Short Communication

TG ANALYSIS OF RANDOM SCISSION POLYMER DEGRADATION

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(Received August 29, 1978; in revised form July 10, 1979)

The usual method of the evaluation of the thermogravimetry of a polymer is shown to be of a questionable value in the case of the random scission degradation. Several physically founded approximations of this type of degradation are given for the homopolymer and for the co-polymer or the co-polycondensate of two differently evaporating monomers. The accuracy of some of these approximations is tested by the mathematical simulation of the degradation process.

The usual equation (cf. [1 – 3])

$$-\frac{\mathrm{d}G}{\mathrm{d}T}=\frac{k_0}{q}G^a\exp(-E/RT) \tag{1}$$

(where G is the momentary sample weight, q the linear heating rate and k_0, a and E appropriate constants) often fails to fit the actual TG curve of polymer degradation. In successful cases the values of k_0, a and E obtained are formal descriptive parameters of the curve, rather than meaningful physical constants of the degradation kinetics.

The mathematical description of the degradation kinetics depends on the mechanism. In the simplest case of random scission [4, 5], the probability p that an arbitrary polymer bond will be conserved follows a simple rate equation

$$-\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{k_0}{q}p\exp(-E/RT) \tag{2}$$

where E is now the true activation energy of bond cleavage.

If the initial distribution of the polymer is given so that $N_x(O)$ is the number of the x-mer molecules, the degradation of the system is described by the following set of equations

$$-\frac{\mathrm{d}N_x(T)}{\mathrm{d}T}=\frac{k_0}{q}\exp(-E/RT)\left[N_x(T)-2\sum_{y=x+1}^{m}N_y(T)\right] \tag{3}$$

with the solution

$$N_x(T)=N_x(O)p^{x-1}+ + \sum_{y=x+1}^{m}N_y(O)[(y-x-1)p^{x+1}-2(y-x)p^x+(y-x+1)p^{x-1}] \tag{4}$$

where m is the length of the highest mer and p is the solution of (2), i.e.

$$p = \exp\left[-\frac{k_0}{q}\int_{T_0}^{T}\exp(-E/RT)\mathrm{d}T\right]. \tag{5}$$

If the only volatile mer is the monomer, the following equation describes the TG curve in the case of instant monomer evaporation (M is the monomer molecular weight):

$$G = G_0 - M\left\{N_1(O) + \sum_{y=2}^{m} N_y(O)[(y-2)p^2 - 2(y-1)p + y]\right\}. \tag{6}$$

Usually, the detailed polymer distribution is not known. In the case of random scission, however, the course of the number average polymerization degree P_n does not depend on the initial distribution [4, 5]. Owing to this, the expression for the initially uniform polymer

$$G = G_0P_n^{-1}[2(P_n - 1)p - (P_n - 2)p^2] \tag{7}$$

is a good approximation to the TG of real polymers with usual distributions. If P_n is high, (7) can be simplified further to

$$G = G_0(2p - p^2). \tag{8}$$

It can be shown by computer simulation [5] that (7) and even (8) can be used for polymers with "most probable", Flory or Poisson-type distributions. The accuracy of the obtained values of k_0 and E are usually better than 5 per cent in the case of instant monomer evaporation, and better than 10 per cent if the probable kinetics of monomer evaporation are assumed in the simulated degradation [5].

From (5) and (8), there follows the expression

$$\int_{T_0}^{T}\exp(-E/RT)\mathrm{d}T = -k_0q^{-1}\lg[1 - (1 - G/G_0)^{0.5}] \tag{9}$$

by means of which the values of E and k_0 can be extracted from the TG curve. Using, for example, the Doyle approximation of the integral [6], a pseudolinear function of $1/T$

$$\lg\{T^{-2}\lg[1 - (1 - G/G_0)^{0.5}]\} = -E/RT + \lg(k_0R/qE) \tag{10}$$

gives crude estimations of E and k_0. Much better results, however, can be obtained by computer optimization of these parameters using (7) and (5), with some more precise approximation of the temperature integral.

The appropriateness of the random scission approximation for the given degradation can be determined from the change of distribution during the degradation, or from the isothermal degradation kinetics [4, 7]. Generally, however, it can be expected to fit the purely thermal cleavage of equilibrium polyadducts and polycondensates under an inert atmosphere or in vacuo. Degradation via a radical chain mechanism will be in rather poor accord with this approximation, but even more so with any simpler mathematical model of the type (1).

References

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