Polym. Bull. (2009) 62:271–280
DOI 10.1007/s00289-008-0014-y

ORIGINAL PAPER

Novel allylic phosphonium salts in free radical accelerated cationic polymerization

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Received: 26 July 2008 / Revised: 16 November 2008 / Accepted: 16 November 2008 /

Abstract In the present study, the synthesis and evaluation of novel allylic phosphonium salts as addition fragmentation agents in combination of conventional (photo-/thermal) free radical source for cationic polymerization are described. The amide based allylic phosphonium salts, namely 2-(*N*, *N*-dimethylcaboxy-propenyl) triphenylphosphonium hexafluoroantimonate (**DMTPH**) and 2-(morpholinocarboxy-propenyl) triphenyl phosphonium hexafluoroantimonate (**MTPH**) were synthesized and characterized. The thermal and photo-latency of these salts was examined with and without free radical sources in bulk polymerization of cyclohexene oxide (CHO) salts at 70 °C and $\lambda > 290$ nm irradiation, respectively. In presence of thermal free radical source, the order of activity was observed as **PAT** > **BPO** > **AIBN**. The order of activity of free radical sources on photopolymerization was found to be **benzoin** > **benzophenone** > **TMDPO**. In addition, photopolymerization of other cationically polymerizable monomers (such as *n*-butyl vinyl ether, isobutyl vinyl ether, N-vinyl carbazole and glycidyl phenyl ether) was also examined at $\lambda > 290$ nm irradiation. It is concluded that the rate of cationic polymerization can be accelerated using novel phosphonium salts with combination of free radical sources, by both thermal and photochemical mode.

Keywords Cationic polymerization · Addition fragmentation agent · Phosphonium salt · Photopolymerization · Initiator

Introduction

In the last few decades, the importance of latent cationic initiators, which show activity by external stimulation such as heat or light, has been recognized in a number

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of different industrial applications such as microelectronics, photolithography, curing, and adhesives [1]. Many technologically important monomers such as vinyl ethers and cyclic oxiranes, are typically polymerized in cationic mode, therefore, the development of more efficient photo- and thermal latent cationic initiators are desired [2–7]. Photo-polymerization by direct initiation of a general onium salts can be performed below 290 nm. This limits its potential use in cationic polymerization, mainly when visible light-emitting sources are used. To overcome this problem, several indirect pathways such as combination of onium salts with free radical sources [8–11], photosensitizers [12–16], and electron-donating compounds [17] have been extensively studied. Among them, the use of free radical sources in combination of allylic onium salt is a simple and flexible method to generate active species for cationic polymerization. The salient features of this method involve the accessibility of appropriate radical sources with broad range of absorption characteristics and temperature. In such system, radical source undergoes fragmentation and generates free radical (photo or thermally), which add to the double bond of allylic onium salt and produce radical cation as initiating species [7]. Yagci et al. have employed various acrylates based allylic onium salts such as sulfonium salts [18, 19], pyridinium salts [20], allyloxy pyridinium salts [21, 22], anilinium [23] phosphonium [24] salts etc. in externally stimulated cationic polymerization.

Considering the requirement of wide variety of activity of initiators, we have aimed to prepare photo/thermo-latent cationic initiators based on novel phosphonium salts. To the best of our knowledge, the chemistry of amide based allylic phosphonium salts as addition fragmentation agent for thermally and photochemically initiated cationic polymerization has not been studied and it is worthwhile to study the same. Thus, in the present study, we describe the synthesis of novel amide based phosphonium salts (**DMTPH** and **MTPH**) and examine their initiation efficiency as an addition fragmentation agent in conjugation of radical (photo and thermal) sources in cationic polymerization.

Experimental

Materials

N, *N*-dimethylacrylamide, acryloylmorpholine, cyclohexene oxide (CHO), isobutyl vinyl ether (IBVE), *n*-butyl vinyl ether (*n*-BVE), glycidyl phenyl ether (GPE) and N-vinyl carbazole (NVC) were purchased from Aldrich chemicals. All other chemicals (>99%) were purchased from S.D. Fine Chemicals Ltd, Mumbai, India. 2-(bromomethyl)-*N*, *N*-dimethyl acryl amide [25], 2-(bromomethyl)-acryloylmorpholine [25] and Phenyl azo triphenyl methane (PAT)[26] were prepared as reported. Monomers (CHO, IBVE, *n*-BVE and GPE) and solvent (CH_2Cl_2) were distilled over CaH_2 and used just before the polymerization. Triphenyl phosphine (Ph_3P) was recrystallized from *n*-hexane. NVC, AIBN, benzoin and benzophenone were recrystallized twice from ethanol while 2, 4, 6-trimethylbenzoyl diphenyl phosphine oxide (TMDPO) and benzoyl peroxide (BPO) were recrystallized from diethyl ether and used just after recrystallization.

Synthesis of 2-(*N*, *N*-dimethylcaboxy-propenyl) triphenylphosphonium hexafluoroantimonate (**DMTPH**)

To a solution of Ph_3P (5 mmol, 1.31 g) in toluene (10 mL), 2-(bromomethyl)-*N*, *N*-dimethyl acrylamide (5 mmol, 1.04 g) was added and allowed to stir for 1 h. The resulting white precipitate was dissolved in H_2O and washed with *n*-hexane. Finally, $NaSbF_6$ was added to the aqueous part in one portion. The resulting white precipitate was filtered, washed with water and dried under vacuum. Yield: 2.2 g (77%), white crystals, elemental analysis cal for: $C_{24}H_{25}NOPSbF_6$ (609.06 g mol^{-1}) C, 47.24%; H, 4.13%; N, 2.30%. Found: C, 47.15%; H, 4.16%; N, 2.27%, IR (KBr): 3,457, 3,400, 3,085, 3,055, 2,911, 2,972, 1,611, 1,586, 1,489, 1,438, 1,110, 960 cm^{-1}, ^1H NMR (CD_3CN): $\delta = 7.6 - 8.1$ (m, 15 H, Ph), 5.55 (s, 2 H, CH_2), 4.41, 4.34 (s, 2H, $=CH_2$), 2.86, 2.66 (s, 3H, $-NCH_3$) ppm.

Synthesis of 2-(morpholinocarboxy-propenyl) triphenylphosphonium hexafluoro antimonate (**MTPH**)

This compound was synthesized in the similar manner as described for **DMTPH**. Yield: 2.8 g (79%), white crystals, elemental analysis Cal for: $C_{26}H_{27}NO_2PSbF_6$ (651.07 g mol^{-1}): C, 47.88%; H, 4.17%; N, 2.15%, found: C, 47.75%; H, 4.16%; N, 2.11%, IR (KBr): 3,408, 3,050, 2,951, 2,863, 1,640, 1,520, 1,480, 1,460, 1,265, 1,208, 1,114, 997 cm^{-1}, ^1H NMR (CD_3CN): $\delta = 7.6 - 8.1$ (m, 15 H, Ph), 5.53 (s, 2H, CH_2), 4.41, 4.34 (s, 2H, $=CH_2$), 3.52 (t, 4H, $-OCH_2$), 3.35 (t, 4H, $-NCH_2$) ppm.

Measurements

Molecular weight of polymers was measured by gel permeation chromatography (GPC) in chloroform as eluent (flow rate: 1 mL/min) on a setup consisting of a pump and six Ultra Styragel column (50–10^5 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. 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.

Polymerization procedure

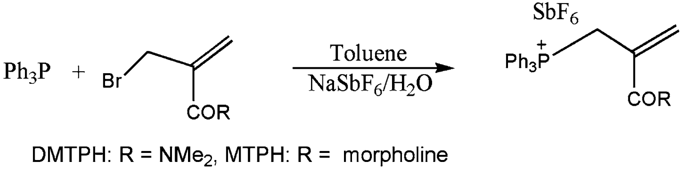
A mixture of monomer and initiator (with or without radical source) was placed in a flame dried ampoule equipped with three way stopcock connected to manifold and degassed for 30 min with three freeze-pump-thaw cycles and sealed off. The ampoule was immersed in an oil bath at constant temperature. Photo polymerization was performed in the similar way of thermal polymerization except Pyrex tubes were employed and reaction mixture was irradiated with 450 W medium pressure mercury lamp with quartz–jacket. After the reaction for a set time, polymerization mixture was dissolved in CH_2Cl_2 and precipitated with excess methanol then dried under vacuum at ambient temperature. The conversion of monomer was determined by gravimetrically.

Results and discussion

Initiators

The allylic phosphonium salts (**DMTPH** and **MTPH**) were synthesized by reaction of corresponding allyl bromide with triphenylphosphine followed by anion exchange of bromide with hexafluoroantimonate anion (Scheme 1). The structure of initiators was well characterized by ^{1}H NMR, IR and elemental analysis as described above.

The UV absorption spectra of **DMTPH** and **MTPH** are shown in Fig. 1, where the main absorbance was observed below 290 nm.



Scheme 1 Synthesis of amide based allylic phosphonium salts

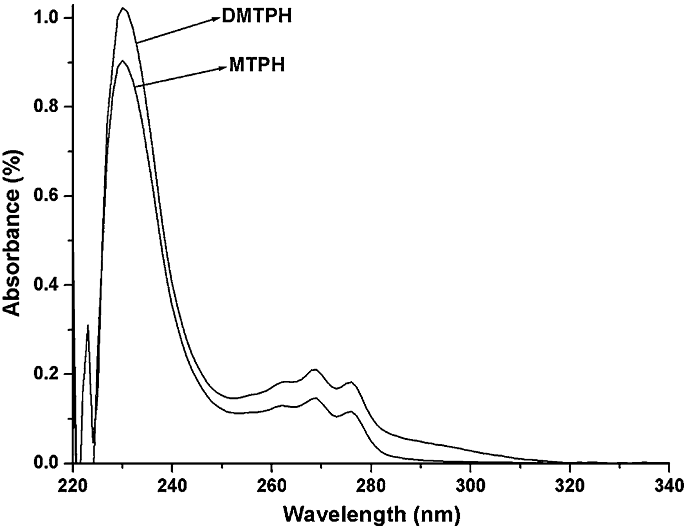


Fig. 1 UV absorption spectra of **DMTPH** (1.20×10^{-5} mol L^{-1}) and **MTPH** (1.20×10^{-5} mol L^{-1}) in CH_2Cl_2 solvent

Polymerization

The bulk polymerization of CHO with 0.1 mol % of phosphonium salt initiators (**DMTPH** and **MTPH**) was performed to examine the efficiency of the prepared initiators in cationic polymerization of CHO in the presence (0.1 mole %) and absence of free radical sources.

Effect of free radicals on thermal polymerization

In the absence of free radical source, the polymerization of CHO was carried out from ambient temperature to 130 °C for 2 h. Figure 2 shows the monomer conversion (%) as a function of temperature. It can be seen that the polymerization with both initiators proceeds above 90 °C and reaches to maximum (100%) conversion at 130 °C.

The conversion without free radical source can be attributed to the thermal decomposition of phosphonium salts. It is assumed that thermal decomposition of the phosphonium salts results in formation of free radicals, which lead to addition fragmentation reaction and further initiate polymerization. This assumption is supported by fact that no polymerization of CHO is observed with benzyltriphenylphosphonium salt at 120 °C [24].

In presence of radical sources (**AIBN**, **BPO** and **PAT),** the polymerization of CHO was carried out at 70 °C for 2 h (Table 1).

Figures 3 and 4 show the time–conversion curve for the polymerization with **DMTPH** and **MTPH**, respectively. It can be seen that with increasing time, the polymerization proceeds and attains respective limiting conversion with each phosphonium salt/radical source combination.

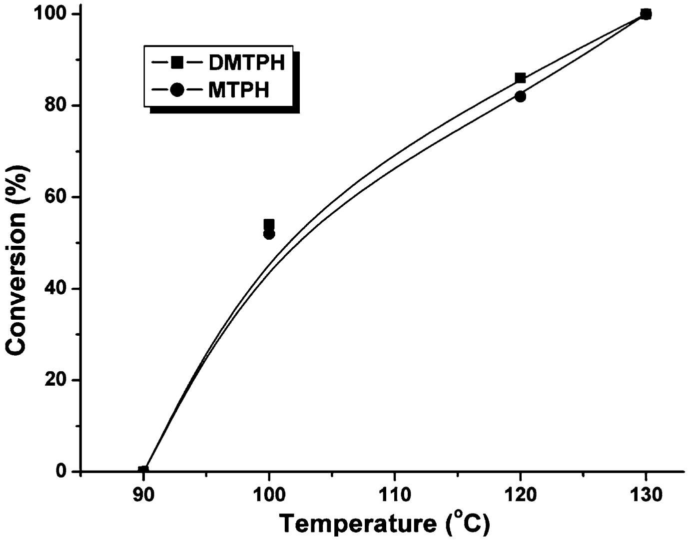


Fig. 2 Temperature–conversion curve in polymerization of CHO with allylic phosphonium salts in the absence of radical sources; [CHO] = 5 mol L^{-1} [DMTPH/[MTPH] = 5 × 10^{-3} mol L^{-1}

Table 1 Thermal polymerization of CHO initiated by thermal radical sources [a]

Initiator	Radical source	Conversion[b] (%)	M_n^c	M_w/M_n
DMTPH	PAT	35	5,600	1.69
	BPO	16	6,766	1.94
	AIBN	8	6,600	1.84
MTPH	PAT	31	6,000	1.79
	BPO	16	6,900	1.81
	AIBN	7	8,200	1.62

[a] Conditions; monomer: initiator: radical source = 5 mol L^{-1} : 5 × 10^{-3} mol L^{-1}: 5 × 10^{-3} mol L^{-1}, time = 120 min

[b] Determined gravimetrically

[c] Determined by GPC based on polystyrene standards

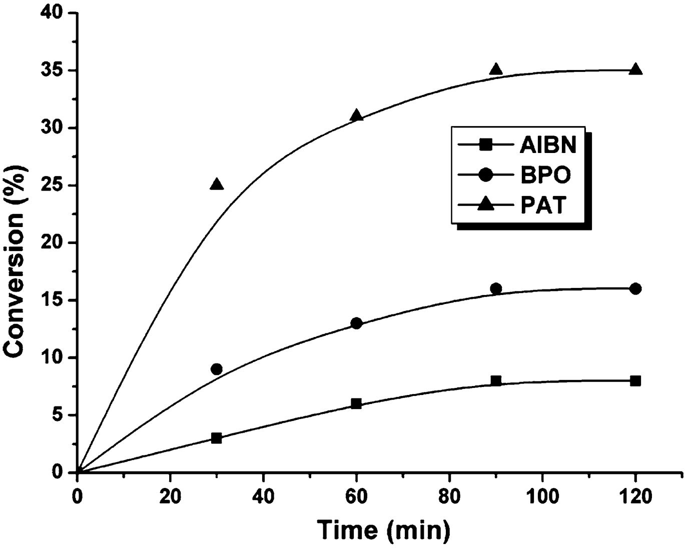


Fig. 3 Time–conversion curve in polymerization of CHO with **DMTPH** in the presence of radical sources at 70 °C; [CHO: DMTPH: radical source = 5 mol L^{-1}: 5 × 10^{-3} mol L^{-1}: 5 × 10^{-3} mol L^{-1}]

The maximum conversion with **DMTPH** in presence of **PAT**, **BPO** and **AIBN** was found as 35, 16 and 8 for 120 min, respectively. The order of initiator activity was observed as **PAT** > **BPO** > **AIBN**. The similar trend was observed with **MTPH** for 120 min, with the limiting conversion around 31, 16 and 7 in presence of **PAT**, **BPO** and **AIBN**, respectively. This trend can be explained by the difference in the decomposition rate constant and the reactivity of radical toward the double bond of phosphonium salts [27].

The above results suggest that by the addition of free radical source, the polymerization rate of CHO can be accelerated even at the temperature (<90 °C).

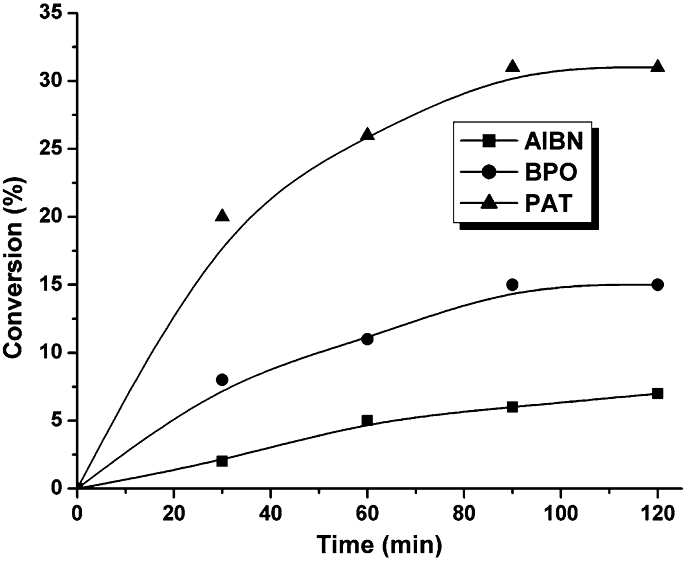


Fig. 4 Time–conversion curve in polymerization of CHO with **MTPH** in presence of radical sources at 70 °C; [CHO: MTPH: radical source = 5 mol L^{-1}: 5 × 10^{-3} mol L^{-1}: 5 × 10^{-3} mol L^{-1}]

Effect of free radicals on photopolymerization

In the absence of free radical source, polymerization of CHO was carried out with 0.1 mol % of **DMTPH** and **MTPH** at $\lambda > 290$ nm irradiation for 1 h and no conversion was observed with both the initiators.

In the presence of photo free radical sources, namely **benzophenone**, **TMDPO** and **benzoin**, the polymerization of CHO was performed with **DMTPH** and **MTPH** at $\lambda > 290$ nm irradiation. It can be seen in Table 2, that the monomer conversion

Table 2 Photopolymerization of CHO with allylic phosphonium salts in presence of various radical sources at $\lambda > 290$ nm[a]

Initiator	Radical source	Time (min)	Conversion[b] (%)	M_n (M_w/M_n)[c]
DMTPH	Benzophenone	120	12	7,030 (2.29)
	TMDPO	120	1	4,436 (1.94)
	Benzoin	10	30	8,236 (1.56)
MTPH	Benzophenone	120	8	6,800 (1.79)
	TMDPO	120	1	4,900 (1.81)
	Benzoin	10	28	9,158 (1.77)

[a] Conditions; monomer: initiator: radical source = 5 mol L^{-1} : 5 × 10^{-3} mol L^{-1}: 5 × 10^{-3} mol L^{-1}, at 25 °C

[b] Determined gravimetrically

[c] Determined by GPC based on polystyrene standards

with **DMTPH** and benzoin (30% conversion for 10 min) was found to be relatively more efficient radical source than others to accelerate the rate of polymerization.

The order of initiator activity with respect to radical source was observed as **benzoin** > **benzophenone** > **TMDPO**. The higher activity with **benzoin** can be explained by its high quantum efficiency to generate radicals and the easier oxidation of these radicals [18]. **Benzoin/DMTPH** system was used for further study due to its higher efficiency compared to other radical source-phosphonium salt combinations.

Effect of free radical source concentration

To examine the effect of free radical source concentration on the initiator efficiency, further polymerization was carried out for 10 min, with (4 times) higher concentration of benzoin by keeping the molar ratio of monomer/salt as constant. Figure 5 shows the kinetics of CHO polymerization with **DMTPH** in presence of **benzoin** at two different concentrations.

The CHO attains 30 and 85% conversion with the concentration of **benzoin** 5×10^{-3} and 2×10^{-2} mol L^{-1}, respectively, without changing the CHO and **DMTPH** concentration. The four times increase in concentration of **benzoin** increases the rate of polymerization approximately three times. The higher efficiency of benzoin can be understood to be the proof of efficiency of the addition-fragmentation process. Thus, the combination of phosphonium salt initiators with radical sources does not only improve the time-conversion behavior but also enables the use of light at extended wavelengths.

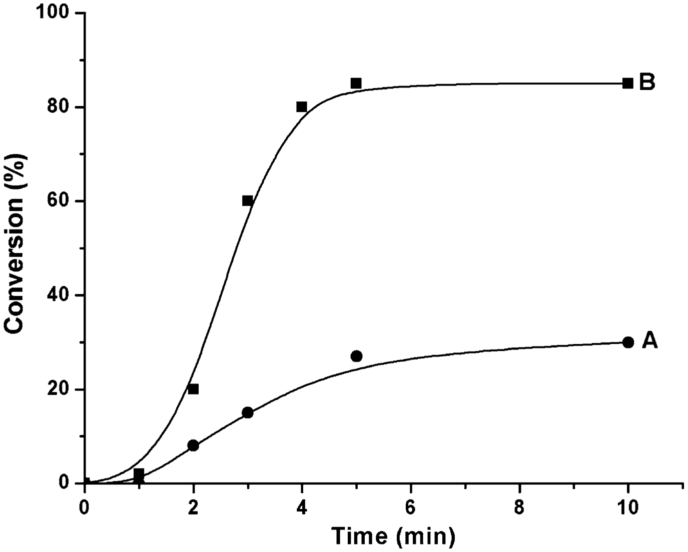


Fig. 5 Time–conversion curves in polymerization of CHO with **DMTPH** at $\lambda > 290$ nm irradiation in presence of different concentration of benzoin [$A = 5 \times 10^{-3}$ and $B = 2 \times 10^{-2}$ mol L^{-1}]

Table 3 Photopolymerization of other cationic monomers with **DMTPH** and **benzoin**[a]

Monomer	Solvent	Conversion[c] (%)	M_n^d (g mol^{-1})	M_w/M_n
CHO	Bulk	85	7,030	2.29
BVE	CH_2Cl_2	63	19,700	2.36
IBVE	CH_2Cl_2	80	24,200	1.29
NVC	CH_2Cl_2	91	41,500	1.69
GPE[b]	Bulk	–	–	–

[a] Conditions; monomer: initiator: radical source = 5 mol L^{-1} : 5 × 10^{-3} mol L^{-1}: 2.0 × 10^{-2} mol L^{-1}, time = 10 min, at 25 °C; $\lambda > 290$ nm

[b] Time = 120 min

[c] Determined gravimetrically

[d] Determined by GPC based on polystyrene standards

Photopolymerization with other monomers

Further, photopolymerization of other cationically polymerizable monomers (*n*-BVE, IBVE, NVC and GPE) was performed with **DMTPH** and **benzoin** at $\lambda > 290$ nm irradiation for 10 min (Table 3).

The monomers, such as *n*-BVE, IBVE and NVC underwent efficiently polymerization, whereas; GPE could not be polymerized up to 120 min under similar reaction conditions due to low reactivity of the monomer.

Conclusions

The amide based allylic phosphonium salts were synthesized and successfully used as photo and thermo-latent initiator in the presence of free radical source as addition fragmentation agent in cationic polymerization. In thermal polymerization, without use of radical source, conversion starts above 90 °C. The rate of polymerization can be accelerated with the use of free radical source at 70 °C and was observed as **PAT** > **BPO** > **AIBN**. No photo polymerization was observed without the use of radical source while it proceeds in the presence of radical source. The rate of polymerization with photo radical source was observed as **benzoin** > **benzophenone** > **TMDPO**. With increasing concentration of radical source, benzoin, the efficiency of both the initiators was increased in photopolymerization. The activity of both initiators was less affected by the presence of different amide group in both thermal and photochemical mode of polymerization. It can also be concluded that a wide range of thermal and photo radical source can be employed to tune the conditions (temperature and wavelength) to enhance the rate of polymerization.

Acknowledgment Authors are grateful to Dr. S. Sivaram, Director, NCL, Pune for providing necessary facilities and fruitful discussions. MKG thanks CSIR, New Delhi, for the award of senior research fellowship.

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