Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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T. Kelen[a]
[a] Central Research Institute for Chemistry, Budapest, Hungary

To cite this Article Kelen, T.(1978) 'Secondary Processes of Thermal Degradation of PVC', Journal of Macromolecular Science, Part A, 12: 3, 349 — 360

To link to this Article: DOI: 10.1080/00222337808061384

URL: http://dx.doi.org/10.1080/00222337808061384

J. MACROMOL. SCI.-CHEM., A12(3), pp. 349-360 (1978)

Secondary Processes of Thermal Degradation of PVC

T. KELEN

Central Research Institute for Chemistry
Budapest, Hungary

ABSTRACT

A brief summary of secondary processes in PVC thermal degradation is given. This includes some details of crosslinking and gel formation, cyclization, chain scission and benzene formation, Diels-Alder reaction with additives, as well as oxidation of polyenes.

I would like to outline some special aspects of PVC thermal degradation to which little attention has been given. These are problems which concern secondary reactions of degradation with the participation of highly reactive polyenes formed in primary processes. The study of these reactions is important with respect both to the interpretation of the mechanism of degradation and to the stabilization of the polymer. Some important secondary reactions include crosslinking, formation of aromatic volatiles, Diels-Alder reactions with additives, and oxidation of polyenes. I will not discuss the interaction between hydrogen chloride and polyenes, for example, as this large subject was discussed in detail in our presentation at the IUPAC Symposium on Macromolecules at Helsinki in 1972.

Investigation of secondary degradation processes was made possible by the fact that the importance of polyenes was recognized in several laboratories in the 1960s, and that their formation kinetics, length distribution and participation in further processes have been intensively studied. It would be impossible to present today

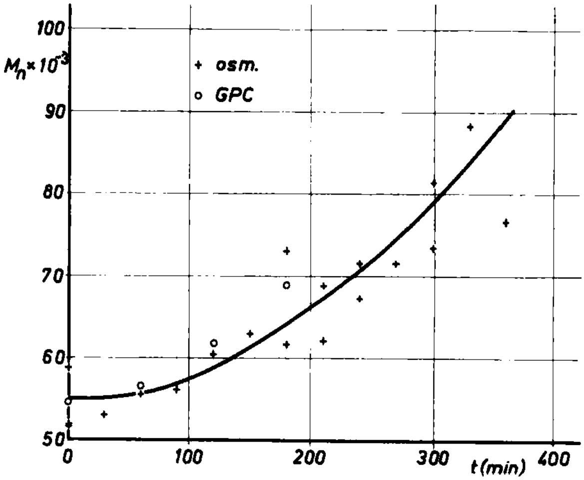

FIG. 1. Change in molecular weight with thermal degradation of PVC (180°C, Ar).

details of all the work which has been performed in this field. I will mention only the well-known investigations of Guyot and his colleagues as well as the results of Braun and co-workers, which are of vital importance.

The most important secondary reactions of polyenes are crosslinking and gel formation. These reactions have been the subject of many investigations [1-6], because of the remarkable consequences observable without direct investigations of the polyenes. I will present some of the most important work performed in this area.

If thermal degradation is carried out on solid samples, a measurable increase in molecular weight can be detected. Figure 1 shows the number-average molecular weight of powder samples degraded at 180°C in a stream of argon as determined by osmometry and GPC.

The intrinsic viscosity also increases in the course of the process (Fig. 2). At a certain crosslinking density, part of the polymer becomes insoluble and a gel is formed. The amount of gel formed, γ, is indicated in Fig. 2. Viscosity values after the gel point are those of the sol phase.

The course of the crosslinking process may also be observed on distribution curves obtained by gel-permeation chromatography. As can be seen (Fig. 3), the distribution becomes wider and shifts towards higher molecular weights. The theory of crosslinking in polymers was developed by Charlesby [7], who studied the effect of

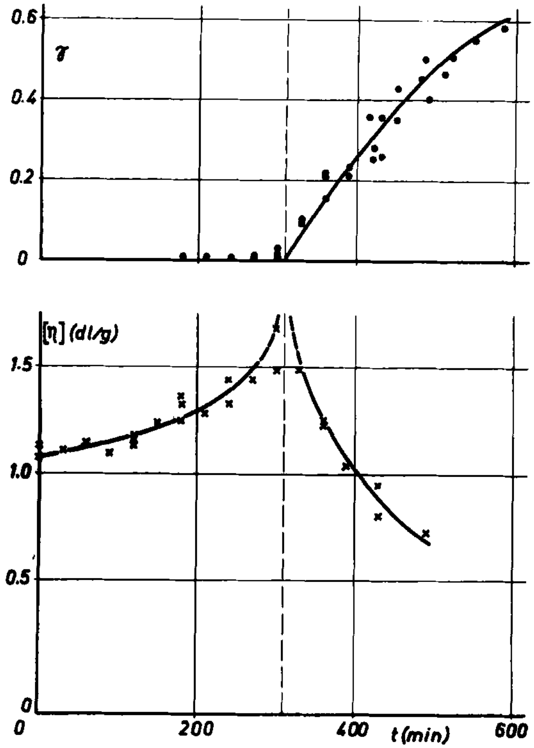

FIG. 2. Change in viscosity of PVC on thermal degradation (180°C, Ar).

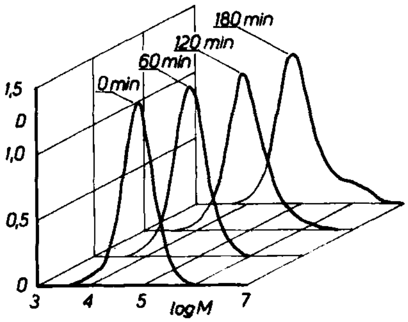

FIG. 3. Molecular weight distribution in PVC on thermal treatment (180°C, Ar).

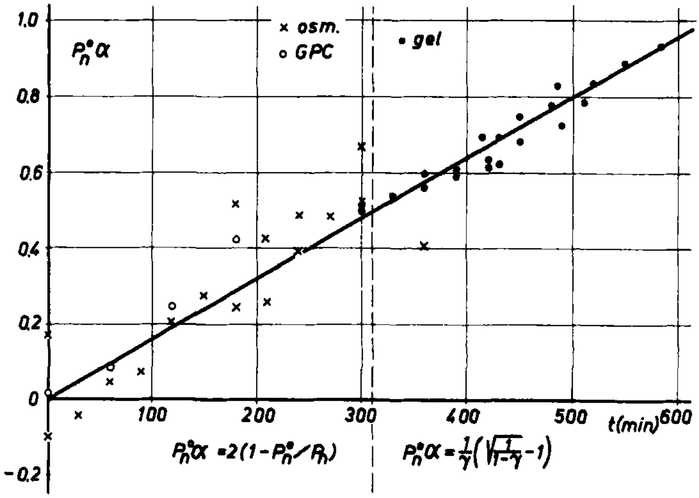

FIG. 4. Dependence of crosslinking density on degradation time. (180°C, Ar).

high energy radiation. He described the number-average degree of polymerization P_n and the amount of gel formed γ as functions of the crosslinking density α:

$$P_n = P_n^0/(1 - 0.5P_n^0 \alpha)$$

$$\gamma = 1 - [1/(1 + \alpha P_n^0)^2]$$

The appropriately transformed relationships of Charlesby fit surprisingly well with the experimental results of thermal crosslinking obtained by osmometry, GPC, and gel fraction measurements (Fig. 4). These show that the dependence of crosslinking density on the degradation time is essentially linear.

As has been shown by several authors [8-12], intramolecular isomerization of polyenes takes place under the conditions of thermal degradation. The process is reflected by the change in concentration of polyenes, which increases in proportion to hydrogen chloride elimination during the first period of degradation only (Fig. 5). Later, the rate of concentration increase slows down, finally almost completely disappearing. The longer the polyene (the greater m is), the sooner this takes place. The effect of the process can also be observed in the ratio of polyene concentrations (Fig. 6). With increasing conversion

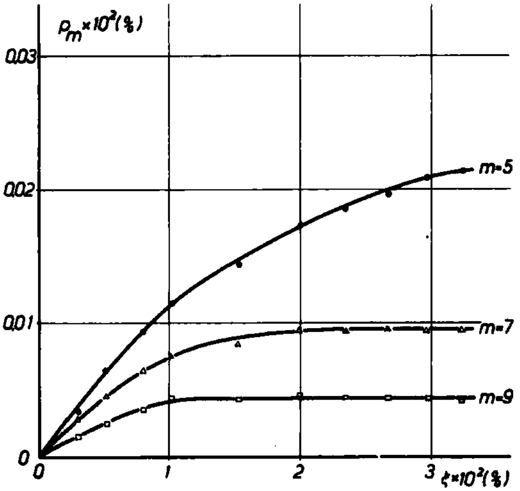

FIG. 5. Relative amounts of polyenes with 5, 7, and 9 double bonds plotted against dehydrochlorination conversion (210°C, Ar).

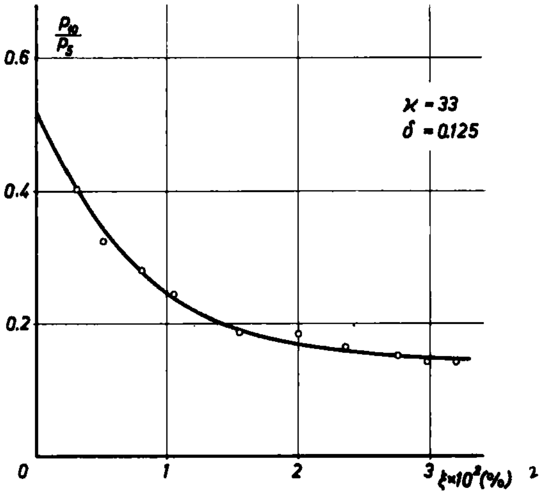

FIG. 6. Concentration ratio of polyenes with 10 and 5 double bonds plotted against the conversion of dehydrochlorination (210°C, Ar).

the distribution shifts to shorter polyenes. I will return later to the meaning of κ and δ.

This phenomenon may be explained by the cyclization of polyenes [1]. It is fully supported by the fact that the reaction can be observed in dilute solution. Because of cyclization, the conjugated polyene becomes shorter or is divided into two shorter sequences separated by a ring. The kinetic treatment of the cyclization process must consider both the secondary decrease and the secondary formation of polyenes.

We have assumed that cyclization proceeds with equal probability on each (m - 2) triad of double bonds in the polyene with m double bonds. The rate of decrease of polyene concentration is $w_m^- = -(m-2)k_c P_m$, where k_c is the cyclization rate constant. On the other hand, the rate of secondary formation of these polyenes is proportional to the concentration of all polyenes containing at least (m + 3) double bonds w_m^+:

$$w_m^+ = 2k_c \sum_{j=m+3}^{\infty} P_j$$

For evaluation the primary formation rate v_m^+ must also be taken into consideration. Then

$$dP_m/dt = v_m^+ - w_m^- + w_m^+$$

There are two limiting cases, depending on whether or not further hydrogen chloride loss, as compared to the number of double bonds in the polyene, can be observed during the chain termination step. In case A, where the termination step leads to a cyclopropane structure, the difference is zero, and

$$v_m^+ = \delta^2 (1-\delta)^{m-1}\, d\xi/dt$$

where δ denotes the reciprocal average length of polyenes and ξ stands for dehydrochlorination conversion. In case B, three hydrogen chloride molecules and a cyclohexadiene structure are formed; then

$$v_m^+ = \delta^2[(1-\delta)^m/(1+2\delta)]/\,d\xi/dt$$

As can be seen in Fig. 7, the experimental data fall between the curves corresponding to the above limiting cases. The relative rate constant of cyclization κ equals 33 in this case. This is for a film sample at 210°C in an atomosphere of argon. The evolution of aromatic hydrocarbons, mainly benzene, in the thermal degradation of

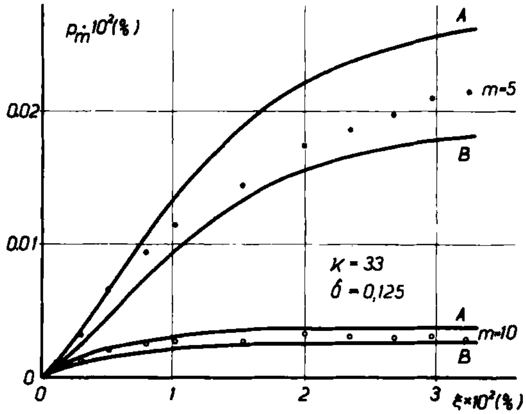

FIG. 7. Amount of polyenes with 5 and 10 double bonds plotted against the dehydrochlorination conversion (210°C, Ar).

PVC has been observed by several authors [1, 13-15]. It seems evident that the formation of these aromatics is related to the cyclization of polyenes.

The kinetics of benzene formation (for example the induction period observed) suggest that the process consists of several steps, and that one of the intermediates may be the cyclized polyene (Fig. 8). Benzene elimination is necessarily accompanied by chain scission, but in the case of solid samples, no decrease in molecular weight caused by chain scission can be observed because of the rapid formation of intermolecular bonds. In dilute solution (1% in trichlorobenzene), however, the rupture is reflected by a small decrease in intrinsic viscosity (Fig. 9).

Diels-Alder reactions, with suitable additives, have been studied by several workers [1, 16, 17]. The problem is of particular importance with regard to stabilization. In studying these reactions, we have carried out, among others, investigations on reactions between predegraded PVC samples and maleic anhydride (MA) or chloromaleic anhydride (CMA), respectively. The decrease in the absorption of polyenes after reaction with maleic anhydride, as shown in Fig. 10, is suitable for kinetic measurements. It is noteworthy that the rate of decrease of the extinction of polyenes of different lengths is independent of polyene sequence length.

The change in extinction corresponds to the expected pseudounimolecular reaction during the initial period only, slowing down later (Fig. 11). It should be noted that in spite of the different reactivities of the additives investigated, the rate of polyene consumption is almost the same in both cases.

The oxidation of polyenes is another extremely important feature,

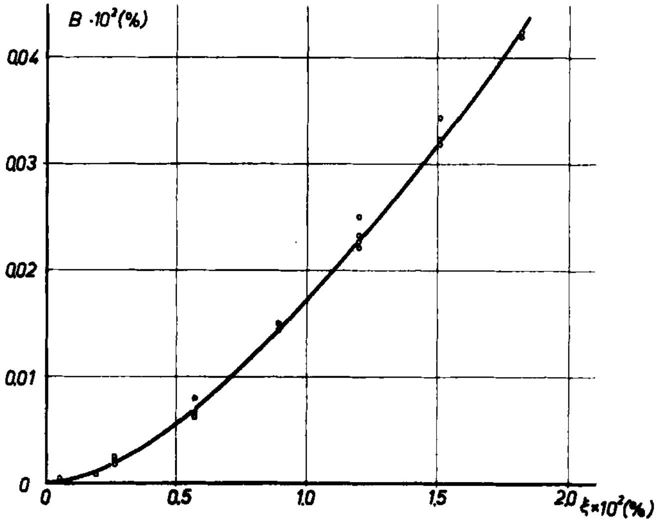

FIG. 8. Amount of benzene plotted against dehydrochlorination conversion (180°C, Ar).

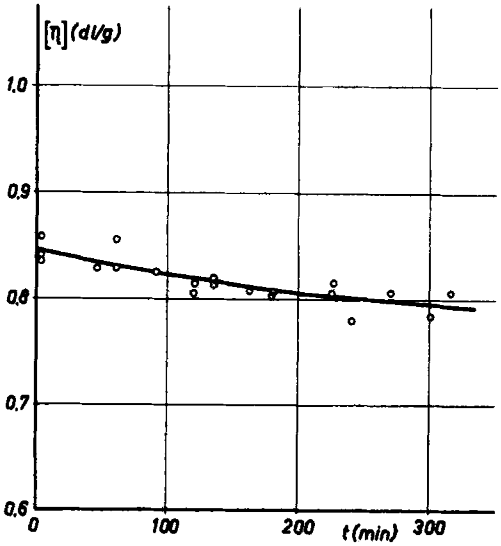

FIG. 9. Intrinsic viscosity of PVC degraded in dilute 1,2,4-trichlorobenzene solution (200°C, Ar).

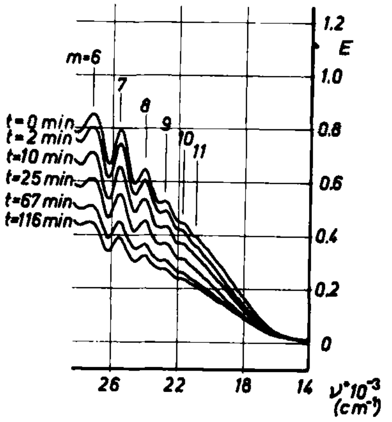

FIG. 10. Change in UV and visible spectrum of degraded PVC on CMA treatment (140°C, 0.058 mole/liter CMA).

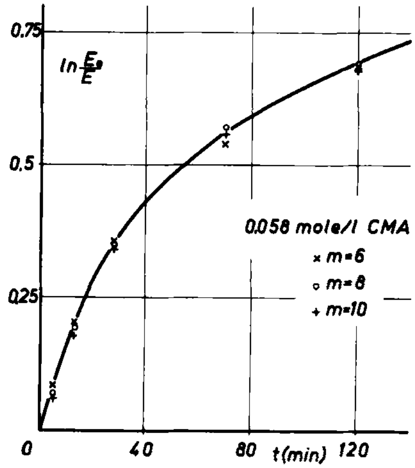

FIG. 11. Change in extinction on reaction of PVC with CMA.

the study of which may lead to a better understanding of PVC degradation under oxidative conditions. Of the great number of important studies carried out in this field, only a few are cited here [8, 18-23]. The process has been studied both as autooxidation and initiated oxidation.

The decreasing extinction of short polyenes approaches a limiting value (Fig. 12), probably because of the formation of oxygen-containing

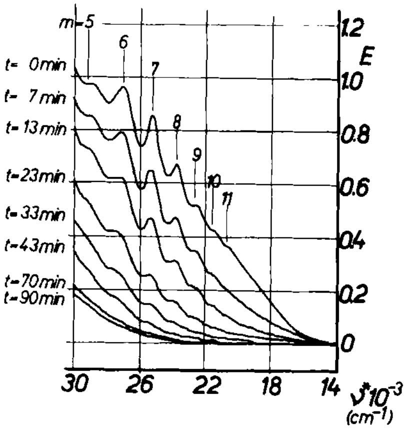

FIG. 12. Change of UV and visible spectrum of degraded PVC during initiated oxidation (60°C, 1.3 × 10^{-3} mole/liter AIBN, O_2).

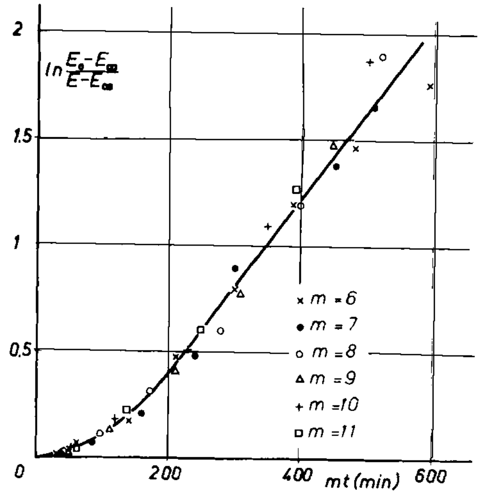

FIG. 13. Change in extinction as a function of mt in the autoxidation of degraded PVC (100°C, O_2).

chromophores. The decrease of extinction in the initiated oxidation differs from that observed in Diels-Alder addition. The rate of decrease is proportional to the length of polyenes (m). The change can be plotted, therefore, uniformly, as a function of the product mt. Figure 13 shows the oxidation of a PVC solution in the absence of initiator, which accounts for the induction period. The peroxide content was followed under the same conditions.

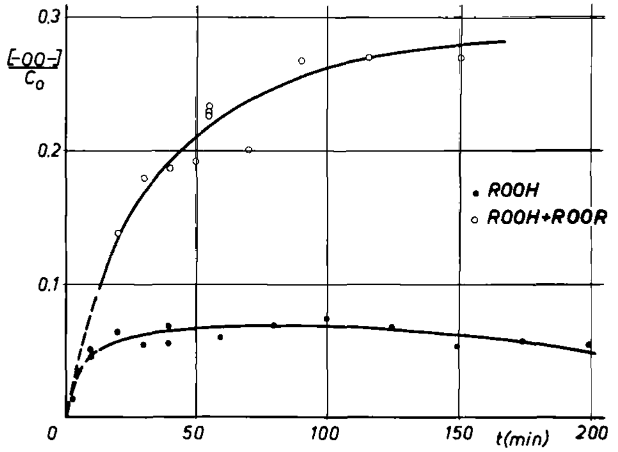

FIG. 14. Formation of peroxides in the autoxidation of degraded PVC (100°C, O_2).

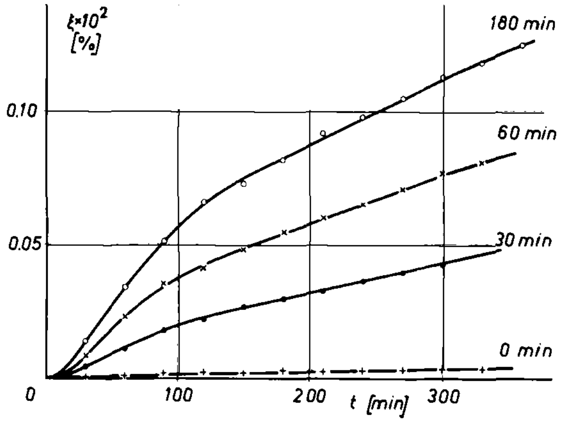

FIG. 15. Dependence of hydrogen chloride elimination on oxidation time (predegradation at 180°C, Ar, for 0, 30, 60, or 180 min; oxidation at 110°C, O_2).

As can be seen in Fig. 14, dialkyl or cyclic peroxides and, in smaller quantities, also hydroperoxides are formed. The concentration of the latter reaches a flat maximum. The radical decomposition of these peroxides is probably the initiating step of oxidative chain reaction. However, the resulting radicals also affect the initiation of hydrogen chloride elimination under these conditions.

Figure 15 shows the dependence of hydrogen chloride elimination on predegradation time at 180°C, in the oxidative degradation of predegraded PVC samples. With increasing polyene content and radical formation the rate of elimination rapidly increases.

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