

The Tg of Amorphous Linear Polyethylene: a Torsion Braid Analysis

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Summary. The Tg of amorphous linear polyethylene has been studied using torsion braid analysis. 4 transitions are observed: at 150°K, 190°K, 260°K and 370°K. Our results indicate that linear polyethylene has 2 glass transitions, a Tg_(L) at 190°K, corresponding to the truly amorphous polymer and a Tg_(U) at 260°K corresponding to the amorphous regions constrained by crystalline regions.

3 different values of Tg (BOYER 1963, MCCRUM et al 1965, and STEHLING and MANDELKERN 1970) have been attributed to linear polyethylene (LPE) -- 150°K, 190°K and 260°K. These values were primarily obtained by extrapolation from data for PE of varying crystallinity, or from ethylene-copolymers of varying ethylene compositions. No direct measurements have been possible on the amorphous polymer itself, since it was not available.

Several years ago, Hendra et al (HENDRA et al 1975) reported that they had succeeded in quenching LPE to the amorphous state. Their infrared data was interpreted as indicating that crystallization from the glass and therefore Tg was below 190°K. Later, Boyer and Snyder (BOYER and SNYDER 1977) reinterpreted Hendra's data and concluded that Tg should be 195°K ± 5°.

We wish to report a torsion braid analysis of LPE ultra-quenched in isopentane. Isopentane has been found to be a satisfactory and reproducible quenchant to quench LPE films into the amorphous state (LAM et al 1978).

Glass braids for the torsion pendulum were coated with solutions of 0.5 % LPE (Dow HB-PE *) in xylene and allowed to dry while taut. The braid was then suspended inside an oven at 160°C that was purged with nitrogen gas. Using a technique described previously for preparing electron microscope samples (JONES et al 1978), the hot braid was then rapidly propelled into a flask of isopentane at its freezing point. The sample was then rapidly inserted into a precooled (82°K) torsion pendulum chamber with all storage, assembly and alignment of the braid to the torsion rod being carried out with the braid under liquid nitrogen.

*Melt index = 1.2, density = 0.965 gm/cc.

Figure 1 is a dynamic mechanical spectrum of LPE as cast on the braid (i.e. a crystalline sample). 2 peaks can be clearly distinguished -- a very small, but reproducible γ peak at 150 K and an α relaxation at ≈ 380 K. Whether there is a peak at 260 K (β) is questionable.

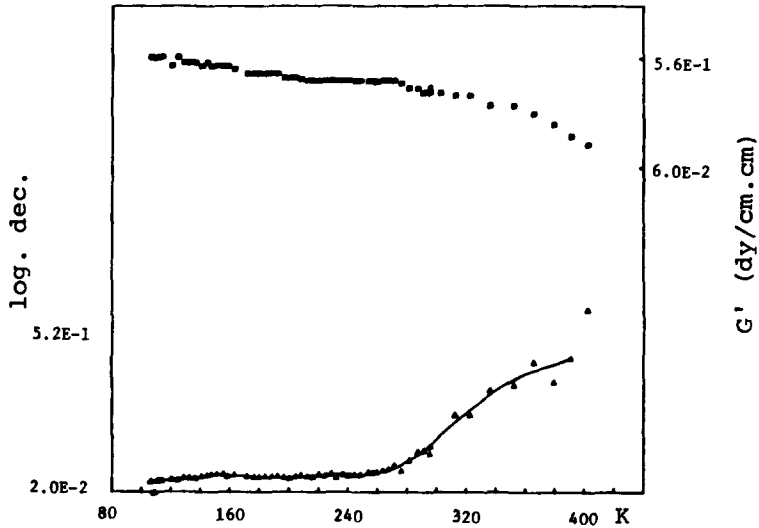


Figure 1. A dynamic mechanical spectrum of the crystalline sample (Dow HB-PE, melt index = 1.2, density = 0.965 gm/cc.).

Figure 2 shows the dynamic mechanical spectrum of the ultra-quenched polymer. 4 peaks corresponding to LPE are observed. The sharp peak at 116°K is attributed to the melting of isopentane ($T_m = 114^\circ\text{K}$). Again, a small γ peak and an α relaxation peak at $\approx 370^\circ\text{K}$ are observed.

There are 2 additional peaks present, however, that are not found in the crystalline polymer -- at 190°K and 260°K. No similar peak at 190°K has been observed for PE (linear/branched) in dynamic mechanical studies, whereas the 260°K peak corresponds to the β relaxation seen most clearly in branched PE.

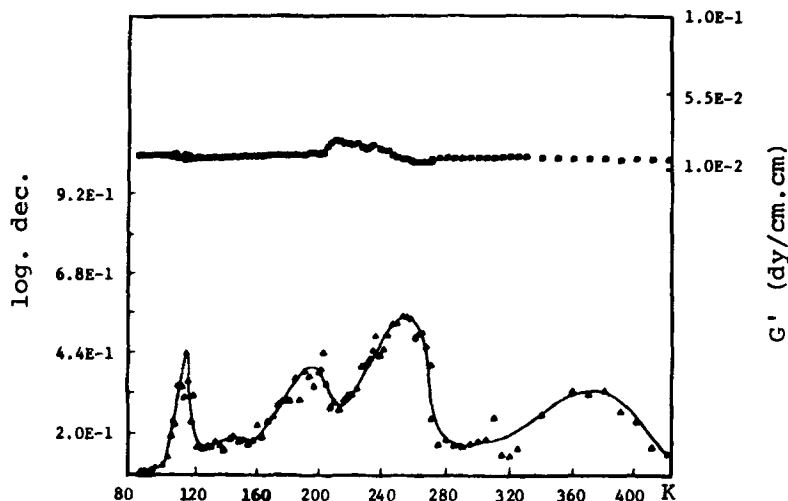


Figure 2. A dynamic mechanical spectrum of LPE ultraquenched in isopentane.

Following the relaxation peak at 190°K, there is a rise in the rigidity of the braid, which we attribute to crystallization. This temperature agrees well with IR (HENDRA et al 1975), electron diffraction and DSC (JONES et al 1978) studies.

On cooling the sample down and re-running the spectrum (figure 3), 3 peaks, at 150°K, 260°K and one at a higher temperature, are observed. The intensity of the 260°K peak depends on the rate of heating and cooling. We point out that in the microcrystalline sample formed by the initial "rapid" heating through T_g (LAM et al 1978), this peak is larger than the α peak, a feature not previously observed for LPE regardless of the degree of crystallinity.

The effect on the spectra of annealing the sample in the vicinity of the 190°K peak will be discussed in detail in a subsequent paper. Electron microscope and electron diffraction studies (LAM et al 1978) show that isolated single crystals of LPE can be formed from uniformly thick films of the glassy polymer if one anneals the films at 200°K for a few hours. Fibers and voids

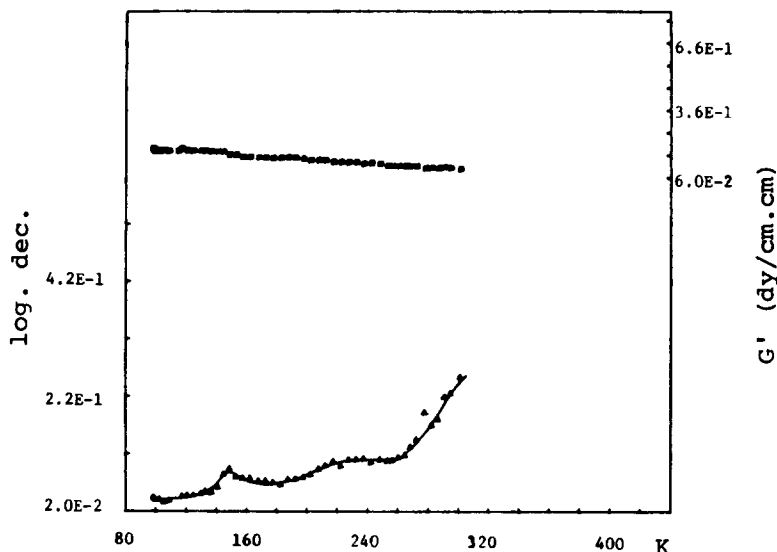


Figure 3. Re-run of the sample shown in figure 2 after cooling down.

between the crystals are formed in the process. These indicate that large scale rearrangement of the polymer molecules occur within the sample during crystallization. If one anneals below 180°K, no such motion can be found. This clearly indicates that 190°K is the Tg of amorphous LPE.

The behaviour of our 260°K suggests that it should also be related to the amorphous content. Since crystallization from the glass takes place well below this temperature, we suggest that it corresponds to the motion of the amorphous regions sandwiched between crystalline regions.

In conclusion, our results support the suggestion of Boyer (BOYER 1973) that there are 2 Tg's for LPE, a Tg_(L) of the truly amorphous polymer at 190°K, and a Tg_(U) at 260°K associated with the amorphous regions constrained by the crystalline regions.

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