

POLYMER-ANALOGOUS REACTIONS OF POLYENES IN POLY(VINYL CHLORIDE)

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ABSTRACT

The primary process in the thermal degradation of PVC in an inert atmosphere and at relatively low temperatures, is the elimination of hydrogen chloride molecules and the formation of polyene sequences of different lengths. The polyenes formed are highly reactive and participate in different secondary reactions.

It has been shown for PVC samples degraded both in dilute solution and in the solid state that the amount of polyenes does not correspond to the degree of dehydrochlorination: proportionality may be observed only at the initial stage of degradation and, later on, the number of double bonds in the system is much lower than the amount of hydrogen chloride molecules split off. With the increase of conversion the increase in the amount of polyenes containing three or more double bonds gradually slows down and, later on, practically ceases. This phenomenon is also quantitatively well interpretable by intramolecular cyclization (backbiting) of polyenes. The reaction leads to cyclohexadiene structures. On completing the kinetic treatment of the process, we determined the relative rate constant of cyclization.

Reactive dienophilic reagents readily react with the polyenes formed in degraded PVC. Based on the changes observed in the u.v. and visible spectra, a kinetic study was made on the Diels-Alder reaction with chloromaleic anhydride. The kinetic treatment, performed on the basis of a presumed mechanism, allowed the determination of the rate constants and their temperature dependence.

Depending on the experimental conditions, the polyenes formed in the course of degradation may participate in other reactions as well. Some of the possible reaction routes are: the change in molecular weight, the formation of low molecular weight aromatic compounds (e.g. benzene) and the considerable proton exchange observed in the reaction of polyenes with hydrochloric acid.

INTRODUCTION

Considering the use and consumption of synthetic materials, polyvinyl chloride stands second in the world. Although it has numerous excellent properties, degradation takes place at a considerable rate at the usual temperature of processing.

Publications dealing with the degradation of PVC (in an inert atmosphere, at 150–250°C) all agree on a dehydrochlorination process and simultaneous

formation of conjugated double bond sequences (polyenes) in the polymer chain¹.

These polyenes give characteristic u.v. and visible spectra of degraded PVC. To each band of these complex spectra, we may assign a very intense main absorption band² appearing at the longest wavelength in the individual spectrum of each polyene.

There is no essential difference of opinion regarding the polyene lengths assigned to the bands. Several authors suggest that the u.v. and visible spectra of degraded PVC can be quantitatively evaluated and the extinction coefficient of polyenes of different lengths can be determined^{3,4}.

Most authors agree that following relatively slow initiation (elimination of the first hydrogen chloride molecule) the reaction will 'zip' along the polymer chain to leave conjugated unsaturated sequences. There is, however, a divergence of opinion regarding the mechanism of the reaction, the initiation step, chain termination, the length of the 'zip' and other important problems, which are the subjects of research all over the world today⁵.

The further fate of the polyenes so formed is, however, a field hardly touched by investigators, although it is both theoretically and practically a very important terrain. The applicability of PVC is much affected by even a relatively small amount of polyenes formed in the course of processing. Conjugated polyenes may initiate further different reactions, e.g. oxidation. Polymer analogous reactions converting the polyenes into other less sensible groups bear, therefore, considerable significance considering the stabilization of PVC. Another important problem in the processing and application of PVC is discolouration, which may also be reduced or eliminated by appropriate polymer analogous reactions.

In the course of our earlier investigations, it has been found and verified⁶, as evidence of polyene reactivity, that polyenes react with hydrogen chloride and thus, evidently, also with the hydrogen chloride formed in the course of degradation. The considerable proton exchange observed in this type of polymer analogous reaction of polyenes supports the possibility of readdition of hydrogen chloride to the degraded polymer.

In this work, we deal with two further polymer analogous reactions: intramolecular cyclization reaction of polyenes and their Diels-Alder reaction with active dienophilic components.

It should be noted that, depending on the experimental conditions, the polyenes formed during degradation take part in other—non-polymer analogous—reactions as well. The changes in molecular weight and the formation of low molecular weight aromatic compounds (e.g. benzene) also point to such reactions.

1. CYCLIZATION OF POLYENES DURING DEGRADATION

In this work we mainly applied the experimental methods described in detail in our previous papers⁶. We used the polymers Ongrovil S 470, a commercial PVC (further on: S 470 PVC), and prepolymerized laboratory PVC (further on: E PVC), both suspension-polymerized Hungarian products.

Our measurements were carried out in a 1,2,4-trichlorobenzene solution of 1 per cent PVC, and on powder or film samples, in the temperature ranges

160–210°C and 160–230°C, respectively. The samples were degraded in glass vessels flushed with purified argon and placed in a silicone oil thermostat. The hydrogen chloride evolved in the reaction was transferred with argon into a conductivity cell; the conductivity was measured and registered. From the calibration, we may obtain the amount of hydrogen chloride evolved, and from this (knowing the weight of the samples) the conversion of hydrogen chloride elimination can be calculated.

The PVC films investigated were prepared from a solution of PVC in previously deperoxidized tetrahydrofuran (THF). In order to remove the solvent, the films were kept *in vacuo* at 80–100°C for several hours. For the purpose of degradation, a 6–7 cm² of the film was glued on a U-form glass frame with a few drops of tetrahydrofuran.

The degradation flask holding the sample was first flushed with an argon stream for about half an hour and then placed in a thermostat preheated to the temperature of degradation. U.V. and visible spectrophotometric investigations were performed on the films by interrupting the degradation. The concentration of polyenes was calculated by using the extinction coefficients determined by Popov and Smirnov for polyenes formed in the degradation of poly(vinyl alcohol) films⁴. It should be noted here that the assignment of the polyene lengths to the individual bands as well as the extinction coefficient values are less reliable for diene and triene and for polyenes containing more than 10–12 conjugated double bonds, than for those containing 5–10 double bonds.

The degraded powder samples were dissolved in peroxide-free tetrahydrofuran, for spectrophotometry. The extinction coefficients of polyenes for THF solution were determined by dissolving in THF the degraded PVC film after spectrophotometry, taking into account the extinction coefficients of the film.

Spectrophotometry of the degraded PVC solution was carried out by taking samples without interruption of the degradation process. In order to prevent polymer precipitation the solution was diluted with THF (1:1) prior to photometry. The extinction coefficients were equivalent to those of pure THF solution. Owing to the self-absorption of TCB, the spectra could be evaluated only for polyenes containing more than four conjugated double bonds.

Our studies on the formation of benzene were carried out with powder samples. The benzene formed in the course of degradation was passed with an argon stream into 0.1–0.2 ml isoctyl acetate in a trap cooled with dry ice-acetone, and the product was determined by gas chromatography.

In our earlier publications dealing mainly with degradation of PVC dissolved in diisooctyl adipate⁶ we showed that, generally, in the initial phase of degradation (up to some tenth per cent conversion) the length distribution of polyenes is approximately a geometrical distribution. Similar results were found in experiments carried out on PVC film and powder samples.

Studying the reaction at somewhat higher—though still low—conversions (of some few per cent), we ascertained that the concentration of polyenes is, in fact, proportional to the extent of dehydrochlorination only in the initial phase of the reaction.

This fact is well demonstrated in *Figures 1 and 2* where the conversion dependence of the concentrations of polyenes containing 5, 7 and 9 conjugated

double bonds (p_5 , p_7 and p_9 in the percentage of monomeric units) and that of the concentration-ratio p_5/p_{10} is shown (S 470 PVC film sample, 210°C).

In the course of degradation, the increase in concentration gradually slows down, first for longer then for shorter polyenes, and the rates become stationary at a certain degree of conversion. Since these changes are faster in the case of long polyenes, it may also be established that polyene distribution changes with the time, and the average length of polyenes decreases with increasing conversion—as illustrated by the increase in the value of p_5/p_{10} .

The amount and length distribution of polyenes change with the conversion as outlined above, irrespective of the sample used for degradation (film, powder or solution), a fact very important in the interpretation of the phenomena.

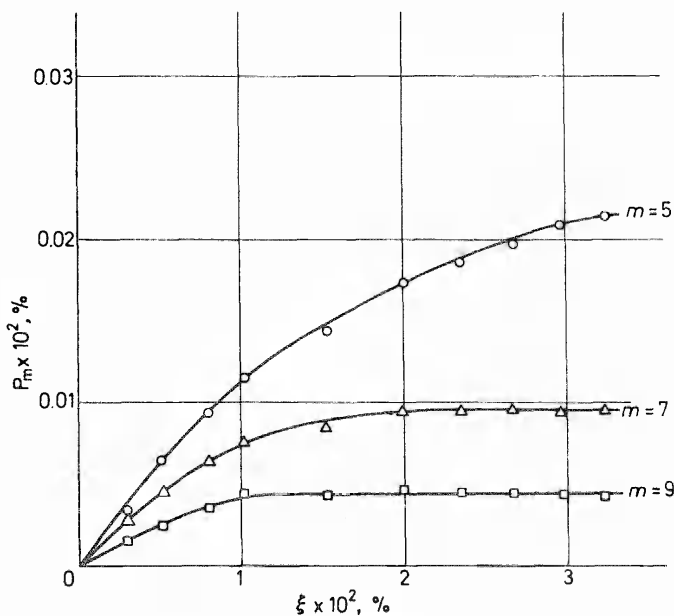


Figure 1. Relative amount of polyenes containing 5, 7 or 9 double bonds, plotted against dehydrochlorination conversion (S 470 PVC film, 18 μ m, 210°C).

Some authors have earlier made qualitative observations⁷ according to which the amount of polyenes formed in the course of degradation is not proportional to the conversion of dehydrochlorination. However, no quantitative conclusions have been drawn, that is, the phenomena have not been interpreted.

Obviously, the decrease in the amount of polyenes (related to the conversion) is not caused by a radical change of the mechanism of degradation. The formation rate of polyenes is proportional to the rate of dehydrochlorination even in the later phases of degradation. This points, therefore, to a chemical reaction consuming the polyenes formed. The fact that the consumption of polyenes in dilute solution takes place at a higher rate than in the solid phase (see later), suggests a first order reaction. On the other hand, under the conditions of degradation there is no such agent which might cause polyene con-

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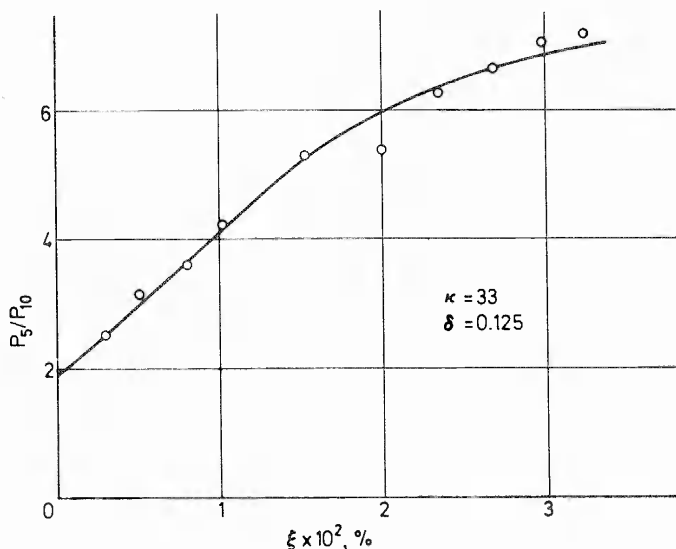


Figure 2. Concentration ratio (p_5/p_{10}) of polyenes containing 5 and 10 double bonds, plotted against the conversion of dehydrochlorination. The curve drawn designates the calculated function (S 470 PVC film, 18 μ m, 210°C).

sumption in its reaction with polyenes: the degradation was carried out in a carefully purified intense argon stream, which assures oxygen-free conditions and removes the volatile products of degradation. Neither can the experimental data be explained by assuming chain scission at the unsaturated sites since this would involve considerable decrease in the molecular weight, which conflicts with the experimental results.

A satisfactory explanation of the observations is the consideration of an intramolecular cyclization reaction (backbiting-like isomerization) of polyenes, in the course of which the conjugated sequences become shorter or split into two shorter parts separated by a ring structure: the number of π bonds decreases by one to bring about ring closure with the formation of a new σ bond (Figure 3).

As is known, compared to rings of other structures, six-membered rings are preferred for steric and energetic reasons. Also in the intramolecular cyclization of polyenes, i.e. the formation of mainly six-membered rings, cyclohexadiene groups is the most probable reaction path. Light absorption of the conjugated diene within the ring structure is not observable in the spectrum studied, so formation of a ring is manifested in the disappearance of three double bonds in the photometric studies.

Such cyclization of polyenes is supported by the fact that—according to other authors⁸ and our own results—at 180–200°C benzene is also formed, although compared to hydrogen chloride in relatively small amount (Figure 4).

The formation of benzene proceeds at first at a low rate and then continuously accelerates in the initial phase of degradation. This suggests that the formation of benzene from polyenes takes place through some intermediate (probably through a cyclohexadiene structure). A closer kinetic study of the formation of benzene is now in progress.

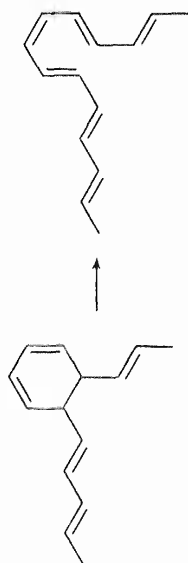


Figure 3. Scheme of intramolecular cyclization of polyenes.

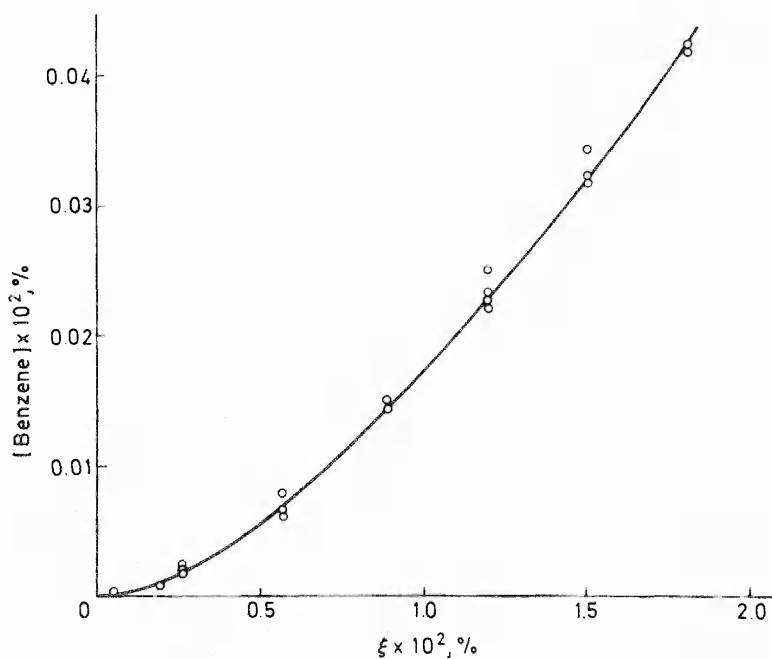


Figure 4. Relative amount of benzene, plotted against dehydrochlorination conversion (S 470 PVC, powder sample, 180°C).

The cyclization isomerization of unsaturated hydrocarbons of low molecular weight (conjugated trienes and tetraenes) has been described by several authors⁹. The presence of cyclohexadiene in degraded PVC has so far not been directly shown, owing to experimental difficulties. There is, however, some reference in the literature to its possible formation¹⁰.

Kinetic treatment of the cyclization model

The kinetics of the formation of polyenes in the course of PVC degradation, as well as their length distribution, has been discussed in our earlier publications⁶ and so the subject will only be briefly outlined here.

The formation of polyenes takes place in a special zip reaction whose initiation step is the primary elimination proceeding randomly or activated by defects. With the consumption of defects the initiation rate decreases and approaches the rate of pure random initiation.

Chain propagation proceeds in a series of activated elimination steps at a rate higher by orders of magnitude than the initiation rate. There are different assumptions for the interpretation of chain termination, which we shall revert to later on. Chain termination will not be considered here as a concrete reaction step but as an approximation described by a probability parameter: hydrochloric acid elimination from a monomeric unit results in a product (double bond) activating further decomposition with $(1 - \delta)$ probability, or in an 'inactive' product with δ probability.

Since chain propagation is very fast compared to initiation, the concentration of chain propagating intermediates becomes stationary (and rather low) from the very beginning of the degradation and the length distribution of polyenes formed in the zip reaction is determined by the δ probability parameter. Based on the above outlined mechanism the primary formation rate of polyenes each containing m double bonds (v_m^+) is:

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

where ξ denotes the conversion of hydrochloric acid elimination.

Accordingly, the amount of polyenes of m length at the onset of the reaction is proportional to the conversion (as long as the effect of secondary consumption and formation reactions is negligible) and the length distribution of polyenes is a geometrical distribution:

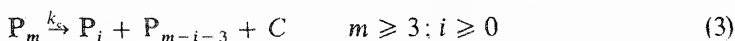
$$p_m = \delta^2(1 - \delta)^{m-1} \xi \quad (2)$$

where p_m stands for the concentration (related to monomeric units) of m length polyenes.

As an approximation, we assume that cyclization occurs with identical probability on an arbitrary double bond triad of polyenes containing at least three conjugated double bonds. In our model only six-membered cyclohexadiene rings have been considered.

Intramolecular cyclization proceeds in several consecutive steps (isomerization processes and ring closure), the rate determining process of which is probably the *cis-trans* isomerization of the double bond. Designating the

cyclohexadiene group with C, we may assume the overall reaction to be :



where k_c is the unimolecular rate constant of the rate determining step of cyclization, and i and $m - i - 3$ stand for the lengths of the new sequences formed.

These new polyenes may then take part in further cyclization provided $i \geq 3$, or $m - i - 3 \geq 3$. These reactions are also considered to have the rate constant k_c ; in other words, the newly formed polyene sequences are not considered to be different from the first-formed polyenes of identical length. (This assumption is essential for the mathematical formulation of the model and is not in contradiction with the experimental results.)

Since the formation of one ring consumes an arbitrary double bond triad of the polyene, m length polyenes may cyclize in $m - 2$ ways. The rate of decrease w_m^- of such polyenes, owing to the cyclization reaction, is as follows :

$$w_m^- = -(m - 2)k_c p_m \quad (4)$$

In the course of cyclization reactions, however, the secondary formation of m length polyenes is also possible, namely from all P_j polyenes containing at least three more double bonds than m ($j \geq m + 3$). This may take place (if $j \neq 2m + 3$) at either one or the other end of a P_j polyene. If, however, $j = 2m + 3$, the only possibility is the simultaneous formation of two polyenes of m length.

According to the above, in the course of cyclization m long polyenes are formed from j long polyenes at $w_{m,j}^+$ rate :

$$w_{m,j}^+ = 2k_c p_j \quad j \geq m + 3 \quad (5)$$

The overall secondary formation rate (w_m^+) of P_m may be obtained by summing the above equation from $j = m + 3$ to $j = \infty$:

$$w_m^+ = \sum_{j=m+3}^{\infty} w_{m,j}^+ = 2k_c \sum_{j=m+3}^{\infty} p_j = 2k_c p(m + 3; \infty) \quad (6)$$

with introduction of the following sum

$$\sum_{j=k}^n p_j \equiv p(k; n) \quad (7)$$

for the total concentrations of polyenes longer than $k - 1$ but shorter than $n + 1$.

The complete time dependence of p_m polyene concentration may therefore be written as

$$\frac{dp_m}{dt} = v_m^+ + w_m^+ + w_m^- \quad (8)$$

Substituting equations 1, 4 and 6, we have :

$$\frac{dp_m}{dt} = \delta^2(1 - \delta)^{m-1} \frac{d\xi}{dt} + 2k_c p(m + 3; \infty) - k_c(m - 2) p_m \quad (9)$$

or in another form :

$$\frac{dp_m}{dt} = \delta^2(1 - \delta)^{m-1} \frac{d\xi}{dt} + 2k_c p(m; \infty) - k_c(m p_m + 2p_{m+1} + 2p_{m+2}) \quad (10)$$

For the amount $p(m; \infty)$ in equation 10, another differential equation may be written, since

$$\frac{dp(m; \infty)}{dt} = \frac{d}{dt} \sum_{j=m}^{\infty} p_j = \sum_{j=m}^{\infty} \frac{dp_j}{dt} \quad (11)$$

After summing, we obtain

$$\frac{dp(m; \infty)}{dt} = \delta(1 - \delta)^{m-1} \frac{d\xi}{dt} + k_c[4p_m + 2p_{m+1} + \xi(m; \infty) - 2(m+1)p(m; \infty)] \quad (12)$$

where we introduced an amount similar to $p(k; n)$

$$\xi_p(k; n) \equiv \sum_{j=k}^{\infty} j p_j \quad (13)$$

for the total amount of double bonds in polyenes longer than $k - 1$ but shorter than $n + 1$. According to this definition we may derive the differential equation of $\xi_p(m; \infty)$

$$\frac{d\xi_p(m; \infty)}{dt} = \frac{d}{dt} \sum_{j=m}^{\infty} j p_j = \sum_{j=m}^{\infty} \frac{j dp_j}{dt} \quad (14)$$

i.e., after summing :

$$\frac{d\xi_p(m; \infty)}{dt} = [1 + (m-1)\delta](1 - \delta)^{m-1} \frac{d\xi}{dt} + k_c\{-3\xi_p(m; \infty) + [6 - (m-1)m]p(m; \infty) + 2(2m-3)p_m + 2(m-1)p_{m+1}\} \quad (15)$$

The system of differential equations 10, 12 and 15 is, in this form, not yet suitable for comparison with the experimental data since the equations contain also the polyene concentrations p_{m+1} and p_{m+2} . If new differential equations were set up for these amounts, they would require the concentration of further longer polyenes (p_{m+3} ; p_{m+4} , etc), which would lead to a system of an infinite number of differential equations. In order to avoid this, we substituted p_{m+1} and p_{m+2} with approximate expressions. This can be done, all the more so since the terms containing these values in the equation are substantially smaller than the others. The approximations were chosen so as to obtain correct values if the length distribution of polyenes is geometrical, a condition well satisfied at the initial stage. The corresponding approximations are :

$$p_{m+1} = p_m \left[1 - \frac{p_m}{p(m; \infty)} \right] \quad (16)$$

$$p_{m+2} = p_m \left[1 - \frac{p_m}{p(m; \infty)} \right]^2 \quad (17)$$

The knowledge of $d\xi/dt$ is also necessary for the calculations. This has been determined parallel to our photometric measurements or in separate experiments by measuring the extent of dehydrochlorination. The conversion curve approached a straight line, in other words, the rate of dehydrochlorination in each experiment (in the low conversion range studied, $0 \leq \xi < 0.05$) was considered constant, and characterized by the overall rate (k_{HCl}) of random elimination. With this approximation, i.e. by neglecting the activated initiation, at the initial stage of degradation (where the effect of the secondary cyclization process is, in any case, not significant) cyclization has received undue consideration.

For better comparison, the measurements were evaluated in the function of conversion. Introducing the relative rate constant

$$\kappa \equiv k_c \frac{d\xi}{dt} \approx k_c/k_{\text{HCl}} \quad (18)$$

and applying equations 16 and 17, the system of differential equations 10, 12 and 15 can be numerically integrated and applied for the evaluation of experimental results.

Comparison of experiments and calculations

Owing to the above-mentioned technical difficulties, we were able to obtain the most reliable data for the concentration of polyenes containing 5–10 conjugated double bonds. Therefore, for comparison of the calculated and experimental results we used the following two quantities:

(a) the concentration ratio of polyenes containing 5 and 10 double bonds, p_5/p_{10} , which is indirectly characteristic of polyene distribution,

(b) the total amount of double bonds in polyenes longer than four but shorter than 11, $\xi_p(5; 10)$, which is indirectly characteristic of the total amount of double bonds present in the system.

The probability parameter δ can be determined by the extrapolation of the ratio p_5/p_{10} to zero conversion. According to equation 2, this ratio is:

$$\frac{p_5}{p_{10}} = \frac{1}{(1 - \delta)^5} \quad (19)$$

The other parameter, the relative rate constant κ , can be determined by a systematic method of trial-and-error, using the $p_5/p_{10}-\xi$ diagram. Thus, both parameters can be determined without applying the experimental results on $\xi_p(5, 10)-\xi$.

As can be seen in *Figures 2* and *5*, the conversion dependence of the ratio p_5/p_{10} , characteristic of the average length of polyenes, is fairly well described by the model for film samples of both polymers under investigation. Similarly, there is good agreement between the calculated and measured p_5/p_{10} values for PVC samples degraded in powder form (*Figure 6*); here and in *Figures 2* and *5* the calculated curve has been plotted.

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With the knowledge of κ and δ , obtained from the diagrams $p_5/p_{10}-\xi$, and on the basis of the model, we calculated the functions $\xi_p(5, 10)-\xi$ (curves A in Figures 7, 8 and 9).

The concentrations of the individual polyenes have also been calculated, as a function of dehydrochlorination conversion. As an example, we present the calculated p_m values for polyenes of $m = 5$ and $m = 10$, plotted in Figure 10 with curves A.

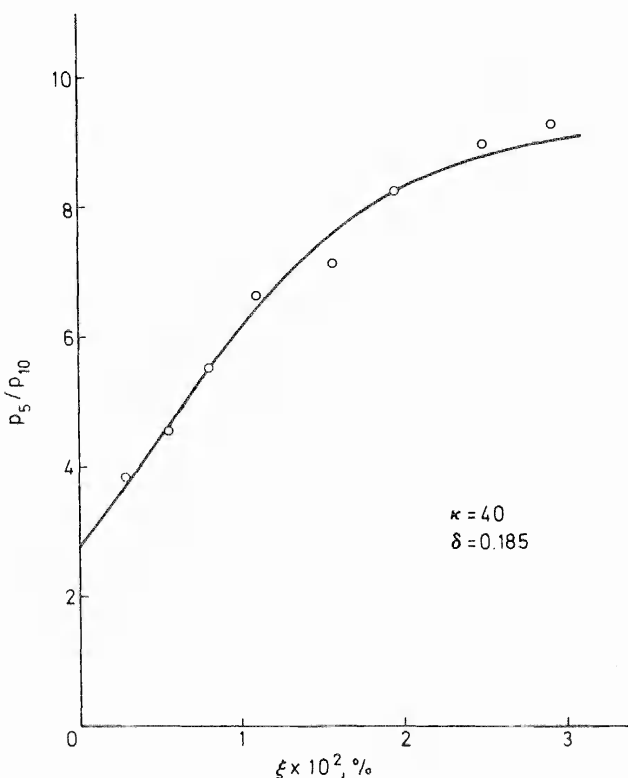


Figure 5. Concentration ratio (p_5/p_{10}) of polyenes containing 5 and 10 double bonds, plotted against the conversion of dehydrochlorination. The curve drawn designates the calculated function (E PVC film, 10 μ m, 210°C).

The calculated amount of polyenes, as well as the calculated amount of $\xi_p(5; 10)$ shows a trend qualitatively similar with that of the measured amounts. The agreement is, however, not satisfactory: the calculated value in the total range under investigation is higher than the measured. But this deviation is not in contradiction with the above described cyclization model: on the contrary, it supports it. Thus, in the above calculations the chain termination has not been given as a concrete reaction step and was only considered with the probability parameter δ . A more detailed analysis shows that among the assumed chain termination steps, some may result in the formation of fewer conjugated double bonds than the number of hydrogen chloride molecules eliminated.

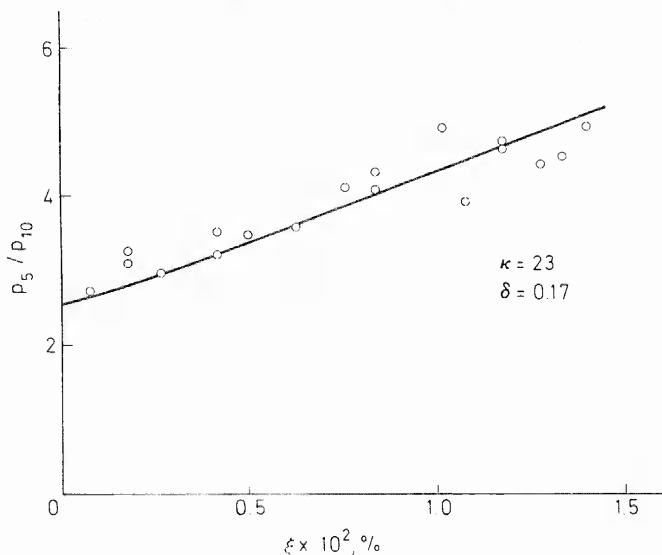


Figure 6. Concentration ratio (p_5/p_{10}) of polyenes containing 5 and 10 double bonds, plotted against the conversion of dehydrochlorination. The curve drawn designates the calculated function (S 470 PVC, powder sample, 210°C).

Such termination occurs also in the α, γ -elimination (cyclopropane formation) earlier proposed by us⁶ and shown in Figure 11.

Chain termination by formation of a cyclohexadiene ring has a similar effect (Figure 12). This may occur if there are three adjacent C—C bonds in *cisoid-cis-cisoid* conformation at the end of the chain still propagating in the course of elimination. Then owing to the favourable steric position, instead of further chain propagation, cyclization may occur immediately after the last elimination step, implying chain termination.

There is a marked difference between this cyclization process and the secondary cyclization discussed earlier. According to our measurements, the rate of secondary cyclization is several orders of magnitude smaller than that of chain propagation and cannot compete with it, owing to slow *cis-trans* isomerization. Chain termination by cyclization will take place only if dehydrochlorination results in a chain conformation favourable for cyclization proceeding at a higher rate than chain propagation.

If the chain termination characterized by δ involved exclusively such cyclizations, the primary formation rate of polyenes would be considerably lower than given in equation 1:

$$v_m^+ = \frac{\delta^2(1 - \delta)^m}{1 + 2\delta} \frac{d\xi}{dt} \quad (20)$$

Considering this primary formation rate of polyenes, the length distribution of polyenes (and the ratio p_5/p_{10}) agrees with that resulting from the model, where no concrete chain termination was formulated and no reduction of the polyene length was taken into account. There are considerable deviations in

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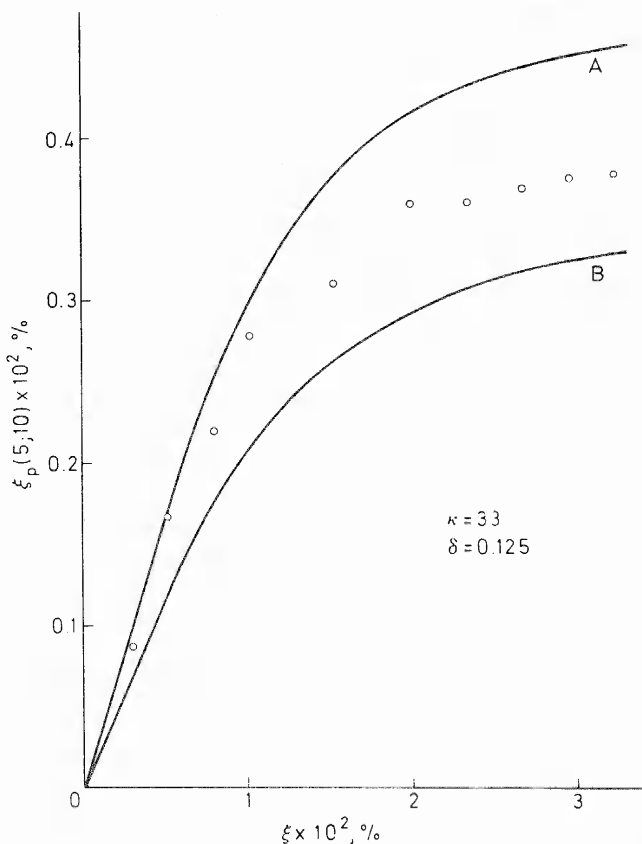


Figure 7. Total amount of double bonds in polyenes of 5-10 length in the function of dehydrochlorination conversion. Curves A and B are the calculated functions (S 470 PVC film, 18 μm , 210°C).

the amount of polyenes and in the sum $\xi_p(5;10)$. The B curves of Figures 7-10 were plotted using equation 20, in other words, as if chain termination would proceed exclusively with cyclization, in the way demonstrated in Figure 12. This calculation resulted in polyene concentrations lower than the experimental values. The polyene concentrations measured are between the values calculated by the two different chain termination models. It may be assumed, therefore, that the average consumption of termination is less than three double bonds.

Detailed examination of the thermal degradation of PVC in trichlorobenzene solution is still under way. From experiments carried out so far, we may state that polyene distribution is shifted towards shorter polyenes with increasing dehydrohalogenation conversion. The conversion dependence of the characteristic p_5/p_{10} ratio is depicted in Figure 13.

The change in the p_5/p_{10} ratio is greater than in the case of samples degraded in the solid phase. The length distribution of polyenes at the beginning of the reaction cannot be approached with a geometric distribution

as shown by the fact that the p_s/p_{10} ratio extrapolated to 0 is less than 1; therefore the experiments cannot be evaluated by the above differential equations.

It may be seen from the conversion dependence of $\xi_p(5:10)$ shown in *Figure 14* that in dilute solution it becomes stationary at a lower conversion than in the solid phase. The value of κ , the relative rate constant, may be estimated on the basis of the diagram $\xi_p(5:10)-\xi$; in dilute TCB solution,

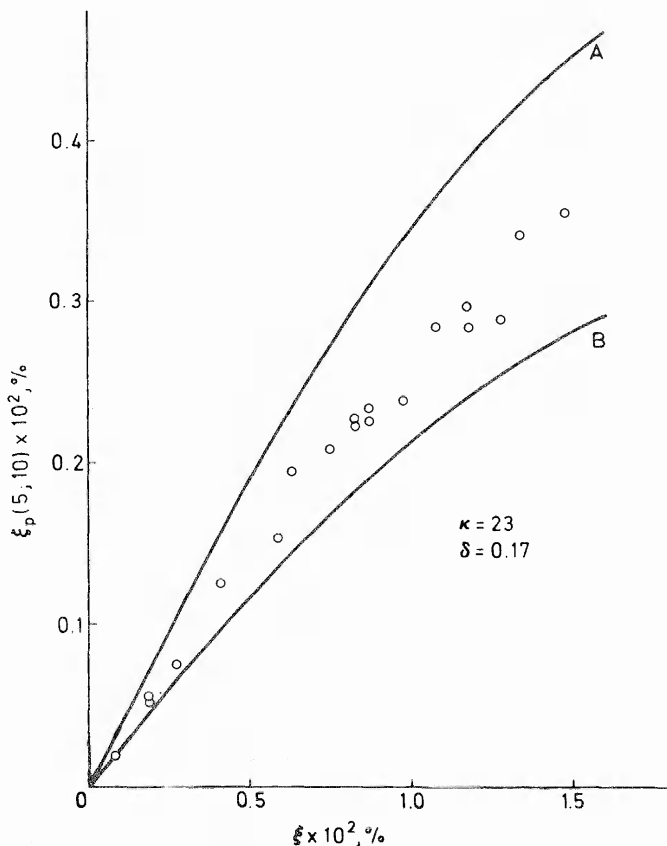


Figure 8. Total amount of double bonds in polyenes of 5-10 length in the function of dehydrochlorination conversion. Curves A and B are the calculated functions (S 470 PVC, powder sample, 210°C).

under the conditions given in *Figure 13*, $\kappa = 55-60$. This value is much higher than those obtained for the same polymer (S 470 PVC) at the same temperature (210°C), for samples of powder ($\kappa = 23$), or for film ($\kappa = 33$). On the other hand, the degradation of the film samples of the other polymer (E PVC) gives a relative rate constant ($\kappa = 40$) fairly similar to that obtained with the film S 470.

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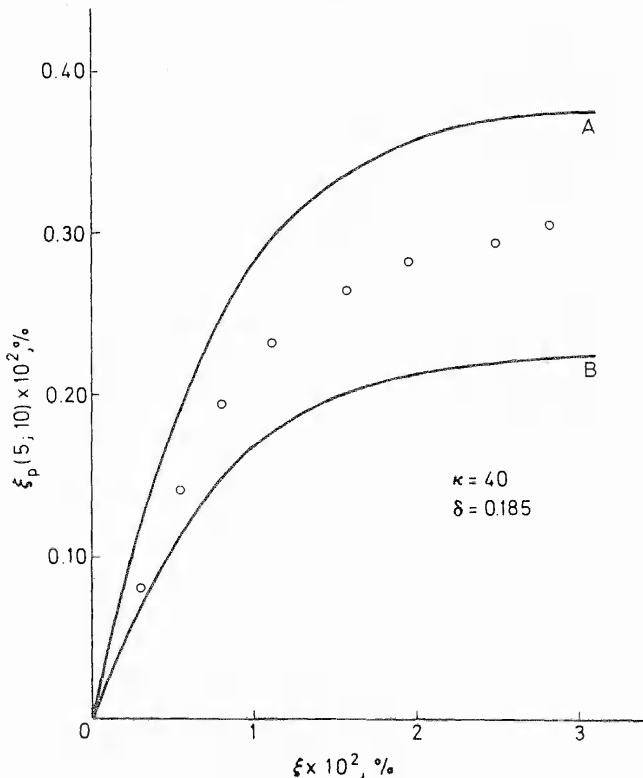


Figure 9. Total amount of double bonds in polyenes of 5-10 length in the function of dehydrochlorination conversion. Curves A and B are the calculated functions (E PVC film, 10 μ m, 210°C).

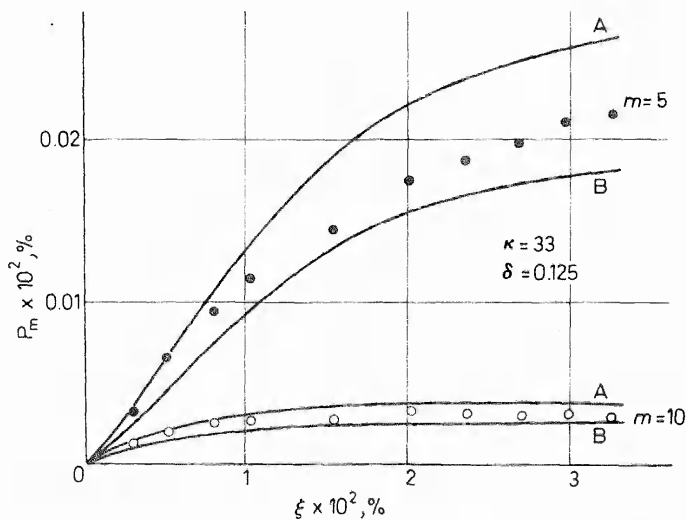


Figure 10. The amount of polyenes containing 5 and 10 double bonds, plotted against the conversion of dehydrochlorination. Curves A and B are the calculated functions (S 470 film, 18 μ m, 210°C).

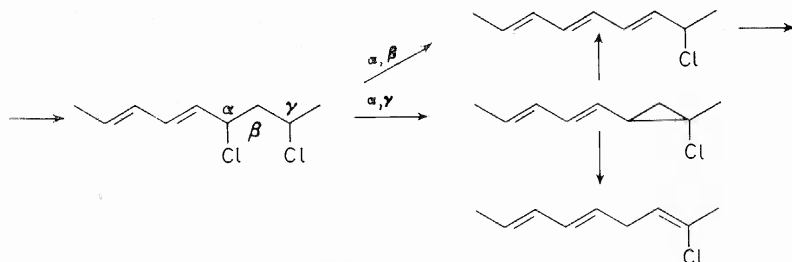


Figure 11. Propagation of activated HCl elimination, and a possible chain termination via cyclopropane ring structure.

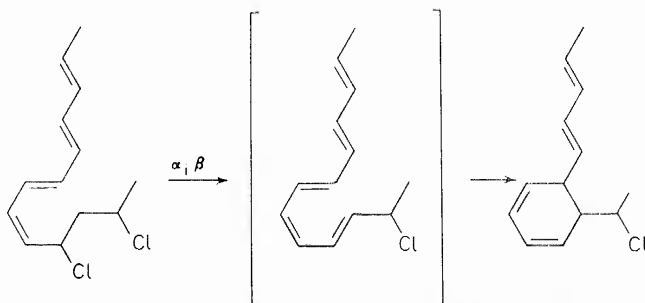


Figure 12. Chain termination due to the cyclization reaction of the propagating chain.

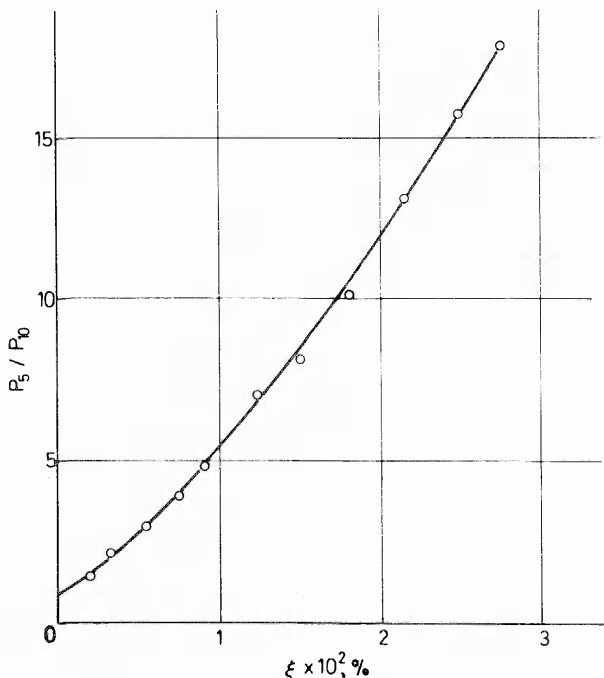


Figure 13. Concentration ratio (p_5/p_{10}) of polyenes containing 5 and 10 double bonds, plotted against the conversion of dehydrochlorination. (Trichlorobenzene solution of 1% S 470 PVC. 210°C, 31.h⁻¹ argon).

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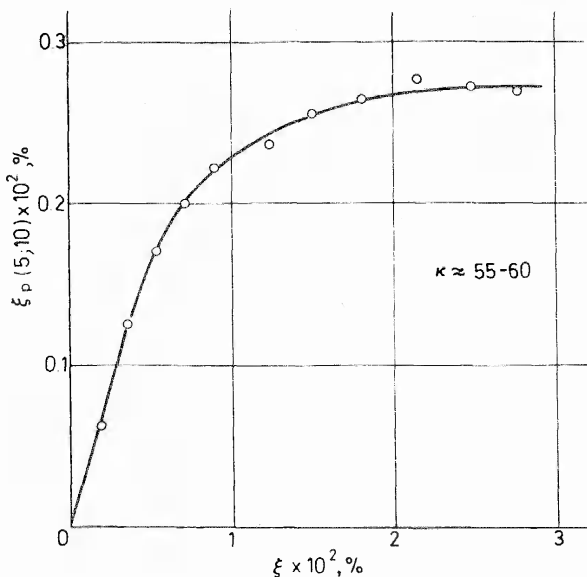


Figure 14. Total amount of double bonds in polyenes of 5-10 length, plotted against the conversion of dehydrochlorination. (Trichlorobenzene solution of 1% S 470 PVC, 210°C, 31.h⁻¹ argon).

The difference between the solid and dissolved samples is remarkable and can be interpreted by the isomerization-cyclization model outlined above, chain mobility in dilute solution being obviously much greater than in the solid phase.

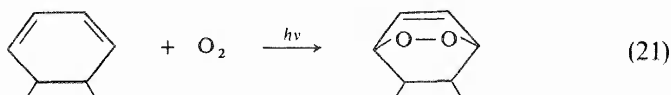
In addition to polymer analogous secondary processes, in the course of thermal degradation, other types of reactions also proceed involving a change in the molecular weight of the polymer. During the thermal degradation of PVC powder samples, osmometric measurements show a slow increase in the number average molecular weight (Figure 15). Such an increase has also been observed by other authors¹¹.

The rise in molecular weight is evidently caused by bimolecular reactions of polyenes. The Diels-Alder type addition between two polyenes or the reaction of polyenes with polyene radicals always present⁶ during thermal degradation, may serve as examples for such reactions. No rise in molecular weight could be observed in samples degraded in dilute solution.

2. THE DIELS-ALDER REACTIONS OF POLYENES

As previously outlined, polyenes primarily formed in PVC degradation may undergo considerable transformation, owing to intramolecular cyclization reactions (backbiting). These processes apparently have a favourable effect since the amount of double bonds as well as the visually observable discolouration of the polymer is smaller than that corresponding to the extent of dehydrochlorination. It may, however, give rise to processes leading to further degradation. It should be noted here that the scission of polymer chain will most probably occur at cyclohexadiene structures

(formation of benzene). Cyclohexadiene structures may also play an important role in the course of oxidative degradation: as is well known, upon excitation, this structure easily reacts with oxygen with the formation of ascaridole type structures¹²:



Thus, owing to thermal degradation, PVC contains reactive polyenes and unsaturated ring structures formed in primary and secondary processes. Therefore all information on their reactivity may provide helpful data for a closer knowledge of the system. Such data may be obtained, e.g., by studying the addition reactions of polyenes.

It is a well established fact that polyenes readily react with different ionic and radical reagents. These processes cannot, however, be considered quantitative as the intermediates formed are relatively stable with long lifetimes. Furthermore, radical addition may give rise to secondary reactions of polyene radicals and ionic processes may lead to equilibrium at an early stage. Our studies on hydrogen chloride incorporation⁶ and the fact that polyenes are capable of halogen addition to only a small proportion of the total amount of double bonds¹³, support the above statements. These observations justified the study of the Diels–Alder reactions of polyenes formed in PVC. The fact that certain important additives of PVC, containing dienophilic sections, have a stabilizing effect¹⁴ also justified a closer study of these processes. Since diene reactions decrease the extent of discoloration on the one hand, and both hinder the formation of and transform cyclohexadiene structures on the other, the Diels–Alder reactions of polyenes may have considerable practical importance.

In our investigations a solution of S 470 PVC (~ 1 wt %) was previously degraded over a period of 300 minutes in an argon stream at 180°C. Purified 1,2,4-trichlorobenzene was the solvent used and the volume of the solution was 40 ml. After degradation, the reaction vessel was placed in a thermostat preheated to the temperature of the Diels–Alder reaction (100, 120, 140, 160°C), under a steady stream of argon gas.

Owing to its great reactivity and easy measurement, we have chosen chloromaleic anhydride (CMA) as the reagent. The commercial product (Fluka) was distilled.

The samples taken from the reaction mixture were diluted with peroxide free tetrahydrofuran of identical volume and then measured by spectrophotometry.

Above 28000 cm^{-1} strong absorption can be observed in the reaction mixture, which may probably be assigned to the charge-transfer complex between the solvent molecules and the reagent. This excluded the possibility of the determination of shorter polyenes. Owing to the considerable error in the spectrophotometry of long polyenes we measured the time dependence of the amount of $m = 6-11$ polyenes during the reaction.

Experimental results; kinetic treatment of the process

Immediately after addition of the reagent, the absorption of polyenes starts to decrease; the extinctions generally remain measurable over a reaction period of 2–3 hours (*Figure 16*).

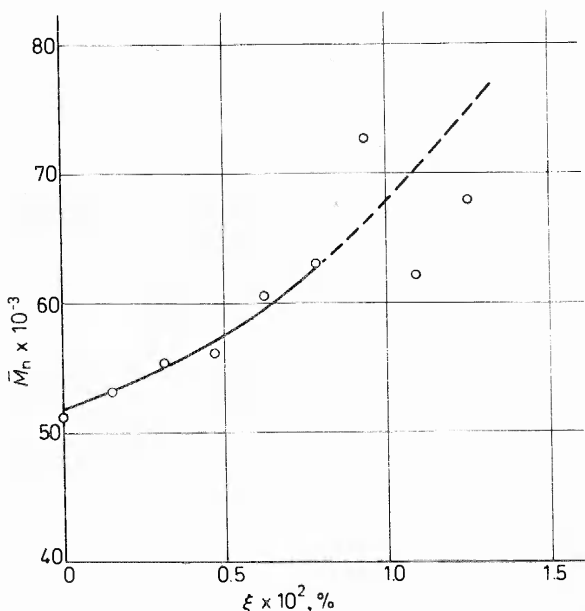


Figure 15. Change in the number average molecular weight of PVC, plotted against the conversion of dehydrochlorination. (S 470 PVC, powder sample, 180°C; above 1% conversion, owing to the decrease in solubility of the samples, the error of determination is greater than at lower conversions).

As is known, the Diels–Alder reaction is for both components a first order process¹⁵. In our experiments we used CMA in great excess compared to the amount of polyenes, so the consumption reaction could be considered as pseudo-unimolecular. Applying different CMA concentrations, we established that the initial rate is proportional to the concentration of the reagent (*Figure 17*).

Plotting the logarithm of extinctions against reaction time, we obtained characteristic curves (*Figure 18*).

It may be ascertained that the decrease in the consumption rate of polyenes is faster than it would be in the case of a simple first order reaction: $\ln(E_0/E)$ is a linear function of time only at the beginning of the reaction. It is notable, however, that the change of relative extinctions for different polyenes proceeds practically in the same way; this means that the reaction rate is independent of polyene length. Therefore, in the following, we considered the average values of results obtained for $m = 6$ –11 polyenes.

The conclusion may be drawn, that the reaction can be regarded as a simple addition only at the initial stage and the complexity of the process becomes evident in the course of reaction. Similar curves may also be

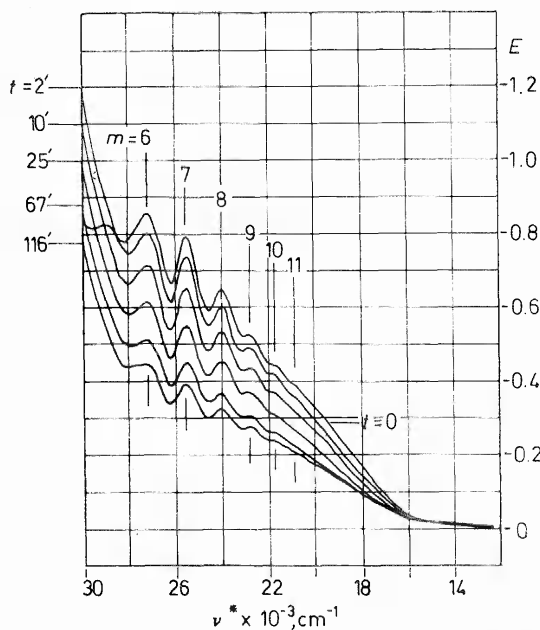


Figure 16. Decrease in the extinction of polyenes, owing to the effect of the Diels-Alder reaction. The spectra are taken at $t = 0$, prior to CMA addition; and at $t = 2, 10, 25, 67$ and 116 min. the corresponding reaction times. 140°C , $[\text{CMA}] = 0.5\% = 5.81 \times 10^{-2} \text{ mol l}^{-1}$. The wavenumbers belonging to the $m = 6-11$ polyenes are designated.

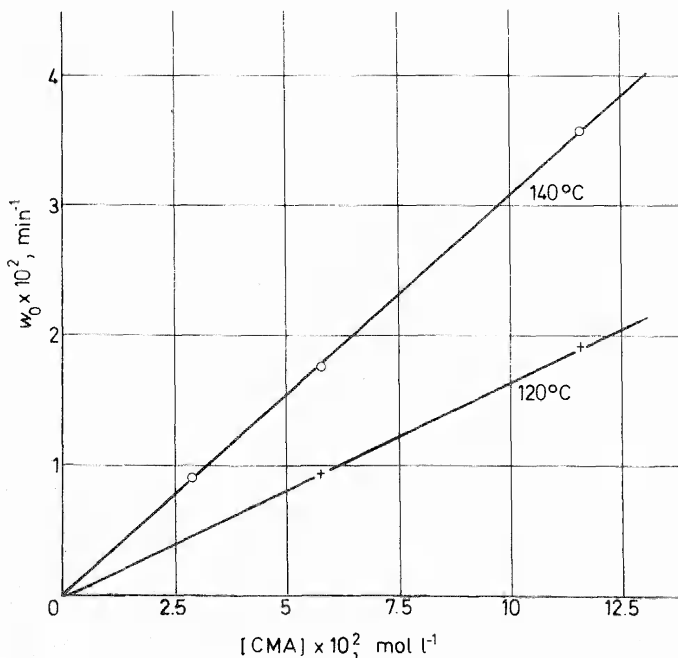


Figure 17. Dependence of the initial rate (w_0) of the Diels-Alder reaction on the concentration of CMA.

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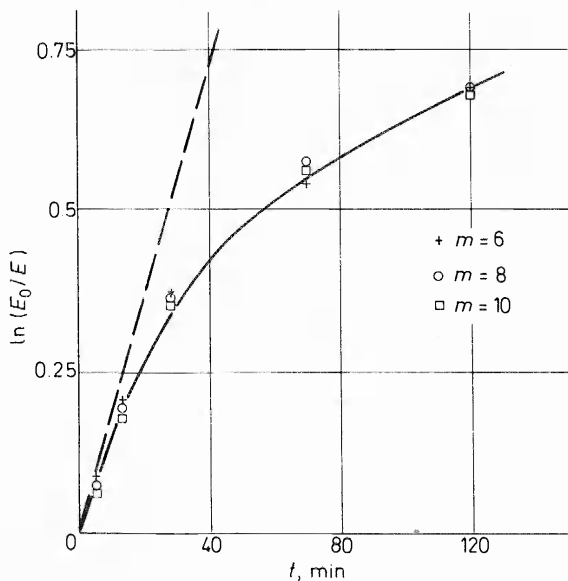


Figure 18. Change in conversion (x) of the Diels-Alder reaction in the function of reaction time. Logarithmic presentation, $\ln(E_0/E) \equiv \ln(1-x)$. 140°C; $[CMA] = 5.81 \times 10^{-2} \text{ mol l}^{-1}$. The continuous curve shows the calculated function and the dotted line represents the first order irreversible reaction.

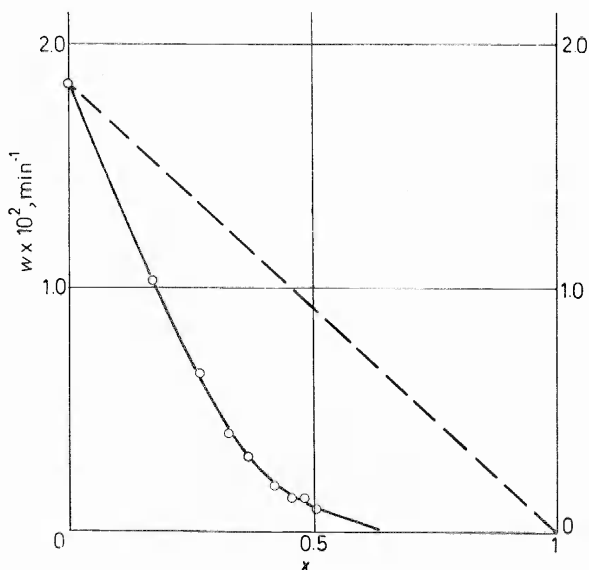


Figure 19. Dependence of the Diels-Alder reaction rate ($w = dx/dt$) from conversion (x). 140°C $[CMA] = 5.81 \times 10^{-2} \text{ mol l}^{-1}$. The continuous curve shows the calculated function and the dotted line represents the first order irreversible reaction.

obtained for reversible first order reactions and, indeed, the reversibility of Diels–Alder reactions is well known¹⁵. In order to clarify the problem we have plotted the rates against conversion. The relationship obtained for experiments carried out at 140°C (0.5 per cent CMA) is given in *Figure 19*.

It may be established that the process is neither an irreversible pseudo-unimolecular addition (dotted line) nor a simple reversible reaction. In the latter case the rate would linearly decrease from the initial value w_0 up to the final conversion x_{∞} .

The bend found in the rate–conversion relationship as well as the fact that the time dependence of the conversion for polyenes of different length is identical, points to a complex reversible addition. We tried to describe the process with the following simplified scheme:

Let us assume that addition always takes place on the two final double bonds of the intact polyene sequence, and that the adduct always dissociates in the position adjacent to the intact polyene sequence. Thus, in these processes the polyene length always changes by two. Owing to steric and polar effects, it may be assumed that once the polyene has reacted with the rate constant k'_a ($k'_a = k_a[\text{CMA}]$), it will take part in the further addition only at a lower rate (rate constant: $k'_b = \alpha k'_a$, $\alpha < 1$). The rate of dissociation of the adduct (rate constant k_d) is, on the other hand, independent of the number of previous additions.

The spectrophotometric method applied does not make any distinction between an intact polyene and an intact sequence of a partly reacted polyene. The extinction measured depends only on the length of the intact polyene sequence. If the concentration of polyenes, which contained originally $m + 2i$ conjugated double bonds, and participated in i number of additions is designated with ${}_iP_{m+2i}$, the complete extinction caused by m length polyenes may be calculated as follows:

$$E_m = c_m \cdot c_m = \varepsilon_m \sum_{i=0}^{\infty} {}_iP_{m+2i} \quad (22)$$

where ε_m is the corresponding extinction coefficient, and c_m stands for the total concentration of m long polyenes. The conversion of the process can be defined as:

$$x = 1 - \frac{c_m}{c_m(0)} = 1 - \frac{E_m}{E_m(0)} = 1 - \frac{E}{E_0} \quad (23)$$

since, as was pointed out before, the conversion is independent of the polyene length:

$$\frac{E_6}{E_6(0)} = \frac{E_7}{E_7(0)} = \dots = \frac{E}{E_0} \quad (24)$$

According to the experimental results, the length distribution of polyenes in the previously degraded PVC used in the study of the Diels–Alder reaction may be well approximated by a geometrical distribution: therefore the following relationship is valid for any m and i value ($m \geq 6$, $0 \leq i < \infty$):

$$P_{m+2i}(O) = \beta^i P_m(O) \quad (25)$$

where $\beta = (1 - \delta)^2$ is the parameter of geometrical distribution.

With the application of the above assumptions and relationships, we discuss first the addition process considered irreversible. In the course of subsequent unimolecular additions, an originally k long polyene is transformed as follows:



The usual treatment of this consecutive set of reactions gives the following result for the concentration of ${}_iP_k$ polyenes formed after the i th addition step:

$${}_iP_k = P_k(O) \frac{(-\alpha)^{i-1}}{(1-\alpha)^i} \left\{ \exp(-\alpha k'_a t) \sum_{j=0}^{i-1} \frac{[-(1-\alpha)k'_a t]^j}{j!} - \exp(-k'_a t) \right\} \quad (27)$$

if $i \geq 1$, and the consumption of the initial polyene can be described by the relationship

$$P_k = P_k(O) \exp(-k'_a t) \quad (28)$$

For summing according to equation 22, we need the concentration of $k = m + 2i$ long polyenes, which may be obtained from equations 25, 27 and 28:

$${}_iP_{m+2i} = P_m(O) \left(\frac{\beta}{1-\alpha} \right)^i (-\alpha)^{i-1} \left\{ \exp(-\alpha k'_a t) \sum_{j=0}^{i-1} \frac{[-(1-\alpha)k'_a t]^j}{j!} - \exp(-k'_a t) \right\} \quad (29)$$

if $i \geq 1$, and the originally m -length polyene is consumed according to the expression

$$P_m = P_m(O) \exp(-k'_a t) \quad (30)$$

After substituting equations 29 and 30 into equation 22 and summing, we obtain the conversion defined in equation 23:

$$x = 1 + \frac{k'_1 - w_0}{k'_2 - k'_1} \exp(-k'_2 t) - \frac{k'_2 - w_0}{k'_2 - k'_1} \exp(-k'_1 t) \quad (31)$$

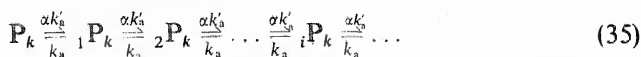
where

$$w_0 = (1 - \beta) k'_a \quad (32)$$

$$k'_1 = \alpha(1 - \beta) k'_a = (1 - \beta) k'_b \quad (33)$$

$$k'_2 = k'_a \quad (34)$$

Exact treatment of the reversible reaction



is even more complicated. Instead, we have applied a method of approxi-

mation analogous with the procedure used for the exact treatment of the simple reversible system



Kinetic treatment of the equilibrium reaction 36 may also be performed in the following way: instead of applying the usual differential equation

$$\frac{dx}{dt} = k(1 - x) - \bar{k}x \quad (37)$$

(where x is the conversion; $x = B/A_0$), we may describe the reaction rate as:

$$\frac{dx}{dt} = k'(x_\infty - x) \quad (38)$$

where the constants k' and x_∞ can be expressed with k and \bar{k} , on the basis of the equilibrium state.

The approximation performed analogously for the reversible consecutive set of reactions 35 and treatment of the results according to equations 22 and 23 gave for the conversion:

$$x = x_\infty + \frac{k_1 x_\infty - w_0}{k_2 - k_1} \exp(-k_2 t) - \frac{k_2 x_\infty - w_0}{k_2 - k_1} \exp(-k_1 t) \quad (39)$$

where

$$x_\infty = \frac{\alpha k_a'^2}{\alpha k_a'^2 + \alpha k_a' k_d + k_d^2} = \frac{k_a' k_b'}{k_a' k_b' + k_b' k_d + k_d^2} \quad (40)$$

$$w_0 = (1 - \beta) k_a' \quad (41)$$

$$k_1 = \alpha(1 - \beta) k_a' \frac{\alpha \beta k_a'^2}{\alpha \beta k_a' - k_d^2 x_\infty} = (1 - \beta) k_b' \frac{\beta k_a' k_b'}{\beta k_a' k_b' - k_d^2 x_\infty} \quad (42)$$

$$k_2 = k_a' \frac{(1 - \beta) k_a'}{(1 - \beta) k_a' - k_d x_\infty} \quad (43)$$

Comparison of the relationships 31–34 and 39–43 showed that in the case $k_d = 0$ (the adduct does not dissociate), the latter convert into the former. In other words, the relationships 39–41 also give a correct description of the irreversible reaction.

The relationship 39 obtained for the reversible process and knowledge of the parameter β , allow the evaluation of experiments. In the course of the previous degradation performed as outlined above, a distribution with parameter $\beta = 0.498$ can be observed. Since $\beta = (1 - \delta)^2$ this value corresponds to $\delta = 0.294$, i.e. $\bar{n} = 3.4$. It should be noted, that polyene distribution remained practically constant during the Diels–Alder reaction, since the time dependence of the conversion was identical for polyenes of different length. The results obtained for the numerical values of constants k_a , k_b , and k_d and their temperature dependence are shown in *Figure 20*.

For the rate constant of the first addition (k_a) we obtained an activation

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energy of $10.4 \text{ kcal mol}^{-1}$, for that of the further additions (k_b): $12.9 \text{ kcal mol}^{-1}$ and that of the adduct dissociation (k_d): $4.0 \text{ kcal mol}^{-1}$.

The applicability of relationship 39 obtained for the conversion is demonstrated by the calculated curves drawn in *Figure 17* and *19*; the calculations were performed with the following values:

$$\begin{array}{ll}
 t = 140^\circ\text{C} & k_a = 0.636 \text{ l mol}^{-1} \text{ min}^{-1} \\
 [\text{CMA}] = 0.0581 \text{ mol l}^{-1} & k_b = 0.151 \text{ l mol}^{-1} \text{ min}^{-1} \\
 & k_d = 9.06 \times 10^{-3} \text{ min}^{-1}
 \end{array}$$

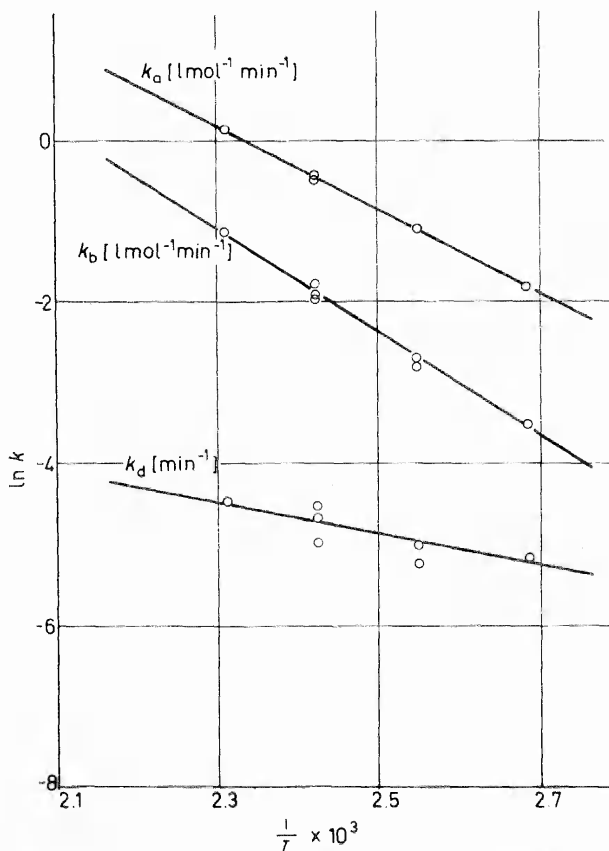


Figure 20. Temperature dependence of rate constants of the polyene-CMA reaction; k_a is the bimolecular rate constant of the first addition, k_b is that of the further reaction and k_d is the rate constant of unimolecular dissociation in the adduct.

The excellent agreement shows that the assumptions applied in the derivation of the conversion are correct enough and the reaction proceeds—at least essentially—according to the mechanism assumed. The rate constant k_a and its activation energy obtained for the first addition process, directly derived from the well reproducible initial rate, are, by all means, reliable. In the temperature range of thermal degradation (in spite of the relatively

low activation energy) the k_a value is considerably higher compared to the overall rate of dehydrochlorination (at 210°C $k_a \approx 4 \text{ l mol}^{-1} \text{ min}^{-1}$, and the rate of elimination is $w_{\text{HCl}} \approx 10^{-4} \text{ min}^{-1}$). In the case of sufficient CMA concentration, the rate of Diels–Alder addition may be expected to compete even with the very high rate component ('zip') of the degradation process: simultaneous study of the addition and degradation may give detailed information on the degradation mechanism.

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