Thermal Degradation of Vinylchloride/α-Olefin Copolymers

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The preliminary results obtained for the thermal degradation of vinylchloride/α-olefin copolymers are, in part, unexpected. Decrease of the initial polyene length with the increase of comonomer content is a reasonable consequence of the shorter viny chloride sequence lengths, but the constancy of these lower values in the course of further degradation indicates, that some secondary reactions of the polyenes (e.g. cyclization) must be absent here. The decrease of the HCl elimination rate in case of copolymers differs from the dependence given by the weak sites model. Formally, the rate is proportional to a netative power of conversion, the value of the exponent depending on the composition. These results indicate the necessity of further research for clearing up the unknown details of PVC degradation mechanism.

KEYWORDS: Copolymers, vinylchloride, α-olefins, thermal degradation, elimination of HCl, formation of polyenes, cyclization

INTRODUCTION

Polyvinylchloride, PVC is, even to-day, one of the most important big-volume plastics. Among the commercial polymers it is unique as an inherently unstable material: HCl eliminates easily from PVC resulting unsaturated structures on the polymer backbone, the further reactions of which give rise to rapid degradation of the polymer. Processing and utilization of PVC is possible only by means of suitable stabilizers.

Because of this commercial importance, the PVC degradation and especially the thermal dehydrochlorination process was thoroughly studied in the last fifty years. It must be stated, however, that in spite of the large amount of the investigations, very important aspects of this degradation process are still obscure. First of all, we do not know the exact mechanism of the elementary HCl-elimination process. During the years of PVC degradation research of a lot of various mechanisms—radical, ionic, molecular—was proposed and rejected. It

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is obvious, however, that because of this ignorance the commercially very important PVC stabilization research cannot step forward from its present state.

The most important result of the study of the dehydrochlorination processes was the recognition of the activated elimination. According to this, the HCl molecules eliminate not independently from each other, with the formation of isolated double bonds on the polymer backbone, but in sequences, forming conjugated polyenes (zip process). It was shown that once initiated, the zip proceeds rapidly and after termination, the polyene formed is generally incapable of further growth, indeed, a decrease of the polyene length is found in consequence of secondary processes.

From the zip mechanism follows that the most important step of the PVC degradation is the initiation of zips. It was postulated that this occurs on the weak sites (defects) of the PVC and even the opinion was proclaimed, that the thermal instability of PVC is caused solely by the various defects. Thus, PVC degradation study concentrated in the last years on the various types of defect structures and their effect on the stability. It was wholly ignored, that the zip termination process has a comparable importance too. Zip length is determined by the relative magnitude of zip growth and zip termination rates, thus, for a given initiation rate, the HCl elimination rate depends on the above relation. For an effective PVC stabilizer there are two possibilities of action: the hindrance of the zip initiation or the enhancement of the zip termination.

The study of the zip termination process is not an easy task, however. Mean polyene length values should give directly the ratio of growth and termination rates but they are influenced by the secondary processes too and the eventual changes of zip termination rate are unseparable from this effect. Thus, the influence of changing conditions in the course of degradation (e.g. the effect of polyenes already formed and of the HCl present in the system) cannot be determined.

It exists, however, an indirect possibility for the study of termination process. Clearly, at the end of a chain of vinyl chloride monomer units the zip process stops (physical termination). If the length of vinyl chloride monomer sequences is short enough, the probabilities of the chemical and physical zip termination become comparable and this must be reflected by the degradation characteristics (kinetics of HCl loss and polyene formation). As the mean zip length is typically less than 10, the effect would be detected in the oligomeric range of PVC, barely accessible for study. Suitable copolymers of the vinyl chloride, however, may have VC monomer sequence lengths in the desired range. Copolymers of vinyl chloride with α-olefins are especially promising. The olefin units can be taken as chemically inert and they are incorporated as isolated ones, dividing the VC chain into short segments. The preliminary results of the study on such copolymers is presented here.

EXPERIMENTAL

Copolymers of vinyl chloride with various α-olefins (propene, 1-butene, 1-pentene) were synthetized by radical polymerization at the Institute of Macromo-

lecular Chemistry of the Czechoslovak Academy of Sciences, Prague. From the actual values of the reactivity ratios it follows that under the applied conditions an isolated incorporation of α-olefin units occurs, this was confirmed by NMR measurements too. In this case the mean length of vinyl chloride monomer sequences, $\bar{s}$, is given by the relation $\bar{s} = (1 - x_{ol})/x_{ol}$, where x_{ol} is the fraction of α-olefin units in the copolymer. According to the model of terminal copolymerization, the VC sequences have the "most probable" length distribution with the parameter $\alpha = (1 - 2x_{ol})/(1 - x_{ol})$. The α parameter gives the probability, that a vinyl chloride unit randomly picked out will be followed by another VC unit.

Thermal degradation of the copolymers and of the VC homopolymer prepared under similar conditions was carried out at 200°C temprature in trichlorobenzene solutions, containing 1% of the polymer, under argon gas. For the spectrophotometric measurements aliquots were taken from the solution at regular intervals and these were measured after dilution with the same volume of tetrahydrofurane. From the absorbance values measured at the maxima of the spectra the concentrations of the polyenes (double bond numbers 4 to 12) were calculated by applying the generally used molar extinction coefficients. For all degradation times, the logarithm of the concentrations of polyenes in function of double bond number gave good linear relationships, indicating a geometrical ("most probable") polyene length distribution. The negative slope of the line is the parameter of the distribution, δ, and then the mean polyene length is given by $\bar{n} = 1/(1 - \delta)$.

HCl loss kinetics was determined by conductometric measurements. The eliminated HCl stripped out by the neutral gas stream was absorbed in water the conductivity of which was registered continuously. Conductivity values at even time intervals were converted into conversion values ξ (mol HCl/mol VC monomer unit). The time course of conversion was smoothed and differentiated by fitting second-order polynomial to five neighboring points and taking the function and derivative value at the middle point.

RESULTS

Even the visual observation of the thermally degrading VC/α-olefin copolymer solutions shows clearly, that the conjugation length of these—depending on the α-olefin content—is less than in case of the VC homopolymer: the coloration of the solutions is yellow, contrary to the reddish hue of the homopolymer solutions. On the spectra the differences are clearly seen in the domain of longer wavelengths corresponding to the longer polyenes (Figures 1–2).

The time course of the mean polyene lengths in course of the thermal degradation is shown on the Figures 3 and 4. The homopolymer has an initial polyene length of approximately 6, diminishing with the degradation time relatively rapidly: after 100 min degradation the value is about 3, and the limiting value is about 2.5. Copolymers having over 10% comonomer are characterized with very low initial polyene lengths (about 3). Diminution of the conjugation length is observable in these cases too, but the effect is small, as the limiting value
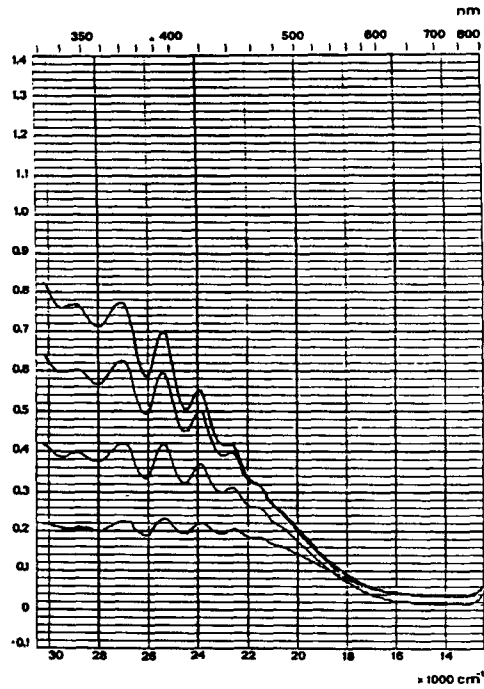
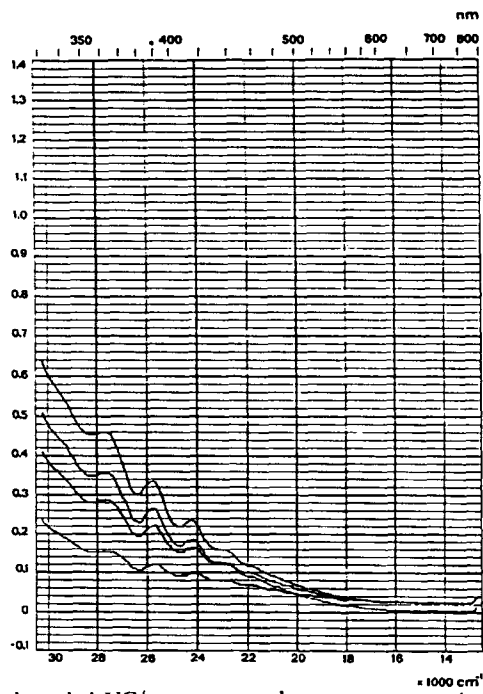FIGURE 1   Spectra of degraded VC homopolymer (degradation times 15, 30, 45, 60 min).

FIGURE 2   Spectra of degraded VC/propene copolymer, propene cntent $x_{ol} = 0.113$ (degradation times 15, 31, 45, 60 min).
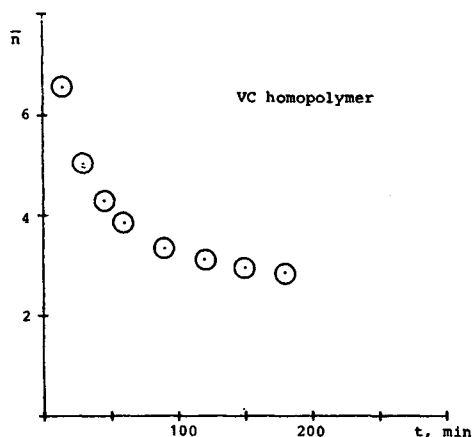
FIGURE 3   Mean polyene length in function of degradation time (VC homopolymer).

seems to be about the same, as in the case of homopolymers. The mean polyene lengths of homo- and copolymers in function of degradation time are given in Table I.

The low initial polyene length observed in case of copolymers is clearly the consequence of the physical zip-termination caused by the short VC monomer sequence length. The quantitative description can be given as follows:

In case of homopolymers, i.e. practically infinite monomer sequence length the formation probability of polyenes with $1, 2, 3 \ldots$ conjugated double bonds is given by the infinite series $(1 - \gamma)$, $\gamma(1 - \gamma)$, $\gamma^2(1 - \gamma) \ldots$ where γ is the probability of the zip growth and $(1 - \gamma)$ is that of the termination. For shorter monomer sequences, however, we have finite series. If the site of zip initiation has only $\underline{k - 1}$ VC monomer unit neighbors, capable of double bond formation,
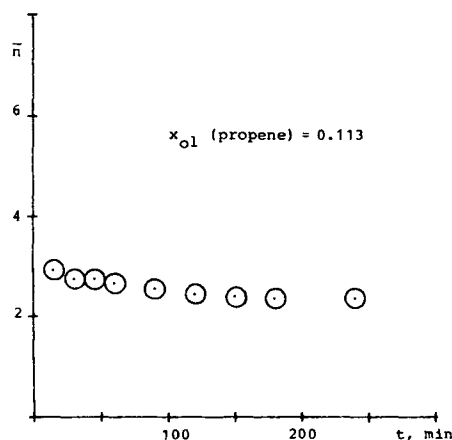

FIGURE 4   Mean polyene length in function of degradation time (VC/propene copolymer, propene content $x_{ol} = 0.113$).

TABLE I

Mean polyene lengths in function of degradation time

Time, min	15	30	45	60	90	120	150	180	240
PVC homopolymer	6.57	5.04	4.30	3.86	3.36	3.13	2.97	2.86	
0.030	6.18	5.07	4.34	3.88	3.77	3.07	2.94	2.83	2.64
0.076 mol. fraction	3.50	3.24	3.06	2.90	2.75	2.62	2.55	2.55	2.48
0.113 propene	2.96	2.77	2.77	2.68	2.56	2.46	2.42	2.38	2.39
0.144	2.95	2.87	2.77	2.65	2.52	2.42	2.38	2.33	2.33
0.020	4.30	3.82	3.54	3.25	3.04	2.90	2.78	2.74	2.67
0.081 mol. fraction	3.58	3.77	3.57	3.31	3.06	2.91	2.79	2.68	2.62
0.101 pentene-1	3.22	3.19	3.03	2.88	2.67	2.58	2.53	2.41	2.40
0.123	3.00	2.92	2.80	2.70	2.56	2.43	2.37	2.38	2.31

the series will be terminated at k double bonds, i.e. $(1 - \gamma)$, $\gamma(1 - \gamma) \cdots$ $\gamma^{k-2}(1 - \gamma)$, γ^{k-1}.

Taking into account only one zip growth direction, the number of possible zip initiation sites having no VC unit neighbor is clearly equal to the total number of VC monomer sequences. The number of possible initiation sites having exactly one VC unit attached is the same less the number of VC monomer sequences of length and so on. The relative numbers of this series can be given then as 1, α, α^2, ..., is the monomer sequence length distribution parameter. Combining these with the finite series of double bond distribution given above and summing up, it becomes clear, that in this case too we have an infinite geometrical distribution of polyene lengths with the parameter $\delta = \alpha\gamma$ and $\bar{n} = 1/(1 - \delta) = 1/(1 - \alpha\gamma)$. The dependence of the mean initial polyene length in function of the copolymer composition can be given then as

$$\bar{n} = \frac{\bar{N}(1 - x_{ol})}{1 + (\bar{N} - 2)x_{ol}}$$

where $\bar{N} = 1/(1 - \gamma)$ is the mean polyene length of the homopolymer and x_{ol} is the molar fraction of the olefin comonomer, incorporated as isolated units in the copolymer. Figure 5 shows the experimentally determined $\bar{n}$ values at 15 min degradation time in function of copolymer composition together with the theoretical dependence calculated by the above expression.

We can state that the experimentally obtained mean initial polyene length values are not inconsistent with the probability model taking into account both chemical and physical zip termination. More accurate experimental determinations are prohibited by the low values of polyene concentrations at the beginning of degradation and later on the kinetically determined distribution will be modified by the secondary processes. These secondary processes were subjects of intensive study earlier and it is thought that the main reaction is the intramolecular cyclization of polyenes, resulting in the reduction of conjugation length. It is assumed, that the polyene length observed at later degradation times approximates a dynamic equilibrium value determined by the (constant) length of the originally formed polyenes and the rate of secondary processes, resulting in
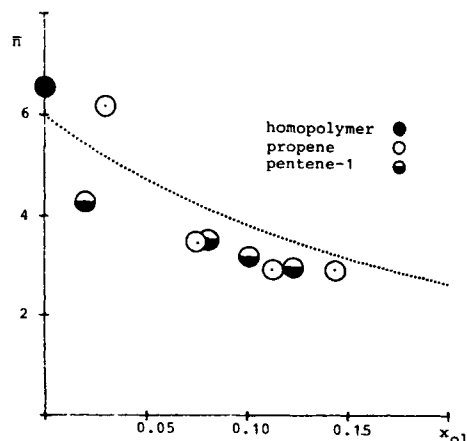
FIGURE 5 Mean polyene lengths determined after 15 min degradation in function of comonomer content. The dotted line was calculated with the initial mean polyene length of the homopolymer $\bar{N} = 6$.

length reduction. The near constancy observed for copolymers with higher α-olefin content is not easily explainable in such a way.

HCl loss kinetics was characterized in case of both homopolymers and copolymers by a decreasing HCl split-off rate. In the study of PVC dehydro-chlorination kinetics it is generally assumed, that this diminution of rate is connected with the consumption of weak, labile sites of the polymer. According to the general opinion, initiation of the HCl elimination of zips occurs preferentially by participation of "weak" (allylic, teritary etc.) chlorines and initiation on regular chain segments (random initiation) is much more slower. At the beginning of the degradation, the rates of these two initiation processes are of the same order of magnitude in case of normal PVC polymers (laboratory polymers, enriched in allylic or tertiary chlorines, can have much higher proportion of weak-site initiation) but the number of labile sites diminishes rapidly and the initiation rate approximates the value determined by the random initiation. As the zip length must be the same for zips initiated on weak and regular sites, the HCl elimination rate can be given as follows:

$$W_{HCl} = \bar{N}(w_i + h_0 \exp(-k_h t))$$

where w_i is the initiation rate on regular structures, taken as practically constant for low conversions, h_0 is the initial concentration of weak sites and k_h the unimolecular rate constant of their decomposition.

In case of copolymers the HCl elimination rate may be influenced by the shorter zip length $\bar{n} < \bar{N}$ and the different number of weak sites. As homo- and copolymers were prepared under the same conditions and the incorporated alkyl groups cannot have an activation effect, we believe that the concentraton of weak sites must be similar in all cases. Then, the time course of conversion rate should be similar of all homo- and copolymers and the rate values proportional to the initial polyene length. This is, however, not confirmed by the experimental observations. With increasing α-olefin content, the initial conversion rate of the
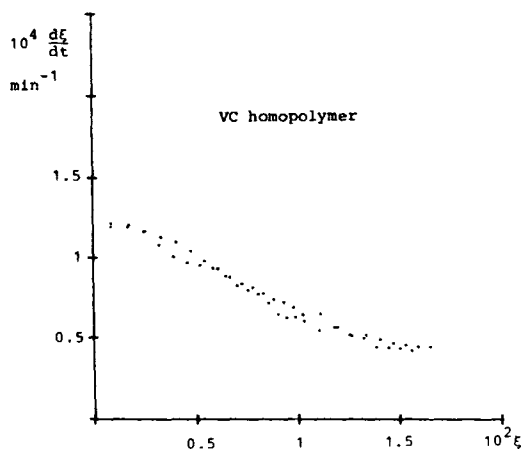
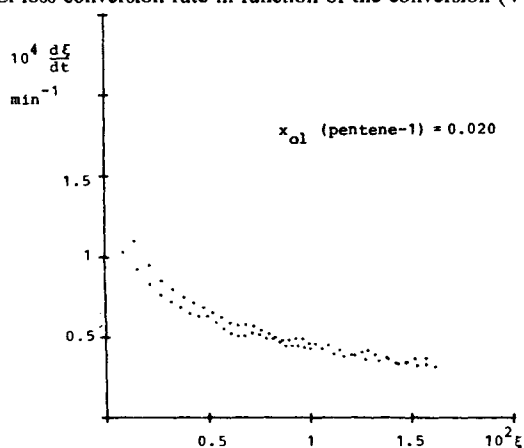FIGURE 6   HCl loss conversion rate in function of the conversion (VC homopolymer).

FIGURE 7   HCl loss conversion rate in function of the conversion (VC/pentene-1 copolymer, $x_{ol} = 0.020$).

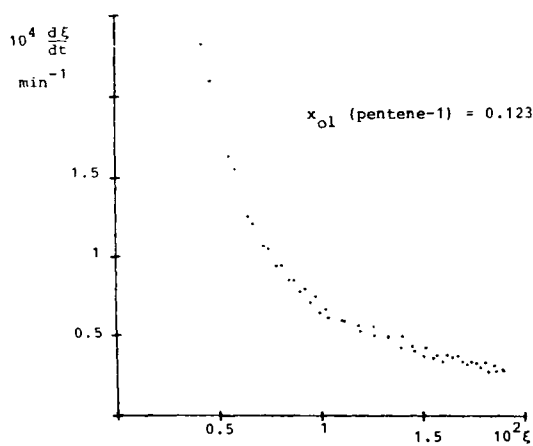FIGURE 8   HCl loss conversion rate in function of the conversion (VC/pentene-1 copolymer, $x_{ol} = 0.123$).
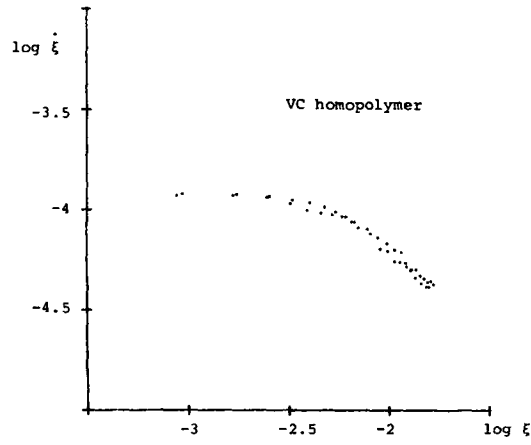
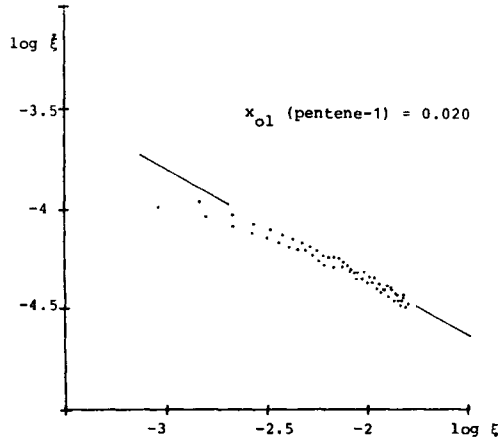FIGURE 9   Log rate vs. log conversion dependence of the VC homopolymer.

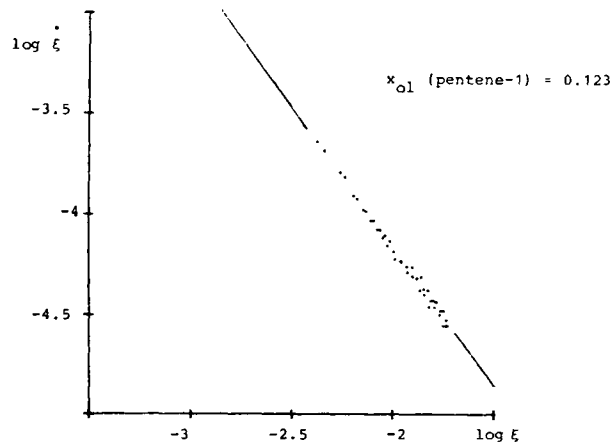FIGURE 10   Log rate vs. log conversion dependence of VC/pentene-1 copolymer, $x_{ol} = 0.020$.

FIGURE 11   Log rate vs. log conversion dependence of VC/pentene-1 copolymer, $x_{ol} = 0.123$.

TABLE II

Apparent reaction order of the conversion
for VC copolymers

mol fraction of comonomer	d log $\dot{\xi}$/d log ξ
comonomer: propene	
0.030	−0.67
	−0.75
0.076	−0.83
	−0.95
0.113	−0.19
	−1.00
0.144	−1.43
	−1.45
comonomer: pentene-1	
0.020	−0.56
0.081	−0.96
	−0.81
0.101	−0.97
0.123	−1.39

copolymers becomes higher (the effect of decreasing zip length is overcompensated) and the decrease of rate with the degradation time is more pronounced.

For comparisons, the conversion rate vs. conversion representations were found more informative, than the conversion-time diagrams. Figure 6 shows, that the homopolymer degradation rate diminishes nearly linearly in the range investigated, after the transient initial period. (If there is only weak-sites initiation, the diagram is perfectly linear with the slope—k_h, if there is random initiation too, after the linearly decreasing section the $\dot{\xi}$ values approximate gradually a constant value). Contrary to this, the diagrams obtained for copolymers indicate hyperbolic decrease of rate with increasing conversion (Figures 7 and 8).

The differences between the homo- and copolymers are even more pronounced on the plots of log $\dot{\xi}$ vs. log ξ values. In case of the homopolymer a transition between the initial and the random-initiation rate is indicated and the dependence is very well described with the parameters $\bar{N}w_i = 3 \cdot 10^{-5}$, $\bar{N}h_0 = 10^{-2}$ and $k_h = 10^{-2} \, \text{min}^{-1}$ by the defect-sites model. For the copolymers, however, good linear dependences were found, with exception of the 2.0% comonomer containing sample, where some curvature is present, but this diagram is distinctly different too from the one obtained for the homopolymer (Figures 9–11). From the slopes of the linear dependences the apparent reaction orders of the conversion can be determined. These are increasingly negative with the increase of comonomer content (Table II).