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ORIGINAL PAPER

Novel addition-fragmentation agent in cationic photopolymerization

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Abstract The aim of present study is to examine the photo-initiation efficiency of *N*,*N*-dimethylacrylamide-based allylic ammonium salt as one component addition-fragmentation agent (cationic photoinitiator cum radical source) in free radical accelerated cationic polymerization. Novel addition-fragmentation agent (AFA), 2-(*N*,*N*-dimethylcarboxy-3-propenyl)(phenylcarbonyl-4-phenylene) dimethyl ammonium hexafluoroantimonate (DMPDA) was synthesized as cationic photoinitiator and its initiation efficiency was examined in polymerization of cyclohexene oxide (CHO), isobutyl vinyl ether (IBVE), and *n*-butyl vinyl ether (*n*-BVE) in CH_2Cl_2 solvent at wavelength $\lambda > 290$ nm. The rate of polymerization increases with the increase in initiator concentration and reaction time. The results demonstrate that DMPDA acts as an efficient photoinitiator (AFA) without use of radical source in free radical accelerated cationic polymerization.

Keywords Photopolymerization · Addition-fragmentation agent · Ammonium salt · Benzophenone · Cationic polymerization · Onium salt

Introduction

In recent years, externally stimulated cationic polymerization has attracted considerable attention due to its control over initiation and curing process [1, 2]. A large number of new latent initiators have been developed because of their ability to initiate polymerization by certain stimulation such as heat or light, which have been industrially used in coating, adhesive, printing ink, microelectronics, and photolithography [3–7]. Among them, photo cationic polymerization became well known to be very useful technology for UV-curable system [8]. Onium salts such as

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iodonium, sulfonium, alkoxy pyridinium, and phosphonium salts are commercially important and well studied as photo cationic initiators [9]. However, the poor absorption of these initiators above 290 nm limits their practical utilization. In recent years, to shift the spectral sensitivity toward higher wavelength region, several indirect systems have been anticipated and extensively studied [10–12]. These systems involve radical initiators, photosensitizers, and electron-donor compounds in combination with onium salts. Among them, radical initiator in combination with allylic onium salt appears to be an easy and flexible way to initiate cationic polymerization [13–15]. The initiation can be stimulated by heat or light with the selection of appropriate radical initiator. However, for the industrial photocuring applications, utilization of one component system with long wavelength absorption characteristics is beneficial over other two component systems due to additional problems associated with the use of co-initiator such as solubility in monomer, compatibility, and cost [16–18]. Considering the requirement of wide variety of one component addition-fragmentation agents with higher initiation efficiency in photopolymerization, we have aimed to prepare cationic initiators based on novel ammonium salts. To the best of our knowledge, the chemistry of amide based allylic ammonium salt, as an addition-fragmentation agent in cationic polymerization has not been studied and it is worthwhile to study the same. Thus, the present study describes the synthesis and use of *N*,*N*-dimethylacrylamide based allylic ammonium salt containing benzophenone moiety with hexafluoroantimonate counter anion (DMPDA) as an addition-fragmentation agent in photocationic polymerization.

Experimental

Materials

N,*N*-dimethylacrylamide, 4-(dimethylamino) benzophenone (DMABP), cyclohexene oxide (CHO), isobutyl vinyl ether (IBVE), *n*-butyl vinyl ether (*n*-BVE), *N*-vinyl carbazole (NVC), and sodium hexafluoroantimonate ($NaSbF_6$) were purchased from Aldrich chemicals. All other chemicals were purchased from S.D. Fine Chemicals Ltd, Mumbai, India and used after purification [19]. 2-(Bromomethyl)-*N*,*N*-dimethyl acryl amide (BMDMA) was prepared as reported [20]. Monomers (CHO, IBVE, and *n*-BVE) and solvent (CH_2Cl_2) were distilled over CaH_2 and used just before polymerization. NVC was recrystallized twice from ethanol and used immediately.

Synthesis of 2-(*N*,*N*-dimethylcarboxy-3-propenyl)(phenylcarbonyl-4-phenylene) dimethyl ammonium hexafluoroantimonate (DMPDA)

In a 50 mL round bottom flask, a mixture of 2-(bromomethyl)-*N*,*N*-dimethyl acrylamide (BMDMA) (0.5 mL, 2 mmol) and 4-(dimethylamino) benzophenone (0.44 g, 2 mmol) in acetonitrile (15 mL) was stirred overnight at ambient temperature. The solvent was evaporated under vacuum and residue was washed with diethyl ether. The resulted bromo salt was dissolved in acetone–methanol (6:4) mixture and stirred with $NaSbF_6$ (0.516 g, 2 mmol) overnight. The solvent was evaporated and the residue was washed with water and recrystallized with dichloromethane. Yield: 0.60 g (63%), Elemental analysis: $C_{21}H_{25}N_2O_2SbF_6$ (572.09 g mol^{-1}), Calcd. C, 44.00; H, 4.40; N, 4.89 Found: C, 44.13; H, 4.43; N, 4.89, ^{1}H-NMR (acetonitrile-d_3) = 8.1–7.5 (m, 9H, Ph), 5.98, 5.81 (d, 2H, =CH_2), 4.80 (s, 2H, N–CH_2), 3.66 (s, 6H, CON$(CH_3)_2$), 2.64–2.77 (s, 6H, N$(CH_3)_2$) ppm, IR (KBr): 3400, 3377, 3028, 3056, 2932, 1702, 1667, 1637, 1610, 1491, 1446, 1415, 1324, 1202, 1137, 970, 897, and 792 cm^{-1}.

Typical polymerization procedure

An appropriate solution of monomer and initiator was placed in a flame dried pyrex ampoule equipped with three way stopcock connected to manifold and degassed for 30 min with three freeze–pump–thaw cycles before irradiation. After reaction for a set time, the mixture was dissolved in CH_2Cl_2 and precipitated with methanol then dried under vacuum at room temperature. The 450-W Hanovia medium pressure mercury vapor lamp was used in this study. The monomer conversion was estimated gravimetrically. The molecular weight of polymer was determined by gel permeation chromatography (GPC).

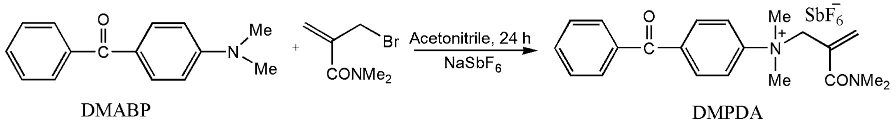
Characterization

Molecular weight of polymers was measured by GPC in chloroform as eluent (flow rate: 1 mL/min) on a setup consisting of a pump and six ultra Styragel column (50–105 Å porosities) and detection was carried out with the aid of UV-100 and RI-150 detectors. Molecular weight (M_n) and polydispersities (M_w/M_n) were determined using a calibration curve obtained by polystyrene standards. ^{1}H-NMR spectra were recorded on a Brüker 200 MHz instrument with $CDCl_3$ and acetonitrile (for initiators) as solvent and tetramethylsilane as internal standard. IR spectra were recorded on a Perkin–Elmer FT-IR (spectrum GX) spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash EA-1112 Microanalyser instrument. The UV spectra were recorded on Perkin–Elmer Lambda 950 UV/VIS spectrometer. After irradiation, the solution was analyzed by gas chromatography (Varian CP-3800 GC) in conjugation with mass spectroscopy (Varian Saturn 2200 GC/MS).

Results and discussion

Initiator synthesis

The synthesis of DMPDA involves a reaction of 2-(bromomethyl)-*N*,*N*-dimethyl acryl amide (BMDMA) with 4-(dimethyl-amino) benzophenone (DMABP) followed by anion exchange reaction of bromide with least nucleophilic SbF_6 anion (Scheme 1).



Scheme 1 Synthesis of DMPDA

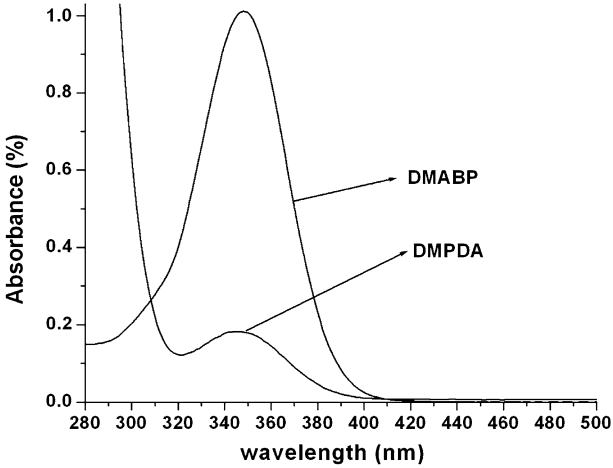


Fig. 1 UV absorption spectra of DMABP (1.20×10^{-5} mol L^{-1}) and DMPDA (10^{-4} mol L^{-1}) in CH_2Cl_2 solvent

DMPDA was well characterized by ^{1}H-NMR, IR, and elemental analysis as described in experimental section. DMPDA is white crystalline compound and showed good stability toward air and moisture at ambient temperature. Figure 1 depicts the UV absorption spectra of DMPDA and DMABP. It can be seen that DMPDA shows absorption above 290 nm.

Photopolymerization

Figure 2 shows time–conversion relationship in polymerization of CHO with two different concentration of DMPDA at $\lambda > 290$ nm for 30 min. It can be seen that conversion to poly(CHO) increases with time and reaches to limiting values. For higher concentration, A (5×10^{-3}), conversion reaches rapidly up to limiting value of 75% within 2 min and remains constant, whereas, for lower concentration B, conversion (%) increases gradually with the time up to 15 min (with 70% conversion).

The increase in concentration of initiator increases the conversion of monomer in short period of time.

Further, the activity of DMPDA was studied in photo-polymerization of IBVE in CH_2Cl_2 solvent above 290 nm. Figure 3, which represents time–conversion relationship for IBVE polymerization, suggests that DMPDA can efficiently

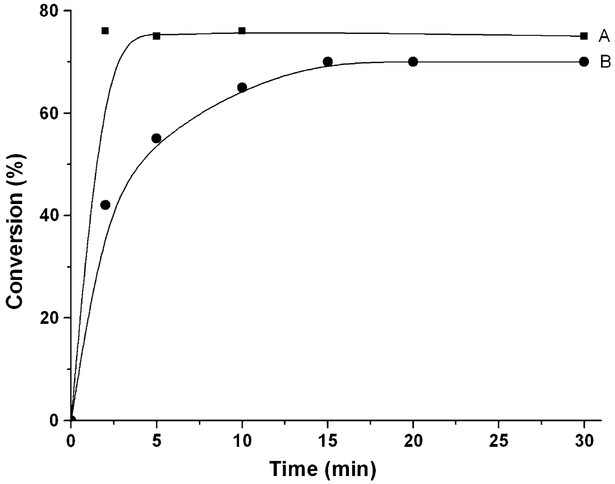


Fig. 2 Polymerization of CHO with DMPDA [CHO] = 5 mol L^{-1}, $\lambda > 290$ nm, 25 °C, (A) DMPDA = 5×10^{-3} mol L^{-1}, (B) DMPDA = 5×10^{-4} mol L^{-1}

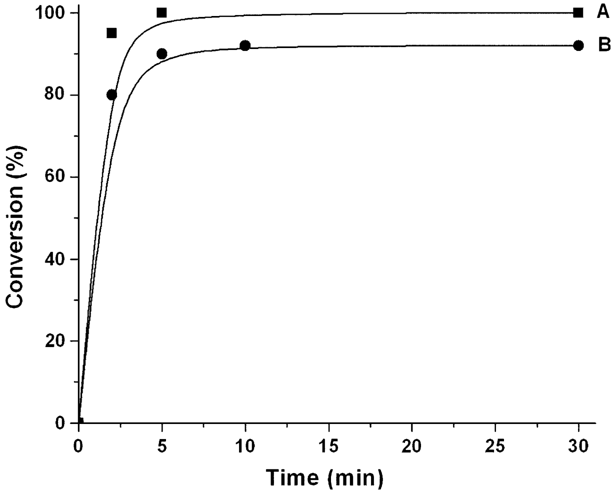


Fig. 3 Polymerization of IBVE in the presence of DMPDA [CHO] = 5 mol L^{-1}, $\lambda > 290$ nm, 25 °C, (A) DMPDA = 5×10^{-3} mol L^{-1}, (B) DMPDA = 5×10^{-4} mol L^{-1}

polymerize IBVE monomer. Within 5 min of reaction, conversion reaches to maximum conversions, 100 and 90% with higher (A) and lower (B) concentrations, respectively.

The photopolymerization of *n*-BVE was also carried out with DMPDA under similar conditions. In Fig. 4, it can be seen that the conversion of *n*-BVE reaches 100% conversion within 10 min with concentration (A), whereas, with lower concentration (B), only 90% was observed after 15 min of reaction time. These

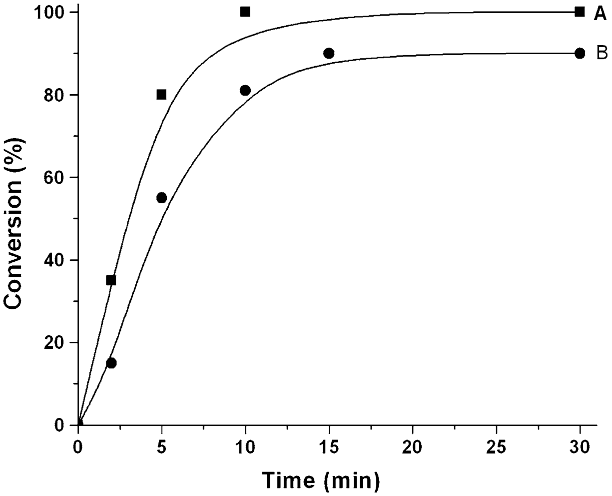


Fig. 4 Polymerization of *n*-BVE in the presence of DMPDA [CHO] = 5 mol L^{-1}, $\lambda > 290$ nm, 25 °C, (A) DMPDA = 5×10^{-3} mol L^{-1}, (B) DMPDA = 5×10^{-4} mol L^{-1}

Table 1 Photopolymerization of cationic monomers in the presence of DMPDA[a]

Monomer	Time (min)	Conversion[b] (%)	M_n^c	M_w/M_n
CHO	15	70	9,400	2.51
NVC	5	92	1,12,000	2.85
IBVE	5	90	25,600	2.36
n-BVE	15	90	17,300	2.05

[a] Monomer: Initiator = 5 mol L^{-1}: 5×10^{-4} mol L^{-1} in CH_2Cl_2 solvent at room temperature ($\lambda > 290$ nm)

[b] Determined gravimetrically

[c] Determined by GPC based on polystyrene standards

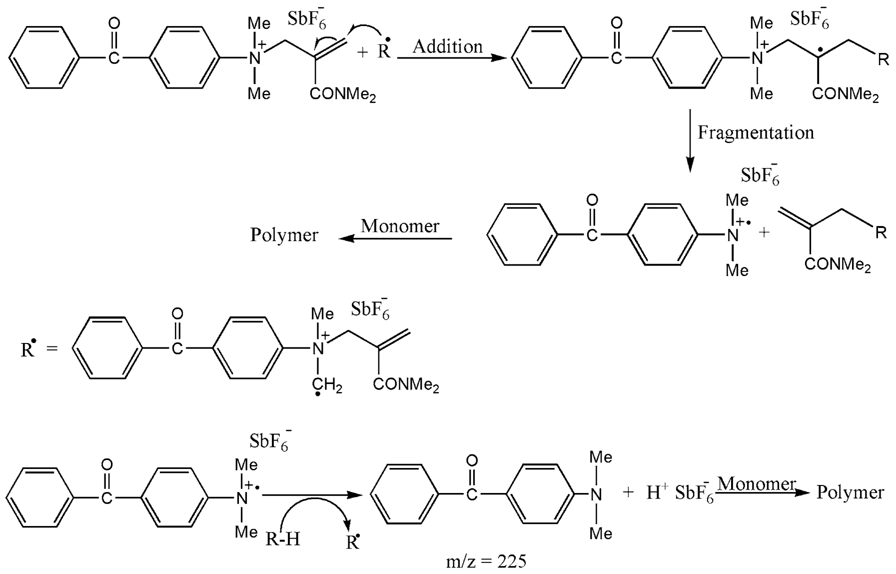
observations indicate that the increase in concentration of DMPDA increases the conversion and rate of polymerization.

Table 1 shows polymerization results of various cationic monomers such as CHO, *n*-BVE, IBVE, and NVC, in the presence of DMPDA in CH_2Cl_2 solvent at room temperature upon photo-irradiation.

All the monomers undergo rapid polymerization in the presence of DMPDA. These results indicate that DMPDA act as an efficient addition-fragmentation agent in free radical promoted cationic polymerization.

Mechanism of photopolymerization

The plausible mechanism for the present system is shown in Scheme 2. In general, benzophenone and its derivatives are well known to act as photoinitiators in radical



Scheme 2 Photo polymerization via radical addition-fragmentation mechanism

polymerization via hydrogen abstraction mechanism [21]. Based on previous literature [16–18], it is believed that benzophenone moiety of DMPDA produces radical species via hydrogen abstraction from ground state DMPDA.

These radicals add to the allylic double bond of initiator and subsequently generate ammonium radical cations, which may initiate the polymerization [22]. Additionally, the possibility of initiation by Bronsted acid generated after hydrogen abstraction from the reaction system (such as monomer, initiator, and solvent) cannot be ignored. In present case, generated ammonium radical cations may abstract hydrogen and generates Bronsted acid as initiating species. To confirm the mechanism via hydrogen abstraction, polymerization of CHO was performed with DMPDA in the presence of 2,6-di-*t*-butyl-4-methyl pyridine (DTBP), a proton scavenger. This system failed to produce any polymer, which proves that initiation is proceeding via hydrogen abstraction pathway.

The presence of DMABP as addition fragment peak at *m*/*z* value of 225 in GC-MS analysis of irradiated solution (5×10^{-3} M) of DMPDA in methanol also support the assumption (Scheme 2, Figs. 5, 6).

Addition-fragmentation reactions

To examine the efficiency of DMPDA as addition-fragmentation agent, polymerization of NVC with DMPDA and DMABP in CH_2Cl_2 solvent at $\lambda > 290$ nm for 5 min. NVC underwent fast polymerization (92% conversion) with DMPDA (as a cationic initiator) (Table 1), whereas, only 8% conversion was observed with DMABP (as a free radical initiator). This also demonstrates the utility of DMPDA as an addition-fragmentation agent. In addition, in order to know the behavior of the

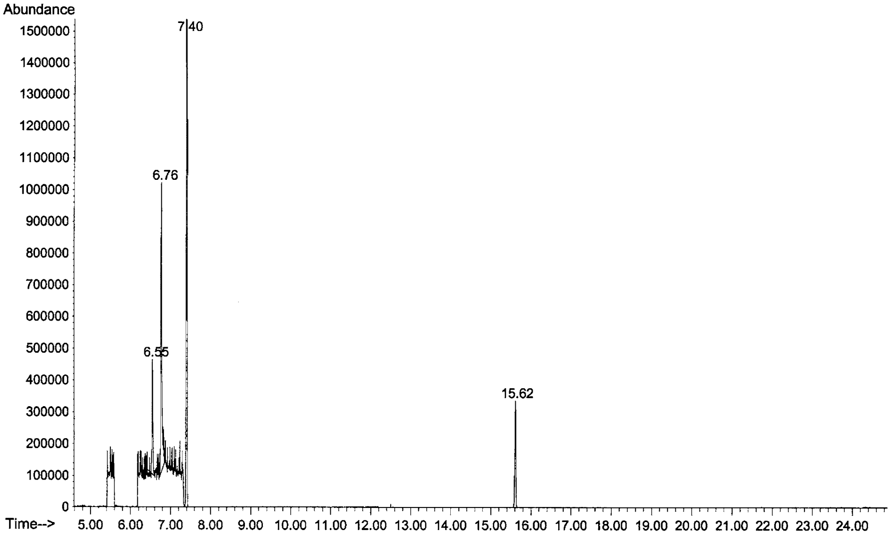


Fig. 5 GC-MS spectrum of DMPDA

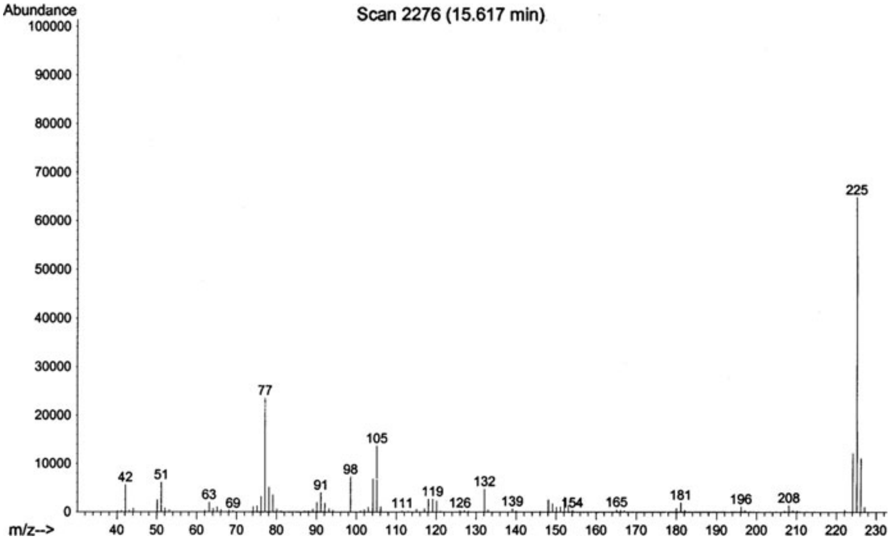


Fig. 6 Photo fragmentation products of DMPDA at 15.62 min in GC-MS analysis

generated free radicals, bulk polymerization of MMA was performed with DMPDA (0.1 mol%) at $\lambda > 290$ nm for 45 min and its initiation activity was compared with DMABP under similar reaction conditions. The initiators, DMPDA, and DMABP give 2 and 5% conversion, respectively. The reduced activity of DMPDA in radical polymerization of MMA may be ascribed by participation of some of the generated free radicals in addition-fragmentation reaction.

Conclusions

The benzophenone containing allylic ammonium salt (DMPDA) was synthesized and used as one component addition-fragmentation agent in cationic photopolymerization. The initiator, DMPDA contains an intrinsic chromophoric group (benzophenone moiety) for the radical generation and an allylic ammonium salt fragment for addition-fragmentation reaction. This initiator was found to be an efficient addition-fragmentation agent in cationic polymerization. Therefore, photo initiation can be induced without use of free radical sources above 290 nm. The properties of DMPDA such as good initiation efficiency, absorption above 290 nm and stability toward air and moisture might imply its use as cationic photo initiator in industrial photo-curing applications.

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