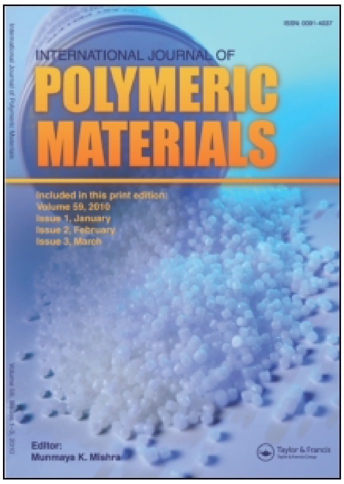

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Troitskii, B. B. and Troitskaya, L. S.(1990) 'The Mathematical Models of the Initial Stage of the Thermal Degradation of Poly(Vinyl Chloride)', International Journal of Polymeric Materials, 13: 1, 169 — 178

To link to this Article: DOI: 10.1080/00914039008039471

URL: http://dx.doi.org/10.1080/00914039008039471

Intern. J. Polymeric Mater., 1990, Vol. 13, pp. 169–178
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Printed in the United Kingdom

The Mathematical Models of the Initial Stage of the Thermal Degradation of Poly(Vinyl Chloride)

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The mathematical models of the initial stage of the thermal dehydrochlorination of PVC are proposed. It is shown that abnormal unstable fragments having constants of rates of degradation equal to 10^{-3}–$10^{-4}\,\mathrm{sec}^{-1}$ have the greatest influence on the thermal degradation of PVC at 180–200°C. The groups having chlorine near tertiary carbon and chloroallylic groups may be such fragments.

KEYWORDS: Thermal degradation, PVC, mathematical models, kinetics, mechanism

There has been considerable discussion about the nature and concentration of unstable fragments of PVC macromolecules and about their influence on the initial stage of polymer degradation.[1–8] It has been established that there are 0.1–0.5 mole per cent of double bonds in the polymer.[2,5,7] PVC contains approximately 0.01–0.05 mole per cent of internal double bonds.[1,2,5,8] The largest part of double bonds places at the ends of PVC macromolecules. Braun, Tüdös *et al.*[1,2] suppose that internal chloroallylic groups have the greatest effect on the stability of PVC. Minsker *et al.*[5] assume all internal chloroallylic groups to be conjugated ketoallylic groups, their concentration is equal to 0.01 mole per cent and they are responsible for low stability of PVC. It has been found 0.1–0.3 mole per cent of branching fragments in PVC having chlorine near tertiary carbon. Berens, Starnes, Abbås, Sorvik *et al.*[3,4] suggest that these groups have the considerable influence on the initial stage of PVC dehydrochlorination. It was shown that PVC macromolecules have 0.01 mole per cent of peroxide and hydroperoxide groups.[1,6,7] Zegel'man *et al.*[6] believe degradation of these fragments to have the greatest effect on the initial stage of dehydrochlorinaion of PVC.

THE THERMAL STABILITY OF IDEALIZED PVC WHICH HAS NO UNSTABLE FRAGMENTS HAS BEEN STUDIED A LITTLE

In this paper it is proposed the mathematical models of the initial stage (up to 6 per cent of conversion) of the thermal dehydrochlorination of PVC by means of is known that average number of conjugated double bonds forming in the thermal degradation of PVC is equal to 3–8.

THE THERMAL DEGRADATION OF LOW MOLECULAR WEIGHT CHLOROHYDROCARBONS HAVING ONLY LINKS OF VC

First of all the thermal degradation of low molecular weight chlorohydrocarbons having only links of VC was considered. The following assumptions were taken into account:

1. Elimination of the first molecule of HCl occurs from the extreme link of VC and dehydrochlorination of chlorohydrocarbon proceeds along the chain without termination. Length of kinetic chain of dehydrochlorination, l_{av}, is equal to the number of monomer links in chlorohydrocarbons. Due to this condition one can use the theory of the consecutive reactions for mathematical models of the thermal dehydrochlorination of chlorohydrocarbons.
2. $k_0 \ll k_1 \ll k_2 \cong k_3 \cong \cdots \cong k_7$, where $k_0, k_1, k_2, \ldots, k_7$ represent the effective constants of rates of dehydrochlorination of VC link and $\sim(\mathrm{CH{=}CH})_n\mathrm{—CHCl}\sim$ groups with $n = 1, 2, 3, \ldots, 7$ correspondingly. It was used the literature values of k_0, k_1, k_2, which have been obtained for the thermal degradation of chlorohydrocarbons in liquid phase in the absence of HCl (Table I).[9] The constants of rates of dehydrochlorination of fragments of PVC macromolecules are equal to the constants of rates of degradation of corresponding low molecular weight chlorohydrocarbons in liquid phase.

Using the theory of the consecutive reactions it is shown that the initial stage of dehydrochlorination of chlorohydrocarbons may be described by the following Eq. (1):[10]

$$[\mathrm{HCl}] = l_{av}c_0^0(1 - e^{-k_0t}) - (l_{av} - 1)c_0^0\frac{k_0}{k_1}(1 - e^{-k_1t}) \tag{1}$$

where c_0^0 represents the initial concentration of model.

TABLE I

Values of rate constants[9] and times of half-conversion in the thermal degradation of fragments of chlorohydrocarbons

Fragment of chlorohydrocarbon, constant of rate of degradation	Temperature of degradation, °C			
	180		200	
	Value of rate constant, sec^{-1}	Time of half-conversion, $\tau_{1/2}$	Value of rate constant, sec^{-1}	Time of half-conversion, $\tau_{1/2}$
$\sim\mathrm{CHCl—CH_2}\sim, k_0$	10^{-7}	1925 hr	$10^{-6.2}$	305 hr
$\sim\mathrm{CH{=}CH—CHCl—CH_2}\sim, k_1$	$10^{-3.9}$	91.6 min	$10^{-3.4}$	28.8 min
$\sim\mathrm{CH{=}CH—CH{=}CH—CHCl}\sim, k_2$	$10^{-1.37}$	12 sec	$10^{-0.97}$	6.5 sec

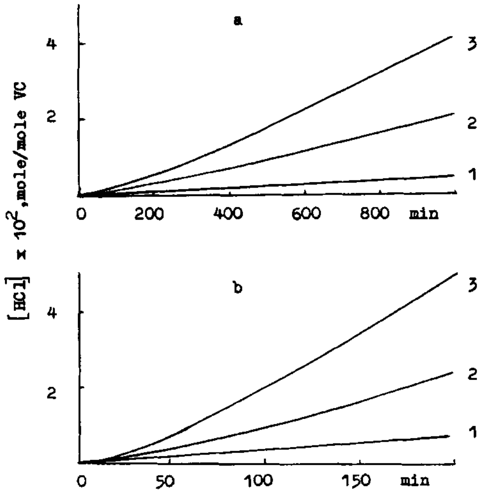

FIGURE 1 Calculated from Eq. (1) kinetic curves of dehydrochlorination of model chlorohydrocarbons having different number of monomer links at 180°C (a) and 200°C (b): $l_{av} = 1$ (1); 4 (2); 8 (3).

Figure 1 shows the calculated curves of dehydrochlorination of model chlorohydrocarbons having 1, 4 and 8 links of VC at 180°C and 200°C.

Differentiation of expression (1) gives the Eq. (2) for the rates of dehydrochlorination of models:

$$\frac{d[\mathrm{HCl}]}{dt} = V_{id} = [l_{av}k_0e^{-k_0t} - (l_{av} - 1)k_0e^{-k_1t}] \cdot c_0^0 \tag{2}$$

From Figures 1 and 2 one can see that except monochlorohydrocarbons the rate of model degradation increases in the early stage and then becomes steady. The increase of rate is connected with accumulation of double bonds (allylic activation, $k_1 \gg k_0$) (Figure 3). Concentration of chloroallylic fragments (c_1) was calculated from the Eq. (3):[10]

$$c_1 = c_0^0\frac{k_0}{k_1}(e^{-k_0t} - e^{-k_1t}) \tag{3}$$

In the stationary part of dehydrochlorination curves the rate of reaction may be described by the following Eq. (4) which is typical for unbranching chain reactions:

$$V_{stat} = V_{init}l_{av} = k_0c_0l_{av} \tag{4}$$

Really in the stationary part of dehydrochlorination curves the rate of formation of chloroallylic fragments is equal to the rate of their degradation:

$$k_0c_0 = k_1c_1^{stat} \tag{5}$$

where c_1^{stat} is the stationary concentration of chloroallylic fragments (Figure 3). On the other hand the time of conversion of diene fragments into polyenes having 3–8 conjugated double bonds is considerably less than the time of degradation of chlorohydrocarbon because $k_2 \gg k_1$ and $k_2 \cong k_3 \cong \cdots \cong k_7$ (Table II).

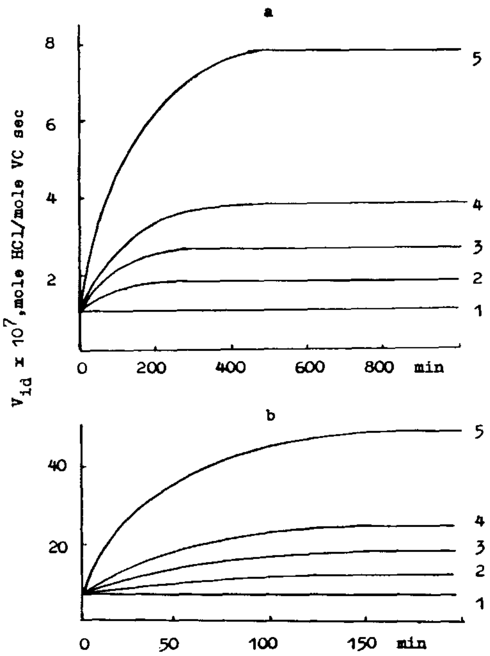

FIGURE 2 Calculated from Eq. (2) curves of dependence of rate of degradation of models having different number of monomer links on time at 180°C (a) and 200°C (b): $l_{av} = 1$ (1); 2 (2); 3 (3); 4 (4); 8 (5).

The times of conversion of diene fragments into polyenes with different number of double bonds were calculated from the Eq. (6):

$$l_{av} = \frac{\sum \text{HCl}}{c_2^0} = \frac{k_2 c_2^0 \cdot t}{c_2^0} = k_2 t \tag{6}$$

where $\sum$ HCl represents summary quantity of HCl which evolves in the thermal degradation of diene fragments up to time t. c_2^0 is initial concentration of diene fragments.

Due to little values of times of conversion of diene fragments into polyenes one can obtain the following expression (7) for the constituent part of rate of model

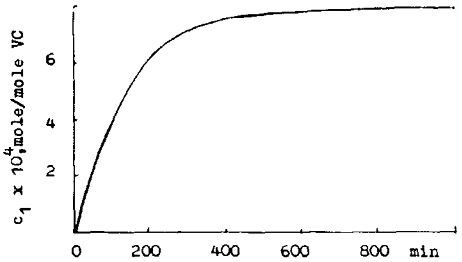

FIGURE 3 Calculated from Eq. (3) curve of dependence of concentration of chloroallylic fragments (c_1) on time in the thermal degradation of model chlorohydrocarbons at 180°C.

TABLE II

Times of conversion of diene fragments into polyenes with different chain length in the thermal degradation of chlorohydrocarbons

Number of conjugated double bonds in polyene	Time of conversion, sec, at degradation temperature	
	180°C	200°C
3	23	9
4	47	19
8	138	56

dehydrochlorination initiated only by degradation of chloroallylic fragments:

$$V_1 = k_1 c_1 (l_{av} - 1) \tag{7}$$

As can be seen from Eq. (2)

$$V_{id} = k_0 c_0 + k_1 c_1 (l_{av} - 1)$$

One obtains the expression (4) under the following conditions: $c_1 = c_1^{stat}$ and the Eq. (5) is realized.

Figures 1 and 2 show that the greater the number of VC links in chlorohydrocarbon (i.e. the greater l_{av}) the greater stationary rate of dehydrochlorination is because after degradation of chloroallylic fragments dehydrochlorination of diene and polyene fragments proceeds with the greater rate up to the end of chain.

The obtained results show that l_{av} is of particular importance in the initial stage of chlorohydrocarbons degradation, i.e. the compound with less number of monomer links are more stable one. If l_{av} is equal to 1 (monochlorohydrocarbon, regular alternating VC-ethylene copolymer, polychlorohydrocarbon in the presence of ideal stabilizer) the rate of model compound degradation is small (Figures 1 and 2).

One can give the detail picture of the initial stage of dehydrochlorination of models of PVC macromolecules. At the beginning the first molecule of HCl eliminates from chlorohydrocarbons with small rate (Table I). Formed double bond increases the degradation rate of adjacent link for 1258 times, $k_1/k_0 = 1258$ at 180 (Table I). Two double bonds accelerate the dehydrochlorination of next link of VC catastrophically, at 180°C $k_2/k_0 = 426579$ (Table I). The time of full conversion of chlorohydrocarbon chain having 3, 4 and 8 links and beginning from diene is very small (Table II), therefore one can say about quasi-chain character of the thermal degradation of chloroallylic fragments. This process may be described by the mathematical expressions which are typical for unbranching chain reactions except the initial period equal to some minutes during which equilibrium between polyenes sets in. After establishment of the stationary concentration of chloroallylic fragments all process of the thermal degradation of model chlorohydrocarbons beginning from elimination of the first molecule of HCl may be described by equation for unbranching chain reactions (Eq. (4)).

It was concluded that the thermal stability of idealized PVC which has no unstable fragments must be lower than that of model chlorohydrocarbons having 1–3 links of VC (the thermal degradation of only these compounds has been studied experimentally)[9] due to large length of macrochain in the polymer.

THE THERMAL DEGRADATION OF LOW MOLECULAR WEIGHT CHLOROHYDROCARBONS HAVING VC LINKS AND UNSTABLE FRAGMENT

It is assumed that the thermal dehydrochlorination of low molecular weight models having unstable fragment (chloroallylic group, fragment with chlorine near tertiary carbon, etc.) and 3–6 links of VC (i.e. $l_{av} = 3\text{–}6$) simulates the thermal degradation of precipitated powders of PVC samples in thin lay with continuous removal of HCl.

Figure 4 shows kinetic curves of degradation of chlorohydrocarbons having chlorine near tertiary carbon which were calculated from the following Eq. (8):

$$[\mathrm{HCl}]_{ter} = c^0_{ter}(1 - e^{-k_{ter}t}) - (l_{av} - 1)c^0_{ter}\frac{k_1}{k_{ter} - k_1}(1 - e^{-k_{ter}t}) + (l_{av} - 1)c^0_{ter}\frac{k_{ter}}{k_{ter} - k_1}(1 - e^{-k_1 t}) \quad (8)$$

where k_{ter} represents the constant of rate of dehydrochlorination of fragment having chlorine near tertiary carbon. c^0_{ter} is the initial concentration of model. The following values of k_{ter} were used: $k_{ter} = 10^{-3,56}\,\mathrm{sec}^{-1}$ at 180°C and $k_{ter} = 10^{-2,94}\,\mathrm{sec}^{-1}$ at 200°C.[11]

The rates of dehydrochlorination of models having chlorine near tertiary carbon (Figure 5) were calculated from the Eq. (9) which was obtained by differentiation of expression (8):

$$V_{ter} = k_{ter}c^0_{ter}\left[e^{-k_{ter}t} + (l_{av} - 1)\frac{k_1}{k_{ter} - k_1}(e^{-k_1 t} - e^{-k_{ter}t})\right] \quad (9)$$

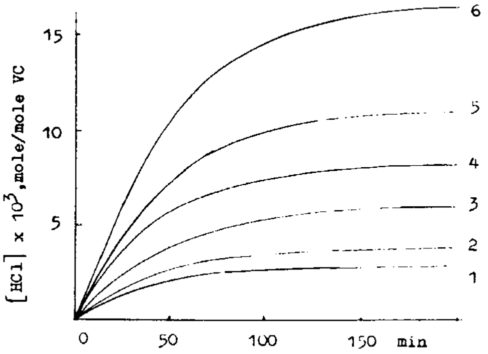

FIGURE 4 Calculated from Eq. (8) kinetic curves of dehydrochlorination of model chlorohydrocarbons having chlorine near tertiary carbon at different chain lengths (l_{av}) and different concentrations (c^0_{ter}) in inert solvent at 200°C. $l_{av} = 3$ (1, 4); 4 (2, 5); 8 (3, 6). $c^0_{ter} = 0.1$ (1, 2, 3) and 0.28 mole per cent (4, 5, 6).

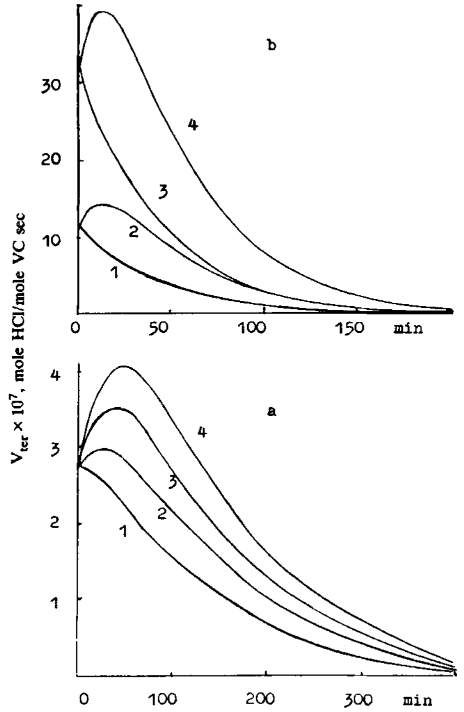

FIGURE 5 Calculated from Eq. (9) curves of dependence of dehydrochlorination rate on time in thermal degradation of chlorohydrocarbons having chlorine near tertiary carbon at different chain lengths (l_{av}) and different concentrations (c^0_{ter}) at 180°C (a) and 200°C (b) in inert solvent. (a) $l_{av} = 3$ (1); 4 (2); 5 (3); 6 (4). $c^0_{ter} = 0.1$ mole per cent. (b) $l_{av} = 3$ (1, 3); 6 (2, 4). $c^0_{ter} = 0.1$ (1, 2); 0.28 mole per cent (3, 4).

As can be seen from Figure 5 the dependences of rates of dehydrochlorination of models with chlorine near tertiary carbon on time have maximum at short times of degradation, the greater l_{av} and c^0_{ter} the more significantly maximum reveals. After maximum meaning the dehydrochlorination rate decreases up to small value during 200 min at 200°C. Thus these models of PVC degrade completely for 200 min at 200°C (Figure 5b). If degradation temperature is reduced maximum rate is observed at greater times. The time of full degradation of models with chlorine near tertiary carbon increases up to 500 min at 180°C (Figure 5a).

Figure 6 shows the dehydrochlorination curves of mixtures of PVC models containing 99.9–99.72 mole per cent of chlorohydrocarbon having only VC links and 0.1–0.28 mole per cent of chlorohydrocarbon having fragment with chlorine near tertiary carbon at different number of links in models at 180°C and 200°C. As can be seen the degradation rates of mixtures increase a little in the early stage and then reduce slowly up to constant value. At small concentrations of model with chlorine near tertiary carbon (at $c^0_{ter} = 0.1$ mole per cent) curves of degradation of mixtures approximate to straight lines after the initial part where increase of rates is observed (Figure 6).

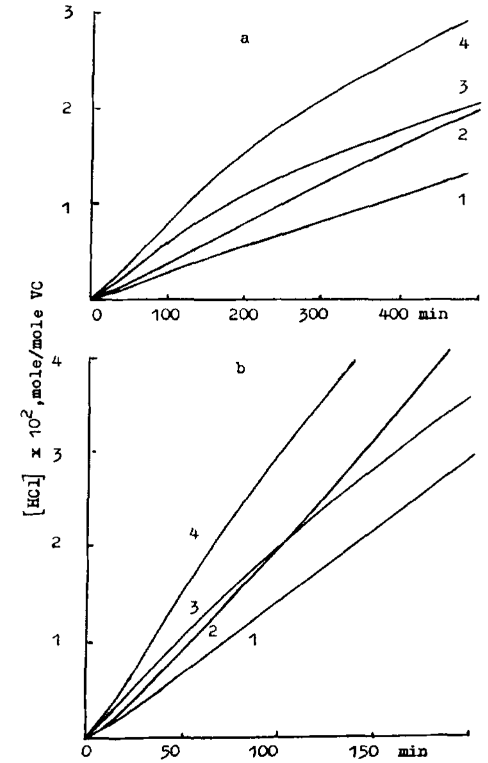

FIGURE 6 Calculated from Eqns (1) and (8) kinetic curves of dehydrochlorination of mixtures of models containing only VC links and models with chlorine near tertiary carbon at different chain lengths (l_{av}) and different concentrations (c^0_{ter}) at 180°C (a) and 200°C (b). $l_{av} = 4$ (1, 3); 6 (2, 4). $c^0_{ter} = 0.1$ (1, 2); 0.28 mole per cent (3, 4).

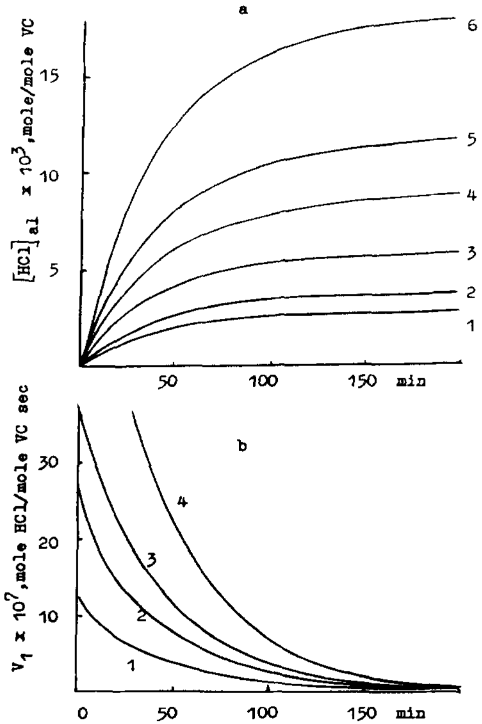

FIGURE 7 Calculated from Eq. (10) kinetic curves of degradation (a) and from Eq. (7) curves of dependence of degradation rate on time (b) in thermal degradation of models having chloroallylic fragments at different chain lengths (l_{av}) and at different concentrations (c^0_1) in inert solvent at 200°C. (a) $l_{av} = 3$ (1, 4); 4 (2, 5); 6 (3, 6). $c^0_1 = 0.1$ (1, 2, 3); 0.3 mole per cent (4, 5, 6). (b) $l_{av} = 3$ (1, 3); 6 (2, 4). $c^0_1 = 0.1$ (1, 2); 0.3 mole per cent (3, 4).

Kinetic curves of degradation of models having chloroallylic fragments (Figure 7a) were calculated from the following Eq. (10):

$$[\mathrm{HCl}]_{\mathrm{all}} = c_1^0(1 - e^{-k_1 t})(l_{\mathrm{av}} - 1) \qquad (10)$$

As can be seen from Figure 7b the initial rate of degradation of models with chloroallylic groups calculated from the Eq. (7) increases in proportion to concentration of chloroallylic fragments and length of chain.

Calculated curves of degradation of mixtures of PVC models containing compounds having only VC links and different concentration of chlorohydrocarbons having chloroallylic group or fragment with chlorine near tertiary carbon at different values of l_{av} were compared with experimental curve of degradation of PVC. Figure 8 shows that experimental curve of PVC degradation at 180°C coincides with calculated ones under the following conditions: 1) $k_0 = 10^{-7}\,\mathrm{sec}^{-1}$, $l_{\mathrm{av}} = 3$, there are 0.27 mole per cent of unstable groups such as fragments with chlorine near tertiary carbon or chloroallylic groups or sum of these fragments in any ratio; 2) $k_0 = 10^{-7}\,\mathrm{sec}^{-1}$, $l_{\mathrm{av}} = 6$; there are 0.13 mole per cent of unstable fragments such as chloroallylic groups of fragments with chlorine near tertiary carbon or sum of these groups in any ratio.

The mathematical models of PVC degradation proposed in this paper give possibility to produce interval of chain lengths, l_{av}, and interval of concentrations of unstable fragments in any sample of PVC.

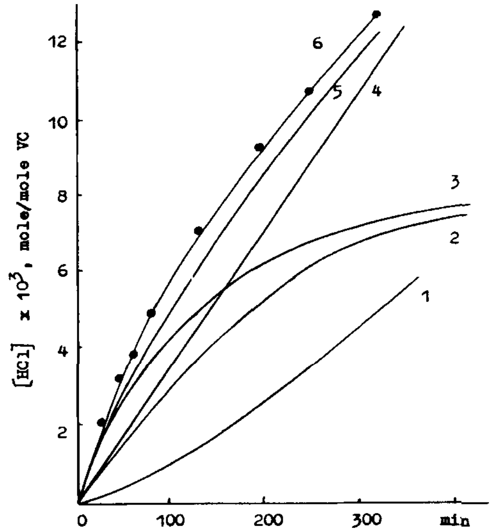

FIGURE 8 Thermal degradation of PVC and mixtures of PVC models at 180°C. (1)–(5) calculated from Eqns (1), (8) and (10) curves of degradation of mixtures of models containing only VC links with models having chlorine near tertiary carbon or chloroallylic groups under the following conditions: $l_{\mathrm{av}} = 3$; there are 0.27 mole per cent of models with chlorine near tertiary carbon or with chloroallylic groups (or $l_{\mathrm{1av}} = 6$; there are 0.13 mole per cent of models with chlorine near tertiary carbon or with chloroallylic groups). Degradation of mixtures of PVC models initiates by dehydrochlorination of different groups: normal links (1); groups with chlorine near tertiary carbon (2); chloroallylic groups (3); normal links and groups with chlorine near tertiary carbon together (4); normal links and chloroallylic groups together (5); (6) experimental curve of PVC degradation in vacuo (~10^{-4} mm) with continuous removal of HCL.

One may neglect the influence of ketochloroallylic groups on the initial rate of PVC degradation at $l_{av} = 3$–6 and their concentration equal to 0.01 mole per cent. At $k_2 = 10^{-0.97}\,\mathrm{sec}^{-1}$ and $l_{av} = 6$ all these fragments degrade during 56 sec at 200°C.

It is known[1] that polymeric peroxides of PVC destroy completely during 5–10 min at 180°C, l_{av} being equal to 1. Pydov[12] has shown by inhibitor method that length of chain of PVC dehydrochlorination initiated by degradation of peroxides is equal to 2. Owing to large values of constants of rates of the thermal degradation of polymeric peroxides, small magnitude of l_{av} and not great concentration of peroxides determined in PVC (0.01 mole per cent) these unstable fragments can not have the greatest effect on the initial stage of PVC dehydrochlorination. But the question about influence of peroxide fragments on the initial stage of polymer degradation is in need of additional study.

Thus, it is shown that abnormal fragments having constants of rates of degradation equal to 10^{-3}–$10^{-4}\,\mathrm{sec}^{-1}$ at concentrations greater or equal to 0.1 mole per cent and at l_{av} equal to 3–6 have the greatest influence on the initial stage (up to 1–1.5 per cent conversion) of the thermal degradation of PVC at 180–200°C. The groups having chlorine near tertiary carbon and chloroallylic groups may be such fragments.

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