

NOTES

Degradation of Polyethylene Terephthalate in Nitrobenzene at 170°C.

The degradation of polyethylene terephthalate (PET) in the melt at 307°C. has been reported by Pohl¹ to involve considerable main chain cracking, with the ester group as an active center and the methylene group beta to the ether oxygen atom as a key weak point. Griehl and Hoffmeister,² also working in the melt, amplified Pohl's results. Marshall and Todd³ found, in the melt at 282.7–320.2°C., a first-order reaction with an activation energy of 32 kcal./mole, accelerated by oxygen.

In the course of preparing block copolymers of PET in nitrobenzene at 160°C., the degradation of the PET under these conditions was examined. Under rigorous exclusion of moisture and air, 15 g. of PET with an intrinsic viscosity of 0.59 were dissolved in 75 ml. nitrobenzene at 190°C. After 30 minutes, when all polymer had dissolved, the solution was brought to and maintained at 170°C. At intervals, 10 ml. portions were withdrawn with a hot pipet and the polymer was precipitated in ether cooled with an acetone-Dry Ice mixture. The precipitated polymer was extracted

TABLE I
Degradation of PET in Nitrobenzene at 170°C.

Time, hr.	$[\eta]$	\bar{M}_n	P	$-\log_{10}(1-x)$
0	0.588	15,900		
0.5 (t_0)	0.577	15,000	78.2 (P_0)	0
11	0.504	13,200	68.9	0.0008
16	0.472	12,100	63.1	0.0013
26	0.433	10,900	56.9	0.0021
46	0.397	9800	51.1	0.0028

with ether for 24 hours in a Soxhlet extractor, dried in a vacuum oven, and stored in a desiccator over P_2O_5 until the determination of $[\eta]$ was carried out.

Molecular weights were extrapolated from Griehl and Neue⁴ using the relationship

$$[\eta] = 1.27 \times 10^{-4} \bar{M}_n^{0.86}$$

The change of \bar{M}_n with time is plotted in Figure 1a. In the first half hour degradation proceeded much faster, since in dissolving the polymer the temperature was kept at 190°C., and any trace of water that might have been present would presumably have been consumed here.

Regardless of where degradation takes place in the chain, the fraction x of bonds broken is given by

$$x = (P_0 - P)/(P_0 - 1)P$$

where P_0 is the \bar{DP}_n at $t_0 = 0.5$ hour, from which point on the temperature was kept constant, and P is the \bar{DP}_n at time t . Assuming the reaction is first order

$$-\log_{10}(1-x) = (k_1/2.303)t$$

A good straight line with $k_1 = 0.49 \times 10^{-7} \text{ sec.}^{-1}$ can be drawn through all but the last point (Fig. 1b).

References

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3. I. Marshall and A. Todd, *Trans. Faraday Soc.*, **49**, 67 (1953).
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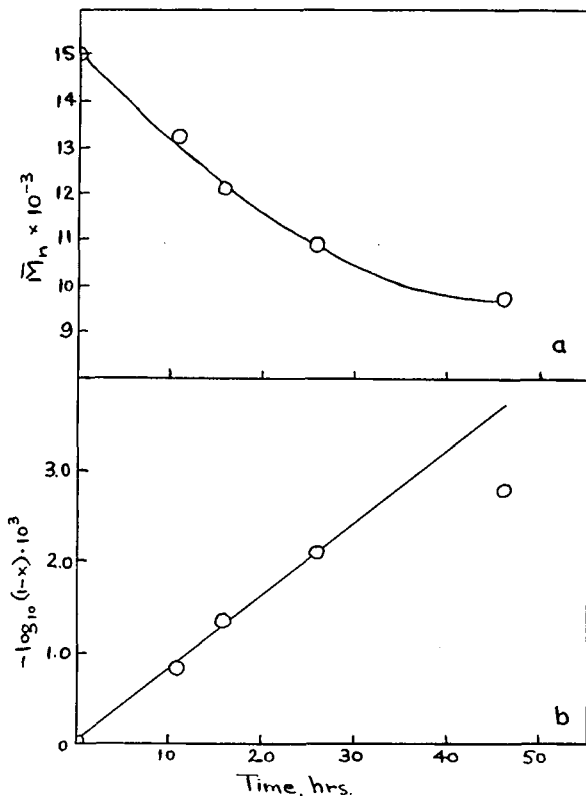


Fig. 1. Degradation of polyethylene terephthalate in nitrobenzene at 170°C.: (a) change in \bar{M}_n with time; (b) bond cleavage with time.