Novel *N*-acyloxytrialkylammonium salts as initiators for free radical polymerization of methacrylates†

Omari E. Ansong,*[a] Susan Jansen,*[a] Yen Wei,*[b] Gregory Pomrink,[c] Hui Lu,[c] Shuxi Li[b] and Yi Guo[b]

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An efficient method for preparing and isolating new derivatives of *N*-acyloxytrialkylammonium salts as initiators for the free radical polymerization of methacrylates and dimethacrylates is reported. The new initiators were evaluated for the free radical polymerization of methyl methacrylate (MMA), triethylene glycol dimethacrylate (TEGDMA) and ethoxylated bisphenol A dimethacrylate (EBPADMA) at 60 °C both with and without sulfuric acid promotion. The resulting polymers were all characterized by TGA and in addition, PMMA was characterized by DSC and SEC. The new initiators are very effective in producing narrow MWDs in PMMA and in effecting crosslinking in the dimethacrylates. The reaction time, polymer yield, molecular weight distribution (MWD), polydispersity index (PDI), decomposition temperature (T_d) and glass transition temperature (T_g), all improved under sulfuric acid promotion at 60 °C. Our attempts at photo-initiated polymerization of the monomers were not successful.

Introduction

i. Organic peroxide/amine system as an initiator for free radical polymerization

Low temperature free radical polymerization of vinyl monomers induced by an organic peroxide/amine system has been well studied. The most common organic peroxide used is benzoyl peroxide (BPO) and the most common amines used are *para*-substituted *N*,*N*-dimethylaniline derivatives such as *N*,*N*-dimethyl-*p*-toluidine (DMT).[1–5] Amines with electron donating substituents in the *para* position are more reactive than those bearing electron withdrawing *para* substituents.[1] The activating strength of the amine increases with the electron density at the nitrogen atom to a level that matches a Hammet substituent constant σ of about −0.14. Additional increases in the electron donating capacity of the substituent beyond this level lower the initiation rate.[6] Bulky substituents also produce a similar retardation of the initiation rate.[7,8] Furthermore, Bowen and Argentar[6] have reported that while the accelerating ability of the amine depends on both the ring and nitrogen substituents, the color stability of the resulting polymer depends more on the ring substituent.

Initiation by the redox BPO/amine system differs from the conventional thermal initiation of BPO with respect to practical applications and chemical kinetics. The redox BPO/amine system has a low activation energy and therefore it can initiate polymerization at room temperature as compared to conventional BPO decomposition, which occurs at 70 °C and above.[2] The mechanism for the acceleration of BPO decomposition by tertiary amines starts with an S_N2 nucleophilic displacement by the amine on the peroxide, yielding an intermediate adduct which finally forms benzoyloxy radical, benzoic acid and *N*-methylene radical.[1,5,8–11] The mechanism is shown in Fig. 1.[1]

ii. Challenges in the reaction chemistry

The mechanism in Fig. 1 shows two radicals as products of the reaction, namely, the benzoyloxy radical and the aminomethyl radical which results from proton loss by the amine radical cation. One group of researchers[12–14] maintains that only the benzoyloxy radical initiates the polymerization and that the amine radical does not. Within this group, Yildiz and Hazer[14] further argue that the dimethylaniline radical is resonance stabilized such that termination by recombination is the only fate of the radical. Two other groups of investigators, namely, Sato *et al.*[15] and De Feng[11] using electron spin resonance (ESR) spectroscopy and UV spectroscopy, respectively, proved that the benzoyloxy radical and the amine radical are both involved in the initiation of polymerization. It is currently fully accepted that both the benzoyloxy radical and the amine radical are involved in the initiation of polymerization.

However, excess radical concentration in the polymerization system, such as would be created by the presence of the multiple radicals, benzoyloxy and amine radicals, typically produces adverse effects such as chain termination and low molecular weights. Furthermore, the structural and stability differences between these radicals would impart different degrees of reactivity to them and this would complicate the kinetics of initiation and polymerization.

A parameter of great influence in the BPO/amine system is the molar ratio of BPO/amine. Oldfield and Yasuda,[2] using ESR to study the curing of bone cement for dental applications, observed that the optimum free radical concentration is

[a]*Department of Chemistry Temple University, 13th and Norris Street, Philadelphia, PA 19122, U. S. A. E-mail: ansong@temple.edu; suebee@temple.edu*
[b]*Department of Chemistry, Drexel University, Philadelphia, PA 19104, U. S. A. E-mail: weiyen@drexel.edu*
[c]*Research and Development, Dentsply International-Caulk, 38 West Clarke Avenue, Milford, DE 19963, U. S. A.*
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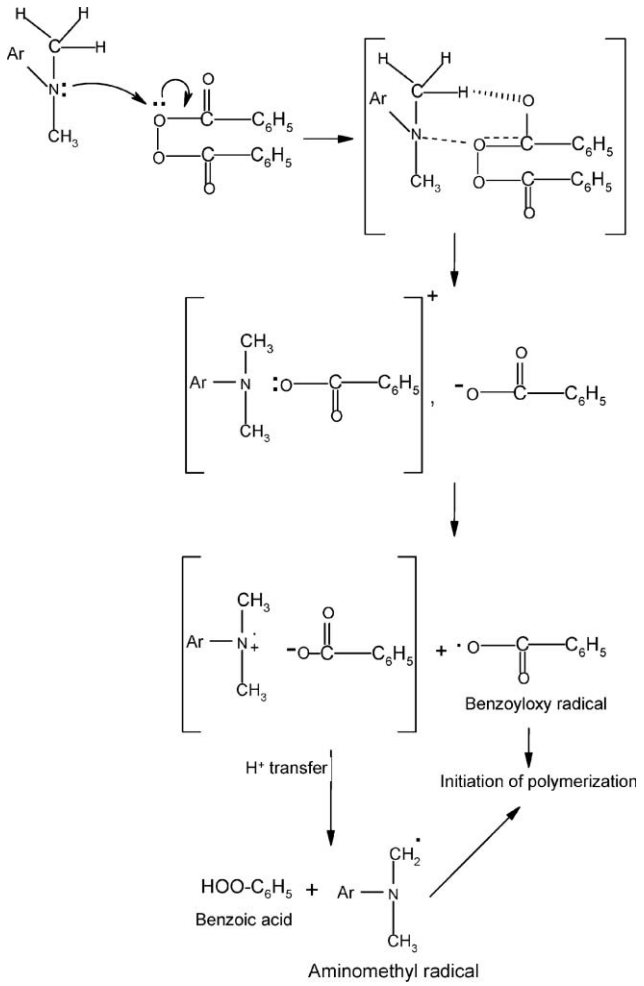

Fig. 1 Mechanism for radical generation in the redox BPO/amine initiator system.

attained when an equimolar BPO/amine ratio is used. They observed further that excess amine leads to a change in the chemical structure of the trapped radical which inhibits the polymerization reaction. Excess amine leads to the formation of nitroxide radicals.[1,2,8,9] The nitroxide radicals produce a side reaction by decomposing BPO to benzoic acid and benzoyloxy radicals.[2] As a side reaction of BPO, it can react with the benzoyloxy radical so formed.[8,13] Another undesirable reaction of BPO is that it can undergo chain transfer reactions.[13] The same applies to the tertiary aromatic amines, which are known to be very good chain transfer agents.[16–18] Yildiz and Hazer[14] have also reported that as the concentration of amine increases, the resulting polymer darkens in color due to adsorption of the amine radicals. Achilias and Sideridou[8] have reported that there is a clear dependence of Mn on the BPO/amine molar ratio.

Another influential parameter in the redox BPO/amine initiator system is the type and choice of amine and its chemistry. The most commonly used amine has been DMT. In dental and prosthesis applications, DMT is very toxic and it is a suspected carcinogen.[1,19] DMT can cause severe prosthesis failure in hypersensitive patients, causing tissue reaction at the bone/cement interface and induce contact dermatitis.[20,21]

Alternative amines that have been proposed include 4-*N*,*N*-dimethylamino phenethyl alcohol (DMPOH), 4-*N*,*N*-dimethylamino phenyl acetic acid (DMAPAA) and ethyl 4-dimethylamino benzoate (EDMAB).[1,5] Alternative amines that have been prepared include 4-*N*,*N*-dimethylaminobenzyl alcohol (DMOH), 4-*N*,*N*-dimethylaminobenzyl methacrylate (DMMO).[22] Bowen and Argentar[6] prepared and evaluated amines similar in structure to DMT but of higher molecular weight. The advantages of the higher molecular weight amines are that they have a reduced solubility in body fluids, which lowers the ease of diffusion into the pulp or other body tissues.[23]

The foregoing discussion shows that for the BPO/amine initiator system the presence of the free amine or free peroxide and their molar ratios account for the undesired side reactions, which compromise on the quality of the polymer product. Therefore, an alternative initiator system, which generates the desired radicals with identical accelerating effect but without the complications or side reactions from free amine or free BPO would be more desirable. The *N*-acyloxytrialkylammonium salts which are stable enough to be isolated, are more desirable alternatives.

iii. Preparation and isolation of *N*-acyloxytrialkylammonium salts

The preparation and isolation of *N*-acyloxytrialkylammonium salts have typically been accomplished by two reaction routes.[15,23] The first route involves the reaction of acyl peroxide, tertiary amine and an anion source. The second route involves the reaction of acyl anhydride, tertiary amine *N*-oxide and an anion source.[15,23] Typical anion sources include sodium tetraphenylborate and sodium perchlorate.[15,23]

The mechanism for both reactions is shown in Fig. 2. The reactions proceed by an *N*-acyloxytriakylammonium intermediate which, upon homolytic cleavage, releases radicals that can initiate the polymerization of vinyl monomers. Because the initiator is isolated and used as the free salt, there is no free amine or free peroxide in the salt. Therefore, this system is free of the undesired side reactions and the stoichiometry issues associated with the free amine and free peroxide that are present in the redox BPO/amine initiator system. By this method Sato and Otsu[23] have prepared and isolated *N*-benzoyloxytriethylammonium tetraphenylborate **1** and *N*-benzoyloxytrimethylammonium tetraphenylborate **2** whose reactions are shown as eqn 1 and 2 respectively (Fig. 3). Sato and Otsu[23] used the salts to initiate the polymerization of MMA at 60 °C.

Some of the *N*-benzoyloxytrialkylammonium salts are unstable and can therefore not be isolated. Among the stable ones which have been isolated are *N*-acetoxy-α-picolinium perchlorate[24] or picrate[25] and acetoxy- or *N*-benzoyloxyquinuclidinium chloride[26] which were prepared by reacting the respective amine oxide with acetic anhydride[24] and acetyl chloride.[26]

iv. Our approach

We have reproduced the preparation of *N*-benzoyloxytriethylammonium tetraphenylborate **1** and *N*-benzoyloxytrimethyl-

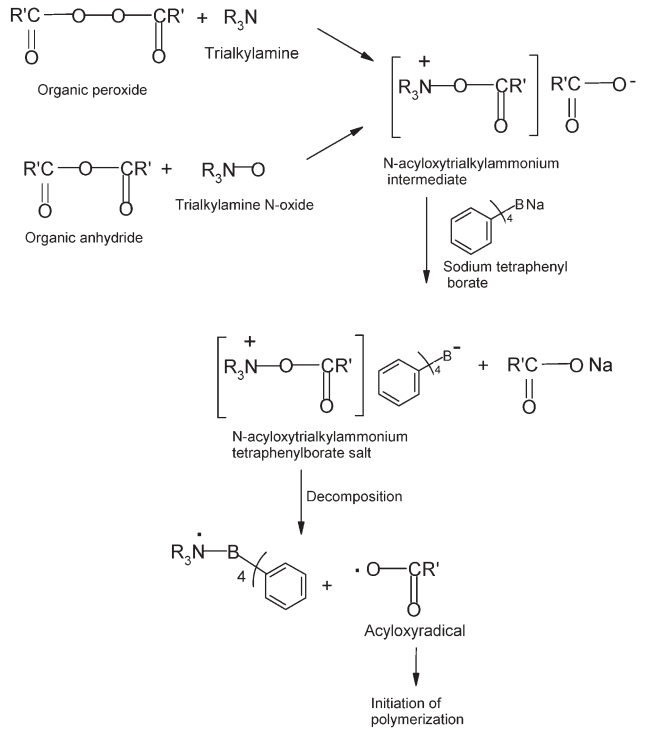

Fig. 2 Mechanism for radical generation from the *N*-acyloxytrialkylammonium tetraphenylborate initiator system.

ammonium tetraphenylborate **2**(Fig. 3) using the procedure by Sato and Otsu.[23] We have prepared, isolated and characterized several new derivatives of **1** and **2** by modifying the reactants in the original reactions. These new reactions are shown in Fig. 4. Unlike reaction 1 (eqn 1, Fig. 3) all the modifications in reaction 2 (eqn 2, Fig. 3) led to the desired derivatives in good yield (65–80%). All the new salts were evaluated as initiators for the free radical polymerization of MMA, TEGDMA and EBPADMA at 60 °C with and without H_2SO_4 promotion and under photochemical conditions. The structures of the monomers that were used are shown in Fig. 5.

Experimental

Materials

Benzoyl peroxide (BPO) was supplied by Dentsply and used as received. All dimethacrylate monomers were supplied by Dentsply. MMA was purchased from Aldrich. MMA and the dimethacrylates were freed of inhibitor by passing them through inhibitor removing columns purchased from Aldrich. The inhibitor removing columns had been packed with quaternary ammonium cation equivalent to amberlite IRA 900 chloride form. Concentrated sulfuric acid and HPLC grade THF were purchased from Fisher Scientific. All the other reagents were purchased from Aldrich. All elemental analyses experiments were performed by Galbraith Laboratories at Knoxville, Tennessee.

Instrumentation

Size exclusion chromatography (SEC) data was recorded on a Waters® GPC system made up of a Waters® 590 pump, a Waters® 410 differential refractometer detector, and a 10 μL Phenogel® column. The column parameters are: pore size = 1×10^3 A; length = 300 mm; inner diameter = 7.80 mm. To the system was connected a computer with software for run control, data storage and analysis. HPLC grade THF was used as a solvent. Sample concentration and injection volume were 0.2% (wt/vol.) and 40 μL respectively. The mobile phase flow rate was 1mL min^{-1}. Commercial grade polystyrene standards were used for internal calibration and it was verified with PMMA standards as well.

The TGA data was recorded on a Q50® TGA (Thermal Analysis Company) attached to a compressed air tank and to a computer using Universal Analysis® software for run control, data analysis and storage. The sample size was in the range 13–14 mg. The temperature range was 20 to 800 °C with a heating rate of 20 °C min^{-1}. The compressed air flow rate was 50 mL min^{-1}.

The DSC data was recorded on a Q100® DSC (Thermal Analysis Company) attached to a compressed air tank and to a computer using Universal Analysis® software for run control, data analysis and storage. The sample size was 3–4 mg. The experiment was done in a stream of compressed air having a

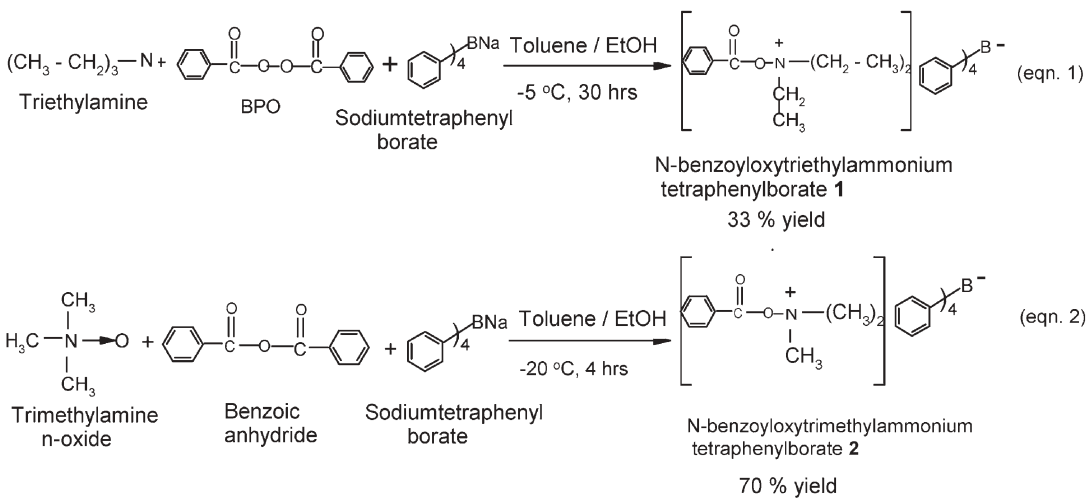

Fig. 3 Reactions for the preparation of *N*-acyloxytriethylammonium tetraphenylborate **1** and *N*-acyloxytrimethylammonium tetraphenylborate **2**.

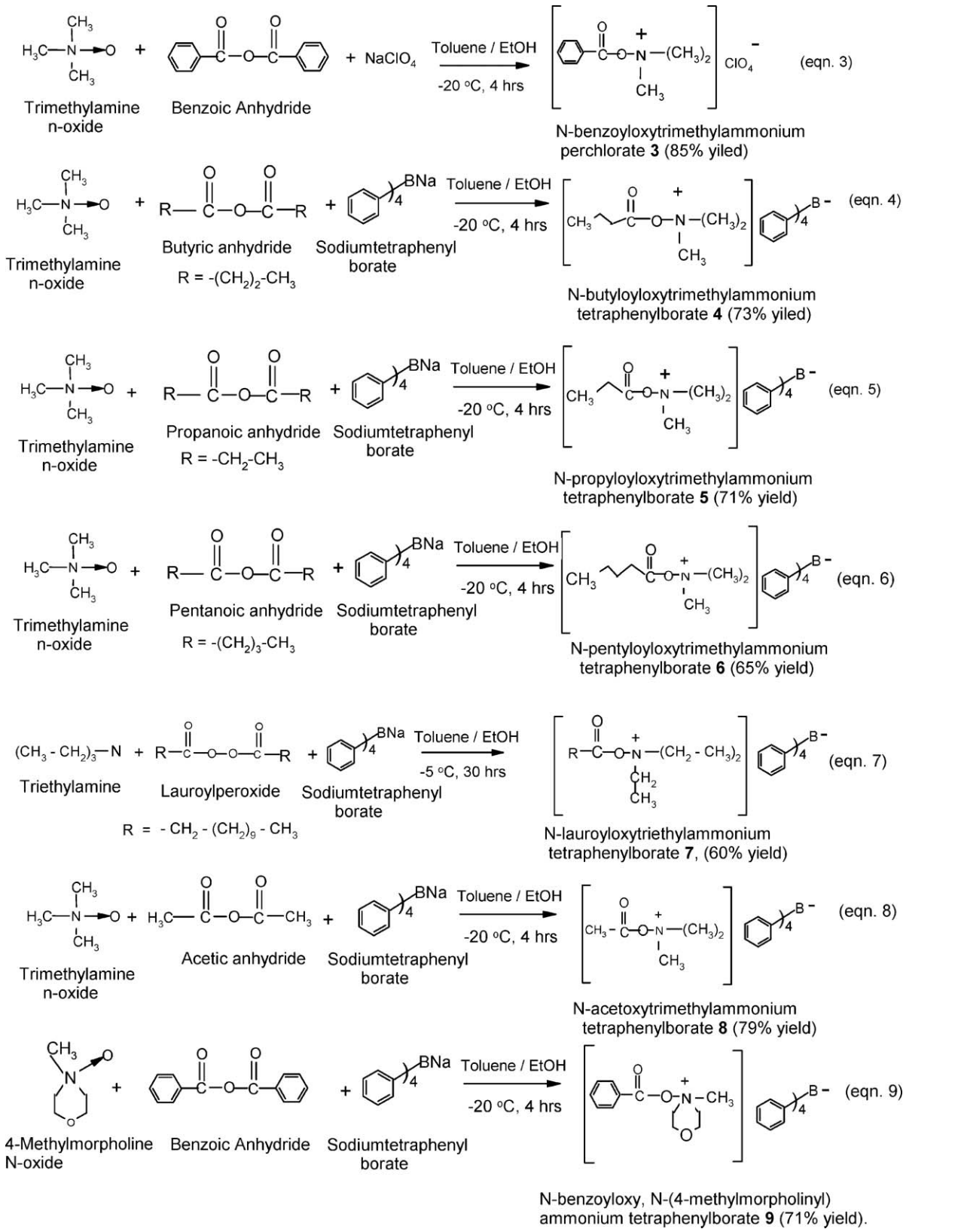

Fig. 4 Preparation of additional derivatives of *N*-acyloxytrialkylammonium salts.

flow rate of 50 mL min^{-1}. The experiment was run from 20 to 200 °C at a rate of 20 °C min^{-1}. The samples were preheated to 150 °C for solvent removal and consistency.

The FTIR experiment was done on a Galaxy Series FTIR model 2020® manufactured by Mattson Instrument. To the FTIR system was connected a computer with WinFirst®

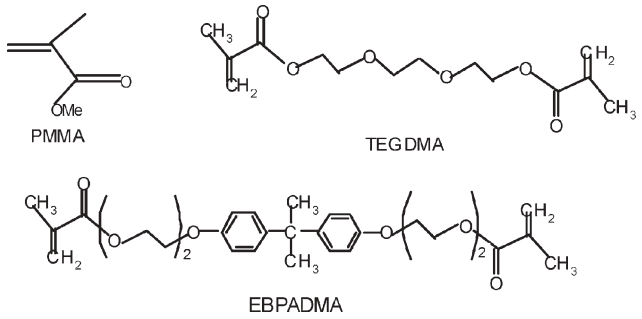

Fig. 5 The structures of the monomers.

software for data collection and analysis. The sample (7 mg) and dried KBr (1mg) were added in a mortar and ground to a smooth powder. The ground powder was loaded into a metallic sample holder and pressed into a transparent wafer. A background spectrum was recorded with an empty sample holder inserted in the path of the FTIR beam. Thereafter, the metal holder bearing the sample wafer was inserted into the path of the FTIR beam to record the sample spectrum.

General procedure for the preparation of *N*-acyloxytriakylammonium salts

All reactants, solvents and a magnetic stirring bar were placed in a one-necked 500 mL reaction flask. The mixture was reacted at −5 °C for 30 h (method 1) or at −20 °C for 4 h (method 2). The product (precipitate) was filtered out and dried under vacuum at room temperature and the yield was calculated. The dried product was recrystallized from an acetone/water (1 : 1) mixture and characterized.

As a typical example, *N*-benzoyloxytriethylammonium tetraphenylborate **1**, was prepared by method 1 as follows. Triethylamine (0.886g, 8.76 mmol), benzoylperoxide (2.12g, 8.76 mmol), sodium tetraphenyl borate (3g, 8.76 mmol), ethanol (50 mL) and toluene (50 mL) were added into a 500 mL one-necked round bottom flask. To the mixture was added a magnetic stirrer. The flask was immersed in ice to which had been added sodium chloride to bring the temperature to −5 °C. The reaction mixture was reacted at −5 °C for 30 h. The white precipitate was filtered out and dried under vacuum at room temperature to give 1.52 g of product (33% yield). The product was recrystallized from acetone/water (1 : 1) mixture. Melting point: 128 °C. IR (KBr wafer, cm^{-1}): 1770, 1050, 3100, 750. Anal. Calcd for $C_{37}H_{40}BNO_2$: C, 82.1; H, 7.45; N, 2.6; B, 2.06. Found: C, 82.41; H, 7.65; N, 2.63; B, 2.06. The details on the experimental procedure for the preparation of the other salts are in the ESI†.

General procedure for the thermal polymerization reactions

All polymerization reactions were done under bulk conditions. A 100 mL Schlenk tube with a Teflon valve was used in all the reactions. The pressure inside the Schlenk tube was kept slightly higher than atmospheric. The initiator, chosen from **1** through **9**, was dissolved in the monomer. The reaction mixture was cooled in liquid nitrogen. At this stage H_2SO_4 was added to the reaction mixture, for those reactions that would be promoted by the acid. The reaction mixture was then degassed three times using a freeze–pump–thaw cycle and N_2 was introduced into the reaction vessel. The reaction vessel was immersed in an oil bath preheated to the desired temperature whereby polymerization occurred. The occurrence of polymerization was indicated by a high increase in the viscosity of the reaction medium. Upon cooling, linear polymers (PMMA) were dissolved in a small amount of methylene chloride and precipitated by adding the solution to a large amount of methanol, filtered and dried under vacuum.

The crosslinked polymers, poly(TEGDMA) and poly(EBPADMA), were obtained by the same polymerization method as described. At the end of the reaction, and upon cooling, because the crosslinked polymer was extremely hard and would not dissolve in any solvent, the Schlenk tube was broken to remove the polymer.

As a typical procedure: to a Schlenk tube were added a magnetic stirrer, initiator adduct **1** (0.6 g, 1.143 mmol) and MMA (11.4 g, 114.3 mmol). The mixture was cooled in liquid nitrogen and sulfuric acid (5.22 mmol) was added to it. The solution was degassed three times using a freeze–pump–thaw cycle. The tube was then filled with nitrogen, capped and immersed in an oil bath preheated to 60 °C with stirring. The viscosity of the solution increased as the polymerization began and the reaction was stopped when the viscosity increased to a point whereby the stirring magnet would no longer turn. After the reaction cooled to room temperature, methylene chloride (60 mL) was added to dissolve the polymer. The polymer solution was added to 500 mL of methanol to precipitate it. The precipitate was filtered and dried under vacuum to give PMMA (5.13 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), 3.5(s, 3H), 2.1–1(br, 2H), 1–1.6(d, 3H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ (ppm), 180, 53, 45, 20, 16. GPC: M_w = 127 000, M_n = 120 000, PDI = 1.06. The M_n obtained (120 000) is higher than the M_n expected from theoretical predictions and this may be due to that fact that the initiator efficiency may be lower than 100%.

Attempted photochemical polymerization

A mixture of the initiator (1 mol%) and monomer were placed on a watch glass and irradiated in the Dentsply 2000 Triad Curing® apparatus for ten minutes.

Results and discussion

In making new derivatives of *N*-acyloxytrialkylammonium salts, all the modifications that we made in reaction 2 (route 2), led to the intended products (compounds **3**, **4**, **5**, **6**, **8** and **9**) in very good yield (> 70%). However, when similar modifications were made in reaction 1 (route 1), only one reaction (reaction 7), led to the intended product (compound **7**), all other reactions failed. The results suggest that route 2 is the more effective method for preparing new derivatives of the salts. The UV and IR traces of **1** and **2** are shown as representative spectra in Fig. 6 and 7 respectively.

All characterization parameters for the polymers initiated under thermal conditions (60 °C) namely, T_g, T_d, PDI and MWD were all augmented under H_2SO_4 promotion. The results are shown in Table 1 and 2. The initiators show effectiveness in crosslinking of the dimethacrylates as

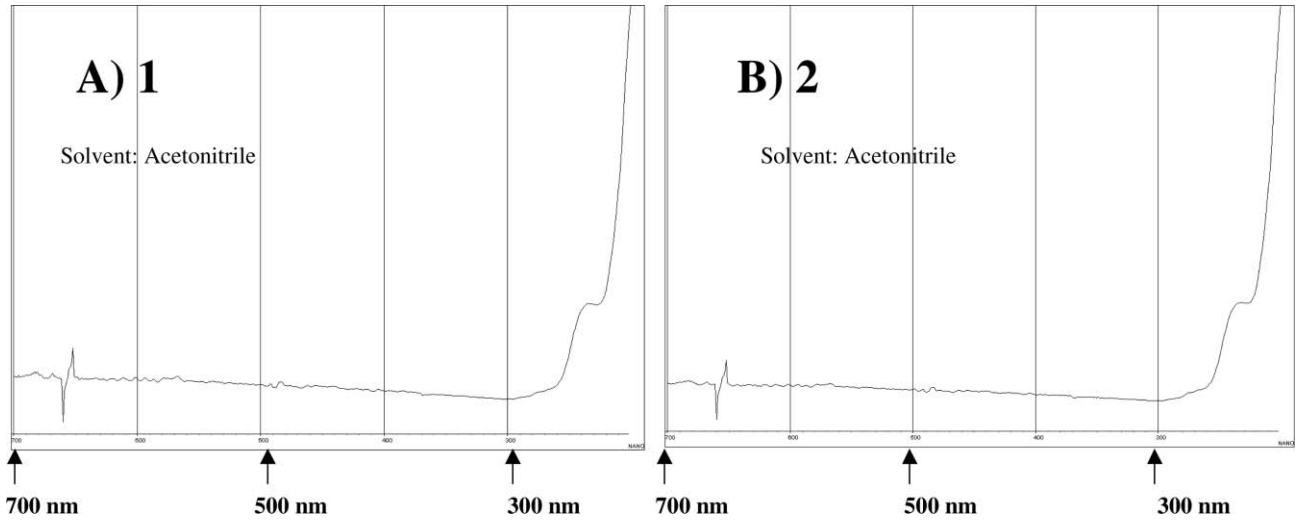

Fig. 6 The UV spectra of (A) initiator 1; (B) initiator 2.

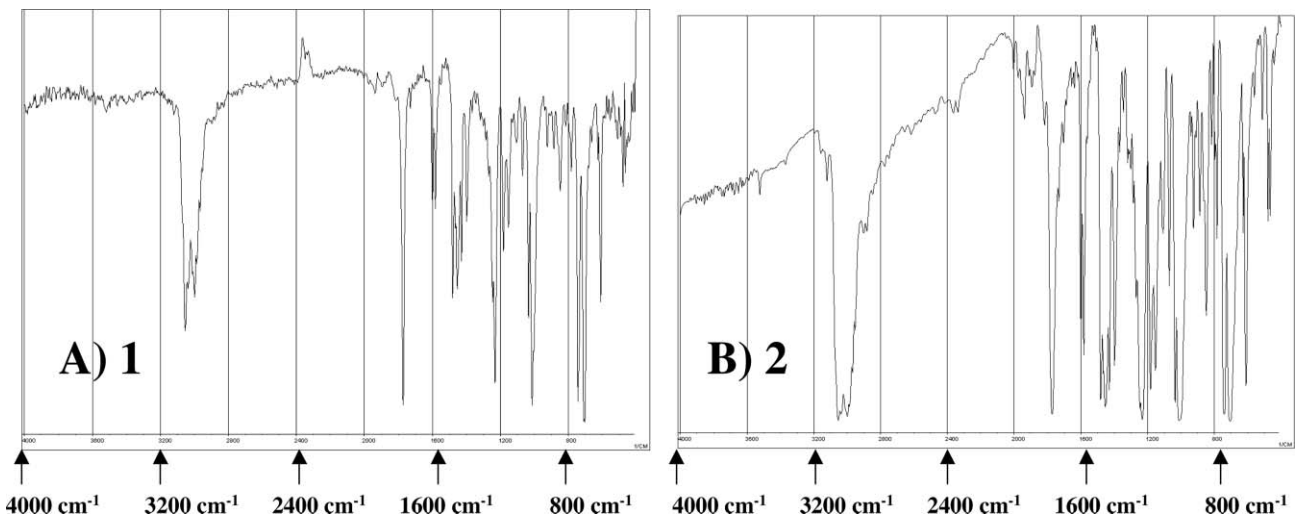

Fig. 7 The FTIR spectra of (A) initiator 1; (B) initiator 2.

evidenced by the physical appearance, the $T_{d,}$ and the lack of solubility in any solvent of all the poly(TEGDMA) and poly(EBPADMA). The polymerization reactions that were promoted by H_2SO_4 had shorter reaction times than the unpromoted reactions. The polymerization times are shown in Table 3.

The high M_n and the narrow PDI obtained from our study attest to the absence of excess radical or its effect in reducing

Table 1 TGA data on polymers

	Decomposition temperature (T_d)/°C					
	Without acid			With acid		
	Monomer			Monomer		
Initiator	MMA	TEGDMA	EBPADMA	MMA	TEGDMA	EBPADMA
N-benzoyloxytriethylammonium tetraphenyl borate **1**	330	300	—	380	311	—
N-benzoyloxytrimethylammonium tetraphenyl borate **2**	335	—	—	370	356	380
N-benzoyloxytrimethylammonium perchlorate **3**	—	—	—	375	374	411
N-butyloyloxytrimethylammonium tetraphenylborate **4**	337	300	380	372	300	410
N-propyloyloxytrimethylammonium tetraphenylborate **5**	365	300	383	381	300	400
N-pentyloyloxytrimethylammonium tetraphenylborate **6**	375	300	380	385	320	386
N-lauroyloyloxytriethylammoniumt etraphenyl borate **7**	340	310	375	370	340	380
N-acetoxytrimethylammonium tetraphenylborate **8**	350	—	—	365	357	—
N-benzoyloxy,*N*-(4- methylmorpholinyl)ammonium tetraphenylborate **9**	—	—	—	—	350	—

Table 2 GPC and DSC data on PMMA

	GPC and DSC results for PMMA							
	Without acid				With acid			
Initiator	M_w	M_n	PDI	T_g/°C	M_w	M_n	PDI	T_g/°C
N-benzoyloxytriethylammonium tetraphenyl borate **1**	118 000	108 000	1.09	121	127 000	120 000	1.06	128
N-benzoyloxytrimethylammonium tetraphenyl borate **2**	119 000	107 000	1.11	122	127 000	120 000	1.06	129
N-benzoyloxytrimethylammonium perchlorate **3**	—	—	—	—	127 000	121 000	1.05	135
N-butyloyloxytrimethylammonium tetraphenylborate **4**	117 000	107 000	1.09	121	129 000	121 000	1.07	134
N-propyloyloxytrimethylammonium tetraphenylborate **5**	112 000	102 000	1.10	120	129 000	128 000	1.01	128
N-pentyloyloxytrimethylammonium tetraphenylborate **6**	112 000	102 000	1.10	121	128 000	121 000	1.06	127
N-lauroyloyloxytriethylammoniumt etraphenyl borate **7**	96 000	92 000	1.04	124	102 000	96 000	1.06	130
N-acetoxytrimethylammonium tetraphenylborate **8**	117 000	110 800	1.06	121	129 000	122 000	1.06	127
N-benzoyloxy,*N*-(4- methylmorpholinyl)ammonium tetraphenylborate **9**	—	—	—	—	—	—	—	—

the molecular weight by chain transfer reactions. The MWD, the PDI, the high M_n and the physical characteristics of the polymers obtained from our study suggest that the method is free from the problems associated with the presence of excess peroxide or excess amine. All the polymers formed from our study were white colored and free of the dark coloration produced by adsorption of amine radicals under conditions where there is excess amine.

The only monomer that polymerized under the Dentsply Triad® lamp was TEGDMA, initiated by a few of the salts. The initiators **5**, **6**, **8** and **9** polymerized TEGDMA giving 6%, 5%, 5% and 7% yields respectively. Although no heat was intentionally applied to the oven, at the end of the ten minute irradiation, the watch glass bearing the sample, felt hot suggesting the occurance of an exotherm. This suggests the operation of thermal initiation and the absence of photo-initiation.

The manufacturers of the Triad Lamp® (Dentsply), through recent private communication, notified us that the lamp can reach temperatures up to 72.5 °C in ten minutes of curing. Therefore, it would be reasonable to conclude that the observed polymerization of TEGDMA was probably thermally initiated by the hot lamp, not through photo cleavage of the initiators. This fact is supported by the UV-VIS spectra of the representative compounds **1** and **2**, which are shown in Fig. 6. The UV-VIS traces of representative compounds **1** and **2** (Fig. 6) show that these initiators do not have significant absorption in the UV-VIS region.

Two groups of investigators namely, Achilas and co-workers[1] and Elvira *et. al*,[21] have reported PDI values of 2.71–3.17 and 2.3–3.1 respectively, for PMMA initiated at 37–40 °C by the redox BPO/amine initiator system. Although our study was done at 60 °C, the PDI for PMMA from our study (1.01–1.11) is much lower than that reported from the other studies. The broad MWD reported for the redox BPO/amine initiator system, may be due to the presence of a large concentration of radicals or the presence of multiple radicals such as the benzoyloxy and methylamine radicals. The nitroxide radical, which results from the presence of excess amine in the BPO/amine system, would serve as excess radical which would also contribute to a broadening of the MWD.

A significant dependence of the polymerization rate on the substituents on the initiators shows up in Table 3. In discussing the substituent effect, it seems better to consider only those reactions that are not catalyzed by acid, because under acid catalysis almost every initiator produced polymerization with the exception of initiators **1**, **8** and **9** in which one or two reactions did not occur. Thus the acid catalysis produced a

Table 3 Polymerization times

	Polymerization reation times					
	Without acid			With acid		
	Monomer			Monomer		
Initiator	MMA	TEGDMA	EBPADMA	MMA	TEGDMA	EBPADMA
N-benzoyloxytriethylammonium tetraphenyl borate **1**	72 h, 20%	72 h, 51%	72 h, no polymer	7 h, 45%	45 s, 61%	26 h, no polymer
N-benzoyloxytrimethylammonium tetraphenyl borate **2**	50 h, 15%	50 h, no polymer	50 h, no polymer	8 h, 60%	1 min, 70%	10 h, 65%
N-benzoyloxytrimethylammonium perchlorate **3**	50 h, no polymer	50 h, no polymer	50 h, no polymer	8 h, 50%	2 h, 95%	10 h, 90%
N-butyloyloxytrimethylammonium tetraphenylborate **4**	48 h, 6%	35 min, 90%	30 min, 50%	8 h, 60%	30 s, 95%	20 min, 90%
N-propyloyloxytrimethylammonium tetraphenylborate **5**	8 h, 5%	20 min, 80%	1 h, 50%	3 h, 40%	15 s, 98%	20 min, 80%
N-pentyloyloxytrimethylammonium tetraphenylborate **6**	7 h, 5%	18 min, 75%	1 h, 55%	3 h, 45%	20 s, 90%	2 h, 23%
N-lauroyloyloxytriethylammoniumt etraphenyl borate **7**	30 min, 50%	40 s, 90%	2 h, 60%	5 min, 60%	15 s, 98%	100 min, 84%
N-acetoxytrimethylammonium tetraphenylborate **8**	50 h, 30%	24 h, no polymer	24 h, no polymer	10 h, 30%	20 s, 90%	50 h, no polymer
N-benzoyloxy,*N*-(4- methylmorpholinyl)ammonium tetraphenylborate **9**	50 h, no polymer	24 h, no polymer	24 h, no polymer	50 h, no polymer	30 s, 90%	24 h, no polymer

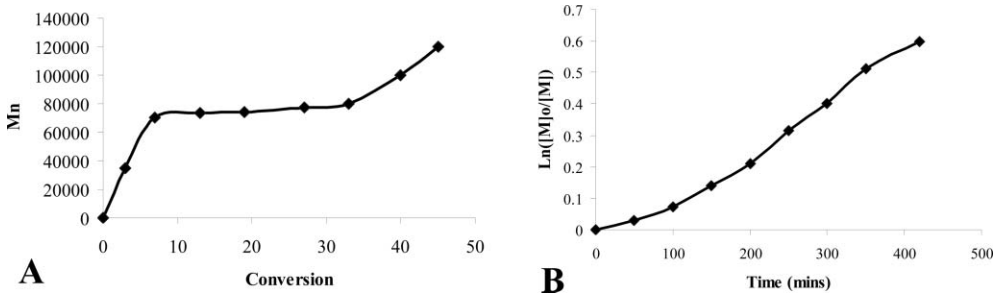

Fig. 8 (A) Evolution of M_n as a function of conversion. (B) The first order kinetic plot for *N*-benzoyloxytriethylammonium tetraphenylborate **1** initiated polymerization of MMA with acid catalysis.

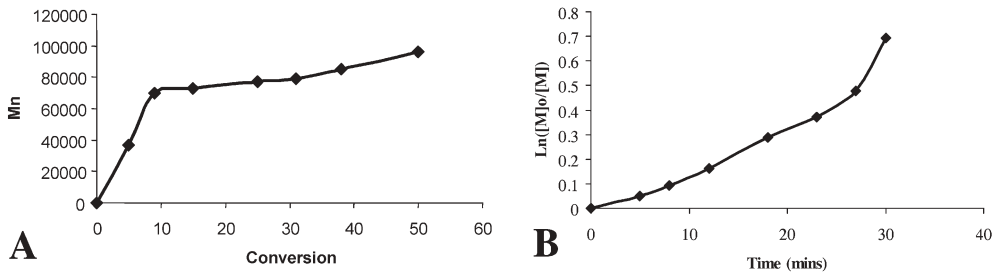

Fig. 9 (A) Evolution of M_n as a function of conversion. (B) The first order kinetic plot for *N*-lauroyloxytriethylammonium tetraphenylborate **7** initiated polymerization of MMA without catalysis.

somewhat "levelling effect" for all the initiators, providing almost no difference in performance with which to contrast the initiators.

The effect of substituents can be evaluated from both structural (steric demands) and electronic perspectives. In Table 3, the best performing initiators are **4**, **5**, **6** and **7**. The polymerization reactions are relatively faster for these initiators and the yields are higher than those of the uncatalyzed reactions. For these initiators, the substituents on both the acyl group and the amine are aliphatic alkyl groups at least one of which has a chain length greater than C_1.

Initiator **8** has only methyl substituents and it performs not so well compared to initiators **4**, **5**, **6** and **7**. The methyl substituents on **8** are the least sterrically demanding while the C_{11} substituent on **7** is the most sterrically demanding. However **7** (like **4**, **5** and **6**) performs much better than **8**. This suggests that sterric factors are not influential in the reactivities of **4**, **5**, **6** and **7**. From electronic perspective, the only polarization effect that these substituents can produce is an inductive electron donating effect. Thus, the superior performance of **4**, **5**, **6** and **7** appears to hinge upon the inductive electron donating effects of the alkyl substituents. The weak performance of **8**, compared to the good performance of **4**, **5**, **6** and **7**, may be due to the difference in inductive electron donating effects between the methyl substituents on **8** and the longer chain alkyl substituents on **4**, **5**, **6** and **7**. In **1**, **2**, **3** and **9** a similar electronic effect appears operative, but the performances of these initiators are lower than those of **4**, **5**, **6** and **7**. Probably, the sterric effects of the phenyl substituent on the acyl groups on **1**, **2**, **3** and **9** are responsible for the lower performances of these salts. This may be particularly true in the case of **9** where, in addition to the phenyl substituent on the acyl group, the nitrogen is a member of the heterocyclic ring.

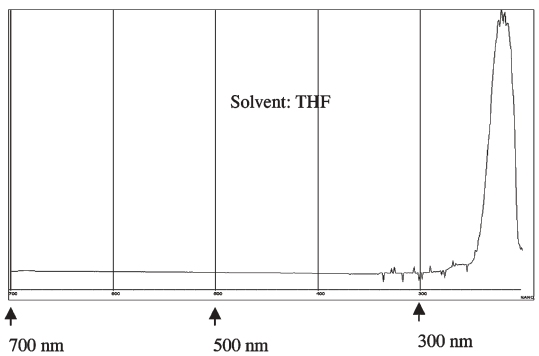

Fig. 10 UV-VIS spectrum of PMMA initiated by **1**.

To summarize the substituent effects, it seems that the electronic features of the substituents on the initiators **4**, **5**, **6** and **7** on one hand and the steric features of the substituents on **1**, **2**, **3** and **9** on the other are responsible for the differences in their performance in polymerization. As our investigations continue, we hope to be able to shed more light on the mechanistic aspects of the impacts of the electronic and structural features of the initiator substituents on both the initiation and polymerizarion rates.

Two representative initiators were chosen for evaluating the kinetics of the polymerization. The initiators **1** and **7** were used to initiate polymerization of MMA at 60 °C with and without acid catalysis respectively. In both reactions, plots of monomer conversion as a function of M_n evolution and the first order kinetics plots were constructed. The plots are shown as Fig. 8

and 9. In the conversion *vs.* M_n plot for both initiators there is a slight linearity at the beginning, resembling living polymerization, and the curve almost levels off at higher conversions and thereby resembles chain polymerization. The first order kinetic plots for both initiators show some slight curvature, suggesting a slight deviation from living polymerization. Additional studies will be needed to conclusively determine whether the polymerization follows a living or a chain mechanism.

To verify the constituents of the polymer chain ends, we measured the electronic spectrum of PMMA initiated by **1**. The UV spectrum, which is shown as Fig. 10, indicates a strong absorption at 240 nm due to the benzoyloxy moiety. The shift of the absorption to a lower wavelength may have been caused by solvent polarity. This confirms the involvement of the benzoyloxy radical in the initiation process.

Conclusions

This study has shown a more efficient method for preparing and isolating new derivatives of *N*-acyloxytrialkylammonium salts as initiators for the free radical polymerization of methacrylates and dimethacrylates. The initiators are very effective in making medium to high molecular weight polymers of narrow MWD and highly crosslinked polymers.

A clear advantage of the initiators is that they are stable enough to be isolated and stored for special applications and are free of the problems associated with the redox BPO/amine system. It is hoped that our continued study on these initiators will lead to the discovery of promoters other than H_2SO_4 and to an enhancement for large-scale practical applications of the initiators.

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