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A kinetic analysis of thermogravimetric data of radically polymerised *N*-phenylmaleimide

Palanichamy Sivasamy
Post-Graduate Department of Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi-626 123 (India)

Chinnaswamy Thangavel Vijayakumar and Klaus Lederer
Institut für Chemie der Kunststoffe, Montanuniversität Leoben, A-8700 Leoben (Austria)

Andreas Kramer [1]
Plastics Research, Ciba-Geigy AG, CH-1701 Fribourg (Switzerland)

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Abstract

The thermal behaviour of the radically polymerised poly(*N*-phenylmaleimide) was studied, adopting the thermogravimetric method at heating rates of 1, 5, 10 and 50°C min^{-1} in a nitrogen atmosphere. The kinetic parameters, such as activation energy, reaction order, Arrhenius pre-exponential factor etc., have been calculated using different mathematical approximations available in the literature. It is observed that the energy of activation values and pre-exponential factors estimated for the degradation of poly(*N*-phenylmaleimide) from a single heating thermogram using different approximations decrease with increase in heating rate, whereas nearly constant values are observed in the Dharwadkar and Kharkhanavala approximation irrespective of the variation in sample size and heating rate. It is also observed that the different approximations, when applied to multiple heating data, give nearly constant values for the kinetic parameters. These values are broadly similar to that calculated using the Dharwadkar and Kharkhanavala approximation from a single heating thermogram.

INTRODUCTION

The synthesis of *N*-phenylmaleimide (NPMI), its solution polymerisation in benzene using benzoyl peroxide as radical initiator and the characterisation of poly(*N*-phenylmaleimide) (PNPMI) using thermo-

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Correspondence to: P. Sivasamy, Post-Graduate Department of Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi-626 123, India.

[1] Present address: Ciba-Geigy Plastics, Duxford, Cambridge CB2 4QA, UK.

gravimetry (TG) and thermal volatilisation analysis (TVA) have been reported [1]. The technique of gas chromatography–mass spectrometry (GC–MS) has been used to separate and identify the pyrolysis products of PNPMI. The TG curve recorded for PNPMI at a heating rate of 10°C min^{-1} in a nitrogen atmosphere reveals the starting temperature of degradation to be 360°C, with the maximum weight loss at 425°C. The TG thermograms for PNPMI have been recorded at heating rates of 1, 5, 10 and 50°C min^{-1} in a nitrogen atmosphere. Using the data, such kinetic parameters as activation energy (E), reaction order (n) and Arrhenius pre-exponential factor (A) etc. have been calculated by adopting different mathematical approximations available in the literature.

EXPERIMENTAL

The synthesis and purification of NPMI monomer and its corresponding polymer (PNPMI) have been described elsewhere [1]. The TG curves for the polymer PNPMI at different heating rates (1, 5, 10 and 50°C min^{-1}) were recorded on a Perkin-Elmer thermogravimetric analyser TGA 7 in a nitrogen atmosphere in the temperature region 100–600°C. Data acquisition and analysis were performed using a Perkin-Elmer 3700 data station.

RESULTS AND DISCUSSION

The thermograms and the first derivatives obtained at heating rates of 1, 5, 10 and 50°C min^{-1} for PNPMI are given in Figs. 1 and 2 respectively. It is obvious that PNPMI undergoes single stage degradation. The kinetic parameters from TG data are arrived at by the various mathematical approximations of the basic equation

$$\mathrm{d}\alpha/\mathrm{d}t = A(1-\alpha)^n \exp(-E/RT) \qquad (1)$$

where α is the fraction undergoing decomposition, E is the apparent activation energy, A is the pre-exponential factor, n is the apparent order of the reaction, R is the gas constant, T is the absolute temperature and $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of decomposition. The various mathematical approximations are classified into different categories by different authors. Flynn and Wall [2] classified them into five categories, namely; (a) "integral" methods utilising weight loss versus temperature data directly; (b) "differential" methods utilising the rate of weight loss; (c) "difference-differential" methods involving differences in rate; (d) methods specially applicable to initial rates; and (e) non-linear or cyclic heating rate methods. Reich and Levi [3] classified the methods as follows: (a) method of Freeman and Carroll; (b) methods involving maximisation of rate; (c) methods with multiple heating rates; (d) method of variable heating rate for a single thermogram; (e) methods for evaluating activation energy which involve double logarithm terms; (f) methods involving approximate

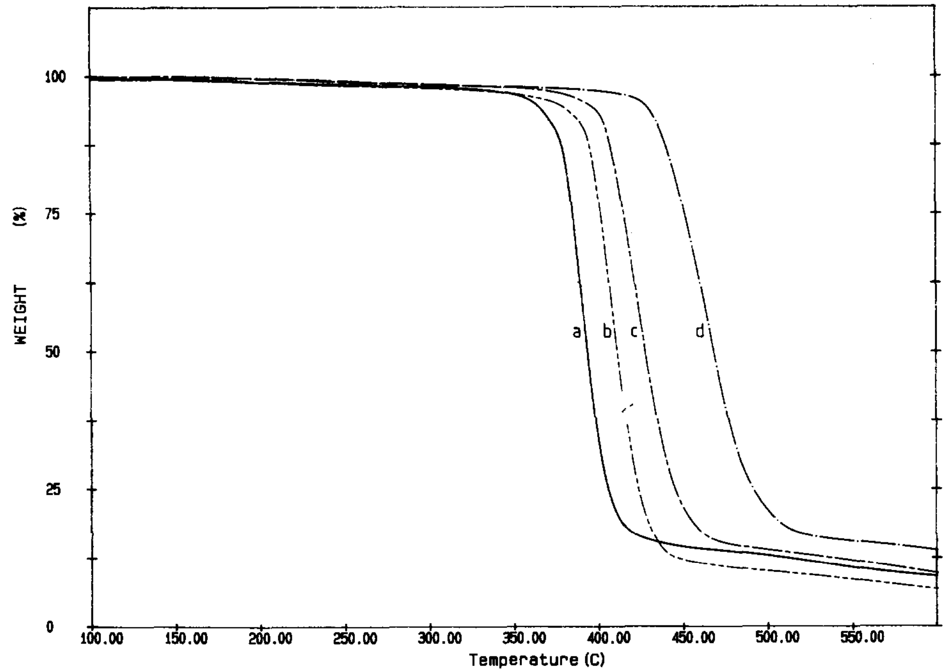

Fig. 1. TG curves for poly(N-phenylmaleimide) in a nitrogen atmosphere at heating rates of 1 (curve a), 5 (curve b), 10 (curve c) and 50°C min^{-1} (curve d).

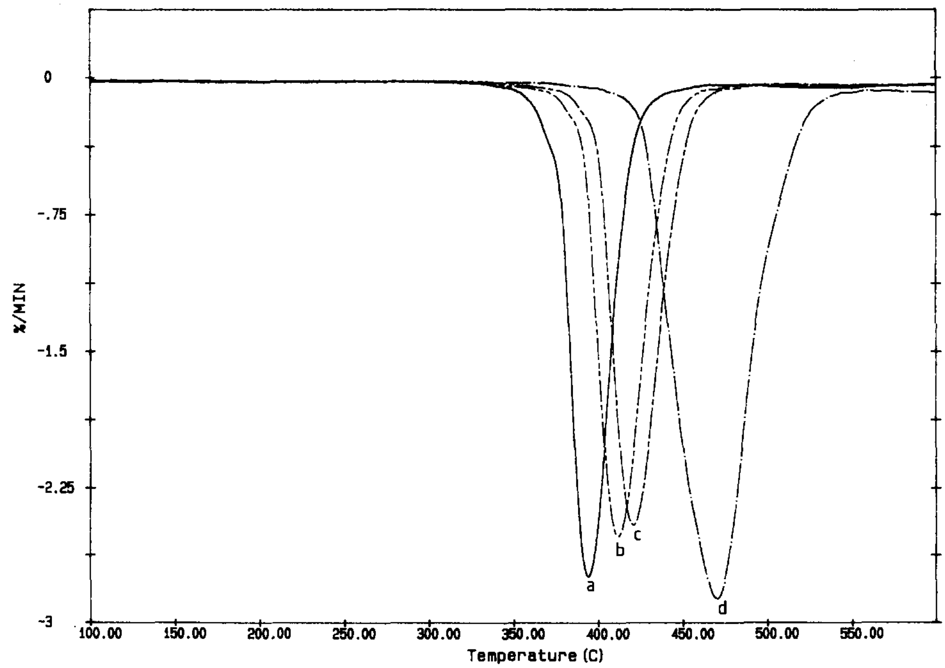

Fig. 2. Differential thermograms (DTG) for poly(N-phenylmaleimide) in a nitrogen atmosphere at heating rates of 1 (curve a), 5 (curve b), 10 (curve c) and 50°C min^{-1} (curve d).

integrations of the rate equation; (g) graphical estimation of reaction order, and (h) miscellaneous methods.

In the present work we have categorised the different methods according to the availability of thermogravimetric data: (a) calculation of kinetic parameters by methods which require only a single heating thermogram, (b) methods which require a single heating thermogram and its first derivative curve (DTG), and (c) methods which require multiple heating thermograms and their first derivative curves. Since the readers are familiar with mathematical expressions derived by various authors, the references pertinent to different methods only are given.

Methods which require a single heating thermogram

The methods due to Murray and White [4], Doyle [5, 6], Horowitz and Metzger [7], Coats and Redfern [8], Broido [9] and MacCallum and Tanner [10] fall into this category. Assuming first order decomposition of PNPMI, the E value (kJ mol^{-1}) and the $\log A$ factor calculated from the above methods using a single heating thermogram are listed in Table 1.

In general, as the heating rate increases, the energy of activation and the frequency factor decrease, independent of the mathematical approximations applied to calculate the above parameters for the thermal degradation of PNPMI. At the slowest heating rate (1°C min^{-1}) the E values obtained from the Horowitz and Metzger, Broido and MacCallum and Tanner approximations are comparatively higher than those calculated from the Murray and White, Doyle, and Coats and Redfern approximations. However, all the approximations except that of MacCallum and Tanner give almost the same E value (258 ± 10 kJ mol^{-1}) at a heating rate of 10°C min^{-1}.

Methods which require a single heating thermogram and its first derivative curve

The methods of van Krevelen et al. [11], Freeman and Carroll [12], Ingraham and Marier [13, 14], Reich et al. [15], Reich [16], Chatterjee and Conrad [17] and Dharwadkar and Kharkhanavala [18] come under this category. The kinetic parameters calculated for the thermal decomposition of PNPMI using the foregoing methods are detailed in Table 2.

It is observed that the E values calculated using the Dharwadkar and Kharkhanavala method are constant irrespective of the heating rate. Further, the E value (259 ± 2 kJ mol^{-1}) obtained by this method is well within the range of the average value derived from the methods belonging to the first category (Table 1) using the 10°C min^{-1} heating rate thermogram (258 ± 10 kJ mol^{-1}). Dharwadkar and Kharkhanavala suitably modified the Horowitz and Metzger equation [7] so as to yield values of the

TABLE 1

The energy of activation (E) and the frequency factor (A) calculated for poly(N-phenylmaleimide) by different approximation methods using a single heating thermogram (reaction order $n = 1$)

No.	Method	E (kJ mol^{-1})				log A			
		Heating rate (°C min^{-1})				Heating rate (°C min^{-1})			
		1	5	10	50	1	5	10	50
1	Murray and White	304.8	291.0	266.0	225.0	22.744	21.816	19.869	15.788
2	Doyle	273.1	279.3	258.2	205.6	23.477	22.238	21.081	16.377
3	Horowitz and Metzger	364.8	354.6	263.8	237.1	27.376	25.911	18.784	15.894
4	Coats and Redfern	297.1	299.1	248.4	212.1	21.672	20.584	17.190	14.418
5	Broido	362.8	291.0	268.6	245.0	–	–	–	–
6	MacCallum and Tanner	346.4	329.5	321.0	252.1	24.564	23.892	23.026	18.300

TABLE 2

The energy of activation (E) and the frequency factor (A) calculated for poly(N-phenylmaleimide) by different approximation methods using TG and DTG traces

No.	Method	E (kJ mol^{-1})				log A			
		Heating rate (°C min^{-1})				Heating rate (°C min^{-1})			
		1	5	10	50	1	5	10	50
1	van Krevelen et al.[a]	281.2	304.8	282.5	246.6	24.256	27.059	23.430	20.605
2	Freeman and Carroll[b]	323.9	237.5	282.7	316.7	24.142	21.053	19.888	16.846
3	Ingraham and Marier[a]	346.4	384.9	356.3	242.5	–	–	–	–
4	Reich et al.[c]	377.9	450.3	386.0	221.7	26.925	28.065	25.995	14.280
5	Reich[a]	348.1	382.9	364.7	277.8	23.967	20.345	19.811	15.577
6	Chatterjee and Conrad[a]	406.4	480.3	436.5	415.7	–	–	–	–
7	Dharwadkar and Kharkhanavala[a]	257.4	260.9	257.3	259.9	–	–	–	–

[a] The reaction order (n) is assumed to be 1.

[b] $n = 0.53$ (1°C min^{-1}), 0.30 (5°C min^{-1}), 1.20 (10°C min^{-1}) and 2.4 (50°C min^{-1}).

[c] $n = 0.013$ (1°C min^{-1}), 0.016 (5°C min^{-1}), 0.018 (10°C min^{-1}) and 0.018 (50°C min^{-1}).

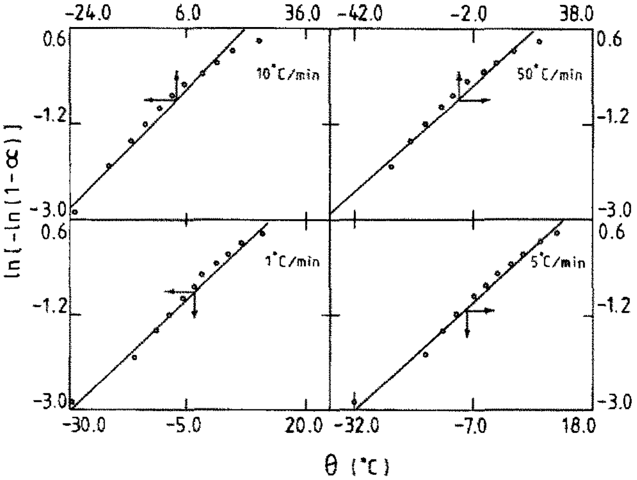

Fig. 3. Application of the Dharwadkar and Kharkhanavala method to the degradation of poly(*N*-phenylmaleimide).

activation energy which are independent of variation in sample size and heating rate. For first order kinetics, the modified equation is

$$\ln[-\ln(1-\alpha)] = (E/RT_i^2)(100/T_f - T_i)\theta + C \qquad (2)$$

where T_i and T_f are the temperatures of inception and completion of the degradation respectively, and $\theta = T - T_s$, where T is the temperature under consideration and T_s is the temperature at the inflection point in the thermogravimetry curve. A plot of $\ln[-\ln(1-\alpha)]$ against θ was made, and is presented in Fig. 3.

Methods which require multiple heating thermograms

This category consists of the Kissinger [19, 20], Friedman [21], Reich [22] and Ozawa [23] methods. Further, if the equations due to Murray and White [4], Doyle [5, 6], Coats and Redfern [8] and MacCallum and Tanner [10] are suitably rearranged, these methods can also fit in this category. The E and A values obtained by various methods except the Kissinger method are given in Table 3.

The E value calculated by the Friedman method is slightly higher than the value (218 ± 16 kJ mol^{-1}) calculated from the other methods. The reason behind this difference is that in all methods except the Friedman method the reaction order is assumed to be 1, whereas according to Friedman's procedure the degradation of PNPMI follows 0.28 reaction order with a frequency factor of 3.72×10^{18}. The activation energy calculated for the degradation of PNPMI as per Kissinger's procedure is 199.5 kJ mol^{-1}. This value is nearer to the average value obtained by other methods.

TABLE 3

The energy of activation (E) and the frequency factor (A) calculated for poly(N-phenylmaleimide) by different approximation methods using multiple heating thermogravimetric data

Percentage conversion	E (kJ mol^{-1})							log A						
	I	II	III	IV	V	VI	VII	I	II	III	IV	V	VI	VII
5.6	222.7	202.3	222.7	265.6	222.7	202.3	202.7	16.735	14.304	16.735	18.804	17.975	14.304	14.638
12.5	237.5	226.5	237.5	318.7 [a]	237.5	226.5	228.1	17.389	16.262	17.389	19.408	18.263	16.262	16.735
19.4	252.3	210.0	252.3	256.7	252.3	210.0	210.9	16.559	14.699	16.559	18.145	17.226	14.699	15.078
26.4	223.6	220.2	223.6	231.9	223.6	220.2	221.5	16.291	16.101	16.291	18.344	16.804	16.101	16.539
33.3	213.8	233.6	213.8	240.8	213.8	233.6	235.4	15.350	16.444	15.350	17.822	15.742	16.444	16.956
40.3	220.6	206.3	220.6	218.7	220.6	206.3	207.0	16.011	15.096	16.011	15.653	16.299	15.096	15.454
47.2	–	222.0	–	212.5	–	222.0	223.4	–	15.803	–	15.144	–	15.803	16.251
54.2	237.5	218.4	237.5	213.0	237.5	218.4	219.7	14.943	15.460	14.943	15.206	15.050	15.460	15.887
61.1	195.6	224.0	195.6	213.1	195.6	224.0	225.5	14.029	16.371	14.029	15.884	14.054	16.371	16.830
68.1	190.0	200.2	190.0	198.0 [a]	190.0	200.2	200.6	13.513	13.728	13.513	14.858	13.455	13.728	14.056
75.0	201.0	201.6	201.0	–	201.0	201.6	202.1	13.730	14.447	13.730	–	13.588	14.447	14.778
81.9	170.0 [a]	–	170.0 [a]	–	170.0 [a]	–	–	12.120 [a]	–	12.120 [a]	–	11.887 [a]	–	–
Average	219.5 ± 19	215.0 ± 15	219.5 ± 19	231.5 ± 26	219.5 ± 19	215.0 ± 15	216.1 ± 15	15.455 ± 2.0	15.338 ± 1.6	15.455 ± 2.0	16.926 ± 2.1	15.846 ± 2.4	15.338 ± 1.6	15.746 ± 1.6

[a] These values are not included for taking the average.

Key: I, Murray and White method; II, Doyle method; III, Coats and Redfern method; IV, Friedman method; V, Reich method; VI, Ozawa method; VII, MacCallum and Tanner method.

The findings lead to the conclusion that the application of the Dharwadkar and Kharkhanavala method to a single heating thermogram and its first derivative curve is sufficient to obtain a reliable assumed first order kinetic E value for a material under investigation.

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