Curing of bismaleimides: 3. Effect of structure on thermal behaviour of bis(amide-maleimide)

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This paper describes the synthesis and characterization of six bismaleimide resins containing amide linkages in their backbones. The effect of structure on thermal behaviour was investigated by introducing phosphine oxide, fluorene, ether, methylene, *m*-phenylene and sulphone groups into the backbone. Thermal characterization of these bismaleimides was achieved using differential scanning calorimetry and thermogravimetric analysis. The presence of an electron withdrawing group in the backbone of the bisimide increased the curing temperature and reduced the reactivity of the maleimide bond. Thermal stability of the cured bismaleimide resins depended on their structure and it was found that the phosphorus and fluorene containing bisimide resins gave high char yields.

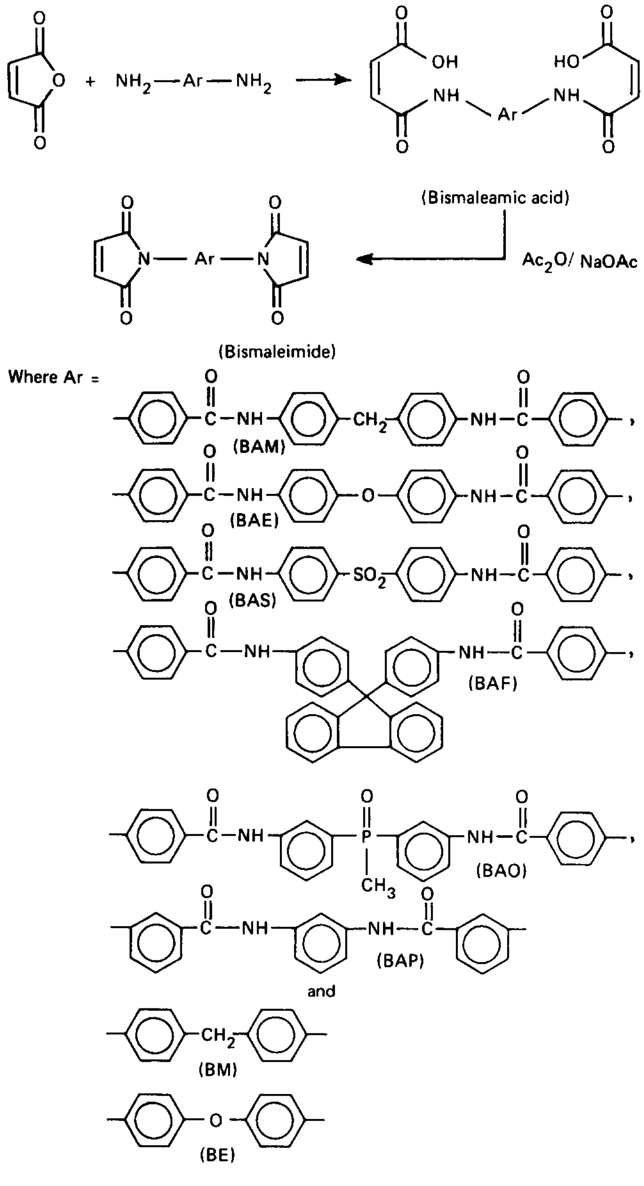
(Keywords: bismaleimides; bismaleamic acid; curing; phosphine oxide; fluorine; sulphone)

INTRODUCTION

The high temperature capabilities and flame resistance of bismaleimides, which are low molecular weight prepolymers end-capped with reactive maleimide rings, is influenced to a great extent by the backbone structure[1,2]. We have earlier reported high char yields in bismaleimides having fluorene, anthrone and phthalein groups as bridging units[3]. Incorporation of elements such as phosphorus and nitrogen into the backbone of synthetic polymers generally leads to an improvement in flame resistance[4-7].

The major disadvantage of bismaleimides is their very low elongation at break. An increase in prepolymer molecular weight may result in increased elongation-at-break and a reduction in the brittleness of the resins. The high temperature stability of aromatic polyamides such as poly(*p*-phenylene terephthalamide) (Kevlar) and poly(*m*-phenylene terephthalamide) is well documented in the literature. It would be interesting to study the thermal behaviour of bismaleimides containing aromatic amide linkages in the backbone. A literature survey has revealed that systematic work on thermal behaviour of bismaleimides containing amide groups has not been reported, although the commercially available Technochemie M-751 resin is based on the poly(amide-maleimide) resin concept[8].

The present studies were, therefore, undertaken to study the effect of structure on thermal behaviour of bis(amide-maleimides). The bismaleimide resins of Scheme 1 were synthesized by the reaction of the appropriate aromatic diamine with maleic anhydride in dry DMF and subsequent cyclodehydration of bismaleamic acid precursor by refluxing with acetic anhydride and sodium acetate using a modification of the method described by Searle[9].



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EXPERIMENTAL

Materials

Dimethyl formamide (BDH) was kept over P_2O_5 for 24 h and was then distilled under reduced pressure and stored over molecular sieves (3 Å) for 24 h before use. Anhydrous sodium acetate (BDH) was obtained by fusion. Maleic anhydride (BDH) was recrystallized from acetic anhydride (BDH). The aromatic diamines containing preformed amide linkages were prepared by reacting 4-nitrobenzoyl chloride with an appropriate diamine in dry DMAc. The dinitro precursor thus obtained was reduced by Pd/C and hydrazine hydrate in DMAc solution. The details of the synthesis of these amines have been described elsewhere[10]. These amines were characterized by elemental analysis and by recording i.r., ^1H n.m.r. and mass spectra.

Synthesis of bismaleimides

The appropriate aromatic diamine (0.01 mol) was dissolved in dry DMF in a three-necked flask fitted with a nitrogen inlet tube, solid transfer tube and a reflux condenser. Maleic anhydride (0.22 mol) was added in two portions over a period of 10 min. The solution was stirred at 50°C for 2 h in a nitrogen atmosphere. Cyclization of the aminic acid intermediate was carried out by adding fused sodium acetate (1.81 g) and acetic anhydride (5 ml) mixture to this solution. The temperature of the reaction mixture was maintained at 50°C for another hour. The solution was then poured into cold water. The precipitate was collected by filtration, repeatedly washed with water and dried at 60°C–70°C in a vacuum oven. The bismaleimides were purified by passing a chloroform solution through a silica gel column. Crystals of the appropriate bismaleimide were separated out after removal of excess chloroform under reduced pressure. The yields of the various bismaleimides ranged from 35–40%.

Characterization

The i.r. spectra of the bismaleimides were recorded in KBr pellets using a Perkin–Elmer (580B) i.r. spectrophotometer. The ^1H n.m.r. spectra of bismaleimides were recorded using a Jeol JNM FX 100 *FT*-n.m.r. spectrophotometer. A solution of bismaleimide in DMSO-d6 was used. The spectra were recorded at 20 ppm with tetramethyl silane as an internal standard. The mass spectra of the bismaleimides were recorded using a Jeol JMS D300 mass spectrometer having a JMS-2000 data processing system. A DuPont 1090 thermal analyser having a t.g.a. module 951 and d.s.c. module 910 was used to evaluate the thermal behaviour of the resins. The measurements were done in air (static) or in nitrogen (flow rate $60\,cm^3\,min^{-1}$) at a heating rate of $10\,K\,min^{-1}$. A sample weight of 11 ± 2 mg was used.

RESULTS AND DISCUSSION

The characterization of the amines used for the preparation of bismaleimides BAM, BAE and BAS has been reported earlier[10]. The aromatic amido-amines AO and AF used for the preparation of bismaleimides BAO and BAF were characterized by elemental analysis and mass spectroscopy. The results of the elemental analysis of these amido-amines agreed well with the assigned structure (observed values for AO, C=66.9, H=5.16; calculated for $C_{27}H_{25}O_2N_4P$, C=67.30, H=5.2; observed values for AF, C=79.86, H=5.12; calculated for $C_{39}H_{30}O_2N_4$ C=78.52, H=5.04).

Electron impact induced fragmentation patterns of these amines at 30 eV have been obtained (*Figures 1 and 2*). Molecular ion peaks in AO and AF were observed at 484 and 586 with relative intensities of 19.67 and 7.59 for base peaks respectively. The scission of the amide bond leads the intense *m/z* 120 fragment ion peaks in both of these diamines. The expected *m/z* (M − 120) fragment ion was not observed in the mass spectra of AO and AF. However, (M − 118) and (M − 119) fragment ions were prominent in AF.

The results of i.r., mass spectroscopy and elemental analysis confirmed the structures assigned to the various diamines used in the present work.

Eight bismaleimides having bridge unit formula weights of 166 to 554 were synthesized to study the effect of structure on thermal behaviour. These prepolymers were characterized by i.r., ^1H n.m.r. and mass spectroscopy.

Characterization of bismaleimides

In the i.r. spectra of all bismaleimides, strong bands due to imido groups were observed at 1720 ± 10 and $1780 \pm 10\,cm^{-1}$. The $\nu_{C=O}$ stretching due to amide linkage was observed at $1680 \pm 5\,cm^{-1}$. The other prominent bands due to phenyl groups at 1600 ± 10 and $1490 \pm 10\,cm^{-1}$ and C–N stretching at $1310 \pm 10\,cm^{-1}$

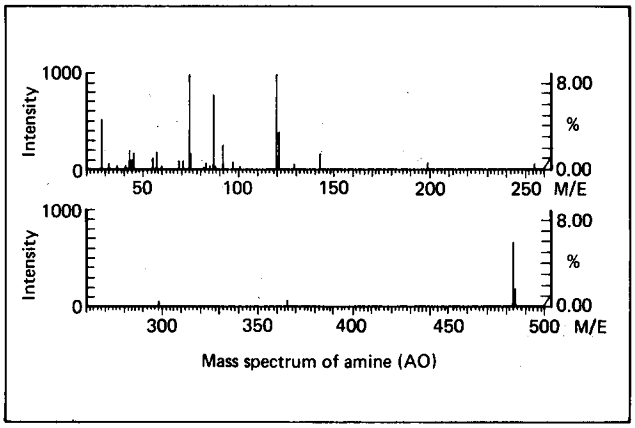


Figure 1 Mass spectrum of amido-amine AO

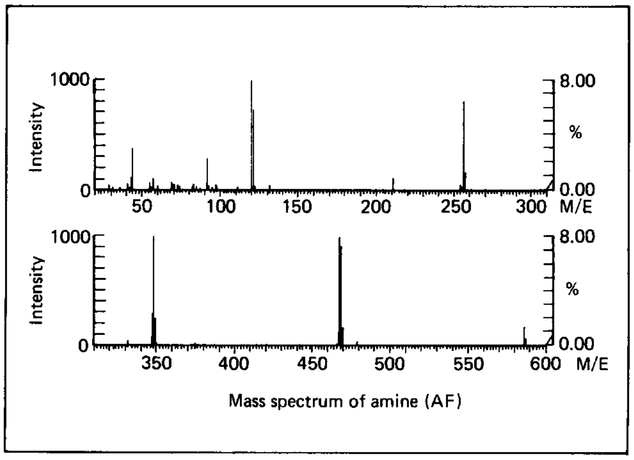
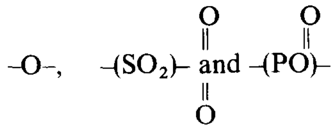
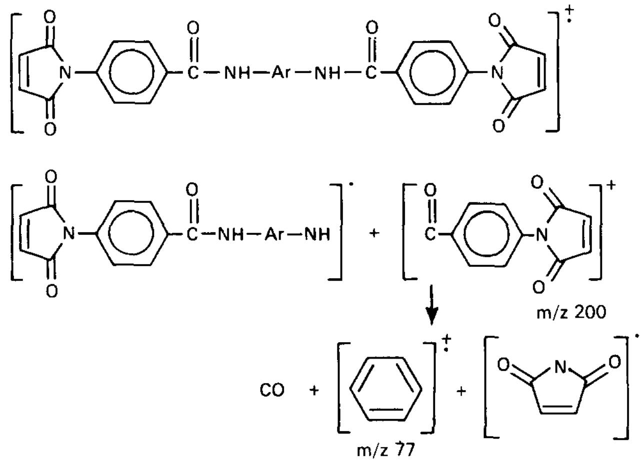


Figure 2 Mass spectrum of amido-amine AF

were also present. In the i.r. spectra of BAE, BAS and BAO, absorption bands were observed at 1230, 1070 and 1150 $\mathrm{cm^{-1}}$ due to  $-\mathrm{O}-$, $\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{\|}}{-(\mathrm{SO_2})-}}}$ and $\overset{\mathrm{O}}{\overset{\|}{-(\mathrm{PO})-}}$ groups respectively.

In the ^{1}H n.m.r. spectra of all the bismaleimides signals due to the protons attached to maleimido double bonds appeared at δ 7.1–7.23 (4H, s). The amido proton appeared at δ 10.3–10.72 (2H, s). A complex pattern was observed in the aromatic region.

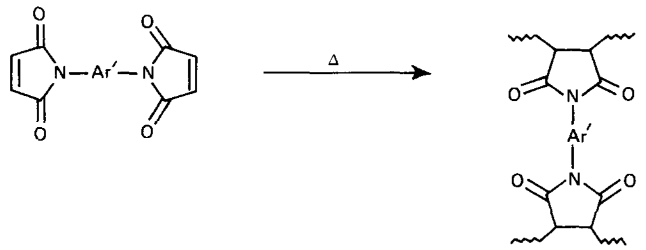
Electron impact induced fragmentation patterns of most of these bismaleimides obtained at 30 eV did not show molecular ion peaks. A molecular ion peak of low relative abundance was observed only in BAM. The high temperature ion source (250°C) may have resulted in crosslinking of these imide prepolymer thereby reducing the volatility. The fragment ions due to scission of amide bonds were observed at *m/z* 200 in each of BAM, BAE, attracting substituents in the maleimide group has been pattern of these bismaleimides can be explained on the basis of the following scheme:



The results of the i.r., ^{1}H n.m.r. and mass spectroscopy thus confirm the assigned structure of the various bismaleimides.

Curing behaviour of bismaleimides

A highly crosslinked network structure is obtained by heating bismaleimides at 150°C–400°C. This curing reaction is believed to proceed via a free radical mechanism. However, the presence of electron donor or electron attracting substituents in the maleimide group has been reported to influence the curing characteristics[11].



Thermal scans of bismaleimides (*Figure 3*) were performed using differential scanning calorimetry in nitrogen. Thermodynamic quantities determined were heat of curing ΔH, exothermic peak temperature (T_{exo}), onset temperature for curing reaction (T_1) and temperature for completion of reaction (T_2). T_1 and T_2 were obtained by extrapolating the front side or back side of the exothermic peak to the base line. From these traces T_1, T_{exo}, T_2 and ΔH were obtained and are reported in *Table 1*.

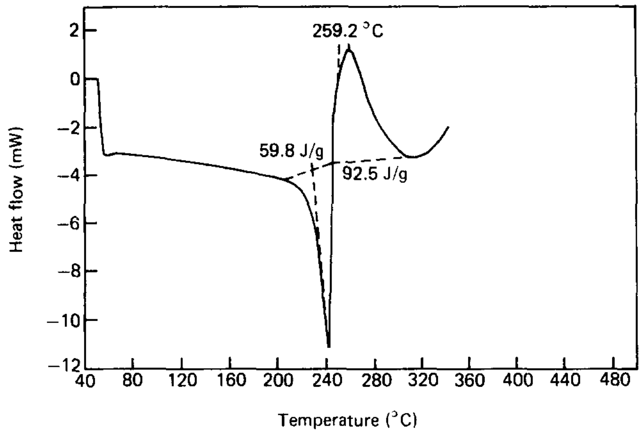


Figure 3 D.s.c. trace of bismaleimide BAP in nitrogen at a heating rate of 10 K $\mathrm{min^{-1}}$

A sharp endotherm associated with melting of bismaleimide was observed only in BM, BE and BAP. In other samples a broad endotherm was observed before the appearance of an exothermic transition. The diffused character of the endotherm may be due to initiation of curing nearing the melting point. The endothermic melting and exothermic curing may be responsible for the broadening of this peak.

In BAM two exothermic transitions were observed having maxima at 260°C and 350°C. The exotherm observed at higher temperatures (i.e. 350°C) is perhaps due to pyrolysis of the cured bisimide.

T_1 and T_{exo} values were at a minimum for BAM and a maximum for BAS (*Table 1*). The relative reactivity of bismaleimides for curing reactions may be judged on the basis of T_{exo} values. The T_{exo} values decreased in the following order:

$$\mathrm{BAS > BAO > BE > BM > BAP > BAF > BAE > BAM}$$

BAS and BAO had strong electron withdrawing groups (sulphone and phosphine oxide, respectively) in the backbone. It may, therefore, be concluded that presence of electron withdrawing group in the backbone of bisimide increased the curing temperature and reduced the reactivity of the maleimide double bond. Similar results have earlier been reported with bis(dichloromaleimides)[12] where curing was observed above 300°C.

Table 1 Results of d.s.c. analysis of various bismaleimides

Resin	Mol. wt.	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH ($\mathrm{J\,g^{-1}}$)	Activation energy ($\mathrm{kJ\,mol^{-1}}$)
BAM	596	205	236	265	92	257
BAE	598	216	244	300	68	243
BAS	646	255	267	294	11	272
BAF	746	221	257	323	47	171
BAO	644	225	265	320	55	184
BAP	506	242	259	290	92.5	163
BM	358	194	260	305	221	152
BE	360	219	262	340	164	137

In the resin under investigation the curing started at much lower temperatures compared with the bis(dichloromaleimides), where electron withdrawing chlorine was directly attached to the maleimide group.

The heat of polymerization (ΔH) obtained from the area under the exothermic peak also depended on the structure of the bismaleimide. However, defining the baseline created some difficulty in those samples where the end of the fusion endotherm and beginning of the curing exotherm were not clearly distinguishable (*Figure 3*). Deviation from the scanning base line has been taken as the onset of the polymerization reaction. A variation in ΔH values is expected by a change in the values of these limits. A very high value (221 J g^{-1}) was obtained for BM followed by BE (164 J g^{-1}). Bis(amide-maleimide) resins BAP and BAM had comparable ΔH values (92 J g^{-1}) while lowest ΔH value was observed in BAS. Since ΔH is a measure of the extent of polymerization (curing) a low value indicates incomplete curing reaction. On the basis of ΔH values (expressed as J mol^{-1}) the following order for the reactivity of bismaleimides is observed:

$$BM > BE > BAP > BAM > BAE > BAF > BAO > BAS$$

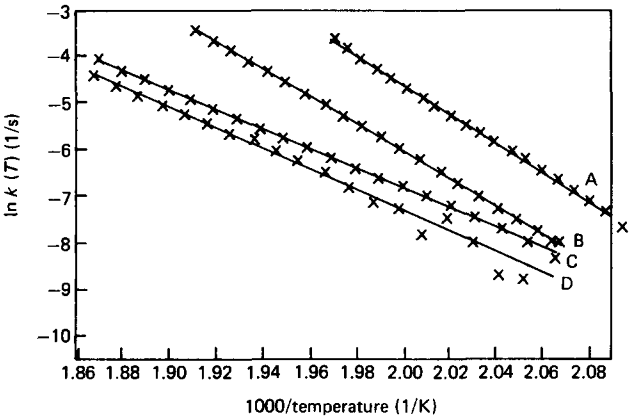


Figure 4 Arrhenius plots of cure rate constants vs. reciprocal temperature. (A) BAM, (B) BAE, (C) BAF and (D) BAO

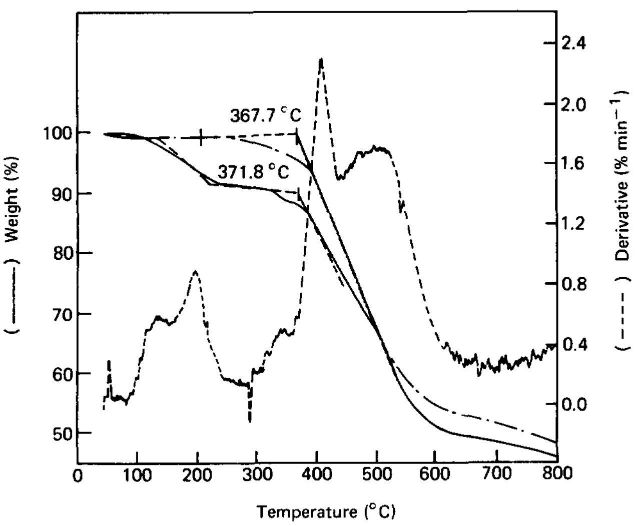


Figure 5 Thermogravimetric traces of BAM heated at 220°C for 0 h (———), and for 2 h (– – –)

Tables 2 Results of thermogravimetric analysis of various bismaleimides (uncured)

Designation	T_i (°C)	T_f (°C)	T_{max} (°C)	Char yield (%)
BAM	138 372	530	197 407	48.0
BAE	125 404	524	144 429	47.0
BAS	166 413	542	194 446	39.5
BAF	140 421	545	173 449	53.5
BAO	143 401	510	163 422	56.0
BAP	198 434	543	245 451	40.0

Table 3 Results of thermogravimetric analysis of bismaleimides (cured at 220°C ± 5°C for 2 h)

Resin	T_i (°C)	T_f (°C)	T_{max} (°C)	Y_c (%)	*IPDT*
BAM	368	560	414	46.5	–
BAE	397	522	428	57.0	–
BAS	417	550	451	43.0	–
BAF	419	545	450	60.0	–
BAO	397	510	418	62.5	–
BAP	421	550	451	44.0	–
BE	274 486	525	343 498	48.0	652
BM	486	532	503	51.0	666

The activation energy for curing reactions was determined according to a dynamic method using the Borchardt–Daniels d.s.c. kinetics programme[13] which permits the calculation of activation energy E, pre-exponential factor (A) and order of reaction (n) from a single d.s.c. scan of a reaction exotherm. The method assumes that the reaction follows nth order kinetics, i.e.

$$\frac{d\alpha}{dt} = k_{(T)}(1-\alpha)^n$$

where α = fractional conversion (dimensionless); $k_{(T)}$ = specific rate constant at temperature T(s^{-1}); n = reaction order (dimensionless).

The method also assumes that the temperature dependence of reaction rate follows the Arrhenius expression. Typical Arrhenius plots of $\ln k_{(T)}$ vs. $1/T$ are given in *Figure 4*. The activation energy ranged between 137 kJ mol^{-1} and 272 kJ mol^{-1} (*Table 1*). It was at a maximum for BAS. It is clear from the d.s.c. results that curing characteristics are influenced by the presence of electron-withdrawing groups in imide propolymers.

Thermogravimetric traces for bismaleimide BAM are shown in *Figure 5*. The t.g. curve was characterized by T_i (initial decomposition temperature), T_f (final decomposition temperature), T_{max} (temperature of maximum rate of weight loss), *IPDT*[14] and per cent char yield in nitrogen at 800°C (Y_c) (*Tables 2* and *3*). The char yields of uncured resins varied from 40% for BAS and BAP to 56% for BAO. A two-step decomposition was observed in uncured bisimide resins. An initial weight loss of ~3–10% was observed in the temperature range of 150°C–250°C. This was followed by a major loss in weight above 300°C. The low-temperature weight loss in the t.g.a. of an uncured resin may be due to loss of imide monomers by the carrier gas from the t.g.a. crucible. No exothermic or endothermic transition corresponding to this temperature was observed in the d.s.c. The anaerobic char yields for cured resins were at a maximum in BAO (62.5%). This imide contains phosphorus in the backbone and it appears that the condensed phase reactions are enhanced by presence of phosphorus (BAO). A high char yield (60%) was obtained in BAF which contains a fused ring structure. Thus the stability of the cured bismaleimide resins is influenced by the structure of the resin.

These results thus indicate that thermal characteristics of bismaleimides are influenced by the bridging units between the maleimide groups. Introduction of amide linkages in bismaleimides (example BM and BAM) although increasing the molecular weight of the prepolymer, reduces the exothermic peak position associated with curing reaction. The char yields of cured resins are also dependent on the structure of bridging units.

ACKNOWLEDGEMENT

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REFERENCES

1 Stenzenberger, H. D. *Appl. Polym. Symp.* 1973, **22**, 77
2 Hummel, D. O., Heinen, K. U., Stenzenberger, H. D. and Siesler, H. *J. Appl. Polym. Sci.* 1974, **18**, 2015
3 Varma, I. K., Fohlen, G. M. and Parker, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 283
4 Sato, M. and Yokoyama, M. *Eur. Polym. J.* 1979, **15**, 75
5 Varma, I. K., Fohlen, G. M. and Parker, J. A. US Patent, 1981, 4 276 344 and 1983, 4 395 557
6 Varma, I. K., Fohlen, G. M. and Parker, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 2017
7 Varma, I. K., Fohlen, G. M. and Parker, J. A. *J. Macromol, Sci., Chem.* 1983, **A-19**, 209
8 Stenzenberger, H. D., Herzog, M., Romer, W., Scheiblich, R. and Reeves, N. J. *Br. Polym. J.* 1983, **15**, 1
9 Searle, N. E., US Patent, 1948, 2 44 536; *Chem. Abstr.* 1948, **42**, 7340
10 Varma, I. K. and Sharma, S. *Eur. Polym. J.* 1984, **20**, 1101
11 Varma, I. K., Fohlen, G. M., Hsu, M. and Parker, J. A. in 'Contemporary Topics in Polymer Science, Vol. 4', (Eds. W. J. Bailey and T. Tsuruta), Plenum Press, 1984, pp. 115–140
12 Varma, I. K., Fohlen, G. M. and Parker, J. A. ACS Symp. Series No. 195, 'Cyclopolymerization and Polymers with Chain-ring Structures', 1982, (Eds. G. Butler and J. Kresta), 253
13 DSC Kinetics data analysis programme, Borchardt and Daniels, E. I. DuPont de Nemours and Co., Wilmington, Delaware 19898, USA
14 Doyle, C. D. *J. Anal. Chem.* 1961, **33**, 77