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DETERMINATION OF THE KINETIC PARAMETERS OF POLYVINYLCHLORIDE

I. Dehydrochlorination at low conversions

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Kinetic equations proposed in the literature for thermal decomposition reactions may be approximated at low conversions by the relation: $\alpha^b = Dp(x)$. This equation reveals three kinds of behaviour under isothermal conditions, as evidenced in the thermal dehydrochlorination of polyvinylchloride. The kinetic parameters were determined with a computing program and its performances were tested. The calculation method was applied to some polyvinylchloride macromodels.

Study of the thermal decomposition of polymers is very important if we are to establish the causes of their thermal instability.

The thermal degradation of polyvinylchloride begins at temperatures over 373 K, although the linear and regular structure of the macromolecular chain implies good thermal stability. This instability may be attributed to some labile structures (tertiary chlorine, internal double bonds, chloromethyl branches, end groups, etc.) appearing in the polymerization process or during polymer processing [1–3]. On the other hand, the tacticity in polyvinylchloride may influence the thermal degradation mechanism [4, 5].

In order to provide evidence of the importance of these structural defects, the thermal degradation of polyvinylchloride must be followed at the lowest possible temperatures. At such temperatures, the dehydrochlorination rate being very low, the conductometric method for the detection of evolved hydrogen chloride is adequate from the aspect of precision.

The thermal degradation of polyvinylchloride may be carried out under isothermal conditions, or under non-isothermal conditions at a constant heating rate. The meain deficiency of the isothermal method results from the fact that the sample is slow to attain the working temperature. In this way the kinetic analysis of the degradation process is difficult [6, 7]. The requirement of remaining in the low

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temperature range under non-isothermal conditions at the available heating rates involves the study of thermal degradation at low conversions (2–3%).

Theoretical

The theoretical study starts from the following separable differential equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion, T is the absolute temperature, $k(T)$ is the reaction constant and $f(\alpha)$ is the conversion function.

The temperature-dependence of the reaction constant is given by the well-known Arrhenius relation:

$$k(T) = Z\exp(-E/RT)$$

where Z is the frequency factor, E is the activation energy and R is the ideal gas constant.

Integrating of Eq. (1) for non-isothermal measurements at a constant heating rate, $\beta = \frac{dT}{dt}$, leads to

$$F(\alpha) = \int_0^{\infty} \frac{d\alpha}{f(\alpha)} = \frac{ZE}{\beta R} p(x) \tag{2}$$

where $x = \frac{E}{RT}$ and $p(x) = \int_x^{\infty} \frac{e^{-u}}{u^2} du$.

The functions $F(\alpha)$ and $p(x)$ are designated as the conversion integral and the temperature integral, respectively.

The function $f(\alpha)$ in Eq. (1) specifies the particular type of kinetic mechanism. Numerous such functions have been proposed in the literature, which may be justified theoretically and/or experimentally [8].

The most usual conversion functions with the corresponding conversion integrals and the first two terms of the power series expansion are listed in Table 1.

Models I, II_b and III_d were tested for polyvinylchloride dehydrochlorination [9–11] (Table 1).

If the experimental study is made at low conversions, we keep only the first term from this power series expansion of the function $F(\alpha)$. In this way, the following relation can be written:

$$a\alpha^b = \frac{ZE}{\beta R} p(x) \tag{3}$$

where a and b are characteristic parameters for each particular mechanism.

Table 1 Main conversion functions and conversion integrals in thermal degradation

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I. Reaction order model

$$f(\alpha) = (1-\alpha)^n;\ F(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} = \alpha + \frac{n}{2}\alpha^2 + \ldots$$

II. Reactions controlled by nucleation

a) $f(\alpha) = \alpha^m;\ F(\alpha) = \frac{\alpha^{1-m}}{1-m},\ m<1$

b) $f(\alpha) = \alpha^n(1-\alpha)^m;\ F(\alpha) = \frac{\alpha^{1-n}}{1-n} + m\frac{\alpha^{2-n}}{2-n} + \ldots$

$1/2<n<1;\ 0.556<m<0.774$

III. Reactions controlled by nucleation followed by nucleus volume increase

a) Introduction period

$f(\alpha) = \alpha^{3/4};\ F(\alpha) = 4\alpha^{1/4}$

b) Bidimensional nucleus growth (Avramî equation)

$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{1/2};$

$F(\alpha) = 2[-\ln(1-\alpha)]^{1/2} = 2\sqrt{\alpha}\left(1+\frac{1}{4}\alpha+\ldots\right)$

c) Tridimensional nucleus growth

$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{2/3};$

$F(\alpha) = 3[-\ln(1-\alpha)]^{1/3} = 3\sqrt[3]{\alpha}\left(1+\frac{\alpha}{6}+\ldots\right)$

d) General case

$f(\alpha) = (1+\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}};$

$F(\alpha) = n[-\ln(1-\alpha)]^{1/n} = n\sqrt[n]{\alpha}\left(1+\frac{\alpha}{2n}+\ldots\right)$

IV. Reactions controlled by nucleation followed by linear nucleus growth

a) Concatenated growth with ramification possibilities

$f(\alpha) = -\alpha$

Explosive reactions: $f(\alpha) = \alpha^n$ $(n>1)$

The conversion function cannot be applied to the initial stages.

b) Nuclei capable of ramification and interaction during growth

$f(\alpha) = \alpha(1-\alpha)$

The same observation as above

V. Reactions controlled by diffusion

a) Unidimensional transport with constant diffusion coefficient (parabolic law)

$f(\alpha) = \alpha^{-1};\ F(\alpha) = \frac{\alpha^2}{2}$

Sintering phenomena

$f(\alpha) = \alpha^{-n};\ F(\alpha) = \frac{\alpha^{n+1}}{n+1};\ 0<n<1$

b) Bidimensional transport

$f(\alpha) = [-\ln(1-\alpha)]^{-1};$

$F(\alpha) = \alpha+(1-\alpha)\ln(1-\alpha) = \frac{1}{2}\alpha^2+\frac{1}{6}\alpha^3+\ldots$

c) Tridimensional transport in a sphere Jander equation

$f(\alpha) = (1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1};$

$F(\alpha) = 3\left\{\frac{1}{2}[1+(1-\alpha)^{2/3}]-(1-\alpha)^{1/3}\right\} = \frac{\alpha^2}{6}+\frac{4\alpha^3}{27}+\ldots$

Ginstling–Brounstein equation

$f(\alpha) = [(1-\alpha)^{-1/3}-1]^{-1};$

$F(\alpha) = \frac{3}{2}[1-(1-\alpha)^{2/3}]-\alpha = \frac{\alpha^2}{6}+\frac{1}{27}\alpha^3+\ldots$

Relation (3) can be put in the following form:

$$\alpha^b = Dp(x) \tag{3}$$

where $D = \frac{ZE}{\beta Ra}$.

The differential equation corresponding to Eq. (3) is

$$\frac{d\alpha}{dt} = \frac{k(T)}{ab}\cdot\alpha^{1-b} \tag{4}$$

which is certainly applicable for low conversions.

From Table 1, for all models excepting the Jander and Ginstling–Brounstein models, it is found that $ab = 1$. The differential Eq. (4) takes the simplest form in this case:

$$\frac{d\alpha}{dt} = k(T)\alpha^{1-b} \tag{5}$$

The relation $ab = 1$ will be considered in the following calculations, in order to specify the value of Z.

Equation (4) shows the existence of three types of behaviour at low conversions under isothermal conditions:

1) The dehydrochlorination rate increases with increasing conversion ($b < 1$). This is the case for reactions controlled by nucleation followed by increase of the nucleus volume.

2) The dehydrochlorination rate is constant (zero-order kinetics; $b = 1$). This behaviour is characteristic for the reaction order model.

3) The dehydrochlorination rate decreases with increasing conversion ($b > 1$), the case for reactions controlled by diffusion.

All these types of behaviour have been found in different studies regarding the thermal degradation of polyvinylchloride at low conversions [12]. In this context, Eq. (5) offers a possibility for quantitative analysis of the process.

As the reaction order model is widely used, we shall point out some consequences resulting from the above-mentioned analysis.

a) The system behaviour is not dependent on the reaction order at low conversions; consequently, this parameter will not be determined from this study.

b) The constancy of the decomposition rate under isothermal conditions is a natural (mathematical) consequence of the conversion function structure. In order to explain the constancy of the decomposition rate of dehydrochlorination at low conversions, a mechanism of the regeneration of defects was proposed [13].

At the end of these considerations, it may be noted that the experimental determination of b from relation (3) does not permit establishment of the kinetic mechanism type without ambiguity. Indeed, the conversion functions:

$$f(\alpha) = \sqrt{\alpha}\,(1-\alpha)^m$$

and

$$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{-1/2}$$

lead to the same approximative expression:

$$F(\alpha) \cong \sqrt{2}$$

Determination of kinetic parameters

For determination of the kinetic parameters of polyvinylchloride dehydrochlorination, the following approximation was used for $p(x)$ [14]:

$$p(x) = \frac{e^{-x}}{x}\left(1 - \frac{2}{x}\right) \tag{6}$$

representing the first two terms from the asymptotic expansion of function $p(x)$.

On substituting (6) into (3) and taking logarithms, we obtain:

$$b \ln c - 2\ln T = \ln \frac{ZR}{\beta Ea}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT}$$

The value of b is estimated by trial; the plot $b \ln c - 2 \ln T$ *vs.* $1/T$ is a straight line. For this purpose a program in FORTRAN language was prepared. The values of b were successively tested from 0.1 to 3.0 with a step of 0.1 (30 values).

The regression line was determined for each value of b utilizing the least square method. The deviation from linearity is given very well by the expression:

$$L = \frac{\sqrt{\sum_{i=1}^{n} \varepsilon_{ri}^2}}{n}$$

where ε_{ri} is the relative error against the regression line and n is the number of experimental data.

The program takes the value of b corresponding to $I_{\min}$. The kinetic parameters E and Z were evaluated with this value of b. The program performances were tested by using relation (3) and calculating the theoretical curves for different values of the kinetic parameters. The approximation proposed by Zsakó [15] for $p(x)$ was used in these calculation in order to increase the accuracy.

The values found in this way

$$p(x) = \frac{e^{-x}}{(x+2)(x-d)},$$

where $d = \dfrac{16}{x^2-4x+84}$ were introduced as input data. The program gave practically the same values of the kinetic parameters as those generated by the input data (Table 2).

Table 2 Testing of program performances estimating the kinetic parameters. Arbitrarily chosen kinetic parameters for the generation of the input data: $b = 1.1$; $E = 175.52$ kJ/mol; $Z = 3.36 \cdot 10^{13}$ min^{-1}. Kinetic parameters obtained from data processing via Eq. (3): $b = 1.1$; $E = 175.68$ kJ/mol; $Z = 3.53 \cdot 10^{13}$ min^{-1}

T, °C	α, %	
	input data	calc. data
182.5	0.0159	0.0159
184.0	0.0184	0.0184
185.5	0.0212	0.0212
187.0	0.0245	0.0244
188.5	0.0282	0.0282
190.0	0.0324	0.0324
192.0	0.0391	0.0391
193.5	0.0448	0.0449
195.0	0.0515	0.0515
196.0	0.0564	0.0564
197.0	0.0617	0.0618

Experimental

Copolymers of vinylchloride with 3-chloro-1-pentene (H_2) [16, 17], isopropenyl chloride (Cl_T) [18] and 4-chloro-1-pentyne (Cl_A) [19] were utilized as macromodels with controlled structural defects for polyvinylchloride (Table 4).

The dehydrochlorination of the samples by thermal degradation was performed by using equipment described previously [7], with 0.2 g samples. The linear heating rate was 45 deg/min, obtained by means of a linear temperature programmer. The amount of hydrogen chloride evolved was measured continuously by conductometry. The degree of dehydrochlorination or the conversion, $\alpha\%$, was determined as the ratio between the hydrogen chloride evolved and the total amount available in the polymer.

The labile chlorine contact was determined by phenolysis [20].

Results and discussion

The time-dependence of the conversion for the macromodels is presented in Fig. 1. In these macromodels for polyvinylchloride, the structural defect content decreases in the following sequence: $H_T > Cl_T > Cl_A$, the thermal stability indicates the same sequence. Thus the conclusion can be drawn that the nature of the structural defect will have the greatest influence on the thermal stability of the samples, at least in the earlier stages of the dehydrochlorination.

Since the first stage of dehydrochlorination is characterized by very low activation energies, this domain must be defined as precisely as possible. From this

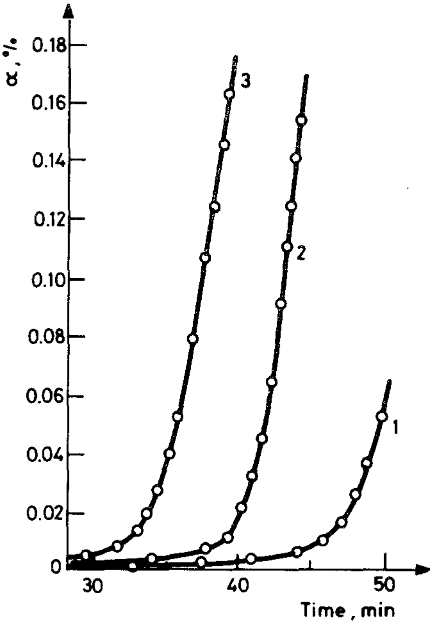

Fig. 1 Experimental curves of PVC macromodel dehydrochlorination in inert atmosphere. 1 – macromodel with H_T; 2 – macromodel with Cl_T; 3 – macromodel with Cl_A

point of view, for a careful analysis of the data it is ncessary to exclude from the calculations conversions below 0.013%.

The kinetic parameters obtained in this way led to the theoretical conversions via Eq. (3). These conversions were then compared with the experimental ones (Table 3). It is evident that the agreement is good.

The kinetic parameters of the macromodels are given in Table 4. (Two measurements were considered for each sample.) Sample Cl_A exhibits different

Table 3 Comparison between experimental data and values computed via Eq. (3) (sample Cl_T)

T, °C	α, %		Relative error, %
	theor.	exper.	
152.0	0.0220	0.0215	−2.28
154.0	0.0276	0.0260	−6.24
155.5	0.0327	0.0320	−2.27
157.0	0.0387	0.0380	−1.92
158.5	0.0458	0.4650	1.54
160.0	0.0541	0.5450	0.81
165.0	0.0933	0.0987	5.47
166.5	0.1100	0.1200	8.64
168.0	0.1290	0.1400	8.08
170.0	0.1590	0.1600	5.73
171.5	0.1860	0.1800	−3.48
174.5	0.2550	0.2600	2.08
176.0	0.2970	0.2870	−3.55
177.5	0.3470	0.3350	−3.45
179.0	0.4040	0.3750	−7.66

Table 4 Kinetic parameters of the macromodels

Sample	Comonomer content, %	b	E, kJ/mol	Z, min^{-1}	$\frac{E}{b}$	$\frac{\ln Z}{b}$
H_T	3.67[a]	1.1	175.52	$3.35 \cdot 10^{15}$	159.56	32. 5
		0.9	138.32	$5.15 \cdot 10^{11}$	153.69	30.0
Cl_T	2.00[a]	1.2	184.63	$1.35 \cdot 10^{18}$	153.86	34.8
		1.2	199.34	$5.74 \cdot 10^{19}$	166.12	37.9
Cl_A	0.20[b]					
first stage		0.9	131.87	$3.71 \cdot 10^{13}$	146.52	34.7
second stage		2.0	180.04	$1.15 \cdot 10^{16}$	90.02	18.5
first stage		0.9	153.36	$4.15 \cdot 10^{16}$	170.40	42.5
second stage		1.9	183.88	$1.69 \cdot 10^{17}$	96.78	20.9

[a] determined via NMR measurements,

[b] determined via labile chlorine content.

behaviour. The kinetic parameters for this sample change suddenly at a certain temperature.

The activation energies obtained for the macromodels are quite similar to the values found for polyvinylchloride [21, 22]. The existence of two stages in the dehydrochlorination process has been pointed out in the literature for less stable samples [23]. Table 4 reveals that the following relation holds between the kinetic parameters of samples H_T and Cl_T and those of the second stage of thermal decomposition of Cl_A:

$$\frac{E_1}{E_2} = \frac{\ln Z_1}{\ln Z_2} = \frac{b_1}{b_2}$$

This relation reveals a new type of compensation effect. A detailed analysis of different types of isoparametrical relations was made by Lesnikovich and Lechik [24]. For the moment, we are not able to state whether the compensation effect we have observed is true. Although, method of the determination of the kinetic parameters provides very good verification on testing, this fact cannot constitute a decisive proof. A systematic study of this phenomenon would provide new data in this respect.

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Zusammenfassung — In der Literatur vorgeschlagene kinetische Gleichungen für thermische Zersetzungsreaktionen können bei niedrigen Konversionen mit der Gleichung $\alpha^b = Dp(x)$ genähert werden. Diese Gleichung offenbart unter isothermen Bedingungen drei Verhaltensweisen, wie an der thermischen Dehydrochlorierung von Polyvinylchlorid bewiesen wird. Die kinetischen Parameter wurden mittels eines Computerprogrammes ermittelt und ihre Leistungsfähigkeit überprüft. Das Rechenverfahren wurden an einigen Polyvinylchloridmakromodellen getestet.

Резюме — Кинетические уравнения, предложенные в литературе для реакций термического разложения, могут быть при низкой степени превращения описаны уравнением $\alpha^b = Dp(x)$. Это уравнение показывает три различных характера термического поведения в изотермических условиях, как это было доказано на примере термического дегидрохлорирования поливинилхлорида. Кинетические параметры были определены с помощью математической программы, действие которой было испытано. Метод расчета был применен для некоторых макромоделей поливинилхлорида.