Copolymerization and activation of peroxide decomposition with acrylic derivatives of tertiary aromatic amines

B. Sandner*, S. Baudach and P. Knoth
Department of Chemistry, Institute of Technical and Macromolecular Chemistry, Martin-Luther-University Halle–Wittenberg, Geusaer Strasse, D-06217 Merseburg, Germany

and M. C. Tanzi
Dipartimento di Chimica Industriale ed Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
(Received 30 November 1993)

The reactivity parameters of the copolymerization of *N,N*-bis(2-methacryloyloxyethyl)-*p*-toluidine (BMAT) (M_1) with methyl methacrylate (MMA) (M_2) in 1,4-dioxane, i.e. $r_1 = 1.07 \pm 0.20$, and $r_2 = 0.11 \pm 0.19$, and with bisphenol-A bis(2-hydroxypropyl methacrylate) (Bis-GMA) (M_2) in benzene, i.e. $r_1 = 0.58 \pm 0.04$, and $r_2 = 0.03 \pm 0.03$, were determined at 60°C at low concentration and low conversion ($\sim 5\%$) of the monomers. Strongly delayed gelation occurred during the copolymerization of BMAT and MMA at monomer conversions of 20–30%, relatively independently of the composition of the monomer mixture. The efficiency of BMAT and *N*-acryloyl-*N'*-phenylpiperazine as activators in the redox initiated copolymerization of Bis-GMA in dental composites at ambient temperatures was found to be comparatively low. In the case where BMAT was used in equimolar proportions to benzoyl peroxide the former component was not detectable in the extract of the cured composite.

(Keywords: copolymerization; redox initiation; dental composite)

INTRODUCTION

The redox system consisting of benzoyl peroxide (BPO) and a tertiary aromatic amine is widely used to initiate free-radical polymerizations at room temperature, e.g. the polymerization of methyl methacrylate (MMA) in bone cements and of low-shrinking dimethacrylates in dental composites. Whereas in the latter case, photoinitiation has become of greater importance, redox polymerization is the only suitable method in the former case. With respect to these medical applications, the toxicity of the tertiary aromatic amines has obviously to be taken into account. Diffusion of the amine into the surrounding tissue is possible during the curing time of bone cements and dental composites, which is ~2–10 min. The diffusion of the amine reaction products may depend on whether or not the amine radicals that are formed are able to start the chain propagation step, a point which has not been clarified decisively until recently[1–4]. Therefore, the application of polymerizable amines as activators in MMA polymerization initiated by BPO was proposed by several authors[4–8].

Dnebosky *et al.*[5] prepared a number of methacrylic esters of various *N*-hydroxyethylaminobenzene derivatives. The monoesters of the *N*-methyl-*N*-hydroxyethyl derivatives were synthesized by transesterification with MMA, while the diesters of the *N,N*-bis(hydroxyethyl) derivatives were prepared by reaction with methacryloyl chloride. The latter method was also used by Qiu *et al.*[4] to prepare the dimethacrylate of *N,N*-bis(2-hydroxypropyl)-*p*-toluidine. Danusso and coworkers described the synthesis of *N*-acryloyl-*N'*-phenylpiperazine (AcrNPP)[6], and the methacrylic derivative (MetNPP)[7], in which *N*-phenylpiperazine was condensed with the corresponding acyl chloride.

The activities of these (meth)acrylic derivatives of *N,N*-bis(2-hydroxyethyl)-*p*-toluidine and *N*-phenylpiperazine as promoters of the decomposition of BPO have been found to be considerably lower than that of *N,N*-dimethyl-*p*-toluidine (DMpT), the activator which is most commonly used[5,8].

The monomer reactivity ratios of AcrNPP (M_1) in its copolymerization reaction with MMA (M_2), determined as $r_1 = 0.25$ and $r_2 = 2.5$[6] corresponds to that of *N,N*-dimethylacrylamide with MMA. It was also found that MetNPP was of a much lower reactivity than AcrNPP in its copolymerization reaction with MMA. Therefore, 30% more MetNPP than AcrNPP was extractable from the poly(methyl methacrylate) produced after redox-initiated MMA polymerization reactions when using MetNPP and AcrNPP in small amounts as a promoter of the BPO decomposition[7].

With respect to low extractability of the amine activator from the cured composite, a polymerizable amine should be used that has a higher copolymerization reactivity than MMA or the other methacrylates which are used in composite materials. This requirement can be met, as the following results show concerning the copolymerization of *N,N*-bis(2-methacryloyloxyethyl)-*p*-

* To whom correspondence should be addressed

0032-3861/94/15/3285–05

toluidine (BMAT) with MMA and also bisphenol-A bis(2-hydroxypropyl methacrylate) (Bis-GMA).

For the synthesis of BMAT, a transesterification method is preferred, since this avoids any potential influence of residual chloride anions[9] (formed by esterification with (meth)acrylic chloride), on the formation of free radicals in the redox reaction between BMAT and BPO.

EXPERIMENTAL

Materials

All solvents were purified by distillation. Methyl methacrylate (MMA) (Röhm Chemische Fabrik) was distilled under vacuum (and argon) after first washing with 10% aqueous NaOH solution, distilled water and drying over Na_2SO_4. Azobisisobutyronitrile (AIBN) (Laborchemie Apolda) was purified by recrystallization from methanol and dried under vacuum. Benzoyl peroxide (BPO) (Laborchemie Apolda) was dissolved in cold chloroform, reprecipitated in methanol and then dried under vacuum.

N-vinylimidazole (NVI) and *N*-methylimidazole (MI) (Riedel-de Haën AG), 2,2-bis[4-(2,3-epoxypropoxy)-phenyl]propane (DGEBA) (EPILOX 17.01, Leuna-Werke AG; epoxy value (groups) = 5.81 eq. kg^{-1}, $M = 344\ g\ mol^{-1}$), methacrylic acid (MAA) (Röhm Chemische Fabrik GmbH; 99.9 wt% acid, stabilized with 200 ppm hydroquinone monomethylether (HQME)), triethyleneglycol dimethacrylate (TEGDMA) (Röhm Chemische Fabrik), 3-trimethylsilylpropyl methacrylate (Fluka AG) and 2,6-di-t-butyl-*p*-cresol (Ionol) (Merck-Schuchardt) were all used as received.

N,*N*-bis(2-methacryloyloxyethyl)-*p*-toluidine (BMAT) was synthesized by a transesterification reaction of MMA with *N*,*N*-bis(2-hydroxyethyl)-*p*-toluidine (Fluka AG) (BMAT: m.p. 42°C). Anal. calcd for $C_{19}H_{25}O_4N$: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.42; H, 7.70; N, 4.16).

N-acryloyl-*N'*-phenylpiperazine (AcrNPP) was prepared as described in ref. 6. It was purified by recrystallization in anhydrous n-heptane in the presence of a small amount of Ionol, and then dried under vacuum (m.p. 76°C).

Quartz powder (Keradenta-Werk Radebeul, average diameter $\bar{d} = 20\ \mu m$) was silanized with 0.5 wt% 3-trimethylsilylpropyl methacrylate before use. The silanized quartz powder was mixed with fumed silica (Wacker HDK) (74/2, w/w). Bisphenol-A bis(2-hydroxypropyl methacrylate) (Bis-GMA) was synthesized by the reaction of DGEBA with a stoichiometric amount of MAA at 90–100°C, in the presence of 0.03 wt% Ionol and 0.8 mol% of either NVI or MI as the catalyst[10].

Copolymerization

Solutions of the monomers in benzene or 1,4-dioxane, containing AIBN, were degassed in a high vacuum system at 10^{-2}–10^{-1} Pa and then polymerized under argon at 60°C. The copolymers were precipitated in methanol or diethylether and then dried at room temperature in vacuum for 2 days. The composition of the copolymers was determined by elemental analysis (N determination).

Conversion at gel point

Mixtures of BMAT and MMA in 1,4-dioxane, containing 1 mol% AIBN as initiator, were degassed in ampoules containing a magnetic stirrer, in the high vacuum system described above. The copolymerizations were carried out under argon at 60°C. The time from the beginning of the reaction until the stirrer stopped was taken as the gel time. The precipitated and dried copolymers were extracted in THF at room temperature with shaking, and the gel content was determined gravimetrically. In order to determine the weight-average degree of polymerization (P_w) of PMMA (needed for calculating the theoretical gel points), $1.79\ mol\ l^{-1}$ of MMA in 1,4-dioxane was polymerized for 5 h by the method described above. The weight-average molecular weight (M_w) was determined by gel permeation chromatography (g.p.c.) (Knauer Wissenschaftliche Geräte; eluent, THF; flow rate, $1\ ml\ min^{-1}$; column, Lichrogel PS 20; detection by RI) using PMMA standards for the calibration.

Preparation of composites

Composites were prepared by chemically curing mixtures of Bis-GMA/TEGDMA (7/3 and 8/2, by weight) in the presence of 76 wt% filler (quartz powder/silica = 74/2, by weight). Initiator (BPO) was added to one half of the monomer mixture, with the activator added to the other half. Equal amounts (by weight) of these initiator and activator pastes were mixed for 20 s. The time taken from the start of mixing until the sample was hard was defined as the curing time.

Determination of water uptake

Samples, 1 mm in thickness and 15 mm in diameter, were postcured at 37°C for 24 h and then stored in distilled water at 37°C for 7 days. After removing any residual water from the surface, the samples were weighed (m_1) and dried in vacuum to constant weight (m_2):

$$\text{water uptake } (\mu g\ mm^{-3}) = 1000\rho\left(\frac{m_1 - m_2}{m_2}\right)$$

using a value of ρ of $2\ g\ cm^{-3}$ for the density of the composite.

Monomer conversion and residual content of activator

A pulverized sample ($m_1 = 0.5$–1 g) was shaken in 10 ml of acetonitrile for 8 h. The solid components were separated using a frit, dried under vacuum and weighed (m_2) to determine the monomer conversion.

$$\text{monomer conversion } (\%) = 100\left(\frac{m_2 - (0.76m_1)}{0.24m_1}\right)$$

The extract was analysed by h.p.l.c. Chromatograms were recorded on a h.p.l.c. apparatus (Knauer Wissenschaftliche Geräte KG), equipped with a LiChrosorb RP-18 column. Samples were analysed by the gradient elution technique, using acetonitrile:water (30:70, until 100:0, by volume), at a flow rate of $1.5\ ml\ min^{-1}$, with u.v. detection at $\lambda = 215$ nm. To determine the proportion of Bis-GMA to TEGDMA, and the content of BMAT in the extract, calibration curves with known mixtures were established.

RESULTS AND DISCUSSION

Copolymerization of BMAT with Bis-GMA and MMA

For the determination of the reactivity ratios, the copolymerization experiments were performed at relatively low molar concentration of the monomers, and in addition were terminated at low conversions ($\leq 5\%$), so

Table 1 Copolymerization of BMAT with MMA in 1,4-dioxane at 60°C: [AIBN] = 1.3×10^{-3} mol l^{-1}; [>C=C<] = 0.692 mol l^{-1}

BMAT in monomer mixture (mol% >C=C<)	BMAT in copolymer (mol%)	Polymerization time (min)	Polymer yield (%)
15	41.0	30	4.2
25	50.0	30	2.2
50	67.9	50	3.1
75	75.8	50	3.6
85	88.1	60	4.5

Table 2 Copolymerization of BMAT with Bis-GMA in benzene at 60°C: [AIBN] = 8.8×10^{-4} mol l^{-1}; [>C=C<] = 0.2925 mol l^{-1}

BMAT in monomer mixture (mol%)	BMAT in copolymer (mol%)	Polymerization time (min)	Polymer yield (%)
15	49.1	15	2.5
25	52.1	15	3.9
50	60.6	15	6.1
75	72.6	15	2.0
85	80.8	25	4.3

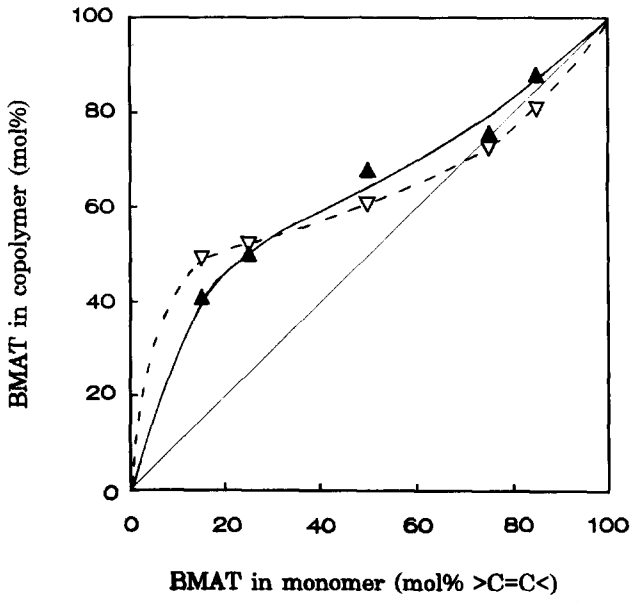

Figure 1 Copolymerization diagram of BMAT with MMA (▲) and Bis-GMA (▽); for conditions see *Tables 1* and *2*

that gelation and crosslinking did not occur. The results are summarized in *Tables 1* and *2* and in *Figure 1*. The reactivity ratios were determined using the method of Kelen–Tüdös[11], with the following values obtained with BMAT = M_1:

M_2	r_1	r_2
MMA	1.07 ± 0.20	0.11 ± 0.19
Bis-GMA	0.58 ± 0.04	0.03 ± 0.03

The copolymerization diagram (*Figure 1*) and the parameters r_1 and r_2 indicate that BMAT is the more reactive monomer.

Both copolymerizations have a tendency to alternation. The copolymerization with MMA is non-azeotropic, but the diagram for the copolymerization with Bis-GMA (*Figure 1*) shows an azeotrope at 69.8 mol% BMAT in the monomer mixture. Using the Q and e values of MMT $e = 0.4$, $Q = 0.74$)[12] we calculated values for BMAT of $e = -0.73$ and $Q = 4.29$, which are rather similar to the corresponding values of -0.39 and 1.78[12] of 2-hydroxyethyl methacrylate, the parent monomer of BMAT.

Conversion at gelation for BMAT–MMA copolymerization

At higher conversions, as expected, BMAT acts as a crosslinker in copolymerization with MMA. *Figures 2* and *3* show, respectively, the gelation time and the conversion level at gelation *versus* the BMAT content in the monomer mixture. Values for the conversion p_c at the gel point were calculated using the following equation[13]:

$$p_c = \frac{(r_1[A]^2 + 2[A][B] + r_2[B]^2)^2}{\bar{P}_w[B]([A]+[B])(r_2[B]+[A])^2}$$

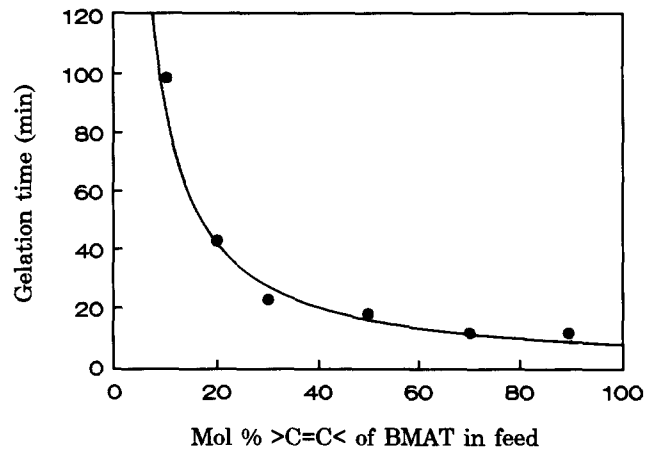

Figure 2 Dependence of the gelation time on the content of BMAT in the monomer mixture for BMAT–MMA copolymerization in 1,4-dioxane at 60°C. [AIBN] = 1.79×10^{-2} mol l^{-1}, [>C=C<] = 1.79 mol l^{-1}

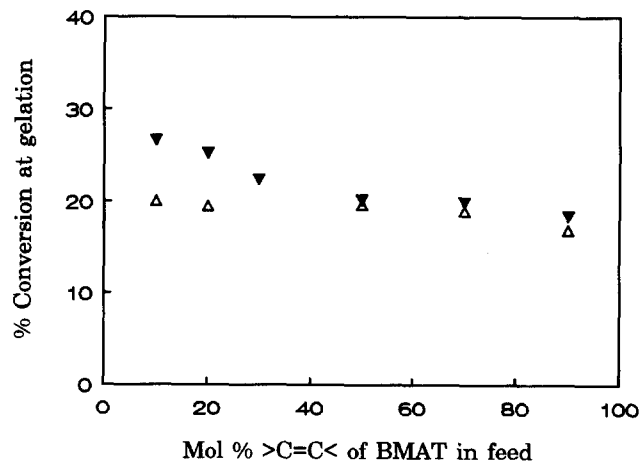

Figure 3 Level of conversion at gelation at different concentrations of BMAT in the monomer mixture for BMAT–MMA copolymerization at 60°C: (▼) total yield of copolymer; (△) yield of crosslinked copolymer. [AIBN] = 1.79×10^{-2} mol l^{-1}, [>C=C<] = 1.79 mol l^{-1}

where [A] is the molar concentration of double bonds of monomer A, [B] is the molar concentration of double bonds of the diene monomer B–B, and P_w is the weight-average degree of polymerization that would be observed in the polymerization of monomer A in the absence of the diene B–B.

This equation is only precise enough for systems with very low concentrations of the diene monomer. The relatively high proportion of BMAT in the monomer mixture may be one reason for the large discrepancies between the observed and theoretical conversions at the gel points, p_c, shown in *Table 3*. Intramolecular cyclization reactions of the pendent vinyl groups of BMAT in the copolymer chain may be a second reason. The preference of cyclization to a crosslinking reaction could be expected on account of the structure of BMAT, as well as the low concentration of the monomers.

The strong tendency of the pendent methacrylic groups to form cyclic species follows also from the difference between the BMAT content of the crosslinked copolymers found experimentally at the gel point and that which was calculated for this conversion without considering the reaction of any pendent methacrylic groups (see *Table 3*). Obviously, the latter react, in preference to the free BMAT, with a radical site of the same macromolecule because their local concentration around the radical grows rapidly with the decreasing hydrodynamic radius of the copolymer coils at higher conversions (>5%) of monomers.

Table 3 Calculated ($p_{c,calc}$) and experimental ($p_{c,exp}$) conversions at gelation for BMAT–MMA copolymerization: $\bar{P}_w = 1450\ g\ mol^{-1}$; for conditions see *Figure 2*

BMAT in monomer mixture (mol% >C=C<)	BMAT in polymer (mol%)		$p_{c,calc}$ (%)	$p_{c,exp}/p_{c,calc}$
	Calcd	Found		
10	31.1	10.8	0.053	500
20	44.3	19.2	0.063	398
30	52.0	29.0	0.072	307
50	64.2	51.8	0.081	246
70	76.2	62.8	0.082	245
90	91.1	79.5	0.074	248

Table 4 Curing times and monomer conversion of composites with AcrNPP as activator[a]

BPO content (wt%)[b]	Temperature[c] (°C)	Curing time (min)	Monomer conversion (wt%)
1	RT	1–2 days	55.0
2	35	35	60.1
3	35	11	
	RT	33	52.9
3.5	35	7	
	RT	20	67.5
4	35	5	
	RT	17	66.1

[a] Bis-GMA/TEGDMA = 7/3, by weight; $n_{BPO}\ mol^{-1} = n_{AcrNPP}\ mol^{-1}$; 76 wt% filler
[b] With reference to total monomer content
[c] RT = room temperature

Composites with polymerizable activator

The ability of the polymerizable aromatic tertiary amines AcrNPP and BMAT to promote the decomposition of BPO in Bis-GMA based composite materials was studied. Setting times of 2–4 min are desirable; these were observed when using the common initiating system BPO/DMpT with 0.8 wt% BPO (with reference to the total content of monomers) (see *Table 5* below).

In the case of AcrNPP, we only found acceptable setting times at concentrations above 3.5 wt% BPO with an equimolar amount of AcrNPP at 35°C (*Table 4*). However, in this case it becomes difficult to dissolve AcrNPP in the monomer mixture.

The activity of BMAT in forming initiating radicals is somewhat higher than that of AcrNPP (*Table 5*). The desired curing times could be attained at the still relatively high content of 2 wt% BPO, with an equimolar amount of BMAT, or with ~1 wt% BPO at molar ratios of BPO/BMAT < 1 (*Table 5*).

One reason for the low efficiency of both AcrNPP and BMAT is steric hindrance on the nitrogen atom, which renders the interaction of amine with peroxide more difficult. It is also probable that the double bond of the acrylic or methacrylic group near the nitrogen atom would substantially reduce the electron donating

Table 5 Properties of composites with BMAT and DMpT as activators after curing at room temperature[a]

No.	BPO content (wt%)[b]	DBPO/BMAT (mol mol^{-1})	Curing time (min)	Monomer conversion (wt%)	Conversion of BMAT (%)	Bis-GMA/TEGDMA in extract (w/w)	Water uptake ($\mu g\ mm^{-3}$)
1	1.0	0.5	>11	68.8	68.8	14.9	12.4
2	1.0	0.1	2.75	79.2	83.0	7.2	14.9
3	0.8	0.1	5.25	85.0	82.2	7.0	9.2
4[c]	2.0	1.0	4.50	84.8	100.0	16.3	13.9
		DBPO/DMpT (mol mol^{-1})					
5	0.8	1.0	2.50	81.3	–	0.5[d]	24.3
6[c]	0.8	1.0	2.00	80.8	–	3.5[d]	17.0

[a] Bis-GMA/TEGDMA = 7/3, by weight; 76 wt% filler
[b] With reference to total monomer content
[c] Bis-GMA/TEGDMA = 8/2
[d] Determination of Bis-GMA, after extraction with 1,4-dioxane, carried out by u.v. spectroscopy at $\lambda = 276$ nm

capability of the latter. In any case, the electron density at the tertiary nitrogen atom of AcrNPP should be lower than that of BMAT because the phenyl ring of the former is not substituted by a methyl group, as in the case of BMAT.

The h.p.l.c. analysis of the residual BMAT content in the extracts of the cured composites shows that it is only in the case where the molar ratio BMAT/DBPO = 1 that the whole of the BMAT is incorporated into the network (*Table 5*). This incorporation of BMAT is possible, both by an addition reaction of its double bonds to the macroradicals, as well as by a termination (combination) or a starting reaction of the radical which originates from the reaction with BPO.

The ratio of Bis-GMA and TEGDMA found in the extracts of cured composites is significantly changed by the presence of BMAT at curing. Bis-GMA is somewhat preferentially incorporated into composites polymerized by using DMpT as the activator (*Table 5*). However, the low reactivity of Bis-GMA in the copolymerization with BMAT, as shown above, results in high residual contents of Bis-GMA in the extracts of composites that have been cured with BMAT as the activator. It is also found that the water uptake of composites with BMAT is lower than that of composites containing DMpT (*Table 5*).

CONCLUSIONS

The high reactivity of the methacrylic groups of BMAT in the copolymerization with Bis-GMA does not bring about a complete incorporation of BMAT into the copolymer at monomer conversion >20% in every case, owing to the cyclization tendency of the pendent methacrylic groups. Therefore, it should be more favourable to use a monomethacrylate, e.g. *N*-(2-methacryloyloxyethyl)-*N*-methyl-*p*-toluidine (MMAT), which has the additional advantage of a higher efficiency in accelerating the peroxide decay[5]. Studies of the copolymerization of MMAT are in progress.

ACKNOWLEDGEMENTS

Financial support of this work by the Ministry of Science and Research of Saxonia–Anhalt, the Dr Otto Röhm Foundation and the Funds of the Chemical Industry of Germany is gratefully acknowledged. Furthermore, the authors would like to thank Gerd Biessmann for providing software for use in the copolymerization calculations, and Barbara Kunth for carrying out the h.p.l.c. measurements.

REFERENCES

1 Imoto, M., Otsu, T. and Ota, T. *Makromol. Chem.* 1955, **16**, 10
2 Huisgen, R., Heydkamp, W. and Bayerlein, F. *Chem. Ber.* 1960, **93**, 363
3 Mallon, H.-J., Unseld, W., Reinhold, G. and Reichenbach, M. *Acta Polym.* 1990, **41**, 460
4 Qiu, K. Y., Guo, X. and Feng, X. *Chin. J. Polym. Sci.* 1989, **7**, 258
5 Dnebosky, J., Hynkova, V. and Hrabak, F. *J. Dent. Res.* 1975, **54**, 772
6 Danusso, F., Tanzi, M. C., Levi, M. and Martini, A. *Polymer* 1990, **31**, 1577
7 Tanzi, M. C., Levi, M. and Danusso, F. *Polymer* 1990, **31**, 1735
8 Tanzi, M. C. and Levi, M. Paper presented at 15th Annual Meeting of Society for Biomaterials, Lake Buena Vista, Florida, USA, April–May 1989, p. 47
9 Hahn, M., Jaeger, W., Wandrey, Ch. and Reinisch, G. *Acta Polym.* 1984, **35**, 350
10 Sandner, B. and Schreiber, R. *Makromol. Chem.* 1992, **193**, 2763
11 Kelen, T. and Tüdös, F. *React. Kinet. Catal. Lett.* 1974, **1**, 487
12 Greenley, R. Z. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 3rd Edn, Wiley, New York, 1989, p. II-268
13 Odian, G. in 'Principles of Polymerization', 3rd Edn, Wiley, New York, 1991, p. 511