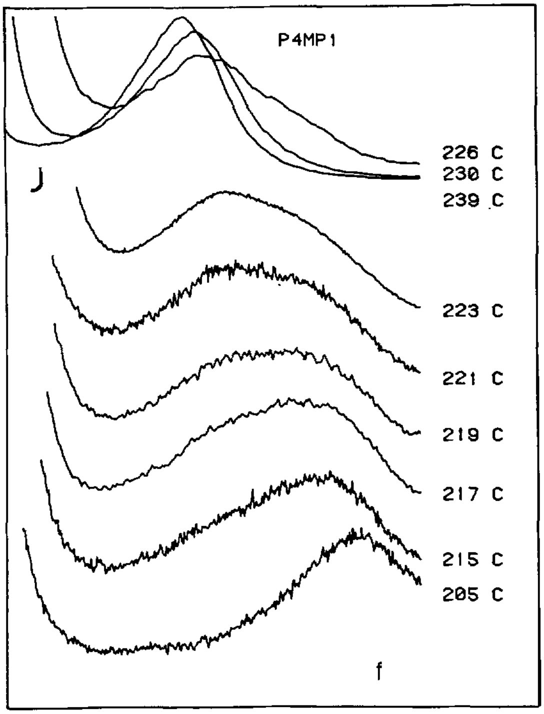

fig. 2a: Several acoustic phonon spectra of P4MP1 around the melt transition. f hypersonic frequency (explanations in the text).

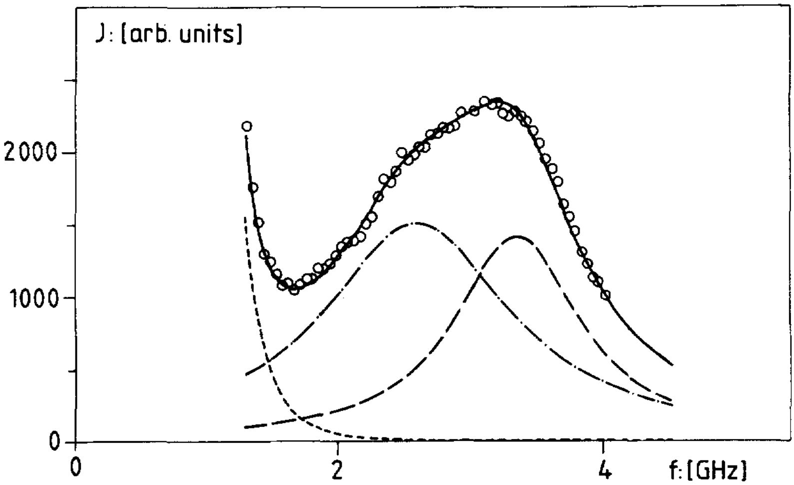

fig. 2b: The phonon spectrum of P4MP1 at 217°C with the appropriate fit curve (——). (···) Rayleigh wing, (-·—·-) "melt phonon", (---) "solid state phonon".

To prevent sample degradation the Brillouin measurements were performed in an helium filled thermostat. The temperature stability was better than 0.1 K. The sample temperature was measured by a miniature chromel-alumel thermocouple close to the scattering volume. The data accumulation took about 2 minutes for a spectrum. After setting a new temperature at least 1 hour passed before starting the data accumulation again.

Fig. 1 also shows the sound velocity v versus temperature T around the melt transition. The sound velocity was measured at decreasing temperature (o, crystallization) and increasing temperature (●, melting). Surprisingly both measurement series led to nearly the same result (no hysteresis).

Several corresponding spectra are shown in fig. 2a,b. As to the phonon spectrum at 217°C it is shown (fig. 2b) that it can satisfactorily be described by an overlap of two phonon spectral lines and the Rayleigh wing. The mean free path of the phonons in the coexistence region is about 2 μm (fig. 2b,3).

Fig. 3 shows the hypersonic velocity, -attenuation and Rayleigh peak intensity of P4MP1 as a function of temperature. In the temperature range between 215°C and 230°C the sound velocity curve is bi-valued, indicating the coexistence of two different longitudinal acoustic phonons in this temperature range.

As to the above mentioned temperature range we assume the coexistence of two species of regions within the scattering volume of different elastic properties. The lateral dimensions of these regions should be a few micrometers at least and their boundaries should be rather sharp, otherwise two different longitudinal acoustic phonons would not coexist. Because of their small size compared to the acoustic wavelength isolated crystals cannot be responsible for the additional spectral line. The spectra of fig. 2 should thus be interpreted in the following way: At high temperatures, e.g. at 239°C only one longitudinal acoustic phonon spectral line corresponding to the "melt phonon" exists. At decreasing temperature a high frequency shoulder in the phonon spectrum is developed with continuously increasing intensity. This additional spectral line originates from a longitudinal acoustic phonon with a 20% larger sound velocity at the same wavelength than the "melt phonon". It can be followed down to room temperature (fig. 3) and is therefore identified as the "longitudinal acoustic phonon of the solid state" composed of spherulites (Inoue, Saunders). Below 205°C the spectral line of the "melt phonon" has disappeared completely, indicating that melt regions of a sufficient size and number are no longer present in the scattering volume. The idea of coexistence of melt- and solid state -regions between 210°C and 230°C is also supported by the Rayleigh scattering (——, fig. 3). Only in the coexistence region the sample is optically opaque indicating that the different regions which are of the order of the laser wavelength have also different refractive indices.

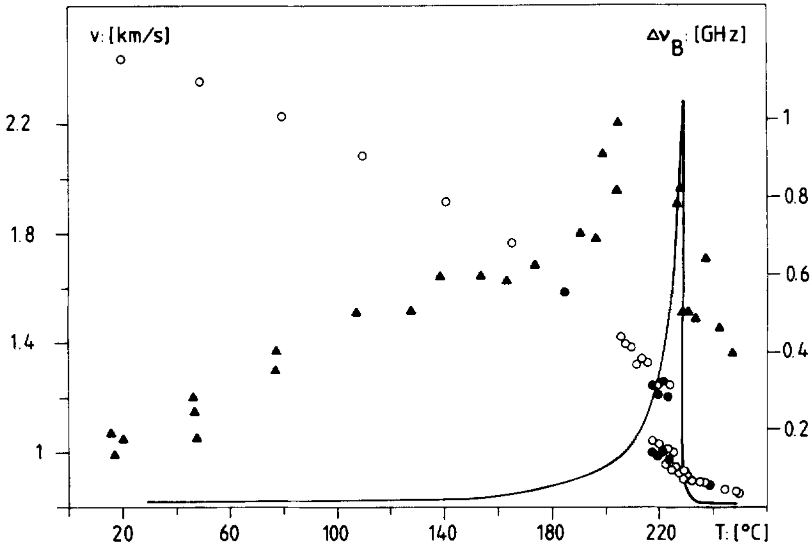

fig. 3: Elastic and optical properties of P4MP1 versus temperature. (——) Rayleigh peak intensity, o, • sound velocity (s.a. fig. 1), ▲ phonon linewidth (full width at half maximum).

The volume fraction of the scattering volume which is in the solid state or in the melt state is roughly given by W_c/W_c^{max} and $(1 - W_c/W_c^{max})$ respectively.

From the fact that the elastic properties of the coexisting different regions change only slightly with respect to the temperature (fig. 1) and that the scattering cross-section for both sort of regions changes continuously with respect to the temperature one can conclude that only the amount of the different regions changes: The structural and elastic properties of the solid state are already fixed and change only slightly with decreasing temperature. The discontinuity of the elastic properties is mainly determined by the elastic stiffness constant which changes by about 45% whereas the density changes only by about 5% (Griffith).

From the discontinuity of the sound velocity it may be concluded that the growth of the spherulites (or aggregation of spherulites) to a minimum size of a few micrometer diameter sets in rather spontaneously and that there exists no significant size distribution of the spherulites on the scale of the acoustic wavelength. Unfortunately the real degree of crystallinity during the Brillouin experiments can not be taken from the appropriate curve in fig. 1 because the crystallinity curve from the DSC measurements might be as well shifted as deformed with respect to the temperature on account of the heating rate.

The question remains whether the amorphous part of the solid state has the same properties as the melt: It follows from fig. 1 that the sound velocity of the "melt phonon" increases significantly (30% of the discontinuity) below 230°C. This can be explained either if the "melt regions" change their properties (structure?) but remain non crystalline or if crystallization without spherulite formation has already taken place. In the former case it could be concluded that the amorphous at the melt transition has significantly changed its elastic properties compared to the melt above the coexistence region. In the latter case the formation of spherulites might be interpreted as a transition from a disordered partially crystalline into the spherulitic state. This question cannot be answered at the moment.

However, the above discussed melting behaviour does not seem to be restricted to P4MP1 because similar elastic behaviour was observed in the meantime at the melting of Polyvinylidenefluoride.

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