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Photoinitiated polymerization of methyl methacrylate by phenacyl type salts

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Abstract

Phenacyl onium salts, namely *N*-phenacyl-*N*,*N*-dimethylanilinium-*N*,*N*-diethyldithiocarbamate (**Ia**), phenacyl-triphenylphosphonium-*N*,*N*-diethyldithiocarbamate (**II**), 1-phenacyl pyridinium-*N*,*N*-diethyldithiocarbamate (**III**), are shown to be efficient photoinitiators for polymerization of methyl methacrylate (MMA). Plausible mechanism of the photoinitiation involves both free radical and zwitterionic processes. Phenacyl radicals formed from the homolytic cleavage of carbon heteroatom bond initiates the free radical polymerization while Lewis bases formed from homolytic cleavage followed by electron transfer or heterolytic cleavage responsible for the zwitterionic initiation. The capability of the salts to act as initiators for the polymerization of multifunctional monomer, trimethylolpropane trimethacrylate (TMPTMA), was also demonstrated.

Keywords: Phenacyl onium salts; Photoinitiated polymerization; Free radical polymerization; Zwitterionic polymerization

1. Introduction

Photoinitiated polymerization forms the basis of numerous applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics [1–3]. Almost all of the commercially significant photoinitiators are organic compounds that produce free radicals and/or cationic species upon irradiation [4]. The most widely used free radical photoinitiators include benzoin and its derivatives, benzyl ketals, acetophenone derivatives, aromatic ketone/amine combinations [4], while onium salts belonging iodonium [5], sulphonium [6] and alkoxy pyridinium [7] families represent a class of cationic photoinitiators. On the other hand, until recently little attention has been paid to the anionic counterpart. Kutal and coworkers [8] have discovered that solutions of ethyl-α-cyanoacrylate (ECA) containing *trans*-$Cr(NH_3)_2(NCS)_4^-$ undergo rapid anionic polymerization upon irradiation with visible light. Initiating species were reported [9] to be NCS^- ions released from a ligand field excited state of the metal complex according to Eq. (1). This anion then adds to the highly electrophilic monomer, ECA, to yield stabilized carbanion from which further chain-growth occurs (Scheme 1, Eq. (2)).

Complexes based on $Pt(acac)_2$, tungsten or chromium carbonyl pyridine [10], acyl-substituted ferrocenes [11] were also reported to function as photoinitiators for the anionic polymerization of ECA. Fukuchi et al. [12] reported the anionic coordination polymerization of epoxides by a catalyst system consisting of titanium tetra-isopropoxide and photochemically generated phenol. We have demonstrated that, besides these organometallic complexes, specially designed organic compounds such as alkoxy pyridinium [13] and phosphonium [14] salts can also act as photoinitiators for anionic polymerization of ECA. It was shown that Lewis bases such as pyridine or triphenylphosphine formed from the photolysis of alkoxy pyridinium salts or tetra-phenylphosphonium salts, respectively, initiates the polymerization via zwitterionic mechanism. The overall polymerization mechanism is represented below for the example of *N*-ethoxy-2-methyl-pyridinium salt photosensitized by anthracene (Scheme 2).

More recently, we have reported [15,16] that *N*-phenacyl-*N*,*N*-dimethylanilinium hexafluoroantimonate initiates the cationic polymerization of appropriate monomers efficiently upon irradiation. Interestingly, the initiation mechanism is quite different from that when using the sulphonium analogues [17]. It was proposed that the phenacyl anilin-

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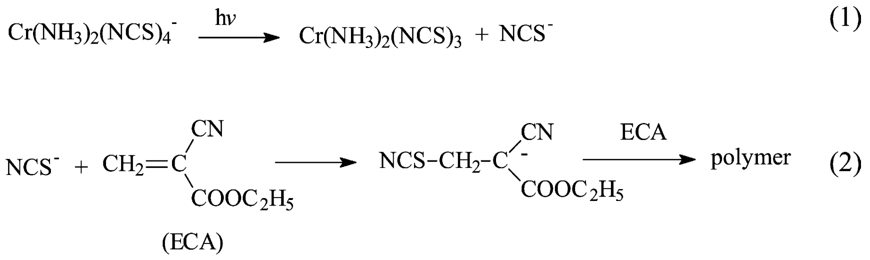
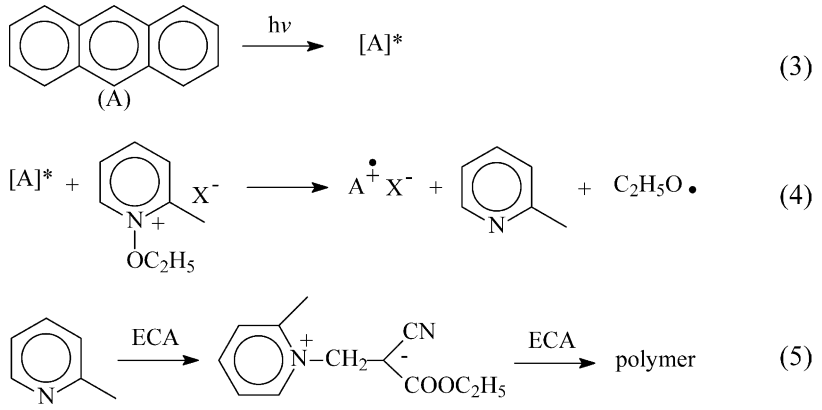


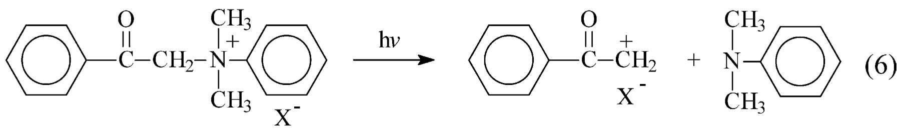
$$Cr(NH_3)_2(NCS)_4^- \xrightarrow{h\nu} Cr(NH_3)_2(NCS)_3 + NCS^- \qquad (1)$$

$$NCS^- + CH_2{=}C(CN)(COOC_2H_5)\ (ECA) \longrightarrow NCS{-}CH_2{-}C^-(CN)(COOC_2H_5) \xrightarrow{ECA} \text{polymer} \qquad (2)$$

Scheme 1.



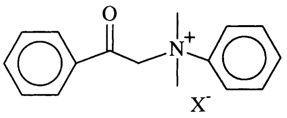
Scheme 2.



Scheme 3.

ium salts undergo irreversible photolysis leading to a fragmentation of the photoinitiator according to Eq. (6). Polymerization and spectroscopic investigations revealed that the benzylic cations are responsible for the initiation (Scheme 3).

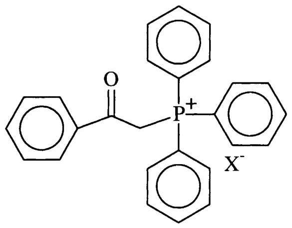
It appears feasible that *N*,*N*-dimethylaniline formed concomitantly, according to Eq. (6), is capable of initiating the zwitterionic polymerization and that, therefore, phenacyl anilinium salts might also be used as photoinitiators for anionic polymerization. Phosphonium and pyridinium salts comprising phenacyl groups may also be efficient in generating reactive Lewis bases such as phosphine and pyridine, respectively. We here report our investigations concerning the possibility of photoinitiation of polymerization of methyl methacrylate (MMA) by using anilinium, phosphonium and pyridinium salts possessing phenacyl chromophoric groups. The structures of the salts used in this study are shown below:



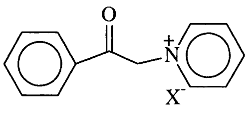
I a, b

a: $X^- = {}^-SC(S)N(Et)_2$

b: $X^- = SbF_6^-$



II, $X^- = {}^-SC(S)N(Et)_2$



III, $X^- = {}^-SC(S)N(Et)_2$

2. Experimental

2.1. Materials

N,*N*-Dimethylaniline (98%, Fluka) was distilled prior to use. Bromoacetophenone (98%, Aldrich), triphenylphosphine (97%, Fluka), pyridine (99.5%, Lab-Scan), sodium *N*,*N*-diethyldithiocarbamate (99 + %, Aldrich), methanesulphonic acid (>98%, Merck), hydroquinone (=99%, Merck) and acetone (=99%, Merck) were used as-received. Methylene chloride was first extracted with sulphuric acid, washed with water, then extracted with 5% NaOH solution, and again washed with water. It was dried over calcium chloride and fractionally distilled. MMA (=99%, Fluka) was distilled over CaH_2 in vacuo. Trimethylolpropane trimethacrylate (TMPTMA) (Aldrich) was used without further purification.

2.2. Synthesis of N-phenacyl-N,N-dimethylanilinium-N,N-diethyldithiocarbamate (*Ia*)

Into a 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 0.50 g (2.5×10^{-3} mol) of bromoacetophenone, 0.30 g (2.5×10^{-3} mol) *N*,*N*-dimethylaniline and 0.43 g (2.5×10^{-3} mol) sodium *N*,*N*-diethyldithiocarbamate and 5 ml of acetone. The reaction mixture was brought to reflux and held at this temperature for 120 min. The solution was filtered to remove NaBr, which was formed during the reaction. Then the solvent was removed on a rotary evaporator, leaving *N*-phenacyl-*N*,*N*-dimethylanilinium-*N*,*N*-diethyldithiocarbamate (**Ia**) as a tan solid. The product was recrystallized twice from ethanol solution and dried at vacuum, m.p. 104 °C, yield 40%. ^{1}H-NMR (δ in ppm): 7.5–8 (C_6H_5); 6.12 (N^+–CH_2–); 3.77 (N^+–$(CH_3)_2$). Elemental analysis: $C_{21}H_{28}ON_2S_2$ (388 g mol^{-1})—Calcd.: C, 65%; H, 7.2%. Found: C, 64.85%; H, 6.6%. UV: $\lambda_{max\,1} = 249$ nm, $\varepsilon_{249\,nm} = 41{,}322$ l mol^{-1} cm^{-1}, $\lambda_{max\,2} = 279$ nm, $\varepsilon_{279\,nm} = 23{,}921$ l mol^{-1} cm^{-1}.

2.3. Synthesis of phenacyl-triphenylphosphonium-N,N-diethyldithiocarbamate (*II*)

Into a 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 0.50 g (2.5×10^{-3} mol) of bromoacetophenone, 0.66 g (2.5×10^{-3} mol) triphenylphosphine and 0.43 g (2.5×10^{-3} mol) sodium *N*,*N*-diethyldithiocarbamate and 50 ml of acetone. The reaction mixture was brought to reflux and held at this temperature for 120 min. The solution was filtered to remove NaBr, which was formed during the reaction. Then the solvent was removed on a rotary evaporator, leaving phenacyl-triphenylphosphonium-*N*,*N*-diethyldithiocarbamate (**II**) as a tan solid. The product was recrystallized twice from ethanol solution and dried at vacuum, m.p. 105 °C, yield 30%. ^{1}H-NMR (δ in ppm): 7.5–7.9 (C_6H_5); 4.4 (P^+–CH_2–). Elemental analysis: $C_{31}H_{32}ONPS_2$ (529 g mol^{-1})—Calcd.: C, 70.3%; H, 6%. Found: C, 70.2%; H, 5.51%. UV: $\lambda_{max\,1} = 249$ nm, $\varepsilon_{249\,nm} = 28{,}833$ l mol^{-1} cm^{-1}, $\lambda_{max\,2} = 279$ nm, $\varepsilon_{279\,nm} = 16{,}330$ l mol^{-1} cm^{-1}.

2.4. Synthesis of 1-phenacyl pyridinium-N,N-diethyldithiocarbamate (*III*)

Into a 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 0.50 g (2.5×10^{-3} mol) of bromoacetophenone, 0.20 g (2.5×10^{-3} mol) pyridine and 0.43 g (2.5×10^{-3} mol) sodium *N*,*N*-diethyldithiocarbamate and 50 ml of acetone. The reaction mixture was brought to reflux and held at this temperature for 120 min. The solution was filtered to remove NaBr, which was formed during the reaction. Then the solvent was removed on a rotary evaporator, leaving 1-phenacyl pyridinium-*N*,*N*-diethyldithiocarbamate (**III**) as a tan solid. The product was recrystallized twice from ethanol solution and dried at vacuum, m.p. 104 °C, yield 40%. ^{1}H-NMR (δ in ppm): 7.5–8 (C_6H_5); 5–5.5 (N^+–CH_2–). Elemental analysis: $C_{18}H_{22}ON_2S_2$ (346 g mol^{-1})—Calcd.: C, 62.4%; H, 6.4%. Found: C, 48.4%; H, 3.3%. $\lambda_{max\,1} = 249$ nm, $\varepsilon_{249\,nm} = 35{,}441$ l mol^{-1} cm^{-1}, $\lambda_{max\,2} = 279$ nm, $\varepsilon_{279\,nm} = 19{,}890$ l mol^{-1} cm^{-1}.

2.5. Polymerization

Appropriate solutions of MMA containing one of the phenacyl onium salts, were mixed in Pyrex tubes and degassed with nitrogen prior to irradiation by a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at $\lambda > 300$ nm and a cooling system. At the end of a given time, polymers were precipitated into methanol, filtered, dried and weighed. Conversions were determined gravimetrically.

2.6. Characterization

^{1}H-NMR spectra were recorded on a Bruker 250 MHz instrument. Elemental analyses were performed on a CHNS-932 LECO instrument. UV-Vis spectra were taken on a Philips PU 8700 UV-Vis spectrophotometer. Gel permeation chromatography (GPC) analyses were performed via set-up consisting of a Waters pump and three styragel HR3, HR4, HR4E columns with THF as the eluent, at a flow rate of 1 ml min^{-1} and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards. The melting points of the salts were determined by differential scanning calorimetry (DSC) Perkin Elmer DSC 6 at a scanning rate of 5 and 10 °C min^{-1}.

2.7. Real-time infrared spectroscopy photopolymerization studies

Uniform samples of photocurable formulations consisting of salt (1%, w/w) and a multifunctional monomer, namely

TMPTMA, were prepared by casting on a KBr pellet. The samples were placed in the compartment of a Fourier transform infrared spectrometer (Mattson 1000 FTIR) and were simultaneously exposed to an UV photolysing light and an IR analysing light beam. The photolysing light was generated by a medium pressure mercury lamp (Flexicure UV system) and was directed through a flexible fibre optic to the IR compartment. The light intensity (4.37×10^{16} photon s^{-1}) was determined by potassium ferrioxalate actinometry [18]. The spectrometer was operated in the absorbance mode and the detection wavelength was set at 810 cm^{-1} (C=C–H twist) to monitor the disappearance of double bonds. The degree of conversion, α, can be expressed by the following relation:

$$\alpha = \frac{A_0 - A_t}{A_0}$$

where A_0 is the initial absorbance at 810 cm^{-1} and A_t the absorbance value at irradiation time.

3. Results and discussion

As stated previously (vide ante), electrophilic vinyl monomers such as cyanoacrylates undergo anionic polymerization with Lewis bases such as amines and phosphines via a zwitterionic mechanism. Although phenacyl onium salts that contain complex metal halides such as SbF_6^-, PF_6^-, AsF_6^-, etc., are an efficient and convenient class of compounds to generate Lewis bases photochemically, they suffer from the drawback of the termination of the anionic species by the photofragments formed from these compounds. The phenacylium cations stabilized with non-nucleophilic counter anions can react with the initiating and propagating centres. For this reason, for potential application of these salts as photoinitiators for anionic polymerization it is necessary to equip them with counter anions with higher nucleophilicity.

A simple one-pot reaction was used for the synthesis of phenacyl onium salts with *N*,*N*-diethyldithiocarbamate anion. Accordingly, phenacyl bromide was reacted with *N*,*N*-dimethylaniline (Eq. (7)), triphenylphosphine (Eq. (8)) and pyridine (Eq. (9)) in the presence of sodium *N*,*N*-diethyldithiocarbamate to yield respective salts according to the following reactions (Scheme 4).

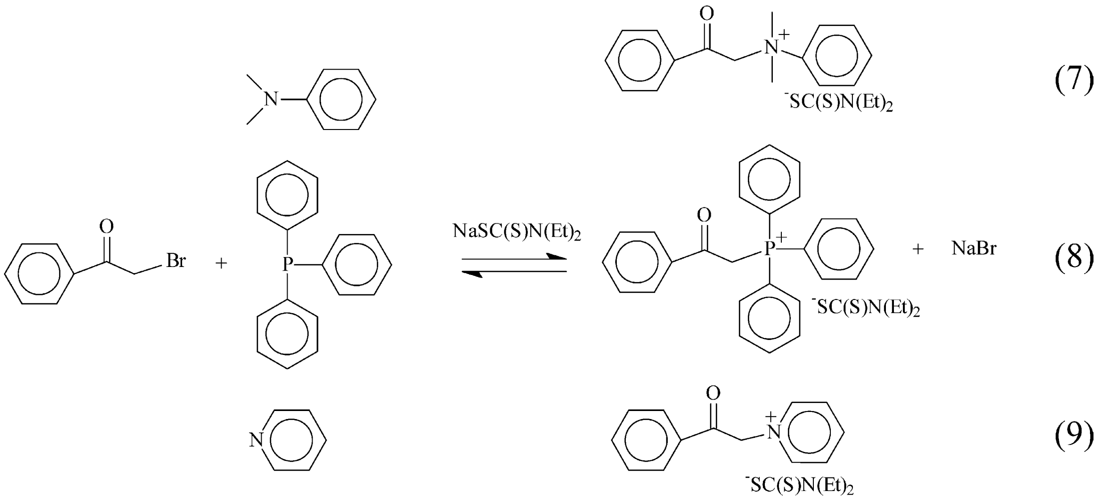
The structure of the salts was confirmed by spectral and elemental analysis (see Section 2). All salts possess similar absorption spectra characteristic to the phenacyl moiety with two maxima at 249 and 279 nm but different molar absorptivity arising from the salt structure. In a previous paper [15], we have already reported that phenacyl anilinium salts undergo an irreversible photolysis leading to decomposition of the salt. This was further confirmed for all salts by the spectral changes on UV irradiation. Representative results for the decomposition of the salts are shown in Fig. 1(a)–(c).

UV spectra were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals of 10 s each. The salts were used as photoinitiators for polymerization of MMA. The results are compiled in Table 1.

Conversion to poly(MMA) increases with the irradiation time as represented in the example of **Ia** (Fig. 2).

As can be seen from Table 1, all salts readily initiate the polymerization. We consider that the same mechanism implies for the initiation by all of the salts, since they are structurally similar, i.e., positively charged heteroatom is located adjacent to phenacyl moiety. Based on the previous studies and present results, the following mechanism for the initiation of the polymerization of MMA is suggested as illustrated for the example of the anilinium salt (Scheme 5).

Electronically excited salt may undergo heterolytic cleavage resulting in the formation of phenacylium cations. Similar photodecomposition was proposed by Tsunooka and coworkers [19], who used phenacyl ammonium salts in photoinitiated crosslinking of epoxy compounds. Reaction (11), path b offers an alternative pathway in which homolytic



Scheme 4.

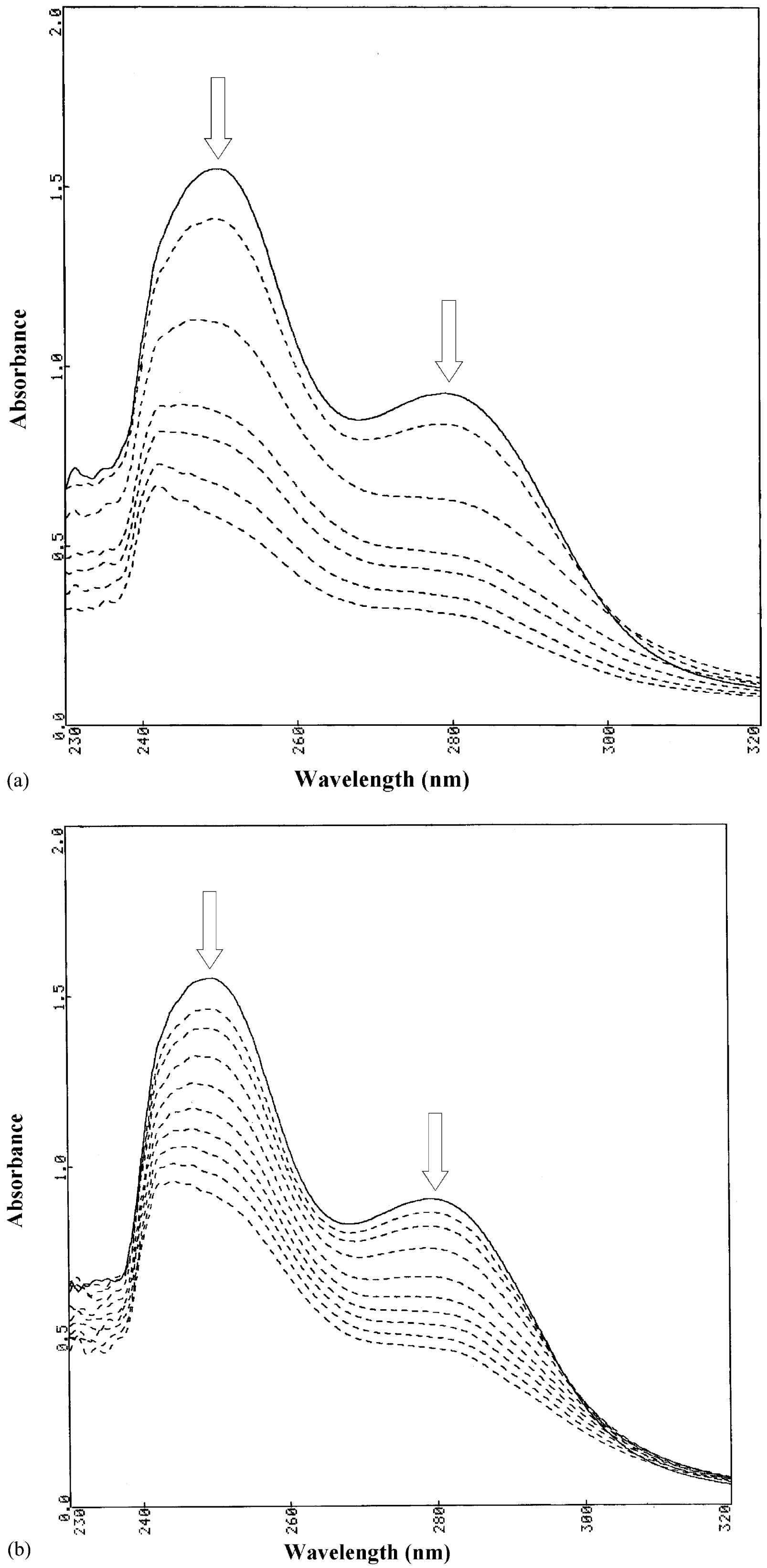


Fig. 1. UV spectral changes of salts on irradiation at λ > 300 nm under nitrogen in CH_2Cl_2: (a) **Ia**; (b) **II**; (c) **III**.

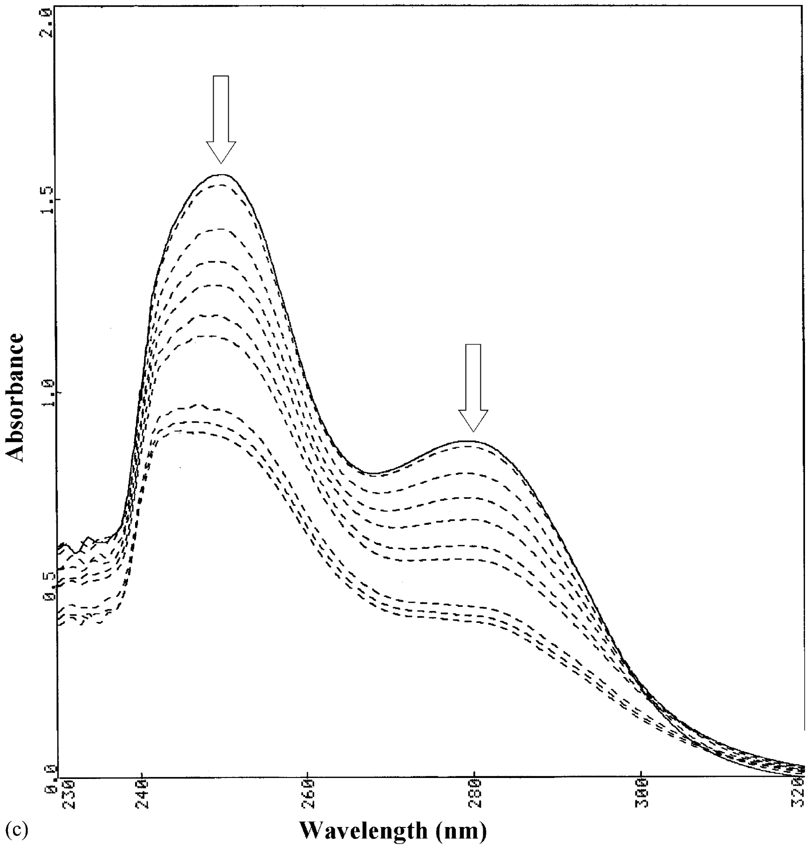


Fig. 1. (*Continued*).

cleavage followed by electron transfer essentially yields the same species. Notably, phenacylium cation is converted to covalently bonded inert compound as a result of the combination of the cation with thiocarbamate anion and free Lewis base, dimethylaniline is liberated. In order to gain some insight into polymerization mechanism we have performed some polymerization experiments in the presence of both radical scavenger and protonation agent. If the polymerization mechanism involves only free radical species, the polymerization would be completely inhibited by a radical scavenger. Accordingly, if the polymerization is initiated via a zwitterionic mechanism, sample containing protonation agent would yield no polymer. Interestingly, the polymerization yield was affected by the addition of hydroquinone and methanesulphonic acid as radical scavenger and protonation agent, respectively, but not totally inhibited in either case. It is therefore most probable that both radical and zwitterionic mechanisms are responsible for the initiation. Under

Table 1
Photopolymerization[a] of MMA in the presence of phenacylium salts at room temperature

Run	Salt	Hydroquinone[b]	Acid[c]	Conversion (%)	M_n[d] ($\times 10^{-4}$)	M_w/M_n
1	**Ia**	−	−	48.7	4.3	1.7
2	**Ia**	+	−	26.3	3.7	1.6
3	**Ia**	−	+	23.0	16.5	1.7
4	**II**	−	−	42.0	3.9	1.8
5	**II**	+	−	28.0	3.5	1.6
6	**II**	−	+	15.0	22.1	2.2
7	**III**	−	−	37.0	5.2	1.6
8	**III**	+	−	25.8	5.0	1.5
9	**III**	−	+	12.5	20.2	1.8

[a] [MMA] = 9.35 mol l^{-1}, [salt] = 5×10^{-3} mol l^{-1}, irradiation time = 90 min, $\lambda > 300$ nm.
[b] [Hydroquinone] = 2×10^{-2} mol l^{-1}.
[c] [Methanesulphonic acid] = 2×10^{-3} mol l^{-1}.
[d] Determined by GPC.

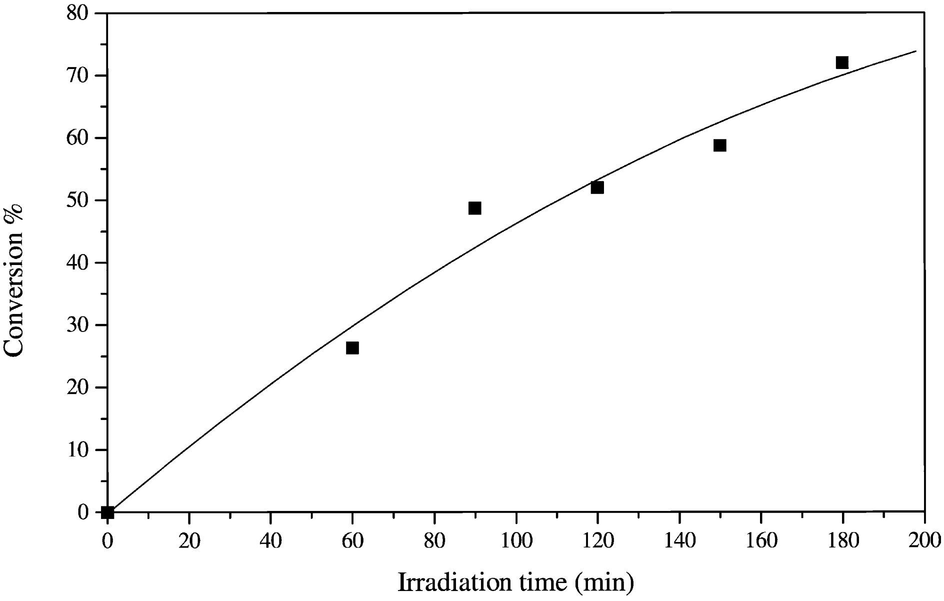
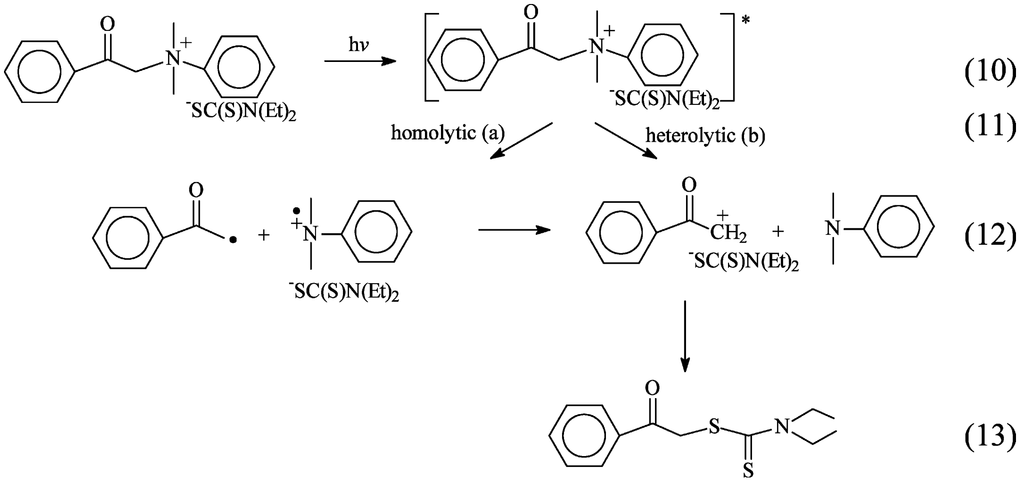
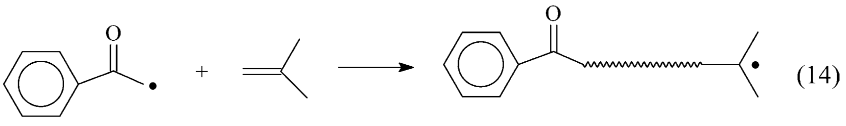


Fig. 2. Photopolymerization of MMA (9.35 mol l^{-1}) by using **Ia** (5×10^{-3} mol l^{-1}) at $\lambda > 300$ nm.

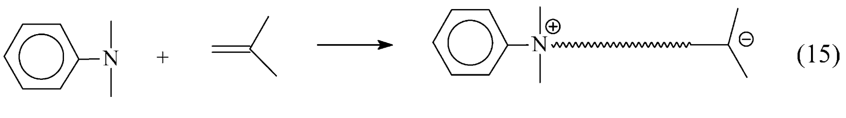


Scheme 5.

Free Radical Polymerization



Zwitterionic Polymerization



Scheme 6.

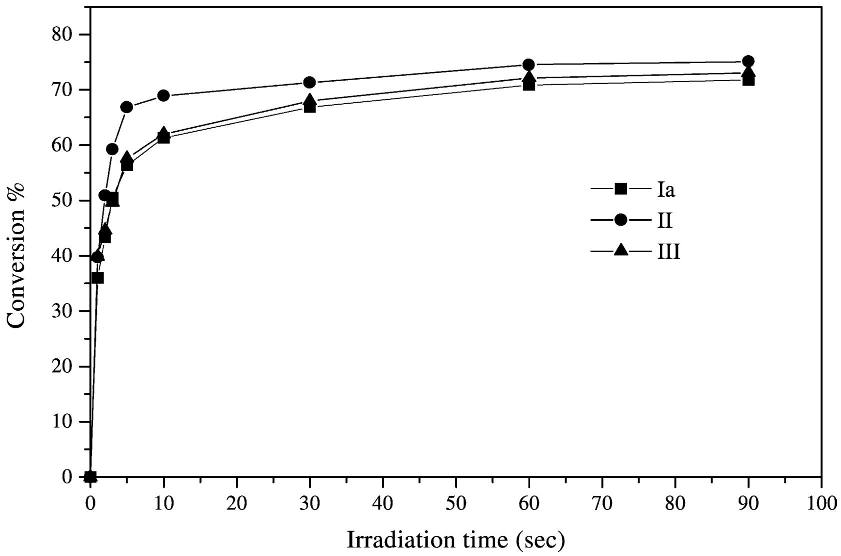


Fig. 3. Real-time FTIR kinetic profiles demonstrating the photopolymerization of TMPTMA containing different phenacyl onium salts (1%) with polychromatic light (unfiltered light from a medium pressure lamp). Phenacyl onium salt: **Ia** (■), **II** (●) and **III** (▲).

this scenario, phenacyl radicals induce free radical polymerization while dimethylaniline initiates zwitterionic polymerization according to the following reactions (Scheme 6).

It is interesting to note that with free radical polymerization, i.e., in the presence of methanesulphonic acid, polymers with lower conversions but higher molecular weights were obtained (see Table 1). Even more convincing evidence for the proposed mechanism was obtained by the polymerization studies using salts with different counter anions as initiators (Table 2).

Notably, the polymerization yield was much lower with the salt possessing non-nucleophilic counter anion, hexafluoroantimonate. In this case the polymerization is initiated exclusively by a radical mechanism since stable phenacylium cations are stabilized with the counter anion and thus terminates the propagating zwitterionic species. Expectedly, the addition of hydroquinone inhibits the polymerization completely.

The efficiency of the salts in the photocuring of formulations containing a multifunctional monomer, TMPTMA, was also studied. The disappearance of double bonds during the photocuring of the formulation was followed by real-time Fourier transform infrared (RT-FTIR) spectroscopy [20,21]. By monitoring changes in the characteristic IR absorption bands of the monomer, it allows the direct monitoring of fast polymerization process continuously. In Fig. 3 kinetic profiles referring to the polymerization of TMPTMA under polychromatic light are shown.

Table 2
Photopolymerization[a] of MMA in the presence of *N*-phenacyl-*N*,*N*-dimethylanilinium salt at room temperature

Run	Salt[b]	Hydroquinone (mol l^{-1})	Conversion (%)	M_w/M_n
1	**Ia**	–	48.7	1.7
2	**Ia**	2×10^{-2}	26.3	1.6
3	**Ib**	–	6	–
4	**Ib**	2×10^{-2}	0	–

[a] [MMA] = 9.35 mol l^{-1}, irradiation time = 90 min, $\lambda > 300$ nm.
[b] [Salt] = 5×10^{-3} mol l^{-1}.

The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1}. The shape of the curves indicates the existence of two stages: a rapid first stage followed by a slow stage. It can be seen that efficient polymerization takes with all salts.

In conclusion, it was shown that photoinitiated polymerization of vinyl monomers can be induced by phenacyl type onium salts with thiocarbamate anions. Polymerizations in the presence of respective scavengers suggest that both free radical and zwitterionic mechanisms play a role in the initiation.

Acknowledgements

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