THERMAL CONDUCTIVITY AT LOW TEMPERATURES IN SEMICRYSTALLINE POLYMERS

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Over the past few years we have studied in detail the influence of (i) crystallinity and (ii) crystallite orientation in determining the thermal conductivity, \( \kappa \), of semicrystalline polymers.\(^1\)-\(^3\) Between about 2K and room temperature the variations in \( \kappa \) with these two parameters are completely different above and below about 25K. At the higher end of the range the conductivity increases both with crystallinity and with orientation, the latter being brought about by drawing or extruding the isotropic polymer. At low temperatures, on the other hand, the specimens with the greatest crystallinity have the lowest conductivity with values in a 50\% crystalline specimen at \( \sim 1.5K \) roughly an order of magnitude lower than those found "universally" for amorphous solids.\(^4\) These low values, furthermore, are found to be more or less independent of crystallite orientation. The overall behaviour just described is shown schematically in figure 1.

This rather dramatic change in behaviour is attributed to the different conditions arising at low temperatures when the phonon mean free path, \( \lambda \), becomes larger than the dimensions, L, of the intercrystalline (amorphous) structural units. As the difference in density between crystalline and amorphous regions can be as great as 20\% the "structure scattering" of the composite polymer gives rise to a thermal resistance that is considerably greater than that of the amorphous material alone.

At still lower temperatures, somewhere in the region of 1K, it is found that, for polyethylene the variation of \( \kappa \) with T undergoes a rather sharp decrease in slope, changing from a dependence in the temperature range 1K to 20K of about \( T^{1.8} \) to a linear dependence below that temperature.\(^3\),\(^5\),\(^6\) This feature has been explained on
Figure 1. Schematic temperature dependence of thermal conductivity (a) parallel to the extrusion direction for various degrees of extrusion, $\lambda$ and (b) with crystallinity, $X$. 