CHEMISTRY

A Secondary Process in the Liquid-induced Crystallization of Polyethylene Terephthalate

IT is known that amorphous polyethylene terephthalate may be crystallized by treatment with certain organic liquids[1]. With the polymer in the form of a film the process is accompanied by the appearance of opalescence, generally attributed to sub-microscopic spherulites, and is a function of time, temperature and film thickness[2]. In these investigations the thickness was at least equal to 2×10^{-2} cm. On extension of the work to include thinner films, it was observed that not only was there an increase of opalescence on treatment with a typical liquid such as acetone but also that after a certain time, afterwards referred to as an induction period, an almost opaque front was seen to move across the sample.

Use of reflectance and transmission microscopy indicates that the phenomenon is basically an internal one and involves a particulate structure, the size of the particles being of the order of a few microns. X-ray diffraction reveals no sharp distinction between samples which have undergone this change and those removed from acetone just before the process would have occurred. Figs. 1 and 2 show that the induction period is both temperature and thickness dependent, the latter suggesting that the reason why the phenomenon has not been previously noted, if it had taken place, was due in part to a high degree of opalescence which may have masked the process. Although it is premature to conclude a mechanism at this stage, it is suggested that it may be due to an internal fracture effect which occurs when the two main diffusion and associated crystallization fronts approach each other, abstracting amorphous material in two directions and resulting in a void in the centre of the sample. In this context it may be significant to note that it is found that the phenomenon does not apparently happen when diffusion is restricted to occur from one direction only.

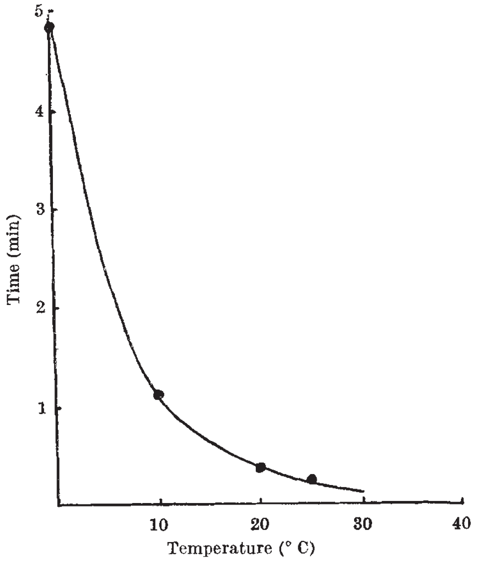

Fig. 1. Induction period versus temperature of acetone

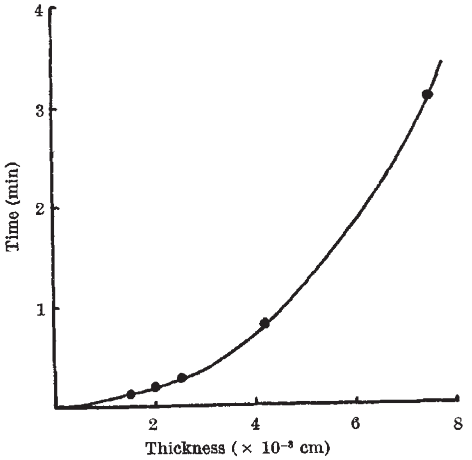

Fig. 2. Induction period versus film thickness

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[1] Kolb, J., and Izard, E. F., *J. App. Phys.*, **20**, 571 (1949). Moore, W. R., Richards, D. O., and Sheldon, R. P., *J. Text. Inst.*, **51**, T 438 (1960).

[2] Sheldon, R. P., *Polymer*, **3**, 27 (1962).

Solvated Electrons in Alkali Glasses

EVIDENCE has recently been obtained which strongly suggests that 'solvated' electrons in water at room temperature have an absorption band in the 15,000 cm^{-1} region[1]. Jortner and Sharf[2] found a similar absorption in frozen aqueous solutions of alkali metal hydroxides at 17,000 cm^{-1} after exposure to 200 kV X-rays, which they attributed to trapped electrons, although they favoured an 'expanded' orbital on the cation as the trapping centre[2].

It has been suggested[3] that 'solvated' electrons, if such species exist, will not normally be produced by radiolysis of molecular solids since there is no opportunity for bulk reorientation of solvent molecules. However, if a frozen ionic solution were irradiated and anion vacancies could be generated by some means, then electrons could well be trapped as in F-centres to give the required 'solvated' electron centre.

Table 1. DETAILS OF THAT FEATURE OF THE ELECTRON SPIN RESONANCE ABSORPTION SPECTRUM OF γ-IRRADIATED AQUEOUS SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE GLASSES AT 77° K ATTRIBUTED TO TRAPPED ELECTRONS

System	g factor ($\pm$ 0·0005)	Line width $\pm$ 1·0 gauss
10 molar NaOH in H_2O	2·0006	16·1
20 molar NaOH in H_2O	1·9995	18·5
10 molar KOH in H_2O	2·0005	11·8
20 molar KOH in H_2O	1·9997	11·6
10 molar NaOH in D_2O	2·0007	6·1
10 molar NaOH in 1 : 1 (by vol.) mixture of H_2O and D_2O	2·0009	11·8

We postulate that this is in fact the reaction observed by Jortner and Sharf, the hydroxyl ion being especially effective as an anion since it is the conjugate base of the solvent and can readily move, on demand, by proton migration. A systematic investigation of such systems by visible and electron spin resonance spectroscopy has been undertaken, and the results seem to support the model. Those features which are particularly relevant are summarized in Table 1 and will be briefly discussed.

There was no marked variation in the visible absorption spectrum with change in concentration of water or in the nature of the cation. On exposure to visible light the band in the 17,500 cm^{-1} region was lost, and a broad absorption in the near infra-red appeared. At the same time, one feature in the complex electron resonance spectrum of the γ-irradiated material was lost.