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THE INTERPRETATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC POLYMER DEGRADATION CURVES

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In addition to the method of Flynn–Wall the Freeman–Carroll method too was employed to determine the kinetic parameters of polymer degradation, since this latter method is also applicable in cases where the kinetic parameters vary during the decomposition process or where the temperature of the sample does not increase according to a strictly linear programme. To interpret the results an extension of Boyd's theory was attempted with a formal model of polymer decomposition by elimination; it was possible to describe the kinetic constants of the reaction with the values obtained. In depolymerization and polymer decomposition by elimination the reaction mechanism may readily be determined using these kinetic parameters.

In the kinetic interpretation of thermogravimetric curves obtained by the thermal degradation of polymers the researcher asks himself whether the results of his research can be utilized, how the kinetic parameters of the process can be determined, and what their significance is.

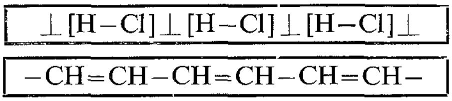
Many methods are described in the literature for the evaluation of kinetic parameters, but these usually assume that the kinetic research is performed at a constant temperature, or that the sample temperature rises at a constant heating rate. In addition it is assumed that the rise of temperature does not lead to a modification of the degradation mechanism, so that the evaluated kinetic parameters have significant and constant values. These restrictions are not always satisfied, especially in the degradation of polymers under dynamic thermal conditions, because the thermal effects of the reactions may alter the linear rise of temperature significantly, while the experimental results show that during the degradation of polymers, the mechanism alters so that the kinetic parameters usually vary with both the heating rate and the transformation degree [1].

One of the literature methods subject to the above reactions is the Freeman–Carroll method [2], which estimates kinetic parameters on the basis of differences between close experimental values, so that both the heating rate and the kinetic parameters can be considered constant. The Flynn–Wall method [3] may also be used, because of the possibility of showing the dependence of the kinetic values on the transformation degree, so that modifications of the degradation mechanism become visible.

The significance of the kinetic parameters of depolymerization reactions was discussed for a large range of mechanism by Boyd [4]. In an attempt to interpret the mechanism of polymer degradation by elimination, Boyd's theory has been extended beyond chain depolymerization.

For polymers which degrade by elimination, it is possible to formulate a model of a "support" macromolecule, an assumed polymer with conjugated double bonds, stable under given thermal conditions, on which is "fixed" a second polymer, given by the sequences of the functional groups, which "depolymerize" by their detachment from the "support" polymer, forming small volatile molecules.

In the special case of polyvinyl chloride, the proposed model leads to the arrangement given in Fig. 1.



$$\begin{array}{|c|}\hline \perp[\mathrm{H{-}Cl}]\perp[\mathrm{H{-}Cl}]\perp[\mathrm{H{-}Cl}]\perp \\ \hline \mathrm{-CH{=}CH{-}CH{=}CH{-}CH{=}CH-} \\ \hline \end{array}$$

Fig. 1

As the dehydrochlorination of PVC is accompanied by the formation of hydrogen chloride and a polymer with a structure similar to that of the "support" polymer, in the kinetic treatment of the process the real dehydrochlorination will be substituted by depolymerization of the imaginary "fixed" polymer, with a symbolical combination of the functional groups, giving hydrogen chloride during degradation. Since the detached micromolecular products are usually volatile substances at degradation temperatures, the degradation process can be studied by the common thermogravimetric methods. But in contrast with the common depolymerization reactions, which proceed in a single thermogravimetric step, polymer degradation by elimination of small molecules formed from the functional groups detached from the main chain, takes place in at least two thermogravimetric steps, the first at a lower temperature corresponding to the detachment of the small molecules.

According to the proposed model, at temperatures not above the degradation temperature of the respective "support" polymer (i.e. when the detachment of small molecules is not accompanied by degradation of the polymeric chain itself), the sample weight at a given moment is given by the sum of the "support" polymer constant weight and the "fixed" polymer variable weight. This also holds even when intermolecular links are formed in the "support" polymer, if the process is not accompanied by the elimination of small molecules different from those giving the "fixed" polymer. In other words, degradation by elimination can be expressed by the weight variation of the "fixed" polymer only, which depolymerizes by a "zip" reaction.

Consequently, the experimental thermal curves allow the quantitative determination of the "fixed" polymer weight variation. In the proposed model, however, this process is comparable to a depolymerization, so that we consider that it can be described kinetically by an extension of Boyd's theory.

Table 1

No.	Initiation	Zip termination	Distribution, initially degree of polymerization	n	h	E_a
1.	Statistical	short first order	each distribution	1	0	S+P−T
		short disproportionation	each distribution	1	0	(S/2) + P − (T/2)
		short recombination	most probable	1	0	(S/2) + P − (T/2)
2.	Statistical	long recombination	mono	1	1	S
3.	Statistical	long recombination	most probable	3/2	1	S
4.	End-group	short first order	mono	0	−1	E + P − T
5.	End-group	short first order	most probable	1	−1	E + P − T
6.	End-group	short disproportionation	mono	1/2	−1/2	(E/2) + P − (T/2)
7.	End-group	short disproportionation	most probable	1	−1/2	(E/2) + P − (T/2)
8.	End-group	short recombination	most probable	1	0	E
9.	End-group	long recombination	each distribution	1	0	E

The correlation which results between the kinetic parameters and the degradation mechanism for both common depolymerization and degradation by elimination is shown in Table 1 (n is the overall reaction order, h the exponent of the polymerization degree in the pre-exponential factor, E_a the overall activation energy of the process, S the activation energy of statistical, E that of end-group initiation, P the activation energy of propagation and T that of termination). It is clear that the experimental values can be correlated with the theoretical ones, only when the degradation rate is determined by the chemical process and not by transport phenomena (diffusion, heat transfer, etc.).

In the selection of degradation mechanism DTA curves of the processes can be used. Depolymerization starting from chain end-groups leads to endothermic effects, while oxidative degradation can usually be considered a statistically initiated reaction and leads to exothermic effects.

In many cases it has been observed that the kinetic parameters of polymer degradation depend on both the heating rate and the transformation degree. This modification of the kinetic parameters may be caused either by a changing of the degradation mechanism, or by the fact that the reaction does not proceed in the stationary state, especially if dynamic thermal conditions are employed.

Numerous data on the thermal destruction of polymers confirm that polymer degradation depends on synthesis and working conditions, so that the mechanisms described in the literature for certain conditions are not generally valid and can seldom be used to evaluate a theoretical criterion for stabilizer selection.

Each new synthesized polymer must be studied from the point of view of thermo-oxidative degradation, and only the exact understanding of its degradation under certain conditions opens the way for future improvements.

The most difficult experimental problem is to determine the conditions under which the chemical process is the rate-controlling step. Our experience shows that this can be achieved as follows: it is known that the dehydrochlorination of PVC starts by statistical initiation, and, in the case of polymers with the most probable distribution, up to a certain molecular weight the kinetic "zip" may be considered long. This process has a global reaction order of 3/2. Consequently, we shall select a PVC with a small molecular weight and, if the reaction order 3/2 is found for its dehydrochlorination, we can consider that under such conditions the chemical process is the rate-controlling step. Now if another polymer is studied under identical conditions, the probability that the chemical reaction is also rate-controlling is high because from the physical point of view (granulation, thermal conductivity, the quantity of liberated gas, etc.) the polymers do not differ very much from each other.

In the study of PVAc we find that no matter what the origin of the sample for small and medium molecular weights the reaction order of the degradation is 3/2. Using the correlation between the expected reaction order and the most probable mechanism, the conclusion was reached from the analysis carried out by the Derivatograph of 20-mg samples that the controlling step of the process is the chemical reaction.

The utility of thermal analysis in research on polymers will be illustrated by a concrete example.

Formaldehyde copolymers containing $-C-C$ links and stabilized by thermal treatment and with antioxidants were studied, the results being presented in Table 2. These results lead to the conclusion that the raw copolymer depolymerizes from the chain end. Now the third method of stabilization is not useful because the process of polymer degradation is characterized by a smaller activation energy. In contrast, the greater activation energies after the first and second methods of stabilization show the good action of the stabilizers. The polymer with the best thermal characteristics is obtained by using the first method of stabilization; the loss of weight at 290° is 5%, similar to that of Hostaform. However, it seems that the degradation mechanism is different.

Table 2

Specimen	E, kcal/mole	n	DTA (initially)	$T_{5\%}$ °C
Hostaform	57	0.9	exotherm	290
S_1	69	1.5	exotherm	290
S_2	74	1.7	exotherm	270
S_3	27	0.5	endotherm	260
Raw copolymer	24	1.0	endotherm	220

Conclusions

Correlations between degradation mechanism, kinetic parameters and experimental conditions for polymer destruction have been discussed. It is important to use samples below 20 mg (granules or very fine films) for the thermogravimetric studies of polymers.

References

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Résumé — Dans le but de déterminer les paramètres cinétiques des polymères, on a utilisé la méthode de Flynn—Wall et celle de Freeman—Carroll qui peut aussi s'appliquer quand les paramètres cinétiques varient pendant la décomposition ou lorsque la température de l'échantillon n'augmente pas suivant un programme strictement linéaire. Pour interpréter les résultats, on a étendu la théorie de Boyd pour la dégradation des polymères par élimination et montré qu'il était possible de décrire les constantes cinétiques de ces réactions à l'aide des valeurs obtenues. On a mis également en relief que, dans le cas de la dépolymérisation et de la décomposition des polymères avec perte de poids, ces paramètres cinétiques se prêtent aisément à la détermination du mécanisme de la réaction.

ZUSAMMENFASSUNG — Bei der Bestimmung der kinetischen Parameter von Polymeren wurde außer der Flynn—Wall-Methode auch die Freeman—Carroll-Methode eingesetzt, da letztere auch in solchen Fällen anzuwenden ist, bei denen sich die kinetischen Parameter während des Abbauvorganges ändern oder bei welchen der Temperaturanstieg in der Probe nicht nach einem genau linearen Programm erfolgt. Zur Deutung der Ergebnisse wurde versucht, die Boydsche Theorie mit Hilfe eines formalen Modells für den Polymer-Abbau durch Eliminierung auszuweitern und somit zu beweisen, daß die Beschreibung der kinetischen Konstanten dieser Reaktionen an Hand der erhaltenen Werte möglich ist. Es wurde auch betont, daß in den Fällen der Depolymerisierung und der Polymerzersetzung durch Eliminierung der Reaktionsmechanismus unter Anwendung dieser kinetischen Parameter leicht bestimmt werden kann.

Резюме — При определении кинетических параметров полимеров использован, помимо метода Флинн—Уалла, метод Фримен—Керролла, поскольку этот метод применим и в тех случаях, когда кинетические параметры меняются в процессе распада или температура образца увеличивается не по линейной программе. Для интерпретации результатов сделана попытка расширить теорию Бойда с помощью формальной модели распада полимера элиминированием и показана возможность описания кинетических констант этих реакций полученными величинами. Установлено также, что в случаях деполимеризации и распада полимера элиминирование этих кинетических параметров позволяет легко определить механизм реакции.