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Addition polyimide—heat and kinetics of polymerization of bismaleimide modified with bisitaconimide

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Abstract

Enthalpy changes and kinetic parameters for the thermal polymerization of N,N'-bismaleimido-p,p'-diphenylmethane, modified by the addition of N,N'-bisitaconimido-p,p'-diphenyl ether, were evaluated from differential scanning calorimetric studies. The Arrhenius parameters, (activation energy E and pre-exponential factor A) were calculated by three kinetic equations for comparison. The heat and kinetics of the polymerization reaction show a systematic decrease with increase in the itaconimide concentration in the polymerizing mixture. A linear correlation between activation parameters and heat of polymerization was also established.

INTRODUCTION

Polyimides are among the most widely used thermosetting polymers which offer high thermal stability and retention of good mechanical and electrical properties on long term aging. Bismaleimides and bisitaconimides belong to this category, and therefore they find applications as high temperature polymers for adhesives, laminates, coatings, electrical insulations, etc. [1,2]. They undergo thermal polymerization from 150–300 °C without evolution of volatile by-products [3]. The major disadvantage of bismaleimides is brittleness. However, the flexibility of maleimides can be enhanced by a number of methods such as the incorporation of meta linkages in the backbone, chain extension by Michael type addition reaction using diamines containing flexible spacers such as methylene, oxygen, sulfur and sulfone, and addition or copolymerization with different anhydrides and imides, such as the comparatively less brittle itaconimides [4,5].

Polymers exhibit a wide variety of thermal behavior as a result of their structural differences, and various thermoanalytical methods have been used to study these aspects. The cure characteristics, thermal stability and thermal decomposition kinetics of four bismaleimides based on maleic anhydride and four different aromatic diamines have been reported by us [6]. The

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synthesis and characterization of the oligomers of *N,N′*-bis(3,3′-itaconimidophenyl)sulfone have been reported in another publication [7]. Differential scanning calorimetry (DSC) has been extensively used to determine the heat and kinetics of the exothermic cure reaction of thermosetting polymers [8,9]. The enthalpy change and the kinetic parameters for the thermal polymerization of four bismaleimide–diamine adducts, prepared by reacting diaminodiphenylmethane with the four bismaleimides, have also been reported [10]. The present paper describes our DSC studies on the thermal polymerization of *N,N′*-bismaleimido-*p,p′*-diphenylmethane, modified by the addition of *N,N′*-bisitaconimido-*p,p′*-diphenyl ether.

EXPERIMENTAL

Materials

*N,N′-Bismaleimido-*p,p′*-diphenylmethane (bismaleimide or BM)*

The bismaleimic acid was prepared by the reaction of maleic anhydride with *p,p′*-diaminodiphenylmethane in acetone medium. The acid thus obtained was imidized with acetic anhydride to obtain the bismaleimide.

*N,N′-Bisitaconimido-*p,p′*-diphenyl ether (bisitaconimide or BI)*

The bisitaconimide was similarly prepared by reacting itaconic anhydride with *p,p′*-diaminodiphenyl ether, followed by the cyclocondensation of the bisitaconamic acid.

The details regarding the preparation and characterization of these compounds are given in our earlier publications [6,7]. Bismaleimide–bisitaconimide mixtures were prepared with the proportions BM : BI = 80 : 20, 60 : 40, 50 : 50, 40 : 60 and 20 : 80 for the present study.

Instrumental

DSC studies were carried out using a Perkin–Elmer DSC model 2C. All the experiments were done in a nitrogen atmosphere, with purging at a rate of 50 cm^3 min^{-1}. A constant heating rate of 10 °C min^{-1} and a sample mass of 5 ± 0.1 mg were employed for the entire study. DSC was calibrated using pure indium metal of m.p. = 156.4 °C and $\Delta H_m = 6.8$ cal g^{-1}. Heat of polymerization was calculated from the DSC peak area. For the calculation of the kinetic parameters for the thermal curing of the samples from DSC curves, the degree of conversion α was determined from the ratio of the fractional area and the total area under the DSC curve. A numerical integration method (trapezoidal) was employed for the purpose [11]. All computational work was done with a CDC computer, using a FORTRAN IV program.

RESULTS AND DISCUSSION

Melting curves

On heating, the bisimides undergo melting, and their melting points are in the ranges BM 148–150 °C and BI 178–180 °C. The mixtures show two melting peaks, differing from the melting peaks of the pure bisimides. The values of the melting points are given in Table 1.

Heat of polymerization

Bismaleimide undergoes thermal polymerization immediately after the completion of melting. The temperature of inception of reaction T_i, peak exothermic temperature T_s and temperature of completion of reaction T_f for the pure bismaleimide and its mixtures with bisitaconimide are given in Table 2. From this table, it can be seen that the T_i values are composition dependent whereas the T_s and T_f values remain almost constant.

TABLE 1

Effect of composition on melting points of bisimides

Composition (%) BM:BI	Melting point (°C) (1)	Melting point (°C) (2)
100:0	149	–
80:60	140	146
60:40	139	143
50:50	140	144
40:60	142	158
20:80	143	174
0:100	–	180

TABLE 2

Effect of bisitaconimide on exothermic reaction temperature and ΔH of polymerization of bismaleimide

Composition (%) BM:BI	T_i (°C)	T_s (°C)	T_f (°C)	ΔH (cal g^{-1})
100:0	155	249	307	38.70
80:20	150	245	305	36.10
60:40	149	243	302	33.54
50:50	162	242	302	32.70
40:60	177	245	301	31.50
20:80	182	242	301	30.20

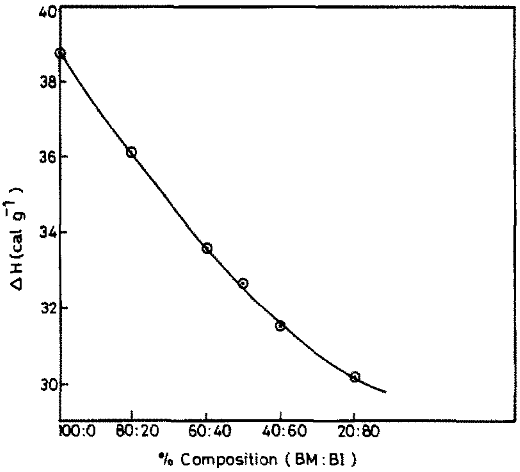

Fig. 1. Effect of composition on ΔH of cure reaction

The heat of polymerization (ΔH) of bismaleimide and its mixtures, calculated from the DSC peak area, is also given in Table 2. It is observed that the ΔH of polymerization of the samples shows a systematic decrease with the increase in bisitaconimide concentration in the mixture. The effect of variation of the composition of bisimides on the ΔH of polymerization is shown in Fig. 1.

Kinetics of polymerization

The kinetic parameters for the thermal polymerization of pure and modified bismaleimides were calculated using three methods. In the first method, described by Rogers and co-workers [12,13], the logarithm of the distance, d, between the baseline and the exothermic curve was plotted against the reciprocal of absolute temperature ($1/T$). From this plot, the best linear portion of the curve was chosen. The distance d_1 and d_2 and the temperatures T_1 and T_2 correspond to the two extremes of the linear portion of the curve. By substituting the values of d_1, d_2, T_1 and T_2 in the equation

$$-E = \frac{4.58 \log(d_1/d_2)}{1/T_1 - 1/T_2} \qquad (1)$$

the activation energy was calculated. The pre-exponential factor was calculated by substituting the value of E in the equation

$$A = \frac{\phi E \, e^{E/RT_{(\max)}}}{RT^2_{(\max)}} \qquad (2)$$

where ϕ = heating rate, R = gas constant and $T_{(\max)}$ is the maximum of the DSC curve. The values of E and A are given in Table 3.

TABLE 3

Kinetic parameters from the Rogers method

Composition (%) BM : BI	E (kcal mol^{-1})	A (s^{-1})
100 : 0	44.46	1.576×10^{15}
80 : 20	36.81	3.946×10^{13}
60 : 40	33.29	3.372×10^{11}
50 : 50	30.89	3.699×10^{10}
40 : 60	29.81	6.615×10^{9}
20 : 80	28.40	1.001×10^{9}

The activation parameters for the polymerization reaction were also calculated using two non-isothermal integral equations, viz., the Coats–Redfern (CR) equation [14]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{3}$$

and the Madhusudanan–Krishnan–Ninan (MKN) equation [15]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^{1.9215}}\right]=\ln\frac{AE}{\phi R}+3.7721-1.9215\ln E-\frac{0.12039E}{T} \tag{4}$$

An iteration method was employed for the evaluation of order parameter n, which was found to be 1.5 in almost all cases (from both the methods). The left hand sides of eqns. (3) and (4) were plotted against $(1/T)$ and, from the slope and intercept, E and A were calculated. Their values, along with the correlation coefficients r are given in Tables 4 and 5 for the CR and MKN methods respectively. The correlation coefficients are above 0.999 in all cases, indicating the goodness of the curve fits.

From Tables 3, 4 and 5 it can be seen that E and A systematically decrease with increase in bisitaconimide concentration in the reaction mix-

TABLE 4

Kinetic parameters from the Coats–Redfern method

Composition (%) BM : BI	E (kcal mol^{-1})	A (s^{-1})	r
100:0	41.45	2.343×10^{15}	0.9999
80:20	36.86	2.312×10^{13}	0.9999
60:40	33.52	6.932×10^{11}	0.9997
50:50	31.43	4.316×10^{10}	0.9998
40:60	29.83	7.457×10^{9}	0.9991
20:80	28.51	1.055×10^{9}	0.9990

TABLE 5

Kinetic parameters from Madhusudanan–Krishnan–Ninan method

Composition (%) BM : BI	E (kcal mol^{-1})	A (s^{-1})	r
100:0	41.68	3.981×10^{15}	0.9999
80:20	37.26	1.122×10^{13}	0.9999
60:40	33.62	6.310×10^{11}	0.9998
50:50	31.57	6.310×10^{10}	0.9998
40:60	29.95	1.000×10^{10}	0.9992
20:80	28.65	1.585×10^{9}	0.9990

ture. The relationships between the kinetic parameters and compositional variations are represented by the plots shown in Fig. 2 for the three equations. Figure 1 shows a similar type dependence of ΔH on the composition of the reaction mixture. This is indicative of the existence of a linear relation between the ΔH of polymerization and the activation parameters.

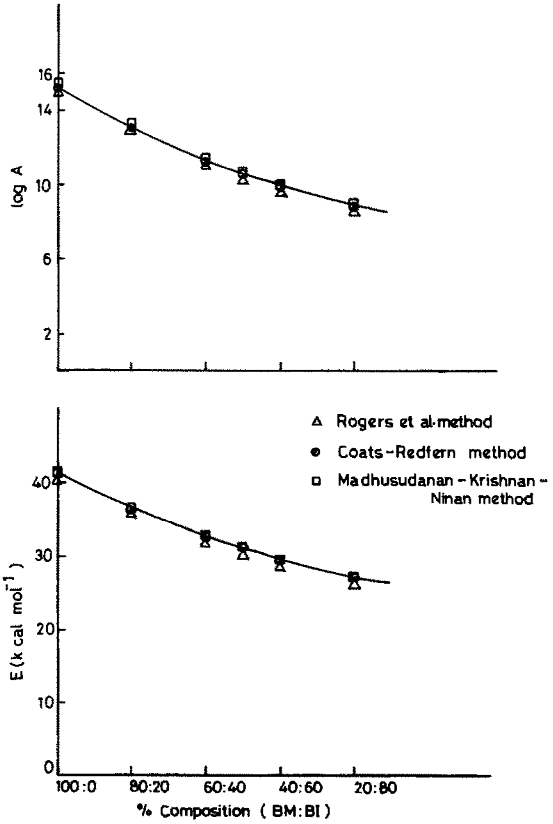

Fig. 2. Effect of composition on activation parameters

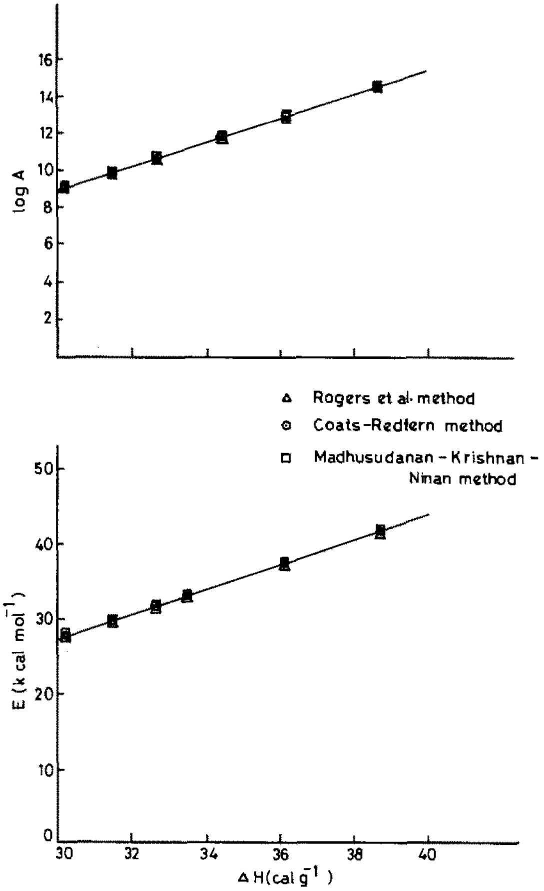

Fig. 3. Relation between ΔH of polymerization and activation parameters

This type of relation between heat of reaction and activation energy was reported for endothermic decomposition reactions of some inorganic compounds [16]. The linear dependence of E and of log A on ΔH of polymerization is shown in Fig. 3. The values of the correlation constants for the above plots for the three equations are given in Table 6. The values of the correlation coefficients are nearly equal to unity in all the cases, confirming

TABLE 6

Correlation constants for activation parameters vs. ΔH of polymerization plots

Method	E vs. ΔH plots			log A vs. ΔH plots		
	Slope	Intercept	r	Slope	Intercept	r
Rogers	1.469	−16.527	0.9952	0.754	−13.867	0.9974
Coats–Redfern	1.543	−18.556	0.9968	0.753	−13.770	0.9967
Madhusudanan–Krishnan–Ninan	1.566	−19.127	0.9972	0.739	−13.234	0.9953

the validity of our assumption regarding the linear dependence of the activation parameters on heat of cure reaction for the system under investigation.

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