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Intra- and interchain thermal conduction in polymers.

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Abstract

It is shown here that oriented polymers are good candidates to get a better understanding of the thermal conductivity in semi-crystalline polymers. By measuring the thermal conductivity parallel and perpendicular to the polymer chains as a function of temperature, the thermal-transfer mechanisms along and across the chains could be identified. The mechanisms leading to the thermal-conductivity increase upon stretching will be discussed.

1. INTRODUCTION

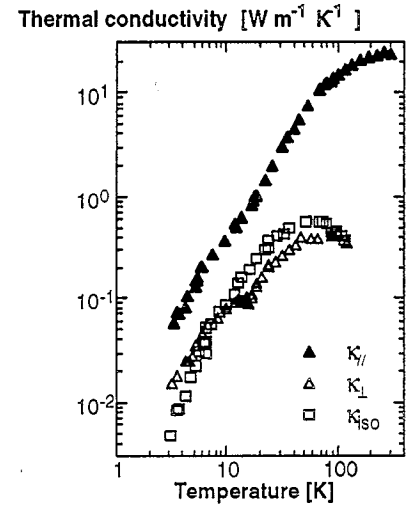
Several models have been proposed to explain the temperature variation of the thermal conductivity of semi-crystalline polymers.[1-4] However, these models do not fully explain the behavior observed in these materials. Since the understanding of polymer thermal conductivity requires the knowledge of the heat-transfer mechanisms along and across the polymer chains, we performed the measurements of the thermal conductivity of model samples : i.e. oriented polyethylene films.

2. EXPERIMENTAL

The polyethylene (PE) films were obtained from ultra-high molecular weight Hostalen Gur 412 (M_w = 2000 kg mole^{-1}). They were prepared by dissolving the polyethylene in xylene at 130 °C. After complete dissolution of the polymer, the solutions were cast and quenched to room temperature. Subsequently, the solvent was evaporated at ambient conditions and dry solution-cast films were obtained. Solid-state drawing of the films was performed on thermostatically controlled hot shoes at 120 °C. The draw ratio of the films, defined as the ratio between their final length after stretching and their initial length before drawing ($\lambda = L/L_0$), ranged from 21 to 98. All the films presented a crystallinity ratio higher than 75%.

The temperature variation of the thermal conductivity was measured by means of a thermal potentiometer especially designed for the measurement of samples with small cross-sections such as fibers or films[5] mounted on the heat sink of a liquid helium cryostat whose temperature may be regulated between 1.5 and 300 K. Contacts on the samples were insured by means of GE7031 varnish. To improve adhesion and thus thermal contact, the surface of the PE films was activated by an etching treatment just before mounting the sample on the thermal potentiometer. This treatment (400 V, 5 mA) was performed under an argon plasma (0.1 mbar).

Figure 1 : Comparison between the temperature dependence of the longitudinal (▲) and the transverse (Δ) thermal conductivity of a drawn polyethylene film ($\lambda = 40$) and that of the pristine isotropic sample (□).

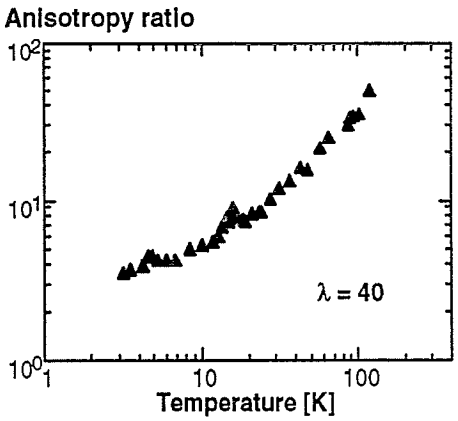


3. RESULTS AND DISCUSSION

In figure 1, the temperature dependence of both the longitudinal, $\kappa_{//}$, and the transverse thermal conductivity, $\kappa_{\perp}$, of a stretched film ($\lambda = 40$) are compared to that of the isotropic sample, κ_{iso}. As expected, the thermal conductivity is greatly enhanced

in the longitudinal direction and the temperature dependence becomes more pronounced. In the transverse direction, the thermal conductivity is slightly lower than that of the isotropic sample at high temperature. For $\kappa_{\perp}$, the temperature variation is close to that of the isotropic sample. We observed similar behaviors for films with draw ratios equal to 21 and 98. The same effects were also observed for polyacetylene films.[6]

Figure 2 : Temperature dependence of the anisotropy ratio, $\kappa_{//}/\kappa$, for a drawn solution-cast polyethylene film ($\lambda = 40$).



The increase of the thermal conductivity in stretched polymers was generally attributed to the alignment of the polymer chains in the crystalline phase.[1] This explanation should certainly account for the increase observed at low draw ratios ($\lambda < 20$) where a strong alignment of the polymer chains in the crystalline phase occurs.[1,8-10] However, for $\lambda \geq 20$, previous studies performed on oriented polyethylene showed that the polymer chains are perfectly aligned in the crystalline phase an that higher stretching levels do not improve this alignment.[8,9] However, other structural changes may account for the increase of the thermal conductivity for draw ratios above 20. First, x-ray diffraction studies showed that the transverse crystallite size slightly increases when the draw ratio increases from 25 to 100.[9] This certainly lead to a weaker scattering of the transverse phonons on the crystallite boundaries and to an increase of the contribution of these phonons to the thermal conductivity. Second, though in the crystalline phase the chains are completely aligned for $\lambda = 20$, the alignment of the polymer chains in the amorphous phase continues to improve for $\lambda > 20$.[8,9] The perfect alignment of the amorphous phase is only obtained for $\lambda > 100$. The thermal conductivity should thus be improved with molecular orientation as it is the case for the Young's modulus.

On the highly drawn polyethylene films ($\lambda > 20$), a dip is observed in the temperature dependence between 8 and 17 K, both in the longitudinal and in the transverse direction (Fig. 1). This anomaly is more pronounced in the transverse direction and was also observed on the films with $\lambda = 21$ and 98. It is not present on isotropic polyethylene. This anomaly appears in the temperature range where the plateau is observed in amorphous materials. In the transverse direction, indeed, the heat flux crosses crystalline and amorphous regions which are in series heat transfer in the amorphous phase could thus dominates the thermal resistance. This cannot be the case in the longitudinal direction where regions of both phases are parallel to the heat flux. The temperature variation suggests rather a resonant scattering mechanism or a scattering of phonons by defect aggregates.

The thermal conductivity of drawn polymers is strongly anisotropic (Fig. 1). At 80 K, the anisotropy ratio, $\kappa_{//}/\kappa_{\perp}$ is approximately equal to 26 for a film with $\lambda = 40$. It decreases with decreasing temperature. The temperature variation of the anisotropy ratio is presented in figure 2 for a solution-cast film with $\lambda = 40$. At 4.2 K, $\kappa_{//}/\kappa_{\perp}$ is reduced by a factor of 10. The decrease of the anisotropy ratio is not surprising since the polymer will behave more and more like a three-dimensional material with decreasing temperature. In other words, as the dominant phonon wavelength increases there is much less discrimination between heat transfer along the polymer chains and across them.

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