Novel Dibenzocycloheptenyl Phosphonium Salts as Thermolatent Initiator in Cationic Polymerization

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ABSTRACT: In this study, novel thermolatent cationic initiators based on dibenzocycloheptenyl phosphonium salts (**1a**, **1b**, **1c**, **1d**, **2a**, and **3a**) were synthesized and their efficiency was examined in bulk polymerization of glycidyl phenyl ether (GPE). The polymerization of GPE was performed with 1 mol % of dibenzocycloheptenyl triphenylphosphonium salts (**1a–1d**) with different counter anions (SbF_6^-, PF_6^-, AsF_6^-, and BF_4^-) at 25–200°C for 1 h. The order of initiator activity was found as **1a** > **1d** > **1b** > **1c**. To examine the effect of phosphine moiety, the activity of **1a** was compared with dibenzocycloheptenyl-tri-*n*-butylphosphonium hexafluoroantimonate (**2a**). The order of initiator activity was observed as **1a** > **2a.** The initiator activity of **1a** was compared with that of 10,11-dihydrodibenzocycloheptenyltriphenylphosphonium hexafluoroantimonate (**3a**) to understand the effect of extended conjugation in dibenzocycloheptenyl ring. In general, with the increase in the polymerization temperature, conversion (%) also increases. The solubility of initiators in various solvents and epoxy monomers was also examined. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3707–3713, 2009

Key words: cationic polymerization; glycidyl phenyl ether; thermolatent; initiators; phosphonium salt

INTRODUCTION

The externally stimulated initiators have gained considerable attention in applications such as curable coatings, paints, packing, fillers, and adhesives, because of their control over initiation and curing process.[1–4] The latent cationic initiators, which exhibit no activity under ambient condition but generate active species on external stimulation such as heating or photoirradiation, have gained momentum over conventional anhydride and amine-based initiators.[5–12] Thus, development of efficient thermolatent cationic initiators having good solubility in monomer and resistance toward air and moisture is more desirable. Several onium salts such as benzyl sulfonium,[13–15] benzyl pyridinium,[16,17] benzyl ammonium,[18] hydrazinium,[19,20] and others[21–25] have been developed as potential thermolatent initiator. Among these initiators, the phosphonium salts offer a great variety of reactivities because of participation of d-orbital.[26,27] Endo and coworkers[28] have reported that benzylphosphonium salts generate protons as active species beside formation of stable ylides. Later, fluorenylphosphonium salts have been reported as more active initiators than benzylphosphonium salts because of the higher acidity of fluorenyl methine proton.[27] The acidity of methine proton, which determines the activity of initiators, depends on stability of resulting ylide. Therefore, it is worthwhile to synthesize novel initiators with good solubility, thermal stability, and higher activity. Considering aforementioned points, it is assumed that dibenzocycloheptene-based phosphonium salts can serve as active initiators for cationic polymerization. This article describes the synthesis of novel thermolatent cationic initiators based on dibenzocycloheptenyl phosphonium salts (**1a**, **1b**, **1c**, **1d**, **2a**, and **2c**) and examines the effect of counter anion (SbF_6^-, PF_6^-, AsF_6^-, and BF_4^-), phosphine moiety (Ph_3P and Bu_3P), and ring conjugation (double bond) on their initiation efficiency in cationic polymerization of glycidyl phenyl ether (GPE).

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EXPERIMENTAL

Materials

Triphenylphosphine (Ph_3P), tri-*n*-butyl phosphine (Bu_3P), dibenzo(a, d)cyclohepten-5-ol, dibenzo(a,d)-cyclohepten-5-yl chloride, sodium hexafluoroantimonate ($NaSbF_6$), potassium hexafluorophosphate (KPF_6), sodium hexafluoroarsenate ($NaAsF_6$), sodium tetrafluoroborate ($NaBF_4$), and glycidyl phenyl ether were purchased from Aldrich chemicals. All other chemicals were purchased from M/s S. D. Fine Chemicals, Mumbai, India and used after

purification.[29] GPE was dried and distilled over CaH_2 just before polymerization.

Initiator synthesis

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium chloride **(1)**

To the suspension of dibenzo(a,d)cyclohepten-5-ol (2.08 g, 10 mmol) in *n*-hexane (20 mL), $SOCl_2$ (1.46 mL, 20 mmol) in *n*-hexane (10 mL) was added at ambient temperature and allowed to reflux for 1 h. The reaction mixture was cooled to ambient temperature and the solvent was removed under vacuum. The resulting residue was dissolve in toluene (20 mL) and Ph_3P (2.62 g, 10 mmol) in toluene (15 mL) was added and stirred for 1 h. The resulted white precipitate was filtered and washed with toluene and dried under vacuum. Yield: 2.87 g (59%), elemental analysis: $C_{33}H_{26}ClP$ (488.01 g mol^{-1}), Found: C, 81.13%; H, 5.32%; Calculated: C, 81.25%; H, 5.40%. ^{1}H-NMR (DMSO-d_6): δ = 7.95–7.05 (m, 23 H, Ph), 6.82, 6.73 (1H, CH), 6.31 (s, 2H, CH) ppm.

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium hexafluoro antimonate **(1a)**

To the solution of **1** (3 mmol, 1.46 g) in methanol (MeOH, 20 mL), was added $NaSbF_6$ (3 mmol, 0.77 g) in H_2O (20 mL) and allowed to stir at room temperature for 30 min. The precipitate formed was filtered, washed with H_2O, and finally recrystallized with ethanol–dichloromethane (CH_2Cl_2) (8 : 2).

Yield: 1.38 g (67%), white crystals, mp: 268–269°C, elemental analysis: $C_{33}H_{26}PSbF_6$ (688.07 g mol^{-1}) Found: C, 57.73%; H, 3.73%; Calculated: C, 57.50%; H, 3.80%. FTIR (KBr) = 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.95–7.05 (m, 23 H, Ph), 6.82, 6.72 (1H, CH), 6.30 (s, 2H, CH) ppm. ^{13}C-NMR(DMSO-d_6): δ = 136.55, 135.12, 134.66, 134.48, 132.3, 132.07, 130.83, 130.47, 129.93, 129.70, 129.48, 128.63, 117.69, 116.09, 51.25, 50.43 ppm. ^{31}P NMR (DMSO-d_6): δ = 23.29 ppm.

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium hexafluoro phosphate **(1b)**

This compound was prepared by reaction of **1** (3 mmol, 1.46 g) with KPF_6 (3 mmol, 0.55 g) in the same manner as described for compound **1a**.

Yield: 1.30 g (73%), white crystals, mp: 265–266°C. Elemental analysis: $C_{33}H_{26}P_2F_6$ (598.14 g mol^{-1}), Found: C, 66.28%; H, 4.32%; Cal: C, 66.22%; H, 4.38%. FTIR (KBr) = 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.95–7.05 (m, 23 H, Ph), 6.82, 6.72 (1H, CH), 6.30 (s, 2H, CH) ppm. ^{13}C-NMR(DMSO-d_6): δ = 136.55, 135.12, 134.66, 134.48, 132.3, 132.07, 130.83, 130.47, 129.93, 129.70, 129.48, 128.63, 117.69, 116.09, 51.25, 50.43 ppm. ^{31}P NMR (DMSO-d_6): δ = 23.29 ppm.

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium hexafluoro arsenate **(1c)**

This compound was prepared by reaction of **1** (3 mmol, 1.46 g) with $NaAsF_6$ (3 mmol, 0.64 g) in the same manner as described for compound **1a**.

Yield: 1.04 g (54%), white crystals, mp: 267–268°C. Elemental analysis: $C_{33}H_{26}PAsF_6$ (642.09 g mol^{-1}) Found: C, 61.72%; H, 4.06%; Calculated: C, 61.69%; H, 4.08%; FTIR (KBr): = 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.95–7.05 (m, 23 H, Ph), 6.82, 6.72 (s, 1H, CH), 6.30 (s, 2H, CH) ppm. ^{13}C-NMR(DMSO-d_6): δ = 136.55, 135.12, 134.66, 134.48, 132.3, 132.07, 130.83, 130.47, 129.93, 129.70, 129.48, 128.63, 117.69, 116.09, 51.25, 50.43 ppm. ^{31}P NMR (DMSO-d_6): δ = 23.29 ppm.

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium tetrafluoro borate **(1d)**

This compound was prepared by reaction of **1** (3 mmol, 1.46 g) with $NaBF_4$ (3 mmol, 0.33 g) in the same manner as described for compound **1a**.

Yield: 0.70 g (43%), white crystals, mp: 268–269°C. Elemental analysis: $C_{33}H_{26}BF_4$ (540.18 g mol^{-1}) Found: C, 73.65%; H, 4.75%; Calcd: C, 73.35%; H, 4.85%. FTIR (KBr) = 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.95–7.05 (m, 23 H, Ph), 6.82, 6.72 (1H, CH), 6.30 (s, 2H, CH) ppm. ^{13}C-NMR(DMSO-d_6): δ = 136.55, 135.12, 134.66, 134.48, 132.3, 132.07, 130.83, 130.47, 129.93, 129.70, 129.48, 128.63, 117.69, 116.09, 51.25, 50.43 ppm. ^{31}P NMR (DMSO-d_6): δ = 23.29 ppm.

Synthesis of 5-H-dibenzo(a,d)cyclohepten-5-yl tri-n-butylphosphonium hexafluoro antimonate **(2a)**

This compound was prepared in same manner as described for **1** and followed by anion exchange with $NaSbF_6$ in MeOH–H_2O mixture and recrystallized by ethanol–CH_2Cl_2 (8 : 2).

Yield: 0.78 g (52%), white crystals, mp: 32–34°C, elemental analysis: $C_{27}H_{38}PSbF_6$ (628 g mol^{-1}) Found: C, 51.46%; H, 6.08%; Calcd: C, 51.53%; H, 6.04%. FTIR (KBr) = 3030, 2930, 2868, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.70–7.25 (m, 8H, Ph), 7.10 (s, 2H, CH), 5.77, 5.67 (CH, 1H), 2.05 (m, CH_2, 6H), 1.24 (m, CH_2, 6H), 1.09 (m, CH_2, 6H), 0.80 (t, CH_3, 9H) ppm. ^{13}C-NMR (DMSO-d_6): δ = 135.53, 131.85, 131.02, 130.48, 130.14, 129.68, 129.08, 48.11, 47.31, 23.50, 23.19, 22.62, 19.30, 18.45, 13.03 ppm. ^{31}P NMR (DMSO-d_6): δ = 37.43 ppm.

Synthesis of 10, 11-dihydro-5-H-dibenzo(a,d)cyclohepten-5-yltriphenylphosphonium hexafluoroantimonate **(3a)**

To the solution of dibenzo(a,d)cyclohepten-5-yl chloride (10 mmol, 2.28 g) in toluene (20 mL), Ph_3P (10 mmol, 2.62 g) in toluene (15 mL) was added at ambient temperature and allowed to stir for 30 min. The resulted white precipitate was filtered, washed with toluene, and counter anion was exchanged with $NaSbF_6$ in same manner as described for **1a** and recrystallized with ethanol–CH_2Cl_2 (8 : 2).

Yield: 2.87 g (72%), white crystals, mp. 248–251°C, elemental analysis: $C_{33}H_{28}PSbF_6$ (690.07 g mol^{-1}): Calculated: C, 57.50%; H, 4.18%; Found: C, 57.22%; H, 4.22%; IR (KBr): 3030, 2930, 2868, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ = 7.95–7.06 (m, 23 H, Ph), 6.69, 6.58 (CH, 1H), 2.75 (CH_2, 4H) ppm. ^{13}C-NMR (DMSO-d_6): δ = 141.78, 135.29, 134.64, 132.65, 131.34, 130.22, 129.98, 126.76, 52.88, 52.18, 36.06 ppm.

Typical polymerization procedure

A mixture of monomer (5 mmol, 0.65 mL) and initiator (0.05 mmol, **1a**, 34.40 mg; **1b**, 29.92 mg; **1c**, 32.10 mg; **1d**, 26.92 mg; **2a**, 31.44 mg; **3a**, 34.50 mg) 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 for the required time and temperature. After reaction, the ampoule was cooled into liquid nitrogen bath. The polymerization mixture was diluted with CH_2Cl_2 and precipitated with MeOH. The polymer was separated from the supernatant by decantation and dried under vacuum. The monomer conversion was determined by ^{1}H-NMR spectroscopy from crude polymerization mixture before precipitation in MeOH.[30] The molecular weight (M_n) of polymer was determined by gel permeation chromatography (GPC). The obtained polymer was identified to be poly(GPE). ^{1}H-NMR ($CDCl_3$) = δ 7.99–7.65 (m, 5H, —C_6H_5), 4.80–3.25 (m, 5H, —$OCH_2CH(CH_2Ph)$—) ppm. IR ($CHCl_3$): 3036, 2930, 2876, 1599, 1495, 1244, 1132, 1044, 754, 661 cm^{-1}.

Measurements

The single-crystal diffraction data were collected on a Brüker AXS Smart Apex CCD diffractometer at 133(2) K. The X-ray generator was operated at 50 kV and 30 mA using graphite-monochromatized (Mo-K_α = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3° and with three different settings of φ (0°, 90°, 180°) keeping the sample-to-detector distance fixed at 6.145 cm and the detector position (2θ) fixed at −28°. The X-ray data collection was monitored by SMART program (Brüker, 2003).[31] All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Brüker, 2003). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[32] Hydrogen atoms were located from a difference Fourier map, and their positional coordinates and isotropic thermal parameters were refined. ORTEPs and geometrical parameters were obtained using SHELXTL program.[31]

The M_n was measured by GPC in tetrahydrofuran (THF) as eluent (flow rate: 1 mL/min) on a setup consisting of a pump and two Ultra Styragel column (50–10^5 Å porosities), and detection was carried out with the aid of UV-100 and RI-150 detectors. M_n and polydispersities (M_w/M_n) were determined using a calibration curve obtained by commercially available monodispersed polystyrene standards from PSS Germany. NMR (^{1}H, ^{13}C, and ^{31}P) spectra were recorded on a Brüker 200 MHz instrument with $CDCl_3$ (for polymerization mixture) and DMSO-d_6 (for initiators) as solvent and tetramethylsilane as internal standard. FTIR spectra were recorded on a Perkin-Elmer model 683 grating IR spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash EA-1112 Microanalyser instrument.

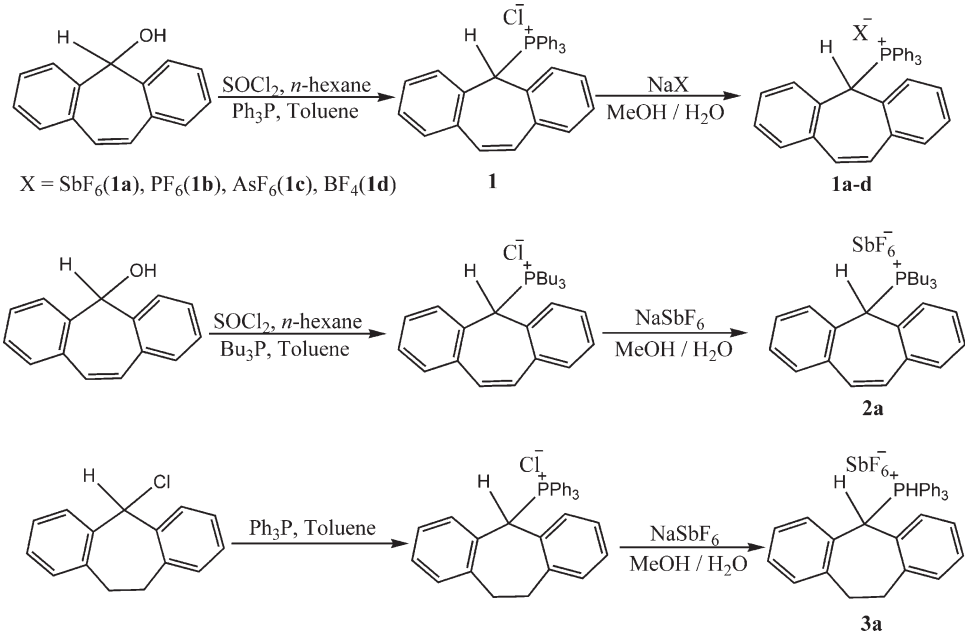
RESULTS AND DISCUSSION

Initiator synthesis

The phosphonium salts (**1a–1d**, **2a**, and **3a**) were synthesized and characterized by NMR (^{1}H, ^{13}C, and ^{31}P), IR, and elemental analysis as described in experimental section (Scheme 1). Figure 1 shows the molecular structure of **1d** obtained by single crystal X-ray analysis. The interatomic distance between the dibenzocycloheptenyl methine proton and carbon (C_1) of **1a*** and **1d**† was found to be 0.78 and 0.95 Å, respectively. The interatomic distance might be

*X-ray data of **1a:** Monoclinic, C2/c, a = 19.982(8) Å α = 90°, b = 13.6036(14) Å β = 103.726(2)°, c = 17.7576(18) Å γ = 90°, V = 6347(5) A^3, Z = 8, 1.620 mg/m^3, F(000) = 3088, μ (Mo-K_α) = 1.148 mm^{-1}. Reflections collected = 29,328/5587 [R(int) = 0.0248], data/restraints/parameters = 5587/0/53, min. and max transmission 0.7492 and 0.5725, respectively, $R1$ = 0.0476, w$R2$ = 0.1303 ($R1$ = 0.0507, w$R2$ = 0.1337) GoF = 1.061, largest diff. peak and hole =1.208 and −1.491 e A^{-3} refinement method, full-matrix least-squares on F^2.

†X-ray data of **1d:** Monoclinic, P 3/n, a = 11.1201(11) Å, α = 90°, b = 17.452(7) Å β = 93.489(7)°, c = 18.233(8) Å γ = 90°, V = 2609.5(5) A^3, Z = 4, 1.375 mg/m^3, F(000) = 1120, μ (Mo-K_α) = 0.156 mm^{-1}. Reflections collected = 18,609. unique = 4592 [R(int) = 0.0306], data/restraints/parameters = 4592/0/456, min. and max transmission 0.9795 and 0.9517, respectively, $R1$ = 0.0463, w$R2$ = 0.1073 (all data $R1$ = 0.0534, w$R2$ = 0.1119) GoF = 1.060, Largest diff. peak and hole =0.616 and −0.308 e A^{-3} refinement method, full-matrix least-squares on F^2.



Scheme 1 Synthesis of phosphonium salts.

related to the labiality of bond (C—H), hence the acidity of methine proton of initiators.

Polymerization

Effect of counter anions

The bulk polymerization of GPE was performed with 1 mol % of initiator (**1a**, **1b**, **1c**, and **1d**) with different counter anion (SbF_6^-, PF_6^-, AsF_6^-, and BF_4^-) at 25–200°C for 1 h (Scheme 2). GPE did not polymerize at all at 25°C for 3 weeks, which reveals the thermolatent nature of the initiators under ambient conditions. Figure 2 shows the effect of counter anion on initiator activity by monitoring monomer conversion as a function of experimental temperature. It shows that the conversion (%) increases with the increase in experimental temperature. The GPE undergoes polymerization with **1a**, **1b**, **1c**, and **1d** above 100, 120, 120, and 100 °C, respectively. With these initiators, rate of polymerization increases with the increase in experimental temperature and reaches to their maximum limiting conversion to afford the polymer with M_n of 2100–3800. At 130°C, the conversion of GPE with **1a**, **1b**, **1c**, and **1d** attains 73, 7, 2, and 27%, respectively. The monomer undergoes 100% conversion with **1a** at 160°C, whereas it gives only 27, 22, and 34% conversion with **1b**, **1c**, and **1d**, respectively, even up to 200°C. The order of initiator activity is observed as **1a** > **1d** > **1b** > **1c**.

However, the molecular orbital calculation for interionic distance between oxonium cation of the

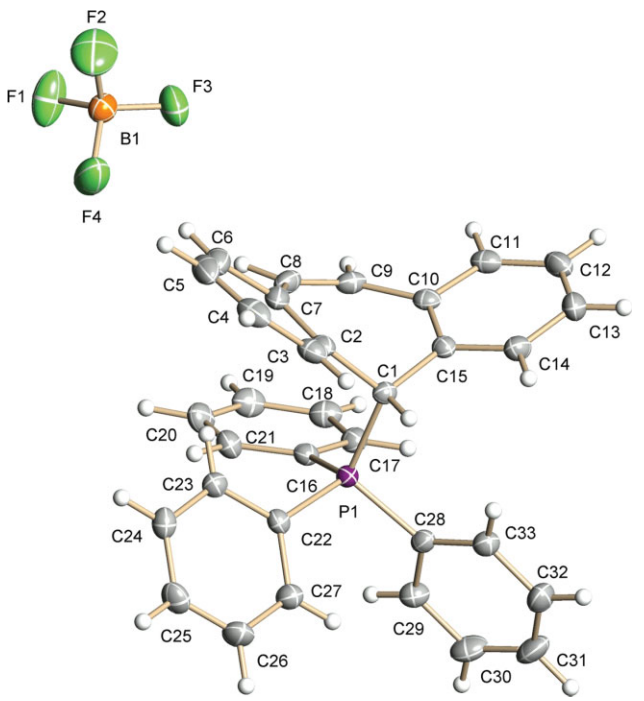
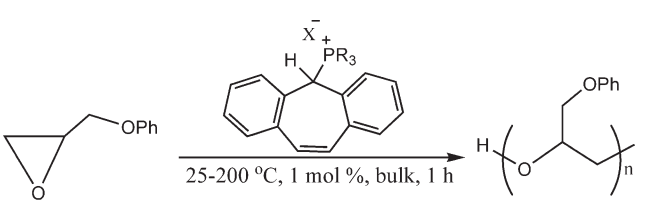


Figure 1 ORTEP drawing of **1d**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



X = SbF_6, PF_6, AsF_6, BF_4
R= Ph_3P, Bu_3P

Scheme 2 Polymerization of GPE.

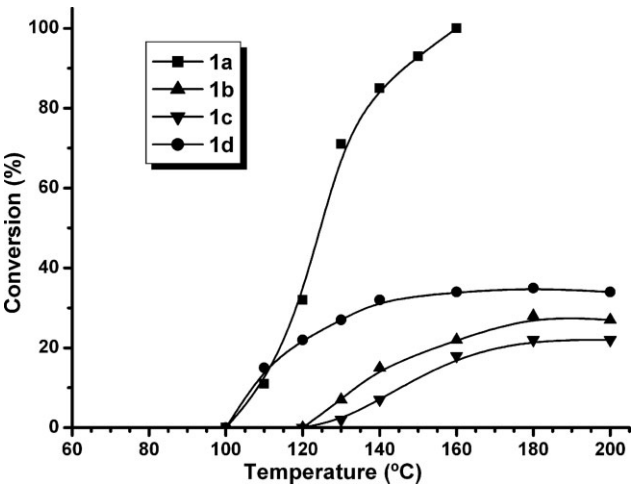


Figure 2 Temperature–conversion relationship in GPE polymerization with **1a–1d** for 1 h.

propagating polymer chain and counter anion[27] shows the order of interionic distance decreases as: $SbF_6^- > PF_6^- > AsF_6^- > BF_4^-$. The longer interionic distance denotes the lesser nucleophilicity of counter anion, which favors the propagation step. Therefore, the order of initiator activity should be as **1a** > **1b** > **1c** > **1d**. In this study, the initiator **1d** (BF_4) exhibits higher initiator activity compared with **1b** (PF_6) and **1c** (AsF_6). For that, it is assumed that methine C—H bond might play some role at the initial stage of initiation. For such purpose, single crystal X-ray measurements of **1a** and **1d** were performed to know bond length of C—H bond. The methine C—H bond length of **1d** (0.95 Å) was found greater than **1a** (0.78 Å). The longer C—H bond length of **1d** might be related to more labiality of the C—H bond, therefore more acidity of methine proton, which is related to rate of initiation.[27] This fact is also supported by our experimental results, which reveals that at low conversion region (110°C), GPE undergoes 11 and 15% conversion with **1a** and **1d**, respectively, whereas no polymerization with **1b** and **1c** (Fig. 2). The single X-ray data and present experimental observation at 110°C reveal that the rate of initiation with **1d** is higher in comparison with other initiators. The conversion (11%) with **1a** is resultant of the longer propagation step, which is favored by least nucleophilicity of SbF_6^- among other counter anions, whereas no polymerization with **1b** and **1c**. After the initial stage of initiation, slow rate of polymerization was observed with **1d**, whereas with other initiators, it increases with the increase in experimental temperature according to their nucleophilicity. In the later stage, the initiator activity is controlled by propagation step, which depends upon nucleophilicity of counter anion. These observations indicate that the order of initiator activity is determined by combined effect of rate of initiation (depends upon acidity of methine proton) and rate of propagation (depending on nucleophilicity of counter anion), which is well supported by experimental results.

Further to confirm the above observed order of initiator activity for longer reaction time in low conversion region (130°C), the polymerization was performed with 1 mol % of **1a–1d** at 130°C for 70 h. Figure 3 shows the time–conversion relationship in polymerization of GPE. The conversion (%) increases with the increase in reaction time and attains respective limiting conversion. The initiator **1a** showed 100% conversion in 5 h, whereas other initiators have shown the maximum limiting conversions, which are 100% (70 h) with **1b**, 45% (70 h) with **1c**, and 100% (50 h) with **1d**. The order of initiator activity remains same in longer duration as similar to temperature-conversion curve and found as **1a**> **1d** > **1b** > **1c**.

Effect of phosphine moiety

To understand the effect of phosphines on initiator activity, polymerization of GPE was carried out with 1 mol % of 5-*H*-dibenzo(a,d)cyclohepten-5-yl-tri-*n*-butylphosphonium hexafluoroantimonate (**2a)** from 25 to 170°C for 1 h. The activity of **2a** was compared with that of **1a** as shown in Figure 4. It demonstrates that polymerization starts above 100 and 130°C with **1a** and **2a**, respectively, to afford the polymer with M_n of 2500–3800. At particular temperature 140°C, with **1a** and **2a**, the conversion was about 85 and 18%, respectively. The conversion (%) increases with the increase in experimental temperature and attains 100% conversion at 160 and 170°C with **1a** and **2a**, respectively. The higher activity of **1a** compared with **2a** may be attributed to the formation of more stable ylide with **1a.** This can be explained by extended conjugation of

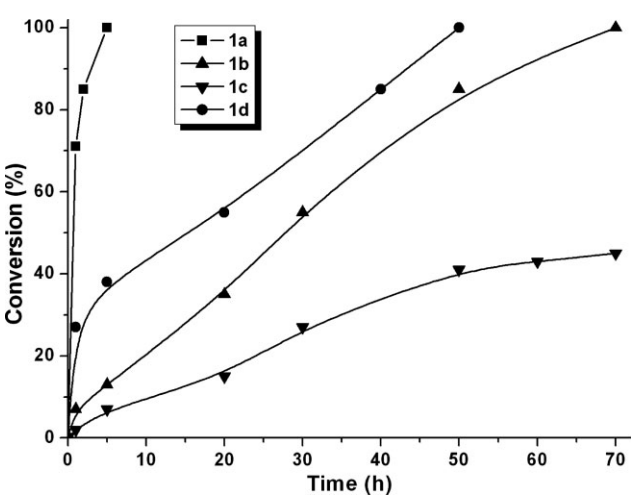


Figure 3 Time–conversion relationship in GPE polymerization with **1a–1d** at 130°C.

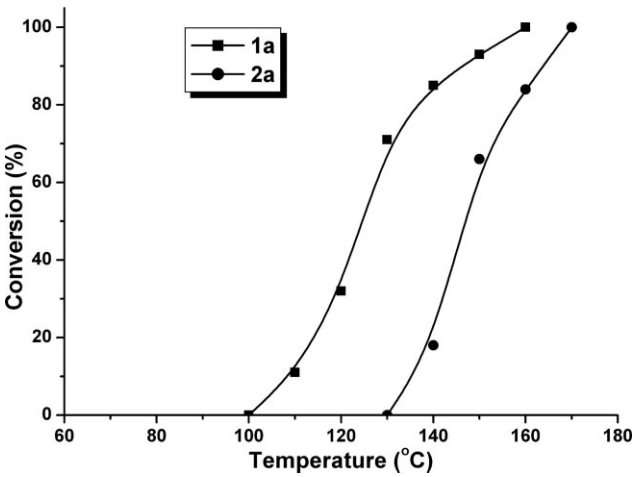


Figure 4 Temperature–conversion relationship in GPE polymerization with **1a** and **2a** for 1 h.

three phenyl rings of phosphine moiety when compared with *n*-butyl groups.[33,34] It is also supported by the higher δ value of methine proton of **1a** (at 6.82 ppm) in comparison of **2a** (at 5.77 ppm) in ^{1}H-NMR spectra. The higher shift in δ value of methine proton can be correlated with higher acidity, which is related to the initiator activity.[26]

Effect of double bond in dibenzocycloheptenyl ring

Figure 5 shows the temperature–conversion relationship in polymerization of GPE with 1 mol % of **1a** and **3a** at 25–160°C for 1 h. It can be seen that the conversion starts above 100°C with **1a**, whereas it begins above 110°C with **3a**, respectively, to afford the polymer with M_n of 2600–3800. With the increase in polymerization temperature, the conversion (%) increases with different rates. At 120°C, with **1a** and **3a** the conversion was about 32 and 15%, respectively. However, GPE attains 100% conversion with both initiators at 160°C. This indicates that at low-conversion region, the order of initiator activity was observed as **1a** > **3a**. This may be ascribed by the stability of resulting ylide with more extended conjugation. This fact is supported by the higher δ value of methine proton in ^{1}H-NMR spectra of **1a** (6.82 ppm) compared with **3a** (6.69 ppm).

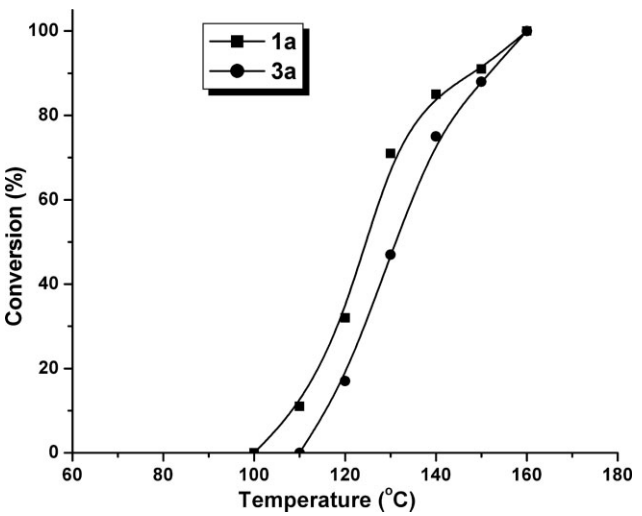


Figure 5 Temperature–conversion relationship in GPE polymerization with **1a** and **3a** for 1 h.

Thermal stability of phosphonium salts

Figure 6 shows the TGA thermogram of all the phosphonium salts under nitrogen atmosphere. The prepared initiators were found to be thermally stable up to 225°C above which their onset degradation temperatures were observed. Therefore, these compounds can be used up to 225°C. The aforementioned thermal properties of these salts might imply their prospective significance as latent thermal cationic initiator.

Solubility of phosphonium salts

The solubility of an initiator plays an important role in polymerization and curing of epoxy monomers.[1] Solubility of all the initiators was examined in various solvents and epoxy monomers (Table I). The solubility of initiators increases with the increase in polarity of solvents. All initiators were insoluble in nonpolar solvents such as toluene and diethyl ether. All the salts are soluble in acetone, dimethylsulfoxide (DMSO), *N*, *N*-dimethylformamide, and acetonitrile. Among the initiators, **2a** has good solubility in chloroform ($CHCl_3$), MeOH, and THF in comparison to other phosphonium salts, which can be attributed because of the presence of aliphatic (three *n*-butyl) groups. The solubility of initiators in epoxy

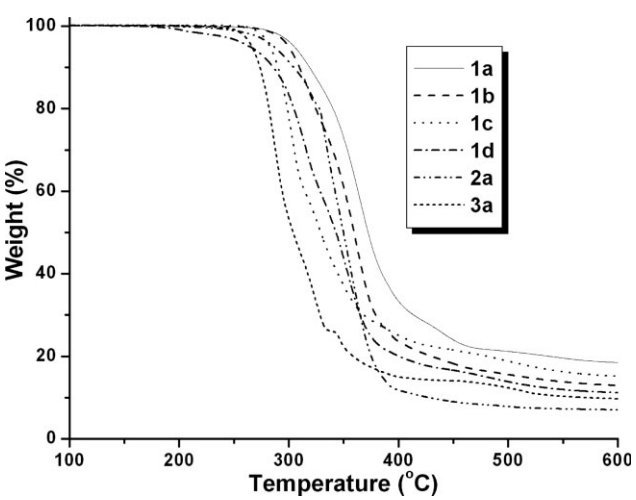


Figure 6 TGA thermograms of phosphonium salts.

TABLE I
Solubility of Phosphonium Salts in Various Solvent and Epoxy Monomers[a]

	Solvent									Epoxy monomer			
Initiator	$PhCH_3$	Et_2O	$CHCl_3$	THF	CH_3COCH_3	MeOH	DMSO	DMF	CH_3CN	GPE	CHO	ECH	PPO
1a	−	−	+	++	+++	+	+++	+++	+++	+++	+	+++	+++
1b	−	−	+	++	+++	+	+++	+++	+++	+++	+	+++	+++
1c	−	−	+	++	+++	+	+++	+++	+++	+++	+	+++	+++
1d	−	−	+	++	+++	+	+++	+++	+++	+++	+	+++	+++
2a	−	−	+++	+++	+++	++	+++	+++	+++	+++	+	+++	+++
3a	−	−	+	++	+++	++	+++	+++	+++	+++	+	+++	+++

PPO, propylene oxide; ECH, epichlorohydrine.
[a] Phosphonium salts (0.1 mmol) in various solvents and monomers at room temperature (+++, soluble in 0.3 mL of solvent; ++, soluble in 0.5 mL of solvent; +, partially soluble in 1.0 mL solvent; −, insoluble).

monomers such as GPE, cyclohexene oxide (CHO), propylene oxide (PPO), and epichlorohydrine (ECH) was also examined. The initiators have shown good solubility in GPE, PPO, and ECH and partial solubility in CHO. It may suggest the relevance of phosphonium salts as latent cationic initiator in curing applications.

CONCLUSIONS

The novel dibenzocycloheptene-based phosphonium salts having different counter anions, phosphine moiety, and dibenzocycloheptenyl nucleus were synthesized and their thermolatent behavior was examined in cationic polymerization of GPE. The order of initiator activity with different counter anions was found as **1a** > **1d** > **1b** > **1c**. The initiator activity was also found to be depending upon phosphine moiety (**1a** > **2a**) and cycloheptenyl nucleus (**1a** > **3a** in low conversion region). The properties of these initiators such as hygroscopic stability, solubility in GPE, and latency under ambient conditions may indicate their utility as latent thermal cationic initiator.

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References

1. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
2. Mark, H. F.; Gaylord, N. G.; Bikajes, N. M., Eds. Encyclopedia of Polymer Science and Technology; Interscience: New York, 1968; Vol. 8, p 303.
3. Yagci, Y.; Reetz, I. Prog Polym Sci 1998, 23, 1485.
4. Yagci, Y.; Endo, T. Adv Polym Sci 1997, 127, 59.
5. González, L.; Ramis, X.; Salla, J. M.; Mantecón, A.; Serra, A. J Appl Polym Sci 2008, 108, 1229,
6. Gupta, M. K.; Singh, R. P. Macromol Symp 2006, 240, 186.
7. Gupta, M. K.; Singh, R. P. Polym Bull, to appear; DOI: 10.1007/s00289-008-0014-y.
8. Gupta, M. K.; Singh, R. P. Macromol Res, to appear.
9. Murai, S.; Nakano, Y.; Hayase, S. J Appl Polym Sci 2001, 80, 181.
10. Gupta, M. K.; Singh, R. P. Polym Bull 2008, 60, 755.
11. Park, S. J.; Heo, G. Y. Macromol Chem Phys 2005, 206, 1134.
12. Garciá, S. J.; Serra, A.; Suay, J. J Appl Polym Sci 2007, 105, 3097.
13. Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. J Polym Sci Part A: Polym Chem 1991, 29, 1675.
14. Shimomura, O.; Tomita, I.; Endo, T. Macromol Rapid Commun 1998, 19, 493.
15. Hyun, D. H.; Patil, P.; Kim, J. Y.; Kim, T. H. J Appl Polym Sci 2007, 103, 3157.
16. Lee, S. B.; Takata, T.; Endo, T. Macromolecules 1991, 24, 2689.
17. Nakano, S.; Endo, T. J Polym Sci Part A: Polym Chem 1996, 34, 475.
18. Nakano, S.; Endo, T. J Polym Sci Part A: Polym Chem 1995, 33, 505.
19. Endo, T.; Sanda, F. Macromol Symp 1996, 107, 237.
20. Kim, M. S.; Lee, S. B.; Lee, K. W.; Endo, T. J Appl Polym Sci 2005, 95, 1439.
21. Kim, H.; Sanda, F.; Nakamura, Y.; Endo, T. Macromol Chem Phys 2000, 201, 1691.
22. Kim, H.; Sanda, F.; Endo, T. Macromolecules 2000, 33, 2359.
23. Kim, H.; Sanda, F.; Endo, T. Macromolecules 1999, 32, 8291.
24. Lee, S. D.; Takata, T.; Endo, T. Macromolecules 1996, 29, 3317.
25. Hino, T.; Endo, T. J Polym Sci Part A: Polym Chem 2004, 42, 362.
26. Toneri, T.; Sanda, F.; Endo, T. J Polym Sci Part A: Polym Chem 1998, 36, 1957.
27. Toneri, T.; Watanabe, K.; Sanda, F.; Endo, T. Macromolecules 1999, 32, 1293.
28. Takuma, K.; Takata, T.; Endo, T. Macromolecules 1993, 26, 862.
29. Armareqo, W. L. F.; Perrin, D. D. Purification of Organic Chemicals, 4th ed.; ButterWorth-Heinemann: Jordon Hill, Oxford, 1980.
30. Hamanzu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. Macromol Chem Rapid Commun 1992, 13, 203.
31. Brüker. SADABS (Version 2.05), SMART (Version 5.631), SAINT (Version 6.45) and SHELXTL (Version 6.14); Brüker AXS Inc.: Madison, WI, 2003.
32. Sheldrick, G. M. Acta Cryst A 2008, 64, 112.
33. Meriwether, L.; Fiene, M. L. J Am Chem Soc 1959, 81, 4200.
34. Jonson, A.; LaCount, R. B. Tetrahedron 1960, 9, 130.