Kinetic study of the crosslinking reaction of flexible bismaleimides

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A series of flexible maleimide-terminated oligoterephthalates with polymerization degree $1 \leqslant X_n \leqslant 22$ have been used as models for the study of bismaleimide crosslinking reactions. Thermal- and initiator-induced polymerizations have been carried out and monitored by differential scanning calorimetry (d.s.c.) for the set of bismaleimides. Kinetic parameters could be obtained by either dynamic or isothermal methods. The results of these experiments are consistent with an overall first-order reaction for the maleimide double bond polymerization, regardless of the length of the imide end-capped oligomers. Activation energies in the range 133–140 kJ mol^{-1} and pre-exponential factors $A \approx 10^{16}$ min^{-1} were calculated for the initiator-induced reactions.

(Keywords: bismaleimides; reactive oligomers; crosslinking kinetics; differential scanning calorimetry)

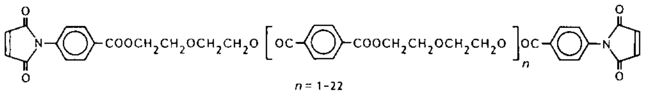
INTRODUCTION

Bismaleimides are increasingly being used as matrix resins for composites[1,2]. They are cured by a thermally induced addition reaction to give highly crosslinked systems. However, the high temperature needed to fully cure bismaleimides (which may be as high as 275°C) to some extent limits their use in conventional composite processing; lower cure temperatures are desirable but not essential. The use of initiators[3–5] or copolymerization with other monomer reactants like allylphenyl[6] or styrene type comonomers[7] can effectively reduce the cure temperature although this does not always represent an ideal compromise between the desire for lower cure temperatures and good final materials properties.

The purpose of this work is to evaluate the crosslinking kinetics of bismaleimides in the presence of radical initiators. This kind of study is an important step for process optimization and for a better understanding of structure–property relations in the crosslinking materials.

Recently we reported[8] on the synthesis of a series of well characterized maleimide end-capped oligoterephthalates with polymerization degrees (X_n) ranging between 1 and 22. The structure of these oligomers, which is shown in *Scheme 1*, makes them very suitable for crosslinking studies due to their low melting points (no overlapping between melting and initiator-induced crosslinking) and low T_g of the networks (no vitrification problems). In addition, having a set of oligomers with the same chemical structure but different chain lengths between maleimide groups allows evaluation of the influence of molecular weight on crosslinking parameters (conversion degree, reaction rate, activation energy, etc.).

Scheme 1



THEORY

Although the crosslinking of bismaleimides has been studied by d.s.c., only a few attempts to study the kinetics have been reported[9–12]. Assuming that the heat generated by the chemical reaction is proportional to the extent of the reaction, α, the reaction rate can be expressed as

$$d\alpha/dt = dH/dt/\Delta H_0 \qquad (1)$$

where dH/dt is the rate of heat evolution and ΔH_0 the total heat of reaction. The kinetic parameters can be obtained from measurements made under either isothermal or non-isothermal conditions.

Due to the complex nature of thermosetting reactions, phenomenological models based on the equation

$$d\alpha/dt = Kf(\alpha) \qquad (2)$$

are frequently used, $f(\alpha)$ being some function of the reactive group conversion (extent of reaction). For most cure reactions, $f(\alpha)$ can be expressed as

$$f(\alpha) = (1-\alpha)^n \qquad (3)$$

for a nth-order reaction or

$$f(\alpha) = \alpha^m(1-\alpha)^n \qquad (4)$$

for an autocatalytic reaction. For multiple bond polymerization, nth-order kinetics have always been reported. K is considered to depend on temperature in an Arrheniüs form. Therefore, the reaction rate can be expressed in the general form

$$d\alpha/dt = Af(\alpha)\exp(-E_A/RT) \qquad (5)$$

for an isothermal experiment, and

$$d\alpha/dt = A/\Phi f(\alpha)\exp(-E_A/RT) \qquad (6)$$

for a dynamic experiment, Φ being the heating rate.

EXPERIMENTAL

Materials

Bismaleimide oligomers with polymerization degree $1 \leqslant X_n \leqslant 22$ were synthesized and characterized as

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described in Reference 8. *N*-phenylmaleimide was synthesized from maleic anhydride and aniline according to the Searle method[13]. The initiators for free radical polymerization were purchased from commercial sources.

Sample preparation

Homogeneous blends of initiators and bismaleimides were obtained by dissolving the initiator in n-hexane and allowing it to precipitate on to the highly pulverized oligomer (non-soluble) as the n-hexane evaporated under vacuum[14]. This method yielded the highest crosslinking enthalpies and the most reproducible results.

D.s.c.

D.s.c. measurements were made by dynamic and isothermal methods with a Perkin–Elmer DSC-4 attached to a Perkin–Elmer 3600 data station, using samples of approximately 8.0±0.1 mg in covered aluminium pans, under nitrogen atmosphere.

Scanning rates of 5, 10, 20 and 40°C min^{-1} were used for the dynamic experiments.

Isothermal runs were carried out at several temperatures selected from the dynamic results (120–160°C). To do the analyses, the samples were placed in the calorimetric cell at room temperature and then heated at 200°C min^{-1} up to the temperature chosen for the experiment. After the isothermal run was completed, the sample was cooled to room temperature and the residual enthalpy of curing (if existing) was measured in a dynamic experiment. Only the four lower molecular weight oligomers were tested isothermally because the low polymerization enthalpy of the higher oligomers prevented accurate measurement.

RESULTS AND DISCUSSION

All the bismaleimide oligomers gave a broad exotherm corresponding to the thermal crosslinking with a maximum at approximately 300°C (20°C min^{-1}), indicating that fairly high temperatures are necessary to complete the cure in a reasonable time.

Since the maleimide thermal polymerization proceeds by a typical radical mechanism[2–5,15], the use of radical initiators has been claimed to be an attractive approach for low temperature cure of bismaleimides. Therefore, we first tested the polymerization of a model compound, *N*-phenylmaleimide ($T_m = 91$°C), in the presence of several radical initiators (1% w/w), determining both polymerization enthalpy and temperature. The results are shown in *Table 1*. Dicumyl peroxide and cumyl hydroperoxide presented the maximum enthalpy and, therefore, the maximum number of reacted double bonds. The low polymerization temperature observed for cumyl hydroperoxide, which caused overlapping with the melting process of the oligomers, lead us to choose dicumyl peroxide as the most suitable initiator for this study.

Table 1 Thermal characteristics of the polymerization of *N*-phenylmaleimide with 1% (w/w) initiator

Initiator	T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})
t-Butylperoctoate	93	104	292[a]
t-Butylperbenzoate	92	105	392
Cumyl hydroperoxide	94	113	464
Methylisobutylketone peroxide	93	135	40[a]
Benzopinacol	127	142	323
Dicumyl peroxide	140	155	439
t-Butylcumyl peroxide	160	177	375

[a] Significant peak at ≈300°C corresponding to thermal polymerization

Table 2 Crosslinking enthalpy per mol of double bond and temperature of the exothermic peak of the series of maleimide end-capped oligoterephthalates

Oligomer	X_n	T_{peak}[a] (°C)	ΔH (kJ mol^{-1})
1	1.3	165	91
2	3.2	162	91
3	8.5	166	81
4	12	161	84
5	16	172	54
6	21	174	46

[a] Heating rate 20°C min^{-1}

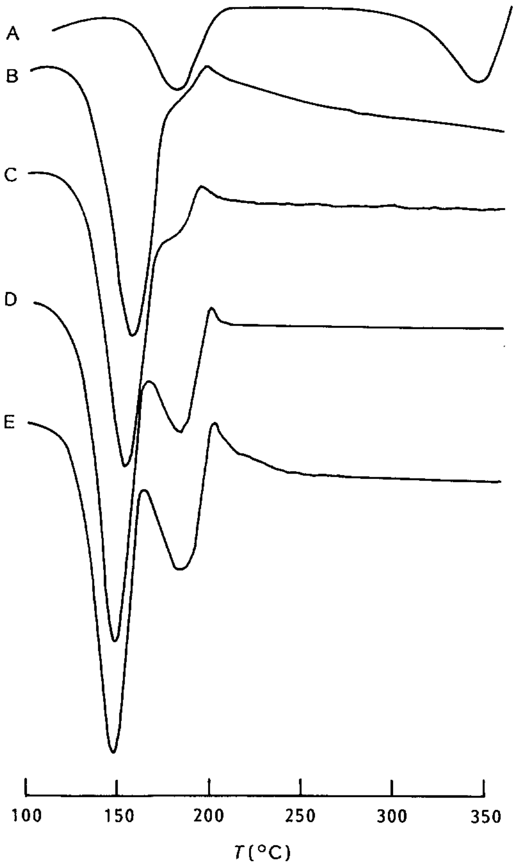

Figure 1 D.s.c. curves at 20°C min^{-1} of oligomer 4 with initiator percentage (in % w/w) as follows: A, 0.1%; B, 0.5%; C, 1.0%; D, 2.0%; E, 3.0%

Several runs were performed with oligomers 1 and 4 to determine the optimal amount of initiator. In *Figure 1* the crosslinking exotherms of oligomer 4 with different initiator percentages are reproduced.

When the concentration is too low, two exotherms are observed, one at ≈180°C corresponding to the peroxide-induced polymerization and another at ≈300°C due to the thermal polymerization. When the amount of initiator increases, only the initiated exotherm appears and it shifts to lower temperature. Furthermore, a shoulder is observed that can be attributed to the decomposition of the excess peroxide. This effect, which was confirmed

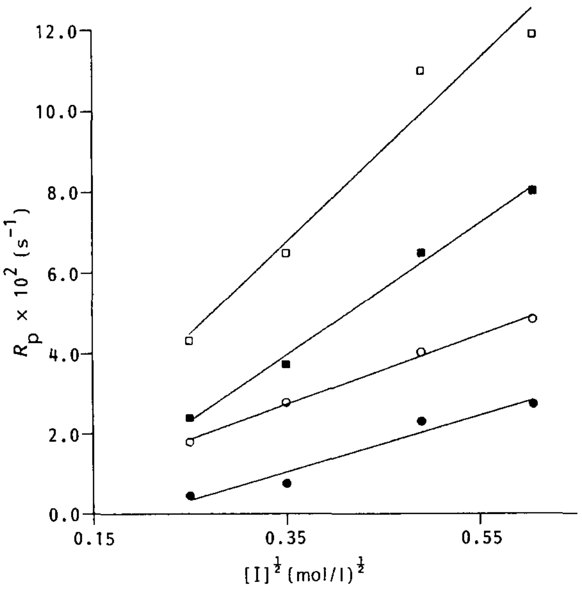

Figure 2 Dependence of overall polymerization rate of oligomer 4 on initiator concentration. ●, 130°C; ○, 135°C; ■, 140°C; □, 150°C

from measurements of initiator decomposition in the presence of the same oligomers before imide end-capping, can be explained by the high half-life time ($t_{1/2}$) of dicumyl peroxide in this range of temperatures[16].

From the cure exotherms the dependence of the overall rate of polymerization on initiator concentration can be studied. It depends on the square root of initiator concentration (see *Figure 2*) according to the general equation of radical polymerization[17,18].

These results made us choose an initiator concentration of 0.03 mol per mol of double bonds. The crosslinking enthalpies of the complete series of oligomers together with the temperatures of the maximum of the exotherm are shown in *Table 2*. The enthalpy values are slightly increased by the presence of the initiator. No significant dependence between molecular weight and temperature of the maximum can be observed. However, the total heat evolved per maleimide group decreases as the molecular weight of the oligomers increases, which can be explained by the effective dilution of end-caps in the larger oligomers[19]. However, the great difficulty in assuring a complete degree of functionalization for the larger oligomers[8] can also explain the lower enthalpy in those cases.

By dynamic methods, the variation of the maximum exotherm temperature as a function of the heating rate can be used to determine the activation energy, E_A, and the pre-exponential factor A[20,21]. The values of E_A calculated from the slope of the Ozawa plots[20] are $130 \pm 5\,kJ\,mol^{-1}$ irrespective of the molecular weight of the oligomer (see *Figure 3*). The values of A also seem to be independent of oligomer size ($A \approx 10^{16}\,min^{-1}$).

The application of the same method to thermal crosslinking in the absence of initiator gives similar values for E_A ($\approx 140\,kJ\,mol^{-1}$), but much lower values for A ($\approx 10^7\,min^{-1}$). Comparison of the two A values clearly shows the increase of polymerization rate due to the initiator[17].

Other similar methods, such as that proposed by Barton[22], yielded remarkably similar values of E_A.

The dynamic curves can also be used to determine the polymerization rate constants at several temperatures if an expression for the conversion function, i.e. a reaction order, is assumed, due to the ability of d.s.c. to report simultaneously the rate and the enthalpy of reaction (1) (Reference 9). The linearity of the Arrhenius representation from these constants can be used as a method to check the validity of the order assumed. As an example, *Figure 4* shows some Arrhenius plots obtained from the reaction rate constants calculated supposing first-order kinetics. The linearity is good for degrees of conversion up to 0.5 for the whole series of oligomers at the different heating rates, giving values of $E_A = 160 \pm 10\,kJ\,mol^{-1}$ and $A \approx 10^{19}\,s^{-1}$. These values are close to those previously calculated by the other dynamic methods that do not imply the assumption of an expression for the conversion function. Although the supposition of second order leads to a similar fit, the

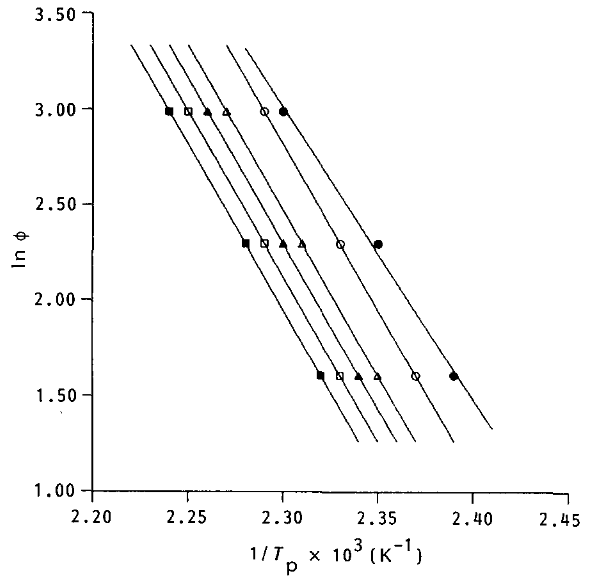

Figure 3 Ozawa plots for the different bismaleimide oligomers (0.03 mol initiator per mol double bond). ■, 6; □, 5; ▲, 4; △, 3; ●, 2; ○, 1

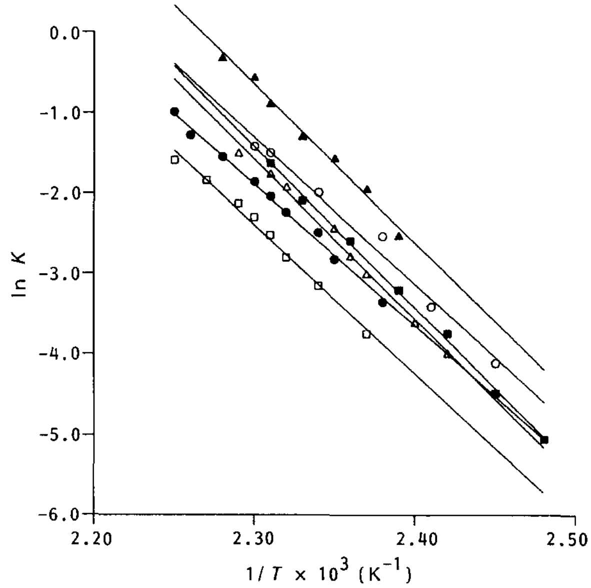

Figure 4 Arrhenius plots of first-order rate constants obtained by dynamic experiments at 20°C min^{-1} for the complete series of oligomers (0.03 mol initiator per mol double bond). △, 1; ■, 2; ▲, 3; ○, 4; □, 5; ●, 6

values of E_A and A are much higher ($200 \pm 10\,\mathrm{kJ\,mol^{-1}}$ and $10^{25}\,\mathrm{s^{-1}}$).

Moreover, simulation of the theoretical curves *versus* T, using the evaluated E_A and A values, by numerical integration of the equation[23,24]

$$d\alpha/dt = (A/\Phi)\exp(-E_A/RT)(1-\alpha)^n \qquad (7)$$

gives better agreement for the first-order model.

The isothermal runs were performed in the temperature range 120–160°C, chosen from the dynamic results. *Figure 5* shows a series of exotherms corresponding to oligomer 2. As can be seen, the maximum of the reaction rate does not appear at $t=0$ and shifts to longer times as the temperature decreases, corresponding in all cases to the same conversion ($\alpha = 0.1$–0.15). This behaviour is not expected either for nth-order kinetics, where the maximum always appears at $t=0$ (maximum concentration of monomer), or for autocatalytic kinetics, where the maximum appears at $\alpha = 0.3$–0.4, the rate being zero at $t=0$ (Reference 9).

In our case, the reaction rate was significant from the beginning and no induction time was detected. As a consequence, the observed shift can be attributed to the low decomposition constant of the initiator at the temperatures used ($t_{1/2}(120°C) = 125\,\mathrm{min}$; $t_{1/2}(140°C) = 85\,\mathrm{min}$)[16]. So, the polymerization process through the double bond does not reach its maximum until a time that is a function of the concentration of free radicals.

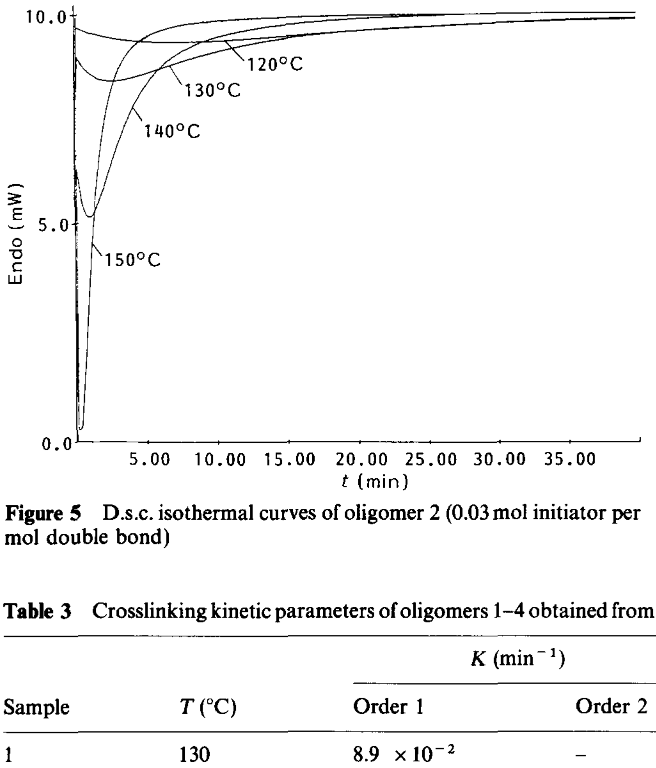

Figure 5 D.s.c. isothermal curves of oligomer 2 (0.03 mol initiator per mol double bond)

All the bismaleimide oligomers react to the same relative extent as a function of time and temperature, reaching values very close to full conversion. That means that vitrification does not take place even for the shorter oligomers.

The direct application of the differential equation (5) to the exotherms gave reaction orders between 1 and 1.5. The actual value slightly changed with temperature. Consequently, the reaction rate constants were calculated by using the following first- and second-order integrated equations:

$$\ln(1-\alpha) = -Kt \quad \text{(first order)} \qquad (8)$$

$$1/(1-\alpha) = 1 + Kt \quad \text{(second order)} \qquad (9)$$

Figure 6 shows the plots corresponding to first-order

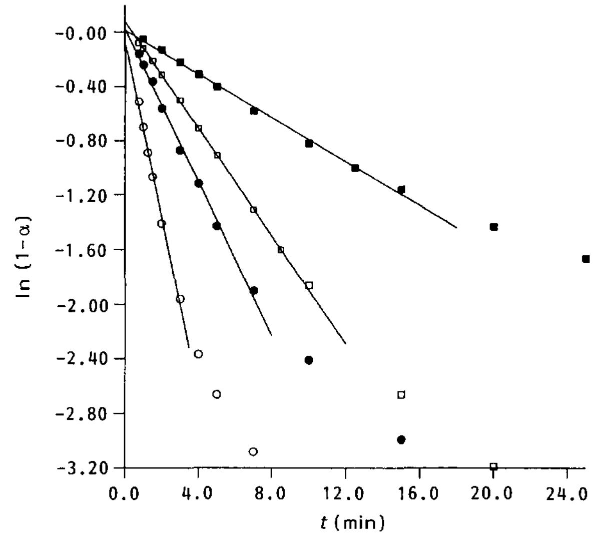

Figure 6 First-order kinetic plots for oligomer 3 at different temperatures (0.03 mol initiator per mol double bond). ■, 130°C; □, 135°C; ●, 140°C; ○, 150°C

Table 3 Crosslinking kinetic parameters of oligomers 1–4 obtained from the isothermal runs by using the first- and second-order integrated equations

		K (min^{-1})		E_A (kJ mol^{-1})		A (min^{-1})	
Sample	T (°C)	Order 1	Order 2	Order 1	Order 2	Order 1	Order 2
1	130	8.9×10^{-2}	–	140	202	10^{17}	10^{25}
	135	1.42×10^{-1}	1.90×10^{-1}				
	140	1.95×10^{-1}	3.25×10^{-1}				
	145	4.04×10^{-1}	8.03×10^{-1}				
	150	6.43×10^{-1}	1.60				
2	120	3.1×10^{-2}	3.6×10^{-2}	130	162	10^{15}	10^{20}
	130	6.0×10^{-2}	7.3×10^{-2}				
	140	1.67×10^{-1}	3.10×10^{-1}				
	150	4.80×10^{-1}	1.09				
3	130	8.1×10^{-2}	1.22×10^{-1}	137	190	10^{16}	10^{23}
	135	1.98×10^{-1}	4.16×10^{-1}				
	140	2.96×10^{-1}	6.72×10^{-1}				
	150	6.43×10^{-1}	1.94				
4	120	2.7×10^{-2}	3.6×10^{-2}	133	165	10^{16}	10^{20}
	130	9.3×10^{-2}	1.50×10^{-1}				
	135	1.04×10^{-1}	3.82×10^{-1}				
	140	2.97×10^{-1}	7.30×10^{-1}				
	150	4.14×10^{-1}	1.14				

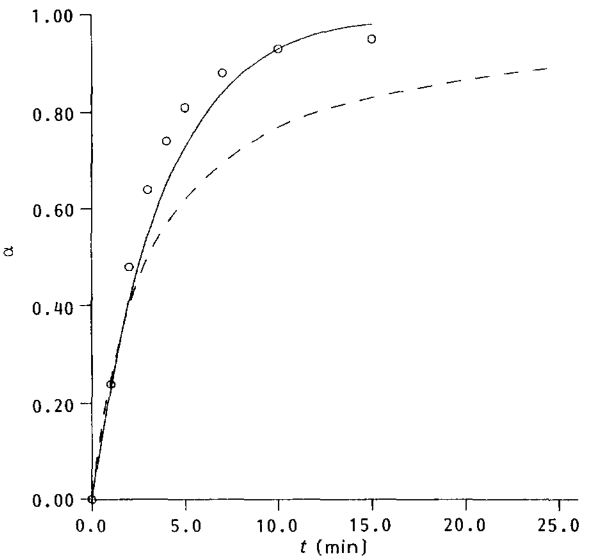

Figure 7 Conversion *versus* time plots for oligomer 3; experimental plots and plots predicted by numerical integration of equation (5) at 140°C (0.03 mol initiator per mol double bond). ——, Order 1; — — —, order 2; ○, experimental

kinetics for oligomer 3. In all the oligomers studied, the data fitted better to a first-order (up to $\alpha = 0.7$) than to a second-order model (up to $\alpha = 0.5$). The values of the kinetic parameters obtained in both cases are summarized in *Table 3*.

The rate constants did not seem to depend on the molecular weight of the oligomers and were higher if second-order kinetics were assumed. Also the values of E_A and A obtained ($\approx 180\,\mathrm{kJ\,mol^{-1}}$ and $\approx 10^{21}\,\mathrm{min^{-1}}$) by considering second order kinetics were higher than those obtained from first order ($\approx 135\,\mathrm{kJ\,mol^{-1}}$ and $\approx 10^{16}\,\mathrm{min^{-1}}$).

Both sets of values were in good agreement with those calculated from dynamic data but, again, only the data obtained from the first-order equation agreed with those obtained by the methods based on the analysis of the change of the exotherm with the heating rate previously discussed.

Furthermore, comparison of the experimental conversion *versus* time profiles with those simulated by numerical integration of equation (5) using the evaluated E_A and A values for both reaction orders[25] (*Figure 7*), gives much better agreement for first order.

CONCLUSIONS

The study of the crosslinking reaction of this series of bismaleimide oligomers has allowed us to quantify the influence of the radical initiators on the kinetics of polymerization, which in turn will permit the control of the cure process in order to obtain highly crosslinked networks. It has been proven that chain length does not exert a significant influence on the polymerization rate for flexible bismaleimides, and that the kinetic parameters fit quite well with an overall first order crosslinking reaction.

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REFERENCES

1 Stenzenberger, H. D., König, P., Herzog, M., Römer, W., Pierce, S., Fear, K. and Canning, M. S. 19th Int. SAMPE Techn. Conf., Covina, CA, USA, October, 1987, p. 372
2 Parker, J. A., Kourtides, D. A. and Fohlen, G. M. in 'High Temperature Polymer Matrix Composites' (Ed. T. T. Serafini), Noyes Data Corporation, Park Ridge, NJ, 1987, p. 54
3 Stenzenberger, H. in 'Structural Adhesives' (Ed. A. J. Kinloch), Elsevier, London, 1986, p. 77
4 Varma, I. K., Gupta, S. P. and Varma, D. S. *J. Appl. Polym. Sci.* 1987, **33**, 151
5 Kwiatkowski, G. T., Robeson, L. M., Brode, G. L. and Bedwin, A. W. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 961
6 Stenzenberger, H. D., Römer, W., Herzog, M., Pierce, S., Canning, M. S. and Fear, K. 31st Int. SAMPE Symp., Covina, CA, USA, 1986, Vol. 31, p. 920
7 Street, S. 25th Nat. SAMPE Symp., Covina, CA, USA, 1980, Vol. 25, p. 366
8 Acevedo, M., de la Campa, J. G. and de Abajo, J. *J. Appl. Polym. Sci.* 1989, **38**, 1745
9 Bruce Prime, R. Thermosets, in 'Thermal Characterization of Polymeric Materials' (Ed. E. A. Turi), Academic Press, New York, 1981, p. 435
10 Varma, I. K., Sangita, and Varma, D. S. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1419
11 Ninan, K. N., Krishnan, K. and Mathew, J. *J. Appl. Polym. Sci.* 1986, **32**, 6033
12 Hammermesh, C. L. and Dynes, P. J. in 'High Temperature Polymer Matrix Composites' (Ed. T. T. Serafini), Noyes Data Corporation, Park Ridge, NJ, 1987, p. 169
13 Searle, N. E. US Patent 2 444 536, 1948; *Chem. Abstr.* 1948, **42**, 7340
14 Lucarelli, M. A., Jones Jr, W. B., Picklesimerand, L. G. and Helminiak, T. E. *Polym. Prepr.* 1981, **22/1**, 19
15 Rätzsch, M., Steiner, V., Giese, B. and Farshchi, H. *Makromol. Chem. Rapid Commun.* 1989, **10**, 195
16 Masson, J. C. Decomposition Rates of Free Radical Initiators, in 'Polymer Handbook', 2nd edn (Eds J. Brandrup and E. H. Immergut), Wiley Interscience, New York, 1975, p. II.1
17 Odian, G. 'Principles of Polymerization', 2nd edn, Wiley Interscience, New York, 1981
18 Cernec, F., Osredkar, V., Moze, A., Vizovisek, I. and Lapaanje, S. *Makromol. Chem.* 1977, **178**, 2197
19 Lauver, R. W. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 2529
20 Ozawa, T. *J. Therm. Anal.* 1970, **2**, 301
21 Kissinger, H. E. *Anal. Chem.* 1957, **29**, 1702
22 Barton, J. M. *Makromol. Chem.* 1974, **171**, 247
23 Gebben, B., Mulder, M. H. V. and Smolders, C. A. *J. Polym. Sci. Polym. Chem.* 1988, **26**, 1743
24 Riccardi, C. C., Adabbo, H. E. and Williams, R. J. *J. Appl. Polym. Sci.* 1984, **29**, 2481
25 Gonzalez-Romero, V. M. and Casillas, N. 45th Ann. Techn. Conf. S.P.E., Covina, CA, USA, 1987, p. 1119