Journal of Thermal Analysis, Vol. 29 (1984) 237–241

RELIABILITY OF THE VOLATILIZATION METHOD FOR DETERMINATION OF THE ACTIVATION ENERGY IN THE THERMAL DECOMPOSITION OF POLYMERS

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(Received August 3, 1983; in revised form November 17, 1983)

The LPTD–MS method, used to determine kinetic parameters in the thermal degradation of polymers by means of volatilization curves, was applied to TG data and the results were compared with those obtained by the methods of Flynn & Wall, Friedman, Freeman & Carroll, and Coats & Redfern.

Problems in modelling polymer degradation kinetics are well documented, and several mathematical methods have been proposed in the literature for calculation of the kinetic parameters associated with the thermal degradation processes of polymers [1–6].

Different analytical techniques can be used to obtain the experimental data [7], but the one most widely used and relied on is dynamic thermogravimetry (TG), where the sample is heated at a linear heating rate and in a controlled atmosphere. However, TG is not particularly informative in most cases of polymer degradation when different degradation species are formed simultaneously or sequentially. In these cases one observes at each temperature the overall end of a superimposition of reactions, and the theoretical significance to be attached to the kinetic parameters obtained is much in doubt.

To overcome this difficulty, rather than monitoring the sample weight loss by TG, effluent gas analysis seems more appropriate, since it allows measurement of the rate of appearance of each species formed in the polymer degradation.

Using a volatilization method, one is limited to selecting, from among the mathematical methods available for the calculation of activation energies and pre-exponential factors, a method which does not make use of initial weight and weight loss data in the calculations.

Linear programmed thermal degradation mass spectrometry (LPTD–MS) [8, 9] has recently been used to monitor the thermal decomposition of high molecular weight samples, and the collection of single ion evolution curves allows differentiation of the thermal reactions occurring in the polymer, and the relation of groups of thermal fragments to a specific process.

The high potential of LPTD–MS in elucidating the mechanism of thermal decomposition of polymers has been recognized in several cases [10], but so far there have been no studies aimed at establishing the reliability of the kinetic parameters derived by this method, by comparing them with those derived by the most established TG methods [11–14].

The LPTD–MS method [9] is based on the generation of a family of volatilization curves, obtained by degrading a polymer sample at different linear heating rates, and the kinetic equation is fitted using ion intensity, i.e. single ion current (SIC), instead of weight data, according to the following expression:

$$\ln\left(\frac{M}{T_m^2}\right) + \ln\left(\frac{E}{RK_0}\right) = -\left(\frac{E}{R}\right)\left(\frac{1}{T_m}\right) \tag{1}$$

where M is the heating rate, E is the activation energy, R is the gas constant, K_0 is the pre-exponential factor and T_m is the temperature at the maximum of a specific single ion curve.

If a polymer decomposes selectivity by a single mechanism, i.e. yielding only one product, its total ion current (TIC) curve is identical to the SIC curve. TIC curves in LPTD–MS experiments are related to the amounts of volatile products evolved from a polymer sample upon heating.

It has been pointed out [10, 15] that TIC curves (at a linear heating rate) reproduce the derivative thermogravimetric (DTG) curves, so that the temperature at the maximum of such a curve corresponds to the temperature of the maximum decomposition rate of polymer in the high vacuum of the MS. Therefore, Eq. 1, developed for the determination of kinetic parameters by LPTD–MS, can be applied to calculate the activation energy and the pre-exponential factor by means of TG, in the special case of polymers decomposing selectivity by a single mechanism. To meet these conditions, we have selected four polymers which decompose by unzipping to monomer, i.e. poly(tetrafluoroethylene) (PTFE), poly(methyl methacrylate) (PMMA), poly(α-methylstyrene) (PαMeSty), and poly(oxymethylene) (POM).

Experimental

Materials

The PMMA, PTFE, PαMeSty and POM used in this study were high-purity commercial samples from Aldrich Chemical Co.

Thermogravimetry

A Perkin–Elmer TGS-2 thermal analyzer was used to determine the weight loss (TG) and the rate of weight loss (DTG) during the thermal degradation of the polymers. The instrument was calibrated with a Curie point standard, as per the manufacturer's specifications. Experiments were carried out on about 1.5 mg of finely ground sample (so that the reaction rate would not be limited by diffusion of the volatile species) under a 60 ml/min stream of dry nitrogen and at furnace heating rates of 5, 10, 15 and 20 degree/min for all the polymers investigated. Higher values of heating rate were not used because the elementary processes could have become slow compared with the heating rate.

Calculations were performed by fitting the experimental results in the kinetic rate equations of each method, with the aid of a PDP 11/23 digital computer.

A least square method was adopted to obtain the kinetic parameters listed in Table 1.

Table 1 Comparison of kinetic parameters for PMMA, PTFE, PαMeSty, POM obtained by various methods

Methods	PMMA			PTFE		
	Ea, kJ/mol	*n*	K_0, 1/S	*Ea*, kJ/mol	*n*	K_0, 1/S
Flynn & Wall	223.5	–	–	313	–	–
Friedman	231	–	–	295.5	–	–
Freeman & Carroll	257.8	1.1	–	318.9	0.8	–
Coats & Redfern	244.5	1.2	–	318.5	0.8	–
LPTD–MS	210	–	$2.5 \cdot 10^{16}$	311.8	–	$2.5 \cdot 10^{18}$

Methods	PαMeSty			POM		
	Ea, kJ/mol	*n*	K_0, 1/S	*Ea*, kJ/mol	*n*	K_0, 1/S
Flynn & Wall	225.2	–	–	105.5	–	–
Friedman	230.6	–	–	114.7	–	–
Freeman & Carroll	234	1.7	–	189.6	0.9	–
Coats & Redfern	118.5	1.0	–	127.7	0.6	–
LPTD–MS	247.4	–	$6.6 \cdot 10^{20}$	90.4	–	$3.4 \cdot 10^{6}$

Results and discussion

In Fig. 1 are reported the linear plots of Eq. 1 for the four polymers studied, as derived from DTG curves.

The activation energy and the pre-exponential factor are determined from the slope and the intercept of the straight lines obtained by plotting ln (M/T_m^2) *vs.* $(1/T_m)$, where M is the linear heating rate and T_m the temperature at the maximum of the DTG curves. The resulting data are collected in Table 1, together with the kinetic parameters determined by the other methods examined here.

The activation energy value of 210 kJ/mol obtained for PMMA from DTG curves compares very well with the values determined by the other methods. For PTFE, all the methods give nearly the same value of 311.8 kJ/mol, in accordance with the values reported in the literature [6]

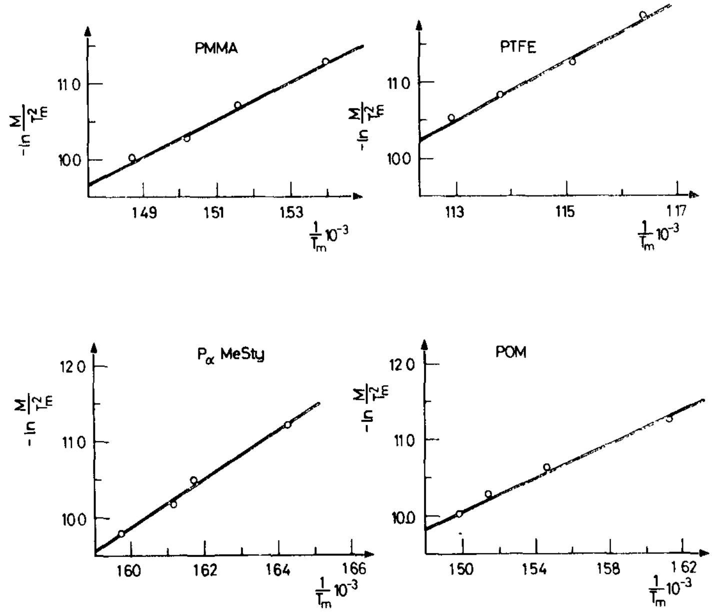

Fig. 1 Linear plot of Eq. 1 as derived from DTG curves for PMMA, PTFE, PαMeSty and POM

For PαMeSty, Eq. 1 gives a value of 247.4 kJ/mol, in good agreement with the results obtained by the methods of Flynn & Wall, Friedman, and Freeman & Carroll. The Coats & Redfern method gives a value of 118.5 kJ/mol, which is very low compared with the others.

For POM, an activation energy of 189.6 kJ/mol is obtained by the Freeman & Carroll method, while the other methods give values of 90–127 kJ/mol. These data show that the LPTD–MS method, applied to TG data, yields activation energy values which coincide reasonably well with the results obtained by the methods of Flynn & Wall and Friedman. The latter are known to be absolute [16], because it is possible to calculate the activation energy without knowledge of the weight loss function in the kinetic equation.

In general, three distinct mechanisms of decomposition of polymers can be considered. A degradation reaction may occur via an irreversible chain reaction, which proceeds through unzipping of monomer units from the degrading polymer. A second case arises when a polymer decomposes by an irreversible stepwise mechanism to yield a mixture of thermal fragments. A third case is given by polymers decomposing by a reversible stepwise mechanism.

The reliability of Eq. 1, shown by the above results, allows the application with more confidence of effluent gas analysis (LPTD–MS) to all types of polymer decomposition processes in order to obtain meaningful kinetic parameters.

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This work was carried out under contract 82.00647.95 of the Consiglio Nazionale delle Ricerche (Rome), Finalized Project on Fine and Secondary Chemistry.

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Zusammenfassung — Die LPTD—MS-Methode, benutzt zur Bestimmung der kinetischen Parameter des thermischen Abbaus von Polymeren aus Verflüchtigungskurven, wurde auf TG-Daten angewandt und die Ergebnisse wurden mit denen verglichen, die nach den Methoden von Flynn und Wall, Friedman, Freeman und Carroll sowie Coats und Redfern erhalten wurden.

Резюме — Совмещенный метод ЛПТД—МС, используемый для определения кинетических параметров реакции термического распада полимеров с помощью кривых испарения, был применен к данным ТГ. Результаты были сопоставлены с теми, которые были получены методами Флинна и Уолла, Фридмена, Фримена и Карролла, а также Коуста и Радферна.