Pile Irradiation of Polyethylene Terephthalate ('Terylene')

IN view of its bearing on the recent communication from Miss Little¹, some simultaneous and independent work, initiated by Charlesby's claim to have cross-linked polyethylene terephthalate by pile irradiation², is perhaps worth recording.

The solution viscosities of two ethylene terephthalate polymers, both before and after varying amounts of irradiation in the BEPO pile at the Atomic Energy Research Establishment, Harwell, were measured in *o*-chlorophenol at 25° C. One polymer ('microdull') contained titanium dioxide as a delustring agent but there was none in the other ('bright'). For both polymers, the limiting viscosity number $[\eta]$ fell and the Huggins's viscosity slope constant³,

$$k^1_H = \frac{d\left(\frac{\eta - \eta_0}{\eta_0 c}\right)}{dc} / [\eta]^2,$$

where η and η_0 are the viscosities of solution and solvent respectively and c is the concentration of the solution in gm./ml., rose with increase of radiation dose. It should perhaps be noted that hydrolysis will contribute to the $[\eta]$ drop for the samples of bright polymer irradiated longest in sealed tubes if the temperature in the pile approaches 100° C.

Polymer	Radiation energy (MW. hr. $\times 10^3$)	$[\eta]$	k^1_H
Microdull	0	76	0.25
"	0.3 in air	65	0.39
"	0.5 "	62	0.41
"	1.0 "	57	0.43
"	2.0 "	52	0.38
Bright	0	65	0.27
"	2 in vacuo	49	0.43
"	4 "	42	0.53
"	8 "	37	0.52

Although the exact significance of k^1_H is not clear, it is generally agreed that it depends on the interactions between the molecules in high polymer solutions: a rise in k^1_H would correspond to a reduction in the effectiveness of *o*-chlorophenol as a solvent for the polymer. The exponent α , which is thought to be unity for spinning-grade polyethylene terephthalate (W. R. Throssell, unpublished work), in the relation between $[\eta]$ and number average molecular weight $\bar{M}_n$, $[\eta] = K\bar{M}_n^\alpha$, would also be expected to fall and cause a reduction in $[\eta]$ uncompensated by the accompanying rise in K . Hence, the observed drop in $[\eta]$ does not necessarily indicate a reduction in $\bar{M}_n$, although the magnitude of the effect suggests that this is probable.

The samples which had been more heavily irradiated *in vacuo* show a small but significant decrease in Vicat softening point of 0.27° C. for unit fall in $[\eta]$. This would be consistent with a modification of the chain structure, for example, by branching. It could be caused by occluded degradation products, but these would probably be removed during the crystallizing pretreatment for one hour at 140° C. before the softening-point test. It cannot be due merely to a reduction in molecular weight, for a fall in softening point is not detected in samples produced by hydrolysis of normal polyethylene terephthalate until $[\eta]$ falls below about 30.

In agreement with the conclusions from X-ray data¹, these results suggest that the effect of pile

radiation, at least up to 800 MW. hr., on polyethylene terephthalate is degradative, although possibly accompanied by branching. Furthermore, the relative ease of solution, unchanged by irradiation, of all the samples in *o*-chlorophenol, together with the lowered softening point are inconsistent with the presence of any measure of cross-linking as reported by Charlesby².

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¹ Little, K., *Nature*, **173**, 680 (1954).

² Charlesby, A., *Nature*, **171**, 167 (1953).

³ Huggins, M. L., *J. Amer. Chem. Soc.*, **64**, 2716 (1942).

A Corrected Guldberg Rule

ACCORDING to the well-known rule of Guldberg¹, the normal boiling point of a liquid is two-thirds of the critical temperature on the absolute scale. The rule is not obeyed by liquids of low boiling point², and even for liquids boiling in the range 20–250° C. the ratio T_b/T_c varies from 0.58 to 0.70. Inasmuch as these deviations arise from the different cohesive forces, and the latter are related to the surface tension, we may write

$$T_b \gamma_b^n / T_c = k,$$

where γ_b is the surface tension of the liquid at the boiling point, and n and k are constants. For ordinary organic liquids the relation

$$T_b \gamma_b^{1/2} / T_c = 4/3 \quad (1)$$

is generally more accurate than the simple Guldberg rule, as may be seen from the following data:

Substance	T_b/T_c	$T_b \gamma_b^{1/2} / T_c$
Carbon disulphide	0.586	1.338
Ethyl bromide	0.618	1.335
Benzene	0.629	1.348
1,1-Dichloroethane	0.633	1.348
Cyclohexane	0.640	1.316
Ethyl ether	0.658	1.305
<i>n</i> -Propyl formate	0.663	1.355
Methyl butyrate	0.677	1.349
<i>iso</i> -Amyl formate	0.688	1.344
<i>n</i> -Butyl acetate	0.690	1.342
<i>n</i> -Octane	0.700	1.303

A relation between the parachor and the critical volume may be derived from (1). Since the molar volume of a liquid at the boiling point is three-eighths of the critical volume³, we have

$$\frac{T_b \gamma_b^{1/2} V_b}{T_c V_c} = \frac{1}{2},$$

so that the parachor is given by

$$P = \frac{1}{2} \frac{V_c T_c}{T_b} \quad (2)$$

A study of the experimental data led Ferguson and Kennedy⁴ to propose the empirical formula

$$P = 0.324 V_c^{1/2} T_c^{1/2}$$