

DYNAMIC THERMAL DECOMPOSITION OF LINEAR POLYMERS AND ITS STUDY BY THERMOANALYTICAL METHODS

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Kinetic schemes allowing to interpret the results of high-temperature gravimetric analysis of linear polymers are proposed. A thermoanalytical method has been developed in which the time for establishing constant temperature in the sample is reduced by 1–2 s. The method can be used to determine to what temperature the polymer can be overheated.

Kinetics of high-temperature depolymerization

Earlier, by thermoanalytical methods [1] the limit of the temperature interval of polymer thermolysis has been determined “from above”, by the characteristic limit temperatures in the range close to the spinoidal point. The relationship between the limit temperatures T_l and the weakening of intermolecular interaction has been established: $T_l = D_i/R$, where D_i is the energy of the intermolecular bonds. However, kinetic relations have not been taken into consideration.

We will demonstrate that in the high-temperature range, the depolymerization process taking place in the total volume of the substance (end-group reaction) largely depends on the destruction rate of associated and non-associated monomeric units. We will assume that in each monomeric unit one reaction center exists, and the rate constants of the destruction of associated monomeric units k_a and of non-associated (isolated) monomeric units k_i are independent of the length^o of the chain. At uniform distribution of the chains in the volume of the polymer, the kinetics of thermolysis are governed by the equaton

$$-dC/dt = k_a N_a + k_i N_i \quad (1)$$

where C is the concentration of the monomeric units formed in the destruction, N_a and N_i are the concentrations of the associated and non-associated (isolated) chain ends, resp.

At lower temperatures the material balance equation is

$$N_a + N_i = zN \quad (2)$$

where z is the mean amount of chain ends in the macromolecule, and N is the concentration of the macromolecules.

For branched (but not cross-linked) molecules $zN = \sum z_i N_i$, where z is the number of reactive end groups of N_i macromolecules. In the simplest case considered here $z=1$, the reaction proceeds from one end of the molecules.

Arranging the terms of Eq. (1) according to initial polymer concentration one obtains

$$-d\omega/dt = k_a(1-p) + k_i p \quad (3)$$

where $\omega = M/M_0$, i.e. the ratio of the masses of reacted and initial polymer, $M_0 = Nn_0$, $k_a = k'_a/n_0$, $k_i = k'_i/n_0$, $p = N_i/N$, $(1-p) = N_a/N$, n_0 is the initial number of monomeric units in the chain.

For elementary reactions the relationship rate constant vs. temperature is usually given by the Arrhenius equation

$$k_a = k_{0a} \exp(-E_a/RT), \quad k_i = k_{0i} \exp(-E_i/RT)$$

where E_a and E_i are activation energies, resp., and k_{0a} , k_{0i} are frequency factors.

The rate of establishing equilibrium of intermolecular interaction substantially exceeds the rate of chemical processes, hence one may write

$$N_i = K_p N_a \quad (4)$$

The relationship equilibrium constant vs. temperature is expressed by the van't Hoff equation:

$$K_p = K_{p0} \exp(-\Delta H/RT)$$

where ΔH is the enthalpy of the dissociation process. The solution of Eq. (3), taking into account Eqs (2) and (4), is

$$\alpha = 1 - \omega = \frac{k_i K_p + k_a}{1 + K_p} \quad (5)$$

The value of the constant coefficient z is included in the constants. Eq. (5) describes experimental data cited in [1] satisfactorily. It follows, in fact, from Eq. (5) that at low temperatures, when $K_{p0} \exp(-\Delta H/RT) \ll 1$ and mainly associated monomeric units exist, $k_i K_p \ll k_a$,

$$\ln(1/t) = -\ln(1-\omega) + \ln k_{a0} - E_a/RT \quad (6)$$

Activation energies determined from the linear sections of the relationship $\ln(1/t)$ vs. $1/T$ cited in [1] satisfactorily coincide with the data of other authors, e.g. [2], confirming the correctness of the above approach.

In the interval of higher temperatures, where $K_{p0} \exp(-\Delta H/RT) \gg 1$ and $k_i K_p \gg k_a$, mainly non-associated monomeric units exist, and hence, if no other processes would take place, at higher temperatures the Arrhenius equation should also be valid, but with another value E_i for the activation energy:

$$\ln(1/t) = -\ln(1-\omega) + \ln k_i - E_i/RT \quad (7)$$

However, experimental data [1] indicate that when the spinoidal point is approached, Eq. (7) does not describe experimental results, and correction is needed. The reason is that at high temperature close to limit temperatures, the increased number of non-associated units leads to the formation of blocks, that is, sections of macromolecules consisting of non-associated monomeric units arranged one after the other in substantial lengths. Since the blocks are unable to occupy a great number of conformations, they possess excess free energy of formation, defined by the entropy of the system. If the excess energy of the block exceeds the energy required for splitting the chemical bond, the splitting reaction in the main chain will be able to proceed not only at the chain end, but also somewhere in between along the chain. Consequently, at high temperatures the reaction mechanism may change: instead of end-group splitting, random splitting will become the prevalent mechanism, accompanied by the elimination of large non-associated blocks. This mechanism is termed avalanche-like decomposition (since large molecule fragments are set free) or dynamic decomposition. It occurs at high temperatures close to the temperature of the spinoidal point, and is accompanied by explosion like effects.

Kinetics of the avalanche-like thermal analysis of polymers

To take into account the dynamic effects of thermal analysis in the kinetic equation, a term must be added, accounting for the formation of non-associated blocks, in the shape of the product of the rate constant with block concentration and with the number of monomeric units in individual blocks. Since the process leading to block formation of a given length has random character, the probability $p = \frac{1}{1+K_p}$ of the existence of non-associated monomeric units and the probability $(1-p) = K_p/(1+K_p)$ of the existence of associated monomeric units must be considered. The probability of formation for a block with a length of n non-

associated units is equal to $p^n(1-p)^2$, and the concentration of such blocks, assuming that at high temperatures a block with the length n is formed on the given chain, is equal to $p^n N(1-p)^2$ [2]. Accepting the principle of the independence of chemical reactions (each block is decomposed independently of the other) the following kinetic equation can be written:

$$-d\omega/dt = k_a(1-p) + k_i p + K \sum_m^{n_0-2} n p^n (1-p)^2 N + K(n-1)p^{n-1} N + K n p^n N \quad (8)$$

For reasons of simplification, in the followings the last two terms of the sum in Eq. (8) will be neglected, without impairing the general validity of the result. The parameter m characterizes the minimum dimension of the non-associated monomeric block at which splitting does not assume an avalanche-like character. It is assumed that evaporation rate is much higher than the block formation rate as the result of the chemical reaction, and decomposition proceeds with the same probability along the total length of the chain.

In the followings it is necessary to take into account the change of the number of molecules with time:

$$dN/dt = KN(1-p)^2 \sum_m^{n_0-2} p^m \quad (9)$$

The solution of this equation at $T = \text{const}$ is

$$N = N_0 \exp \left[K(1-p)^2 \sum_m^{n_0-2} p^m t \right] \quad (10)$$

where N_0 is the initial concentration of the molecules in the system.

Introducing the value of N into Eq. (8) one obtains

$$-\frac{d\omega}{dt} = k_a(1-p) + k_i p + \sum_m^{n_0-2} K n p^n (1-p)^2 \exp \left[K(1-p)^2 \sum_m^{n_0-2} p^m t \right] \quad (11)$$

The solution of this equation at temperatures close to the limit temperatures, when the concentration of associated units is close to zero, while $p \rightarrow 1$, leads to the following expression:

$$\ln \frac{1}{t} \simeq \ln \frac{K p^{n_0} + k_i}{1-\omega} \simeq \ln \frac{K p^{n_0}}{1-\omega} \quad (12)$$

When reaching the temperature T_l , the system becomes thermodynamically unstable, the isolated macromolecules represent a labile "polymeric gas",

decomposing at a high rate in the moment of its formation. Each bond, at free rotation, has the entropy $\bar{\alpha} R$, $\bar{\alpha}$ being a numerical coefficient, $\bar{\alpha} \leq 1$. The entropy loss in the process will then be $\bar{\alpha} R$ at each monomeric unit. Taking into account the additivity of free energy one may write that $K = k_e/exc \cdot k_{chem}$, where k_{chem} is the rate constant of the chemical reaction in the gas phase and k_{exc} is the multiplication coefficient due to the excess free energy of formation of the "polymeric gas". In the physical sense k_{exc} is purely entropical in its origin, caused by the presence of long macromolecular chains in the polymers, $k_{exc} = \exp \bar{\alpha} n$. Since n is a large number in the order ($10^4 - 10^5$), the constant K will approach in its value the maximum possible values for chemical reactions, i.e. $K = 10^9 - 10^{12}$ 1/s, and the gasification period of the polymer at $T = T_i$ will be defined essentially by the time for the dispersion of the gaseous decomposition products.

The above analysis demonstrates that to describe the dynamic, avalanche-like thermolysis of polymers it is necessary to determine experimentally a great number of parameters of the proposed mathematical model. For this purpose, isothermal thermogravimetric analysis with short heating periods of the sample are best suited.

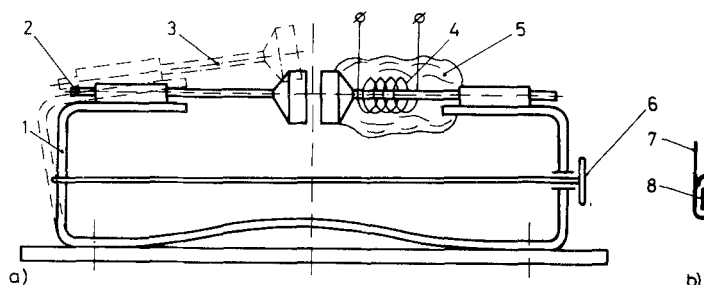


Fig. 1 Schematic representation of the contact heater for thermogravimetric studies of polymers. a) 1 – spring clamp, 2 – stainless steel rods, 3 – rods in the deflected position, 4 – spiral of the electroheater, 5 – thermal insulation, 6 – arrester catch, 7 – foil pack, 8 – sample. b) Pack with the sample

Experimental

To determine kinetic parameters, an experimental technique has been developed characterized by low thermal inertness of the heating system. To reduce the period for reaching the $T = \text{const.}$ régime in the samples we used the method proposed earlier to heat the sample by means of contact with metal rods heated to constant temperature [3]. The apparatus is represented schematically in Fig. 1. The sample 8 is placed in a pack of metal foil 7 (aluminium, brass, steel) and preliminarily

weighed. After releasing the arrester catch 6 containing a flat spring pressure clamp 1, the samples are pressed together between the heated rods. The temperature of the rods is measured by a fixed instrument: a millivoltmeter, by means of thermocouples fixed to the ends of the rods.

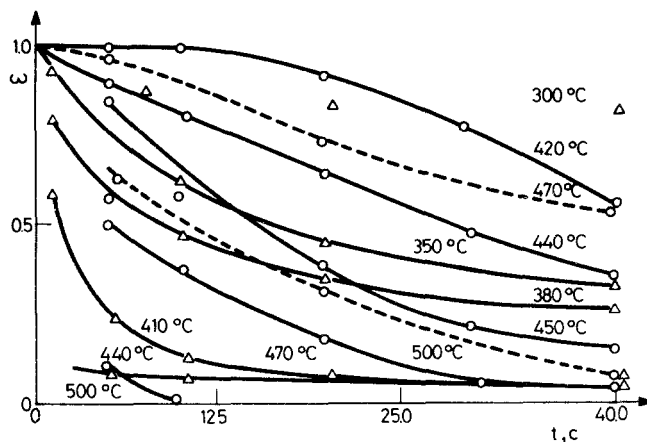


Fig. 2 Kinetics of thermolysis of polymers under isothermal heating conditions (continuous line: block polystyrene, molecular mass 600,000; broken line: high density polyethylene, molecular mass 175,000; spinoidal commercial-grade polymethyl methacrylate. Numbers at the curves: temperature, °C

Calculations and control experiments with thermocouples placed in the samples demonstrated that minimum time during which sample temperature became equal to the temperature of the rods depended on the thickness of the sample and did not exceed 1–2 seconds in the experiments. The calculation of the experimental error in temperature measurement is discussed in the next paragraph. After temperature equalization of the sample with the heater, the samples were kept at constant temperature for a given exposure time, one sample e.g. for 5 s, another for 10 s, a third one for 20 s etc. After exposure the samples were taken out, the rods were removed, the samples were again weighed on analytical scales and the relative mass of the residue $\omega = M/M_0$ was calculated. The results of some experiments are represented in Fig. 2.

For processing experimental results and determining T_i values ω was plotted versus temperature (Fig. 3) or versus reciprocal absolute temperature as in [1]. The use of fixed instruments for measuring temperature and mass of sample allowed to increase accuracy of measurements as compared to traditional methods.

Error in temperature measurement

With increasing sample thickness the error in temperature measurement will increase. To establish the minimum sample thickness for obtaining the required accuracy we calculated the processes of non-steady-state thermal conductivity in the samples taking into account heat absorption due to chemical reactions. The equation of thermal conductivity has the following form:

$$\frac{\partial T_1(x,t)}{\partial t} = a_1 \frac{\partial^2 T_1(x,t)}{\partial x^2} + \frac{W}{c\rho} \quad (13)$$

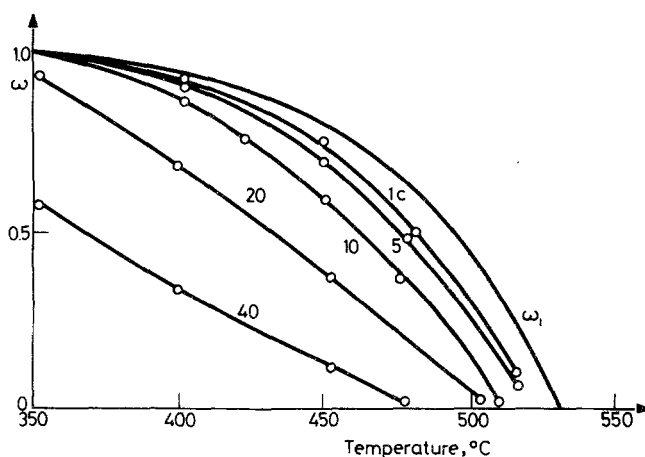


Fig. 3 Isochronous curves of block polystyrene thermolysis determined by isothermal experiments. Numbers at the curves—decomposition time in seconds

The equation of thermal conductivity in the metallic rods (cf. Fig. 1) is

$$\frac{\partial T_2(x,t)}{\partial t} = a_2 \frac{\partial^2 T_2(x,t)}{\partial x^2} \quad (14)$$

In these equations T_1 and T_2 are temperatures of the sample and of the plates of the heater, resp., a_1 and a_2 are temperature conductivities of the sample and heater rod, resp., $c\rho$ and W are volumetric heat capacity and volumetric heat discharge owing to chemical transformations in the sample, $2R$ is sample thickness.

In the followings we will consider the worst case from the view of estimating the error, when the chemical transformation proceeds with constant rate and not, as usual, with a decreasing rate. Then $W = Q/t$, where Q is the thermal effect of the reaction, t is time of the reaction.

The conditions for ideal thermal contact between the sample and the heater are

$$\pm \lambda_1 \frac{\partial T_1(\pm R, t)}{\partial x} = \pm \lambda_2 \frac{\partial T_2(\pm R, t)}{\partial x}; \quad T_1(\pm R, t) = T_2(\pm R, t) \quad (15)$$

where λ_1 and λ_2 are thermal conductivities of the sample and the rods, resp.

The initial and boundary conditions of the thermal conduction process are

$$T_1(x, 0) = T_0; \quad T_2(x, 0) = T_c; \quad \frac{\partial T_1(0, x)}{\partial x} = 0; \quad (16)$$

$$\frac{\partial T_2(\pm \infty, t)}{\partial x} = 0$$

where T_c is the temperature of the medium (i.e. the heater rods).

The solution of the system of Eqs (13)–(16) is known in the literature [4]. Let us write, based on this solution, the value of maximum temperature decrease, originated between the temperature in the center of the sample $T_{1(x=0)}$ and the temperature of the heater T_c as a function of heating time t :

$$\frac{T_1(0, t) - T_c}{T_0 - T_c} = 1 + \frac{Q}{c\rho(T_0 - T_c)} - \frac{1}{1 + K_\varepsilon} \sum_{n=1}^{\infty} (-h) \left\{ 2 \operatorname{erfc} \frac{(2n-1)R}{2\sqrt{a_1 t}} + \right. \quad (17)$$

$$\left. + 4 \frac{Q}{c\rho(T_0 - T_c)} i^2 \operatorname{erfc} \frac{(2n-1)R}{2\sqrt{a_1 t}} \right\}$$

where $K_\varepsilon = \sqrt{\frac{\lambda_1 c_1 \rho_1}{\lambda_2 c_2 \rho_2}}$ = the criterion of thermal activity of the sample related to the heater,

$$h = \frac{1 - K_\varepsilon}{1 + K_\varepsilon} \quad \text{and} \quad i^2 \operatorname{erfc} u = \int_u^{\infty} i \operatorname{erfc} u.$$

By means of Eq. (17) we calculated the experimental error for two investigated substances: polystyrene ($Q = -70$ kJ/mol) and polytetrafluoroethylene (PTFE) ($Q = -155$ kJ/mol). The calculated values are listed in Table 1.

The above equations demonstrate that for any given thickness of the sample one can always find the minimum exposure time from which on the temperature in the sample may be assumed to be equal to the temperature of the heater. This is usually 1–2 s for 0.1 mm sample thickness.

Table 1 Temperature decrease in polystyrene and polytetrafluoroethylene samples with differing thicknesses versus exposure time (in per cents of the temperature T_0)

Heating time, s	Sample thickness R , mm					
	Polystyrene			PTFE		
	0.1	0.2	0.3	0.1	0.2	0.3
	Temperature decrease, %					
1	0.4	0.6	1.0	0.5	1.1	1.7
2	0.2	0.5	0.8	0.4	0.7	1.2
3	0.2	0.4	0.6	0.3	0.7	1.0
4	0.1	0.4	0.6	0.2	0.6	0.9
5	0.1	0.3	0.4	0.2	0.5	0.9

Experimental results

Using the described method a number of polymers were studied; some of the results are represented in Figs 2–4. The study demonstrated that scattering of the experimental data is small and reproductibility is satisfactory. The data in Fig. 2 demonstrate that the relationship $\omega(t)$ at high temperatures is close to exponential, but the initial exponent does not coincide with the value $\omega=1$. Plotting the

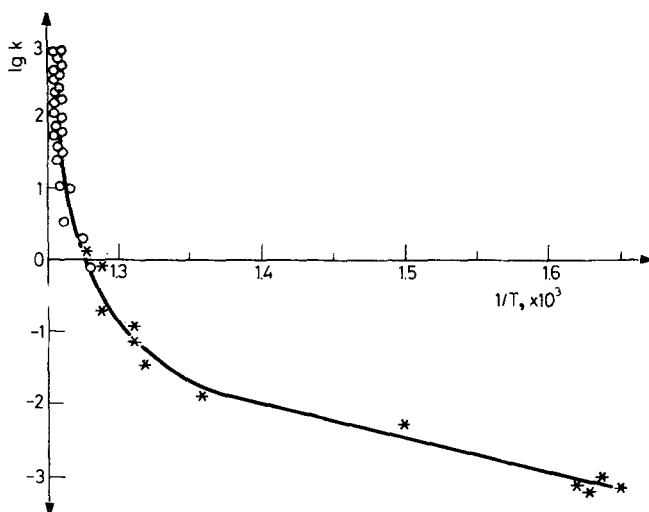


Fig. 4 Logarithm of polystyrene thermolysis rate versus reciprocal temperature, determined by the contact method (\times) and by the imprint method (\circ)

relationship $\omega(T)_t$, satisfied for constant exposure times (isochronous curves) demonstrates that a boundary curve ω_t exist, corresponding to the condition $t \rightarrow 0$. (infinitely high heating rate).

The boundary $\omega_t(T)$ separates the region of metastable and labile states (above the points $\omega_t(T)$) of the polymer. It follows from the above physical and mathematical model that the boundary $\omega_t(T)$ is formed as the result of mass loss accompanying the depolymerization process and due to the formation of blocks of non-associated monomeric units, removed in the non-reacted state from the polymer and decomposed only in the gas phase outside the sample. This conclusion is confirmed by the plot of the logarithm of thermolysis rate *versus* reciprocal temperature (cf. Fig. 4), which in the temperature interval 300–450° is linear and follows the Arrhenius law with the values $E_a = 24.700$ cal/mol and $k_{a0} = 3.9 \cdot 10^5$ 1/s. Above 450° it deviates from the straight line, and the apparent activation energy increases up to 71.000 cal/mol at 500°. This deviation proves that the thermolysis mechanism has changed. The figure clearly shows the shift towards the limit temperature $T_l = 803$ K = 530 °C ($\pm 6^\circ$).

On the same plot, the results of determining T_l for block polystyrene by the imprint method are marked. At $T = T_l$, thermolysis time for polystyrene in the shape of a 1–3 μm thick film, recorded by means of an accelerated movie camera was found to be less than 10^{-3} s. The value established for T_l agrees well with the theoretical value, determined from the energy of dipole–dipole interaction [1] $D_i = 1620$ kcal/mol, namely $T_l = D_i/R = 810$ K. At this temperature, $\Delta H = 0$ in the van't Hoff equation and in Eq. (4), and the length of the non-associated blocks becomes equal to the length of the macromolecules: $n \rightarrow n_0$, all macromolecules will be in the isolated state (a “polymeric gas” will be formed). The coefficient k_{exc} will reach its maximum value and thermolysis proceeds explosion-like, analogously to spinoidal decomposition or phase transition. Therefore the temperature T_l is the final point of the line $\omega_t(T)$.

The experimentally determined limit $\omega_t(T)$ for a given polymer substantially simplifies the description of its thermolysis process at high temperatures, for this purpose the theory of indistinct phase transitions described in detail in [6] can be applied. In particular for block polystyrene, experimental data are satisfactorily described by the function $\omega_t(T) = 0.139 (803 - T)^{0.375}$, and also by the *arcus tangens* equation.

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Zusammenfassung — Es werden kinetische Schemata dargelegt, die die Interpretierung der Ergebnisse von gravimetrischen Hochtemperaturanalysen linearer Polymere ermöglichen. Eine thermoanalytische Methode zur Reduzierung der Zeit zum Erreichen einer konstanten Temperatur in der Probe auf 1–2 s wird beschrieben. Diese Methode kann benutzt werden, um festzustellen, bis zu welcher Temperatur Polymere überhitzt werden können.

Резюме — Предложены кинетические схемы, позволяющие интерпретировать результаты высокотемпературного гравиметрического анализа термолиты линейных полимеров. Разработан метод ТА, в котором время установления постоянной температуры в образце сокращено до 1–2 сек. Метод применим для определения температур достижимого перегрева полимеров.