Macromolecular Research, Vol. 17, No. 4, pp 221-226 (2009)

Thermally Induced Cationic Polymerization of Glycidyl Phenyl Ether Using Novel Xanthenyl Phosphonium Salts

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Received May 8, 2008; Revised October 7, 2008; Accepted October 7, 2008

Abstract: The present study firstly describes the synthesis of novel, thermo-latent initiators based on xanthenyl phosphonium salts with different counter anions and phosphine moieties and secondly examines their efficiency in the bulk polymerization of glycidyl phenyl ether (GPE). The polymerization was performed with phosphonium salt initiators ($\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$ and $\mathbf{I}_{BF4}$) at ambient temperature to 200 °C for 1 h. The order of initiator activity was $\mathbf{I}_{SbF6}$ > $\mathbf{I}_{PF6}$ > $\mathbf{I}_{AsF6}$ > $\mathbf{I}_{BF4}$. To examine the effect of the phosphine moiety on the initiator activity, polymerization was carried out with $\mathbf{I}_{SbF6}$ (Ph_3P) and $\mathbf{II}_{SbF6}$ (Bu_3P) at ambient temperature to 170 °C for 1 h. The order of reactivity was $\mathbf{I}_{SbF6}$ > $\mathbf{II}_{SbF6}$. In general, the conversion percentage increased with increasing polymerization temperature. The thermal stability of these salts was measured by thermo gravimetric analysis (TGA). The solubility of phosphonium salts in various organic solvents and epoxy monomers was also investigated.

Keywords: cationic polymerization, glycidyl phenyl ether, thermo-latent, phosphonium salts.

Introduction

In last few decades, importance of latent cationic initiators, which show activity by external stimulation such as heat or light, has been recognized in number of different industrial applications such as curing, adhesives, microelectronics and photolithography.[1-9] The development of efficient thermo-latent cationic initiators is desirable for their inherent storage stability, handling and solubility in monomers.[10] The glycidyl phenyl ether (GPE) monomer is widely used, as mono functional diluent in epoxy resins and modifier for dyes and fibers,[11] is used as model monomers to study the activity of thermo-latent cationic initiators.[2] The onium salts initiators such as benzylsulfonium,[12-14] benzylpyridinium,[15-17] benzyl ammonium,[18] hydrazinium,[19] and benzylphosphonium[20] have been developed as potential thermo-latent initiators for cationic polymerization of GPE. Unlike other benzyl onium salts those generate benzyl cations, benzyl phosphonium salts generate protons as an active species and form stable ylides.[20] It is also well established that in comparison of sulfonium, pyridinium and ammonium salts, phosphonium counter parts offer a great variety of reactivities because of their d-orbital participation.[20,21] Earlier, Endo *et al.*[21,22] have employed fluorenyl phosphonium salts, which exhibited the better activity than benzyl phosphonium salts[20] due to the higher acidity of fluorenyl methine proton. The acidity of methine proton, which determines the activity of initiators, depends on stability of resulting ylide. Therefore, it is worthwhile to synthesize novel phosphonium salt initiators with good solubility, thermal stability and higher activity. Considering the above-mentioned points, it was aimed to prepare thermo-latent cationic initiators based on novel xanthenyl phosphonium salts, which can produce stable ylides on thermal initiation, which are responsible for higher initiator activity. The present article describes the synthesis of novel xanthenyl phosphonium salts with different counter anions and phosphine moiety and examines their efficiency ($\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$, $\mathbf{I}_{BF4}$ and $\mathbf{II}_{SbF6}$) as thermo-latent initiator in cationic polymerization of glycidyl phenyl ether.

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Experimental

Materials. Xanthydrol, triphenylphosphine (Ph_3P), tri-*n*-butylphosphine (Bu_3P), sodium hexafluoroantimonate ($NaSbF_6$), potassium hexafluorophosphate (KPF_6), sodium hexafluoroarsenate ($NaAsF_6$), sodium tetrafluoroborate ($NaBF_4$), glycidyl phenyl ether (GPE) were purchased from Aldrich Chemicals. All other chemicals (AR grade) were purchased from S.D. Fine Chemicals Ltd, Mumbai, India and used after purification.[23] GPE was dried and distilled over CaH_2 just before polymerization.

Characterization. Molecular weight was measured by GPC in THF as eluent (flow rate: 1 mL/min) on a setup consisting of a pump and six Ultra Styragel column (50 to 10^5 Å porosities) and detection was carried out with the aid of UV-100 and RI-150 detectors. Molecular weight (M_n) and poly-

dispersities (M_w/M_n) were determined using a calibration curve obtained by polystyrene standards. NMR (^1H, ^{13}C & ^{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. IR spectra were recorded on a Perkin-Elmer (model 683) grating FT-IR spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash EA-1112 Microanalyzer instrument. Thermal stability was analyzed using Perkin-Elmer TGA-7, by heating the initiators from 50-900 °C with a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate 20 mL/min.

Synthesis of Xanthenyltriphenylphosphonium Chloride (I_{Cl}). To the magnetically stirring suspension of xanthydrol (1.96 g, 10 mmol) in *n*-hexane (20 mL), was added drop-wise a solution of $SOCl_2$ (1.46 mL, 20 mmol) in *n*-hexane (10 mL) at ambient temperature. After complete addition, reaction mixture was allowed to reflux for 30 min till the solution becomes clear. This solution was cooled up to ambient temperature and evaporated under vacuum. The residue was dissolved in toluene (30 mL) and Ph_3P (2.62 g, 10 mmol) in toluene (15 mL) was added drop-wise and stirred for 1 h. The resulting white precipitate was filtered, washed with toluene and recrystallized from ethanol-CH_2Cl_2 (8:2), Yield: 2.24 g (47 %), Elemental analysis: $C_{31}H_{24}ClOP$ (478.05 g mol^{-1}) Calcd. C, 77.82; H, 5.01. Found: C, 77.86; H, 4.98.

Synthesis of Xanthenyltriphenylphosphonium Hexafluoroantimonate (I_{SbF6}). To a solution of I_{Cl} (1.43 g, 3 mmol) in methanol, a solution of $NaSbF_6$ (0.77 g, 3 mmol) in deionised water was added and allowed to stirr at ambient temperature for 30 min. The white precipitate was filtered, washed with plenty of water and finally recrystallized with ethanol-CH_2Cl_2 (8:2), Yield: 1.57 g (77 %), mp. 248-249 °C, Elemental analysis: $C_{31}H_{24}OPSbF_6$ (678.05 g mol^{-1}) Calcd. C, 54.82; H, 3.56. Found: C, 54.82; H, 3.60. IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^1H NMR (DMSO-d_6): δ= 7.97-7.09 (m, 23H, Ph), 7.05 (1H, CH) ppm, ^{13}C NMR (DMSO-d_6): δ= 153.84, 135.35, 134.46, 130.95, 130.52, 130.10, 129.86, 124.27, 117.12, 116.43, 114.82, 113.60, 39.76, 38.88 ppm. ^{31}P NMR (DMSO-d_6): δ = 21.42 ppm.

Synthesis of Xanthenyltriphenylphosphonium Hexafluorophosphate (I_{PF6}). This compound was prepared by reaction of I_{Cl} (1.43 g, 3 mmol) with KPF_6 (0.55 g, 3 mmol) in the same manner as described for I_{SbF6}. Yield: 1.11 g (63 %), mp. 246-247 °C, Elemental analysis: $C_{31}H_{24}OP_2F_6$ (588.12 g mol^{-1}) Calcd. C, 63.27; H, 4.11. Found: C, 63.38; H, 4.09. IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^1H NMR (DMSO-d_6): δ= 7.97-7.09 (m, 23H, Ph), 7.05 (1H, CH) ppm. ^{13}C NMR (DMSO-d_6): δ= 153.95, 135.34, 134.65, 131.02, 130.51, 130.09, 129.86, 124.33, 117.19, 116.42, 114.82, 113.61, 37.91, 38.88 ppm. ^{31}P NMR (DMSO-d_6): δ= 21.41 ppm.

Synthesis of Xanthenyltriphenylphosphonium Hexafluoroarsenate (I_{AsF6}). This compound was prepared by reaction of I_{Cl} (1.43 g, 3 mmol) with $NaAsF_6$ (0.64 g, 3 mmol) in the same manner as described for I_{SbF6}. Yield: 1.31 g (69%), mp. 251-252 °C. Elemental analysis: Cal for: $C_{31}H_{24}OPAsF_6$ (632.07 g mol^{-1}) Calcd. C, 58.88; H, 3.83. Found: C, 58.80; H, 3.83. IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^1H NMR (DMSO-d_6): δ= 7.97-7.09 (m, 23H, Ph), 7.05 (1H, CH) ppm. ^{13}C NMR (DMSO-d_6): δ= 153.95, 135.34, 134.65, 131.02, 130.50, 130.09, 129.85, 124.27, 117.13, 116.42, 114.82, 113.61, 39.72, 38.89 ppm. ^{31}P NMR (DMSO-d_6): δ= 21.41 ppm.

Synthesis of Xanthenyltriphenylphosphonium Tetrafluoroborate (I_{BF4}). This compound was prepared by reaction of I_{Cl} (1.43 g, 3 mmol) with $NaBF_4$ (0.33 g, 3 mmol) in the same manner as described for I_{SbF6}. Yield: 0.67 g (42%), mp. 248-250 °C, Elemental analysis: $C_{31}H_{24}OPBF_4$ (530.16 g mol^{-1}) Calcd. C, 70.21; H, 4.56. Found: C, 70.16; H, 4.57, IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}, ^1H NMR (DMSO-d_6): δ= 7.97-7.09 (m, 23H, Ph), 7.05 (1H, CH) ppm. ^{13}C NMR (DMSO-d_6): δ= 153.94, 135.31, 134.65, 130.96, 130.52, 130.11, 124.28, 117.19, 116.43, 114.83, 113.70, 39.70, 38.86 ppm. ^{31}P NMR (DMSO-d_6): δ= 21.42 ppm.

Synthesis of Xanthenyltri-*n*-butylphosphonium Hexafluoroantimonate (II_{SbF6}). This compound was synthesized in similar manner as described for I_{Cl} and followed by anion exchange with $NaSbF_6$.Yield: 1.98 g (65%), mp. 216 °C,

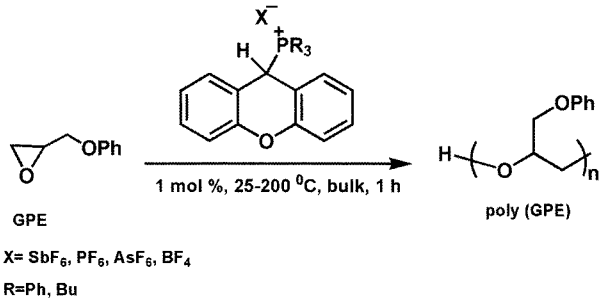
Table I. Solubility of Phosphonium Salts in Various Solvents and Epoxy Monomers

Initiator	Solvent										Epoxy Monomer				
	$PhCH_3$	Et_2O	$CHCl_3$	THF	CH_3COCH_3	MeOH	DMSO	DMF	CH_3CN	H_2O	GPE	PPO	ECH	CHO	EEC
I_{SbF6}	-	-	+	++	+++	+	+++	+++	+++	-	+++	+++	+++	+	-
I_{PF6}	-	-	+	++	+++	+	+++	+++	+++	-	+++	+++	+++	+	-
I_{AsF6}	-	-	+	++	+++	+	+++	+++	+++	-	+++	+++	+++	+	-
I_{BF4}	-	-	+	++	+++	+	+++	+++	+++	-	+++	+++	+++	+	-
II_{SbF6}	-	-	+++	+++	+++	++	+++	+++	+++	-	+++	+++	+++	+	+

Conditions: 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).

Elemental analysis: $C_{25}H_{36}OPSbF_6$ (665.39 g mol^{-1}) Calcd. C, 48.54; H, 5.81 Found: C, 48.46; H, 5.75, IR (KBr): 3030, 2930, 2868, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}, ^1H NMR (DMSO-d_6): δ= 7.60-7.25 (m, 8H, Ph), 5.70, 5.63 (CH, 1H), 2.09 (m, CH_2, 6H), 1.30 (m, CH_2, 12H), 0.86 (t, CH_3, 9H) ppm, ^{13}C NMR (DMSO-d_6): δ= 153.06, 130.65, 129.57, 124.94, 117.30, 115.38, 34.87, 34.03, 23.53, 23.23, 22.45, 16.68, 15.82, 13.06 ppm. ^{31}P NMR (DMSO-d_6): 37.08 ppm.

Polymerization Procedure. A mixture of GPE (5 mmol, 0.65 mL) and initiator (0.05 mmol, $\mathbf{I}_{SbF6}$, 33.90 mg, $\mathbf{I}_{PF6}$, 29.40 mg, $\mathbf{I}_{AsF6}$, 31.59 mg, $\mathbf{I}_{BF4}$, 26.50 mg, $\mathbf{II}_{SbF6}$, 31.44 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 at the required temperature. After the reaction for set time, the ampoule was cooled in liquid nitrogen bath. The monomer conversion was determined by ^1H NMR spectroscopy from the crude polymerization mixture before precipitation.[24] The polymerization mixture was dissolved in CH_2Cl_2 and precipitated with methanol. The polymer was separated from the supernatant by decantation and dried under vacuum. The molecular weight of polymer was determined by gel permeation chromatography (GPC). The obtained polymer was identified to be poly(GPE). ^1H 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}.



Scheme II. Polymerization of GPE.

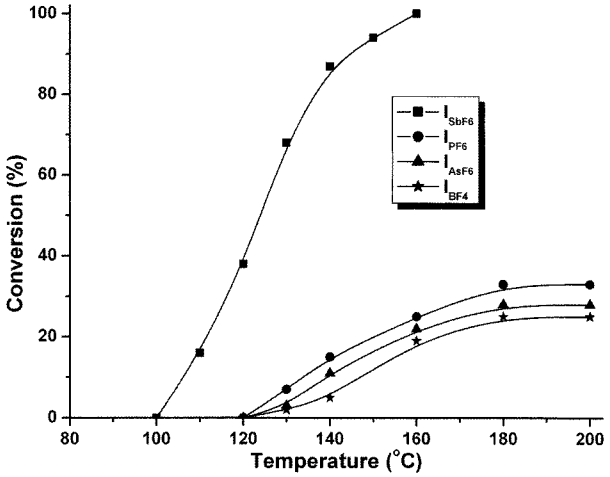


Figure 1. Effect of temperature on polymerization of GPE with $\mathbf{I}_x$ for 1 h.

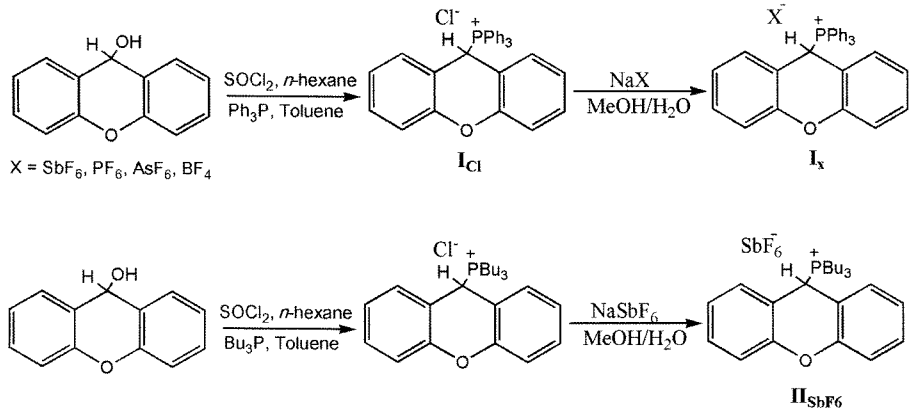
Results and Discussion

Initiators. The xanthenyl phosphonium salts ($\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$, $\mathbf{I}_{BF4}$ and $\mathbf{II}_{SbF6}$) were synthesized and characterized by NMR (^1H, ^{13}C & ^{31}P), IR and elemental analysis as described in experimental section (Scheme I).

Polymerization.

Effect of Counter Anion: The polymerization of GPE was carried out with 1 mol% of initiator ($\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$ and $\mathbf{I}_{BF4}$) at 25-200 °C for 1 h (Scheme II). The phosphonium salts were completely soluble in GPE at ambient temperature but GPE did not polymerize at all under ambient condition.

Figure 1 shows the temperature-conversion curve of the polymerization. The polymerization of GPE proceed above 100, 120, 120 and 120 °C temperature with $\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$, and $\mathbf{I}_{BF4}$, respectively to afford the polymer with molecular weight (M_n) of 1,400-3,400. This reveals the thermal latency characteristic of these phosphonium salt initiators. Above



Scheme I. Synthesis of phosphonium salts.

these temperatures conversion (%) increases with various rates with the increase in polymerization temperature and attains their limiting conversion. Among all the initiators, the maximum conversion (100%) has been found with $\mathbf{I}_{SbF6}$ at 160 °C with highest rate of conversion. For example, above the threshold temperature, at particular point, $\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$ and $\mathbf{I}_{BF4}$ have shown 16% (at 110 °C), 7% (130 °C), 3% (130 °C) and 2% (130 °C) conversion, respectively. Similarly, other than $\mathbf{I}_{SbF6}$, which attains 100% conversion at 160 °C, other initiators have shown the limiting conversions at 200 °C, which are 33% with $\mathbf{I}_{PF6}$, 28% with $\mathbf{I}_{AsF6}$, and 25% with $\mathbf{I}_{BF4}$. The overall order of initiator activity was found as $\mathbf{I}_{SbF6} > \mathbf{I}_{PF6} > \mathbf{I}_{AsF6} > \mathbf{I}_{BF4}$. The difference in activity can be explained by nucleophilicity of the counter anion ($SbF_6^- < PF_6^- < AsF_6^- < BF_4^-$), which depends on inter-ionic distance between the oxonium cation and counter anions. The longer inter-ionic distance denotes the lesser nucleophilicity of counter anion, hence more activity of the initiator.[22]

Further to confirm the order of initiator activity in low conversion region (at 135 °C) for longer reaction time (70 h), the polymerization of GPE was performed with 1 mol% of initiator ($\mathbf{I}_{SbF6}$, $\mathbf{I}_{PF6}$, $\mathbf{I}_{AsF6}$ and $\mathbf{I}_{BF4}$). Figure 2 shows time-conversion curve in the polymerization of GPE. The monomer conversion increases with the increase in reaction time and attains respective limiting conversion. The initiator $\mathbf{I}_{SbF6}$, which showed 100% conversion in 4 h, while other initiators have shown the maximum limiting conversions after 70 h, which are 100% with $\mathbf{I}_{PF6}$, 80% with $\mathbf{I}_{AsF6}$, and 69% with $\mathbf{I}_{BF4}$. The order of initiator activity remains same in longer duration and found as $\mathbf{I}_{SbF6} > \mathbf{I}_{PF6} > \mathbf{I}_{AsF6} > \mathbf{I}_{BF4}$.

Effect of Phosphine Moiety. Figure 3 shows temperature-conversion curve in polymerization of GPE with Ph_3P ($\mathbf{I}_{SbF6}$) and Bu_3P ($\mathbf{II}_{SbF6}$) based phosphonium salts (1 mol%) at 25-170 °C temperature for 1 h. It can be seen that the conversion is started above 100 and 130 °C with $\mathbf{I}_{SbF6}$ and $\mathbf{II}_{SbF6}$,

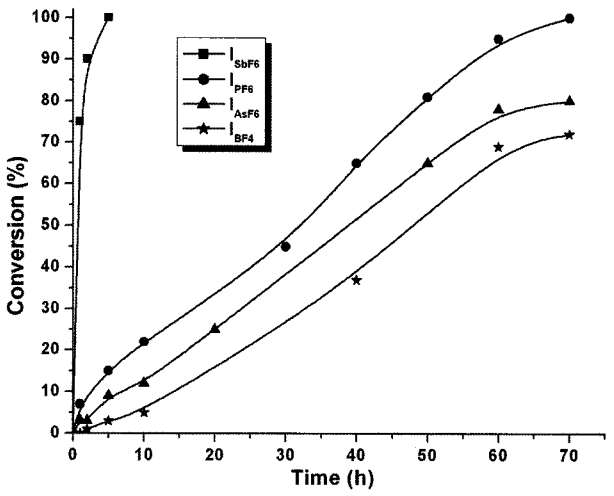


Figure 2. Effect of time on polymerization of GPE with $\mathbf{I}_x$ at 135 °C.

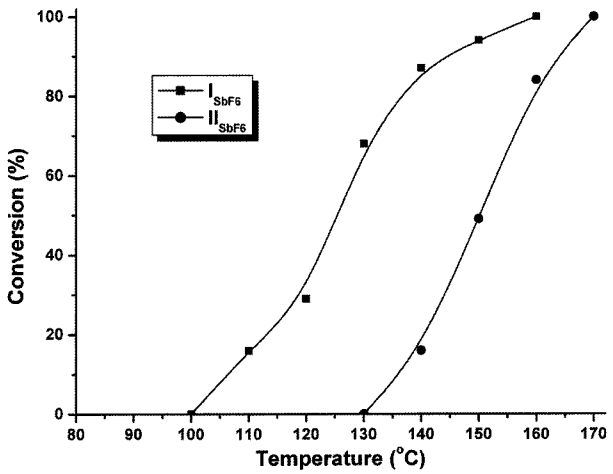


Figure 3. Effect of temperature on polymerization of GPE with $\mathbf{I}_{SbF6}$ & $\mathbf{II}_{SbF6}$ for 1 h.

respectively to afford the polymer with molecular weight (M_n) of 2,600-3,400. With the increase in polymerization temperature, the conversion (%) increases with different rates. The maximum conversion (100%) has been found with $\mathbf{I}_{SbF6}$ and $\mathbf{II}_{SbF6}$ at 160 and 170 °C, respectively. The order of initiator activity was observed as $\mathbf{I}_{SbF6} > \mathbf{II}_{SbF6}$. It can be attributed to the fact that the acidity of methine proton, which is higher for $\mathbf{I}_{SbF6}$ than $\mathbf{II}_{SbF6}$. The increase in acidity of methine proton in $\mathbf{I}_{SbF6}$ can be explained by – I effect of three phenyl rings of phosphine moiety, whereas + I effect of butyl groups in $\mathbf{II}_{SbF6}$ decrease the acidity of methine proton. This phenomenon is supported by chemical shift of methine proton of xanthenyl phosphonium salts $\mathbf{I}_{SbF6}$ and $\mathbf{II}_{SbF6}$ at 7.05 and 5.70 ppm in ^{1}H NMR, respectively (Figures 4 & 5). In addition, the higher reactivity of $\mathbf{I}_{SbF6}$ can also be attributed to the formation of more stable ylide on thermal initiation. The stability of ylide can be explained by extended conjugation of three phenyl rings of triphenyl phosphine with xanthene nucleus compare to *n*-butyl groups.[25,26]

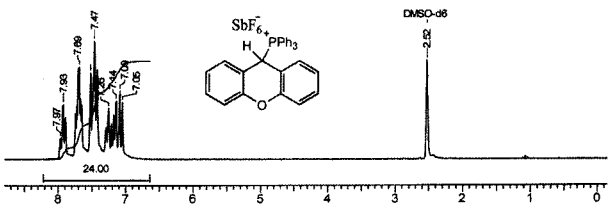


Figure 4. ^{1}H NMR spectra of $\mathbf{I}_{SbF6}$.

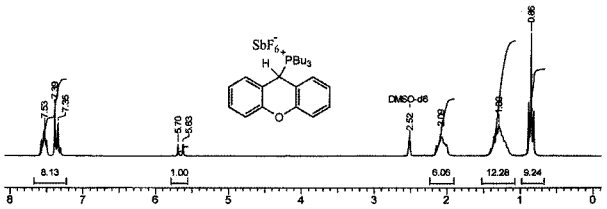


Figure 5. ^{1}H NMR spectra of $\mathbf{II}_{SbF6}$.

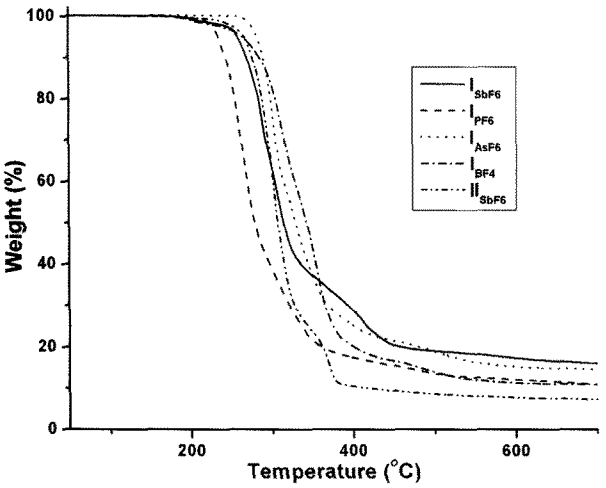


Figure 6. TGA thermograms of xanthenyl phosphonium salts.

Thermal Stability of Phosphonium Salts. Figure 6 shows TGA thermograms of xanthenyl phosphonium salts under nitrogen atmosphere. It can be seen that these salts are stable up to 225 °C and above which the onset degradation temperature were observed. Thus, the thermal stability of these salts up to 225 °C may indicate their use as thermo-latent cationic initiator in curing applications.

Solubility of Phosphonium Salts. The solubility of initiators in various solvents and monomers plays an important role in curing applications.[27] The solubility of prepared salts in various organic solvent and epoxy monomers was examined at room temperature (Table I). These salts are fairly soluble in polar solvents such as acetone, acetonitrile, dimethylsulfoxide and *N,N*-dimethylformamide. Among the phosphonium salts examined, $\mathbf{II_{SbF6}}$ show better solubility in tetrahydrofuran and chloroform in comparison of other salts. This enhanced solubility can be attributed to presence of three *n*-butyl groups in $\mathbf{II_{SbF6}}$. These initiators are insoluble in less polar solvent such as toluene and diethyl ether. The solubility of initiators in epoxy monomers such as GPE, CHO, propylene oxide (PPO), epichlorohydrine (ECH) and 3,4-epoxycyclohexylmethyl-3, 4-epoxycyclohexanemethylcarboxylate (EEC) was also examined. The prepared initiators have good solubility in GPE, PPO and ECH whereas they are sparingly soluble in CHO and insoluble in EEC. The counter anion has no significant effect on solubility of the initiators in monomers and solvents. However, the presence of aliphatic groups in phosphine moiety enhances the solubility. The above solubility characteristics might indicate their use as thermo-latent cationic initiator in curing applications.

Conclusions

In summary, novel thermo-latent initiators based on xanthenyl phosphonium salts with different counter anions and phosphine moiety were synthesized and their efficiency was studied in polymerization of glycidyl phenyl ether (GPE). These initiators are thermally stable, well soluble in monomer (GPE), easy to handle and initiates polymerization of GPE on thermal initiation. The order of initiator activity with respect to counter anion was found as $\mathbf{I_{SbF6} > I_{PF6} > I_{AsF6} > I_{BF4}}$ and with different phosphine moiety was observed as $\mathbf{I_{SbF6} > II_{SbF6}}$. Therefore, initiator activity of phosphonium salts can be controlled by modification of phosphine and nucleophilicity of counter anion.

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

References

(1) H. F. Mark, N. G. Gaylord, and N. M. Bikajes, *Encyclopedia of Polymer Science and Technology,* Interscience, New York, 1968, Vol. **8**, pp 303.
(2) Y. Yagci and I. Reetz, *Prog. Polym. Sci.*, **23**, 1465 (1998).
(3) Y. Yagci and T. Endo, *Adv. Polym. Sci.*, **127**, 59 (1997).
(4) S.-J. Park, F.-L. Jin, and J.-R. Lee, *Macromol. Res.*, **13**, 8 (2005).
(5) Y.-M. Jeon, S.-H. Kim, and M.-S. Gong, *Macromol. Res.*, **13**, 553 (2005).
(6) D. Ratna and A. K. Banthia, *Macromol. Res.*, **12**, 11 (2004).
(7) S. Y. Pyun and W. G. Kim, *Macromol. Res.*, **11**, 202 (2003).
(8) P. H. Kang, J. S. Park, and Y. C. Nho, *Macromol. Res.*, **10**, 332 (2002).
(9) J. K. Lee, Y. Choi, J. -R. Lee, and J. Park, *Macromol. Res.*, **10**, 34 (2002).
(10) S. Murai, Y. Nakano, and S. Hayase, *J. Appl. Polym. Sci.*, **80**, 181 (2000).
(11) H. Morikawa, A. Sudo, H. Nishida, and T. Endo, *J. Appl. Polym. Sci.*, **96**, 372 (2005).
(12) F. Hamazu, S. Akashi, T. Koizumi, T. Takata, and T. Endo, *J. Polym. Sci. Polym. Chem.*, **29**, 1675 (1991).
(13) O. Shimomura, T. Sato, I. Tomita, and T. Endo, *Macromolecules,* **31**, 2013 (1998).
(14) O. Shimomura, I. Tomita, and T. Endo, *Macromol. Rapid Commun.*, **19**, 493 (1998).
(15) S. B. Lee, T. Takata, and T. Endo, *Macromolecules,* **23**, 431 (1990).
(16) S. B. Lee, T. Takata, and T. Endo, *Macromolecules,* **24**, 2689 (1991).
(17) S. Nakano and T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 475 (1996).
(18) S. Nakano and T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **33**, 505 (1995).
(19) M. S. Kim, S. B. Lee, K. B. Lee, and T. Endo, *J. Appl. Polym. Sci.*, **95**,1439 (2005).
(20) K. Takuma, T. Takata, and T. Endo, *Macromolecules,* **26**, 862 (1993).
(21) T. Toneri, F. Sanda, and T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **6**, 1957 (1998).
(22) T. Toneri, K. Watanabe, F. Sanda, and T. Endo, *Macromole-*

cules, **32**, 1293 (1999).
(23) W. L. F. Armareqo and D. D. Perrin, *Purification of Organic Chemicals*, 4th ed., ButterWorth-Heinemann, Linecre House, Jordon Hill, Oxford OX2 8 DP.
(24) F. Hamanzu, S. Akashi, T. Koizumi, T. Takata, and T. Endo, *Macromol. Chem. Rapid Commun.,* **13**, 203 (1992).
(25) L. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.,* **81**, 4200 (1959).
(26) A. Jonson and R. B. LaCount, *Tetrahedron,* **9**, 130 (1960).
(27) H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.