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Note

THE EFFECT OF MOLECULAR WEIGHT ON THE THERMAL STABILITY OF POLYVINYL CHLORIDE

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During an earlier programme of research, we fractionated several samples of polyvinyl chloride by fractional extraction [1]. It has been shown that the thermal stability of PVC depends greatly on the concentration of labile groups such as allylic groups [2], since the concentration of such labile groups varies with the molecular weight of the polymer and its distribution. In the course of this programme we observed a number of previously unreported correlations between molecular weight and thermal stability characteristics, although such behaviour has been shown with other polymers [3].

EXPERIMENTAL

Materials

Several commercial samples of PVC were obtained from the Basrah Petrochemical Complex, with characteristics shown in Table 1. The samples were purified by reprecipitation to exclude the effect of stabilizing additives.

The commercial samples were fractionated by column fractionation which was carried out using mixtures of cyclohexanone and ethanol with several different ratios. The extractions were carried out at constant temperature, i.e. 60 ± 1°C. Several fractions with different molecular weights were separated and characterized via their molecular weight. The characteristics of these fractions are shown in Table 2.

Thermal analysis

Thermogravimetric analysis was carried out on a MOM derivatograph. The measurements were obtained (a) isothermally at 160°C following the

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TABLE 1

Characterization of commercial PVC samples and their thermal characteristics

Sample	$[\eta]$ (cm^3 g^{-1})	$\overline{M}_v$ $\times 10^{-3}$	K	DT(°C) from		Rate of decompn. [a]	Activation energy (kJ mole^{-1})
				DTG	50% decompn.		
Ongrovil	92.3	156.4	76	270	295	11.0	88.2
Sicron	91.4	153.5	70	269	294	11.6	80.3
Low M.W. PVC	68.2	88.3	55	263	283	13.2	61.4

[a] Rate of wt.% loss/min.

TABLE 2

Characterization of some PVC fractions obtained from commercial PVC by fractional extraction

Fraction No.	$[\eta]$ (cm^3 g^{-1})	$\overline{M}_v$ $\times 10^{-3}$	K	DT(°C) from		Rate of decompn. [a]	Activation energy (kJ mole^{-1})
				DTG	50% decompn.		
1	36.0	26.4	37.9	260	281	14.9	30.6
2	52.5	53.8	48.0	261	282	14.3	40.0
3	86.0	136.8	63.1	262	283	13.2	68.0
4	89.5	147.5	66.6	265	285	12.7	72.6
5	95.3	165.1	67.4	266	288	12.1	78.6

[a] Rate of wt.% loss/min.

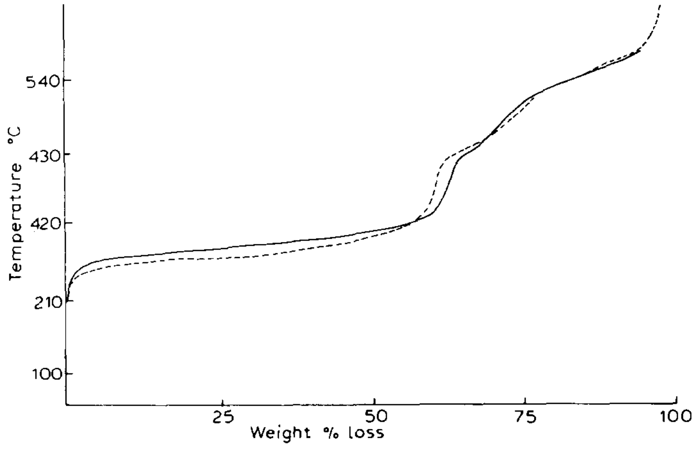


Fig. 1. Thermogravimetric analysis of commercial PVC samples. ———, Ongrovil; ······, low M.W. PVC.

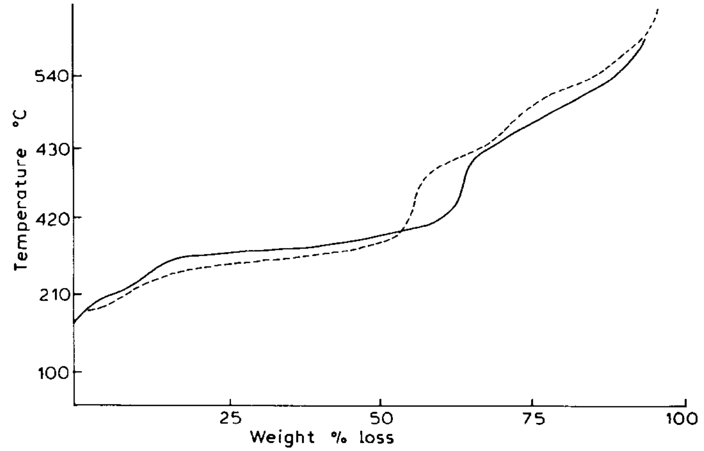


Fig. 2. Thermogravimetric analysis of PVC fractions. ————, Fraction 1; - - - - - -, fraction 3.

procedure used by Askar and Adam [4], and (b) by raising the temperature of the sample at a steady rate (10°C min^{-1}), until the polymer was substantially decomposed (Figs. 1 and 2). All the measurements were carried out against standard α-Al_2O_3 in the presence of air.

(iii) Oxidative degradation

The oxidative degradation experiments were carried out by heating the samples of different molecular weight at 170°C in the presence of atmospheric oxygen. The oxidative degradation behaviour was followed as a function of heating time by measuring the intrinsic viscosity of the samples.

RESULTS AND DISCUSSION

Several thermal stability characteristics were obtained from the thermograms, i.e. decomposition temperature (DT), rate of decomposition at DT and 50% weight loss DT. The results obtained are shown in Tables 1 and 2. The thermogravimetric curves show that the thermal stability of PVC increases with increasing the molecular weight both for commercial (Fig. 1) and fractionated samples (Fig. 2).

The results obtained from the isothermal study at 160°C confirm the molecular weight dependence of thermal stability. Typical isothermal graphs are shown in Fig. 3.

The energy of activation of the decomposition process over the initial 15% weight loss was calculated from the instantaneous slopes of the thermograms at different temperatures. The results obtained for the different samples are

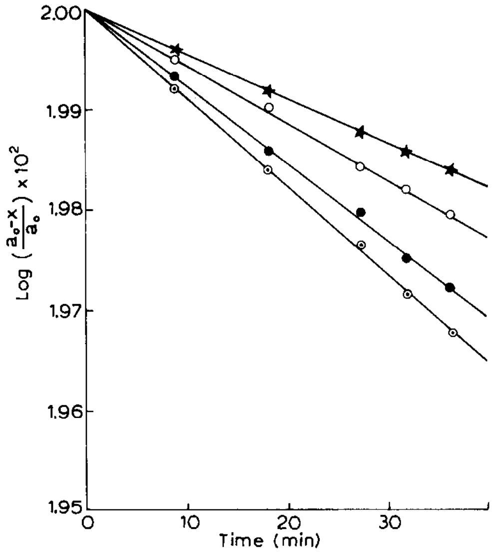


Fig. 3. Isothermal study of PVC fractions at 160°C. ★, Fraction 5; ○, fraction 4; ●, fraction 2; ⊙, fraction 1.

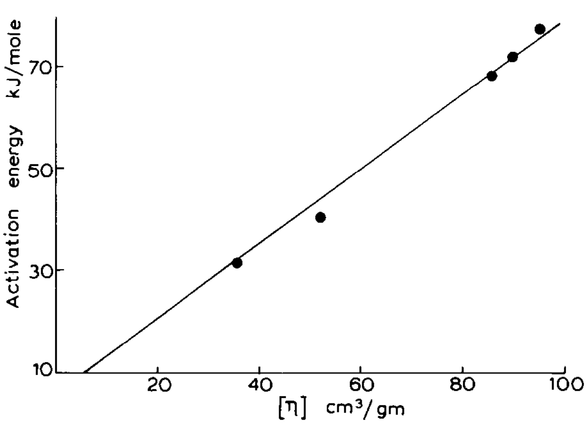
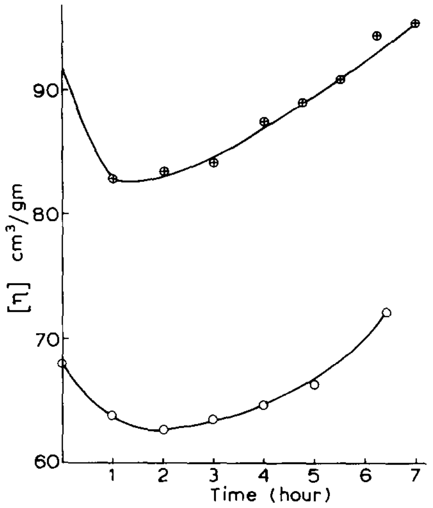


Fig. 4. The relation between intrinsic viscosity and activation energy of PVC fractions.

shown in Tables 1 and 2. The activation energy varies with molecular weight (see Fig. 4).

Concerning the oxidative degradation dependence on molecular weight, the results obtained (Figs. 5 and 6) indicate the occurrence of chain scission and crosslinking during the oxidative degradation process. Thus the stabilized commercial PVC undergoes chain scission then crosslinking because [η] decreases, then begins to increase due to crosslinking reactions while the fractionated samples undergo crosslinking.



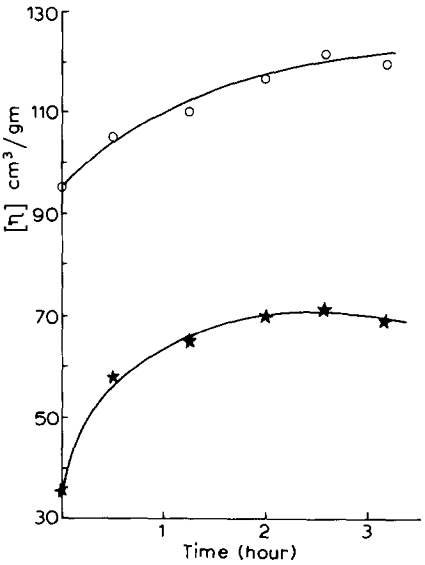


Fig. 5. Thermooxidative degradation of commercial PVC samples at 170°C. ⊗, Sicron; ⊙, low M.W. PVC.

Fig. 6. Thermooxidative degradation of PVC fractions at 170°C. ⊙, $\overline{M_v} = 164\,500$; ★, 35400.

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