Crosslinking and Scission in Thermooxidative Degradation of PVC

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Summary

Crosslinking and chain scission in thermooxidative PVC degradation have been studied. Gel formation was found to give linear Charlesby-Pinner plots, consistent with the constant rate of crosslinking and scission. Similarly to thermal degradation, partial reversibility of crosslinking was observed also in oxygen.

Introduction

In an earlier publication (NAGY et al., 1976) we reported results on the kinetics of gel formation in the thermal degradation of solid PVC. It has been stated that chain scission is negligible in inert atmosphere. It was also shown (KELEN et al., 1978), that gel formation is, at least partially, reversible.

Degradation of PVC in the presence of oxygen is in many respects different from the pure thermal process, e.g., HCl elimination rates are higher. It was recently understood that here the primary elimination process and radical chain oxidation of the polyenes formed are intimately connected, giving a positive feedback system (NAGY et al., 1978; TÜDÖS et al., in press).

Literature data on crosslinking and chain scission in thermooxidative PVC degradation are scarce. Early studies based on viscosity measurements suggest that both processes are effective (DRUESEDOW and GIBBS, 1953; ARLMAN, 1954). A more recent paper claims that in pure oxygen at low conversions ($\xi < 1.5$ %) only chain scission occurs, in air, however, both reactions take place (ABBÅS and SÖRVIK, 1973)

In this publication we present our results obtained from the gel-formation kinetics of thermooxidative degradation of PVC.

Experimental

PVC samples were obtained from the Borsod Chemical Works, Hungary. Sample 70 is a virgin commercial polymer, all others are laboratory products. Sample 38 was polymerized in the presence of a chain-transfer agent. The code numbers correspond to the Fikentscher K values of the samples.

The details of MWD determination by gel permeation chromatography were published earlier (KELEN et al., 1978). The MWD of all samples correspond with good approximation to the most probable (Flory) distribution. Number average polymerization grade (P_n) values see in Table I.

The powder samples were degraded at $180^{\circ}C$ in pure oxygen under atmospheric pressure. The gel content (THF-insoluble fraction) was determined gravimetrically. The reversibility of gel formation was studied by reaction with maleic anhydride (MA) in a cyclohexanone solution (KELEN et al., 1978).

Results and Discussion

All PVC samples degraded in oxygen gave gel-formation kinetic curves with rapid initial increase and well-defined gel points (Fig. 1).
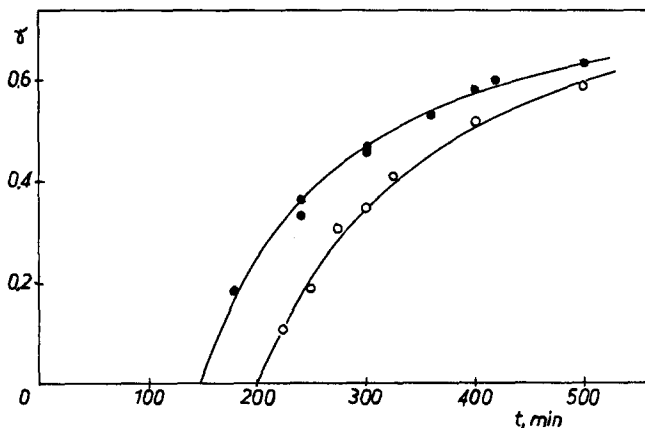

Figure 1.   Typical gel-formation curves of thermo-
oxidatively degraded PVC (o sample 70,
● sample 79; $180^{\circ}C$, pure oxygen).

For systems, where the initial MWD corresponds to the most probable distribution and the probabilities of crosslinking and scission are for all monomer units independent of each other and constant, the following equation was derived (CHARLESBY and PINNER, 1959):

$$s + \sqrt{s} = \frac{p}{q} + \frac{1}{P_n^0 \cdot q} \tag{1}$$

where s is the sol fraction of the polymer (1-s=γ is the gel content), P_n^0 is the number-average polymerization degree, q is crosslinking density (the relative number of crosslinked monomer units to all monomer units) and p is scission density.

If both the crosslinking and the scission processes have a constant rate, i.e., $q = v_q \cdot t$, and $p = v_p \cdot t$, Eq. (1) assumes the following form:

$$s + \sqrt{s} = \frac{v_p}{v_q} + \frac{1}{v_q \cdot P_n^0} \cdot \frac{1}{t} \tag{2}$$

The experimentally determined (s + $\sqrt{s}$) values plotted as a function of the reciprocal degradation time (1/t) give good linearity for all samples. A typical example is shown in Fig. 2.
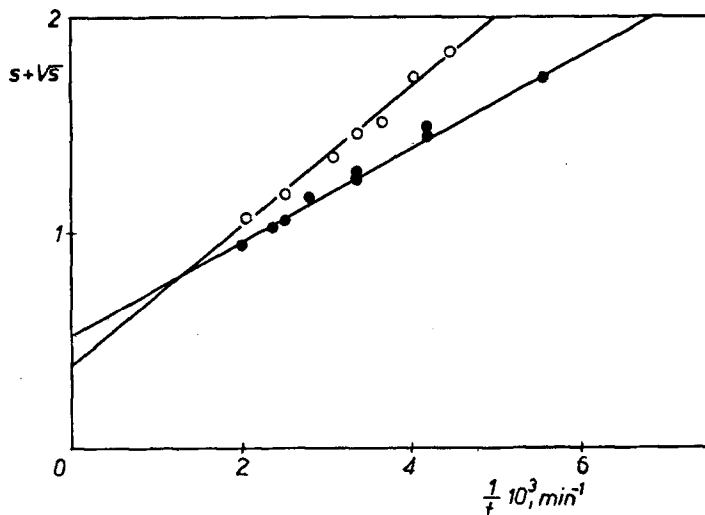

Figure 2. The Charlesby-Pinner plot of PVC samples 70 and 79, degraded at 180°C in oxygen (o sample 70, ● sample 79).

According to our model calculations the linearity of Charlesby-Pinner plots is not too sensitive to changes of crosslinking (v_q) and scission (v_p) rates. Thus the observed linearity does not necessarily mean that v_q and v_p are absolutely constant from the beginning of degradation. The numerical results are collected in Table I.

TABLE I

Parameters of crosslinking and scission in the thermooxidative degradation of different PVC samples.

| K | P_n^O | t_g | ξ_g | $v_p \cdot 10^6$ | $v_q \cdot 10^6$ |
		min	%	min^{-1}	min^{-1}
38	232	179	3.6	12.3	18.2
49	344	174	3.5	3.8	10.3
62	630	176	2.7	2.7	5.9
70	874	200	2.8	1.4	3.6
79	1117	148	2.3	2.2	4.1

K	Fikentscher K value
P_n^O	number average polymerization degree of the virgin sample
t_g	gel point
ξ_g	HCl loss conversion at the gel point
v_p	rate of chain scission
v_q	rate of crosslinking

In some cases, the gel formed in oxidative degradation was treated with maleic-anhydride in cyclohexanone solvent at 80-85⁰. Complete or partial dissolution of the gel (depending on the gel content) was observed, similarly as in thermal degradation (KELEN et al., 1978). Fig. 3 shows a typical example.
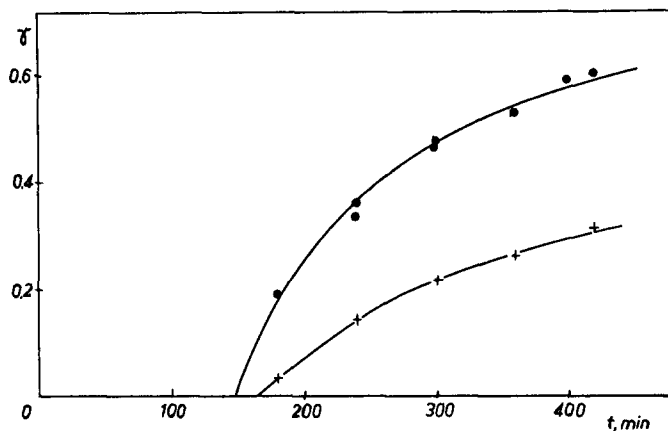
Figure 3. Gel fraction of thermooxidatively degraded
PVC sample 79, before (●) and after MA
treatment (+)

Our present knowledge about the mechanism of
scission and crosslinking is incomplete. It may be
presumed that chain scission is due to polyene oxida-
tion for in the absence of oxygen no scission was
observed. Radical addition and combination as side
reactions of the oxidation process are expected to
play a decisive role in crosslinking as well. Reversi-
bility of the intermolecular bonds formed by radical
reactions seems however improbable. From the reversi-
bility observed it can be concluded that the process
causing gel formation in the thermal degradation is
also operative in the presence of oxygen.

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