

CCA-737

535.34-1:678.742

Note

Half-widths of the Infrared Bands in Polyethylene

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Received June 27, 1972

There are a few papers¹ treating the temperature dependence of the half-width of IR bands of polymers. The importance of such an experimental work lies in the fact that it is possible to infer from it the mechanism that causes the broadening of the IR bands. The aim of this work is, to report the temperature dependence study of the half-widths of IR bands of polyethylene. The following bands were studied: at 2016 cm^{-1} (combination band²), at 1080 cm^{-1} (vibration due to the amorphous polyethylene³) and at 908 cm^{-1} (vibration of the vinyl end-group³).

The measurements were done on samples of various crystallinities and thicknesses so that the studied bands were well separated from the others. A high crystallinity sample was used to study the band at 2016 cm^{-1} and a low one for the band at 1080 cm^{-1} . The results are plotted in Fig. 1.

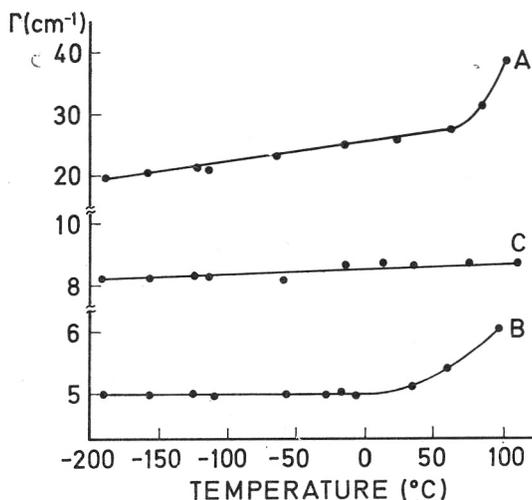


Fig. 1. Temperature variations of the half-widths. A: band at 2016 cm^{-1} ; B: band at 1080 cm^{-1} . C: band at 908 cm^{-1} .

In order to analyse the temperature dependence of the half-widths we can use the theory developed for crystals⁴. The half-width is written as:

$$\Gamma(\Omega) \sim \sum_{\omega_1, \omega_2} [V_{\Omega, \omega_1, \omega_2}]^2 (1 + n_1 + n_2) \{ \delta(\omega_1 + \omega_2 - \Omega) - \delta(\omega_1 + \omega_2 + \Omega) \} + (n_2 - n_1) \{ \delta(\omega_1 - \omega_2 - \Omega) - \delta(\omega_1 - \omega_2 + \Omega) \} \quad (1)$$

where $V_{\Omega, \omega_1, \omega_2}$ is the coupling constant (anharmonic constant of the third order) between phonons with frequencies Ω and ω_1, ω_2 and n_i is the Bose-Einstein distribution. The conservation rules⁴ are satisfied by taking ω_1 as the frequency from the optical dispersion curve and ω_2 from the acoustical one. With this approximation then follows: $\Gamma(\Omega) \propto T$. The above described interpretation seems to be correct for the band at 2016 cm^{-1} . At higher temperatures (slightly below melting) other mechanisms can contribute to the half-width (anharmonic constant of the fourth order, modulation mechanism⁵, hydrodynamic motion of the chain *etc.*) to produce a greater dependence on the temperature. The temperature dependence of the band at 1080 cm^{-1} has two different parts. In the first one the half-width does not change with the temperature. The band at 1080 cm^{-1} is due to the amorphous polyethylene and equation 1 does not apply to it. Below room temperature the disorder of the chains does not vary with the temperature to any large extent and this is reflected in the constant value of the half-width. Above room temperature the disorder of the chains varies with the temperature.

This explanation seems to be in accordance with the recent calculations reported by Zerbi *et al.*⁶ The temperature dependence of the 908 cm^{-1} band half-width is very small. This can be interpreted as if the environment had a small influence on the vibration of the vinyl end-group. The temperature dependence of the peak-height was found to be a useful indicator of the phase changes⁷ (Fig. 2). DTA measurements on the same samples as used in the

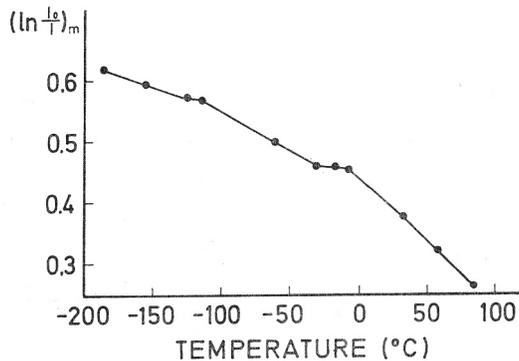


Fig. 2. Temperature variation of peak-height (908 cm^{-1} band).

spectroscopic work have shown phase changes at approximately: -120°C , -20°C , 50°C and 120°C . The first two (at T_g) have been attributed to the amorphous polyethylene. Fig. 2 indicates that the peak-height of the 908 cm^{-1} band is a sensitive indicator of the changes at T_g .

Acknowledgement. This work was supported by Boris Kidrič Fund.

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IZVLEČEK

Polširina IR trakov polietilena

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Merjene so polširine IR trakov polietilena. Njihova temperaturna odvisnost omogoča določiti mehanizem razširitve. Pri traku 2016 cm^{-1} je ta mehanizem anharmočni člen tretjega reda, pri traku 1080 cm^{-1} pa možnost različnih konformacij polietilena.

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Sprejeto 27. junija 1972.