Polymer Bulletin 60, 755–763 (2008)
DOI 10.1007/s00289-008-0910-1

Polymer Bulletin

Cationic Polymerization of Epoxides using Novel Xanthenyl Phosphonium Salts as Thermo-latent Initiator

Mukesh Kumar Gupta and Raj Pal Singh (✉)

Polymer Science and Engineering Division, National Chemical Laboratory, Pune – 411 008, India
E-mail: rp.singh@ncl.res.in; Fax: +91-20-25902615

Received: 6 January 2008 / Revised version: 6 February 2008 / Accepted: 6 February 2008

Summary

The present article describes the effect of steric and electronic factors on the efficiency of initiators based on novel xanthenyl phosphonium salts for cationic polymerization of epoxide monomers. 2-substituted ($I_{H,}$ $I_{Cl,}$ $I_{Me,}$ and I_{OMe}) xanthenyl phosphonium hexafluoroantimonate were synthesized and characterized by NMR (^{1}H, ^{13}C and ^{31}P) and IR spectroscopy. The order of initiator activity in polymerization of glycidyl phenyl ether (GPE), was found as $I_H > I_{Cl} > I_{Me} > I_{OMe}$. To understand the effect of steric factor, the polymerization of cyclohexene oxide (CHO) was performed and the order of activity was found as $I_{Cl} > I_H > I_{Me} > I_{OMe}$. All the initiators were found to be latent at ambient temperature and initiates polymerization on thermal initiation. The order of initiator activity was influenced by electronic and steric factors in the system. The thermal stability of these salts was measured by Thermo gravimetric analysis (TGA). The solubility of the initiators in various organic solvents and epoxy monomers is also discussed.

Introduction

Externally stimulated cationic polymerization has received considerable attention in various industrial applications such as printing inks, adhesive, surface coating and photolithography [1, 2]. Since a few decades, a variety of latent cationic initiators, which show no activity under ambient condition but results active species on external stimulation such as heating or photo-irradiation, have been developed [3-6]. In recent years, for preparation of thermosetting resins, the availability of broad variety of cationic initiators has gained momentum, in comparison to anhydride and amine based initiators that are highly toxic and have low storage stability. Therefore, the development of efficient thermo-latent cationic initiators is more desirable to overcome these shortcomings [7, 8]. The onium salts such as benzyl sulfonium, [9-11] benzyl pyridinium, [12-14], benzyl ammonium [15], hydrazinium [16], and phosphonium salts [17] have been developed as thermo-latent initiator for cationic polymerization of glycidyl phenyl ether (GPE). This monomer is widely used, as mono functional diluent in epoxy resins and modifier for dyes and fibers [18, 19], and has been used as model monomers to study the efficiency of latent thermal cationic initiators [5]. The chemistry of phosphonium salts is well recognized as Wittig salt and is used to prepare various olefinic intermediates in organic synthesis [20]. It is well known that phosphonium salts have an advantage over other onium (sulfonium, pyridinium and ammonium) salts and offer a great variety of reactivity due to participation of d-orbital [21-23]. Therefore, the synthesis of initiators with good solubility, thermal stability and higher activity is desirable. Considering the requirement of wide variety of activity of initiators, we have aimed to prepare thermo-latent cationic initiators based on novel phosphonium salts, which can produce more stable ylides on heating which are responsible for higher initiator activity. Recently, we have prepared novel xanthenyl phosphonium salts, for cationic polymerization of GPE, with variety of initiator efficiency by changing counter anions (SbF_6^-, PF_6^-, AsF_6^- and BF_4^-) and phosphine moiety [24]. It was planned to examine the control over the initiation by having different substituents on xanthenyl ring. This report describes the synthesis of novel thermo-latent cationic initiators based on 2-substituted xanthenyl phosphonium ($I_{H,}$ $I_{Cl,}$ $I_{Me,}$ and I_{OMe}) salts with SbF_6^- counter anion and discusses the effect of the substituents on their initiation activity in polymerization of epoxides.

Experimental

Materials

2-Chloro xanthone, 2-methyl xanthone and 2-methoxy xanthone were prepared as reported [25, 26]. Xanthydrol, sodium hexafluoroantimonate ($NaSbF_6$), triphenylphosphine (Ph_3P), glycidyl phenyl ether (GPE) and cyclohexene oxide (CHO) were purchased from Aldrich Chemicals. All other chemicals (> 99 %) were purchased from S.D. Fine Chemicals Ltd, Mumbai, India and used as received. The monomer (GPE and CHO) and solvent (CH_2Cl_2) were dried and distilled over CaH_2 just before polymerization.

Synthesis of 2- Chloro xanthydrol

To the solution of 2-chloro xanthone with NaOH in ethanol, Zn dust was added at 70 ºC and allowed to stir for 2 h. The reaction mixture was cooled and poured in ice-cold water. The resulting white precipitate was filtered and dried under vacuum.
Yield: 89 %, Elemental analysis: $C_{13}H_9ClO_2$ (232.52 g mol^{-1}) Calc. C 67.11 H 3.90. Found: C 67.03, H 3.87. ^{1}H NMR ($CDCl_3$): $\delta = 8.20\text{-}6.80$ (m, 7H, Ph), 6.94 (d, 1H, CH), 2.0 (s, 1H, OH) ppm.

Synthesis of 2- Methyl xanthydrol

This compound was synthesized in similar manner as described for 2- chloro xanthydrol. Yield: 85 %, Elemental analysis: $C_{14}H_{12}O_2$ (212.08 g mol^{-1}) Calc. C 79.22 H 5.70. Found C 79.13 H 5.74. ^{1}H NMR ($CDCl_3$): $\delta = 8.20\text{-}6.80$ (m, 7H, Ph), 6.94 (d, 1H, CH), 2.37(s, 3H, CH_3), 2.0 (s, 1H, OH) ppm.

Synthesis of 2- Methoxy xanthydrol

This compound was synthesized in similar manner as described for 2- chloro xanthydrol. Yield: 80 %, Elemental analysis: $C_{14}H_{12}O_3$ (228.08 g mol^{-1}) Calc. C 73.67, H 5.30. Found C 73.63, H 5.38. ^{1}H NMR ($CDCl_3$): δ = 8.20-6.80 (m, 7H, Ph), 6.94 (d, 1H, CH), 3.73 (s, 3H, CH_3), 2.0 (s, 1H, OH) ppm.

Synthesis of Xanthenyltriphenylphosphonium Hexafluoroantimonate (I_H)

To the suspension of xanthydrol (10 mmol, 1.96 g) in *n*-hexane (20 mL), $SOCl_2$ (20 mmol, 1.46 mL) was added and refluxed for 30 minute till the solution become clear. The reaction mixture was cooled and concentrated under vacuum. To the resulting residue, Ph_3P (10 mmol, 2.62 g) in toluene (15 mL) was added and allowed to stir for 1 h. The appeared precipitate was filtered, washed with toluene and its anion was exchanged with $NaSbF_6$ (10 mmol, 2.58 g) in MeOH/H_2O mixture, which gives white precipitate, which was recrystallized with ethanol-CH_2Cl_2 (8:2). Yield: 72 %, White crystals, Elemental analysis: $C_{31}H_{24}OPSbF_6$ (678.05 g mol^{-1}) Calc. C 54.82. H 3.56. Found C 54.72, H 3.60 ppm. IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.97-7.09 (m, 23 H, Ph), 7.01 (1H, CH) ppm. ^{13}C NMR (200 MHz, 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 (200 MHz, DMSO-d_6): δ = 21.42 ppm.

Synthesis of 2-Chloro-xanthenylphosphonium Hexafluoroantimonate (I_{Cl})

This compound was synthesized in similar manner as described for $\mathbf{I_H}$.
Yield: 75 %, White crystals, Elemental analysis: $C_{32}H_{23}ClOPSbF_6$ (714.01 g mol^{-1}) Calc. C 52.17, H 3.25. Found C 52.17, H 3.18. IR (KBr): 3030, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.98-7.09 (m, 22 H, Ph), 7.02 (s, 1 H, CH) ppm. ^{13}C NMR (200 MHz, DMSO-d_6): δ = 153.61, 152.66, 135.42, 134.54, 131.55, 130.11, 129.88, 127.55, 124.55, 118.65, 117.24, 116.30, 115.56, 114.69, 113.26, 39.41, 38.57 ppm. ^{31}P NMR (200 MHz, DMSO-d_6): 21.72, 25.67 ppm.

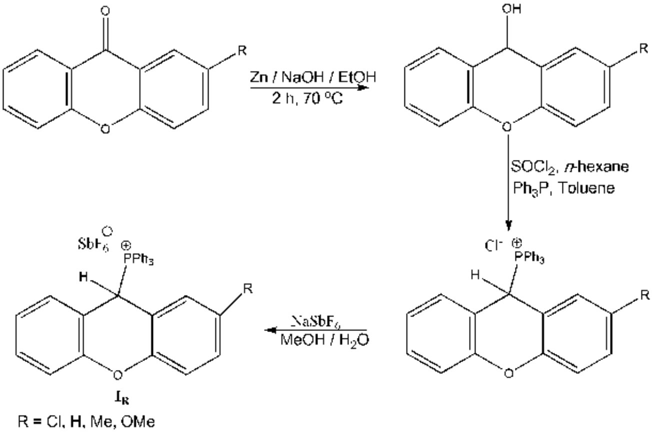
Synthesis of 2-Methyl xanthenylphosphonium Hexafluoroantimonate (I_{Me})

This compound was synthesized in similar manner as described for $\mathbf{I_H}$.
Yield: 65 %, White crystals, Elemental analysis: $C_{33}H_{26}OPSbF_6$ (692.07 g mol^{-1}) Calc. C 55.44 H 3.78. Found C 55.38 H 3.75. IR (KBr): 3030, 2926, 2835, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.98-7.09 (m, 22 H, Ph), 6.94 (d, 1H, CH), 2.15 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz, DMSO-d_6): δ =154.13, 151.84, 135.25, 134.75, 133.02, 131.18, 129.97, 128.86, 124.02, 116.66, 115.07, 113.71, 39.76, 38.95, 20.07 ppm. ^{31}P NMR (200 MHz, DMSO-d_6): 21.14, 25.88 ppm.

Synthesis of 2-Methoxy xanthenylphosphonium Hexafluoroantimonate (I_{OMe})

This compound was synthesized in similar manner as described for $\mathbf{I_H}$.
Yield: 59 %, White crystals, Elemental analysis: $C_{33}H_{26}O_2PSbF_6$ (708.06 g mol^{-1}) Calc. C 54.19 H 3.69. Found C 54.19 H 3.75. IR (KBr): 3030, 2941, 2832, 1625, 1600, 1500, 1463, 1439, 1065, 743, 720, 687 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 7.98-7.09 (m, 22 H, Ph), 6.70 (s, 1H, CH), 3.75 (s, 3H, CH_3) ppm. ^{13}C NMR (200 MHz, DMSO-d_6): δ = 155.11, 154.28, 147.75, 135.24, 134.72, 134.54, 131.55,

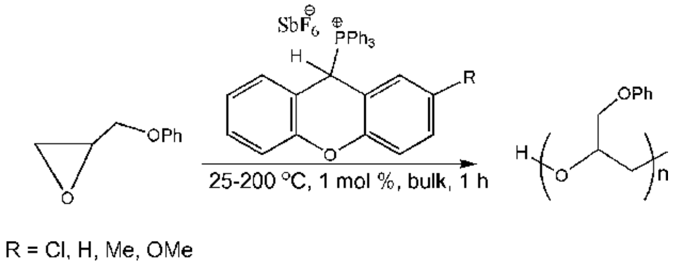
130.80, 120.02, 129.78, 128.86, 123.87, 117.00, 114.58, 55.38, 40.00, 39.18 ppm. ^{31}P NMR (200 MHz, DMSO-d_6): 20.99, 25.67 ppm.



Scheme 1. Synthesis of phosphonium salts

Typical polymerization procedure

GPE (5 mmol, 0.69 mL) and initiator (0.05 mmol, I_H, 33.90 mg; I_{Cl}, 35.90 mg; I_{Me}, 34.70 mg; I_{OMe} 35.44 mg) were placed in a flame dried ampoule equipped with three way stopcock connected to manifold and degassed for 30 minutes 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 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 monomer conversion was determined by ^1H NMR spectroscopy from crude polymerization mixture [27]. The molecular weight of polymer was determined by gel permeation chromatography (GPC).



Scheme 2. Polymerization of GPE

Measurements

Molecular weight was measured by GPC in $CHCl_3$ 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 polydispersities (M_w/M_n) were determined using a calibration curve obtained by polystyrene standards. NMR (^1H, ^{13}C and ^{31}P) spectra were recorded on a Brüker 200 MHz instrument with $CDCl_3$ and DMSO-d_6 (for initiators) as solvent and tetramethylsilane as internal standard. IR spectra were recorded on a Perkins–Elmer model 683 grating IR spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash EA-1112 Microanalyser 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.

Results and Discussion

Initiators synthesis

All the compounds were synthesized and characterized by NMR, IR and elemental analysis as described in the experimental section (Scheme 1). All the initiators are white crystalline salts and showed good stability towards air and moisture at ambient temperature.

Thermal Stability of Phosphonium Salts

Figure 1 shows TGA thermo-gram of all the 2-substituted phosphonium salts under nitrogen atmosphere. The prepared initiators were found to be thermally stable up to 200 °C above which their onset degradation temperatures were also observed.

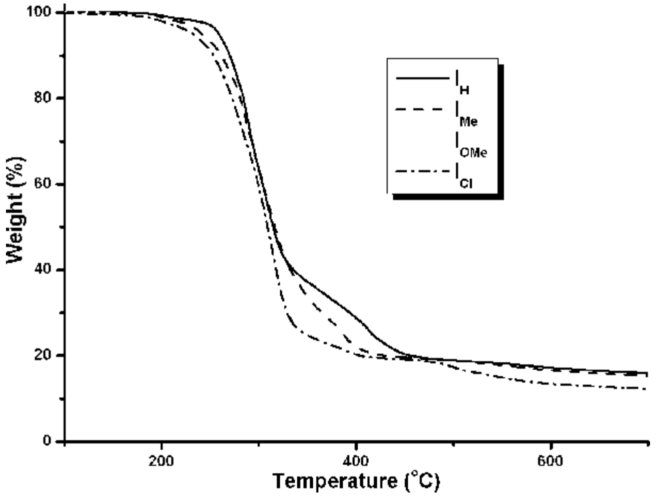


Figure 1. TGA thermo-grams of substituted phosphonium salts

It indicates that substituents have no significant effect on thermal stability of phosphonium salts. Therefore, these initiators can be used up to 200 °C temperature. The above thermal properties might suggest the potential relevance of phosphonium salts as latent thermal cationic initiator.

Polymerization of GPE

The bulk polymerization of GPE was carried out with 1 mol % of initiator (I_H, I_{Cl}, I_{Me} and I_{OMe}) in 25-200 °C temperature range for 1 h (Scheme 2). The effect of substituents on initiator activity was rationalized by monitoring monomer conversion as a function of reaction temperature (Figure 2). It shows the effect of substituents on initiator activity, which exhibit that the conversion (%) increases with the increase in reaction temperature. GPE undergoes polymerization with I_H I_{Cl}, I_{Me} and I_{OMe} above 100, 120, 130 and 140 °C, respectively.

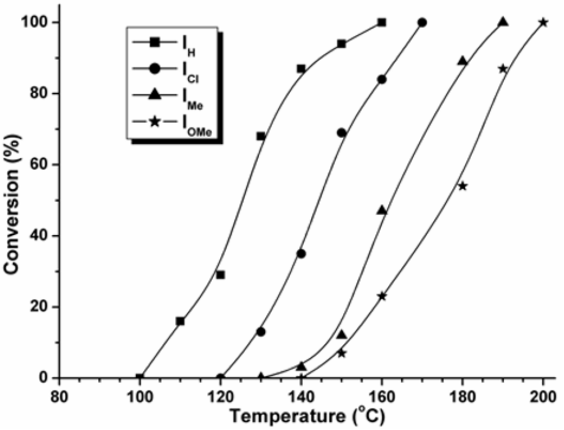


Figure 2. Temperature - conversion curve in polymerization of GPE with I_R for 1 h

For the above-mentioned initiators, the rate of polymerization increases faster after corresponding threshold temperature of initiation to afford the polymer with M_n of 2100-3400. A quantitative conversion with I_H, I_{Cl}, I_{Me} and I_{OMe} was observed at 160, 170, 190, and 200 °C, respectively. The order of initiator activity was found as $I_H > I_{Cl} > I_{Me} > I_{OMe}$. This order of activity can be explained by electronic effect of substituents in the xanthenyl ring of phosphonium salts. This trend is similar to the observation by Endo et. al. [23]. Additionally, the change in ^{1}H NMR chemical shift [28] of xanthenyl methine proton and ^{31}P NMR chemical shift [29] of phosphine in phosphonium salts supports the order of initiator activity. According to δ values of methine proton, I_{Cl} must be initiator with highest activity but I_H shows highest activity. For the reduced activity of I_{Cl} compared to I_H, may be ascribed to the combined effect of steric hindrance caused by the monomer and the bulkiness of chloro-substituent on xanthenyl ring [23].

Polymerization of CHO

To understand the steric effect of monomer on initiator activity, polymerization of CHO was performed with substituted phosphonium salts (0.1 mol %) in CH_2Cl_2 solvent at 60 °C for 1 h and 5 h (Table 1).

It can be observed that the conversion (%) and molecular weight increase with increasing time of reaction. However, CHO attains the substantial percentage conversion after 5 h. The molecular weight of poly(CHO) was found comparatively higher than poly(GPE) due to its higher polymerizability. This can be explained by stability of resulting cyclohexyl cation during polymerization and more nucleophilicity of the CHO monomer due to its restricted conformation [30]. In polymerization of CHO, the order of reactivity was found as $I_{Cl} > I_H > I_{Me} > I_{OMe}$, which is in accordance with the electronic effect of substituents on initiator activity. This also suggests that the steric effect of monomer alters the order of initiator activity in GPE polymerization.

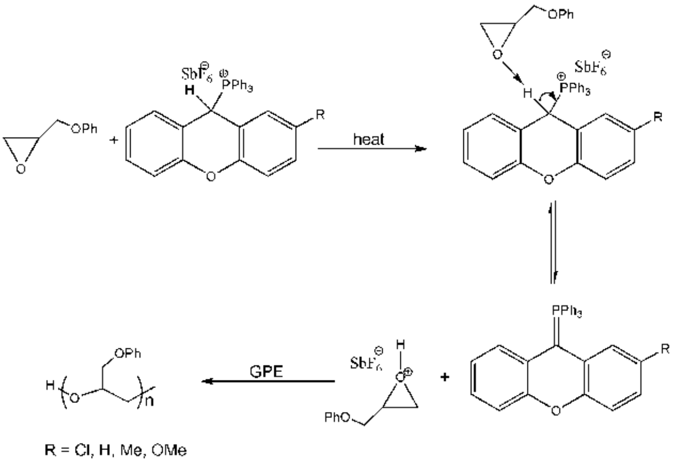
Table 1. Polymerization of CHO with xanthenyl phosphonium salts[a]

Initiator	Conversion (%)		M_n (g mol^{-1}) [b]		M_w/M_n	
	1 h	5 h	1 h	5 h	1 h	5 h
I_H	25	55	25,600	1,10,000	2.35	2.81
I_{Cl}	37	72	26,500	1,16,000	2.21	2.55
I_{Me}	11	23	15,900	40,100	1.85	1.87
I_{OMe}	7	19	13,300	31,300	1.70	1.72

[a] Conditions; initiator 0.1 mol % (3.4 mg) vs. CHO (5 mmol, 0.5 mL) at 60 °C in CH_2Cl_2.
[b] Determined by GPC based on polystyrene standards.

Polymerization Mechanism

Based on the literature of phosphonium salts [17, 21], it is believed that the initiating species in the present system could be methine protons, beside formation of phosphonium ylide (Scheme 3).



Scheme 3. Polymerization mechanism of GPE

It suggests that on thermal initiation, phosphonium salt undergo thermal cleavage of methine C-H bond in presence of GPE and generates oxonium cation, which further propagate the chain polymerization. To confirm this mechanism through formation of ylide, a Wittig reaction of I_H with sodium hydride in THF was performed at ambient temperature. The appearance of red color during the reaction indicates formation of ylide, which was found to be unstable under ambient condition. To this reaction mixture benzaldehyde was added and stirred overnight, which gives a yellow color solid, alkene, whose structure was confirmed by ^{1}H NMR spectra (Figure 3).

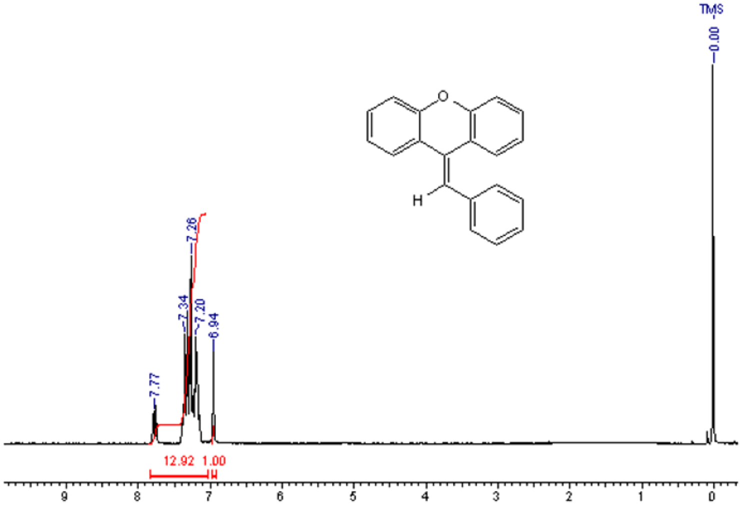


Figure 3. ^{1}H NMR spectra of alkene formed by Wittig reaction

Therefore, the methine proton can be regarded as the initiation species.

Solubility of Phosphonium Salts

The solubility of an initiator has an important role in polymerization and curing of epoxy monomers. For the very reason, solubility of all the prepared xanthenyl salts was evaluated in various organic solvent and epoxy monomers. All the salts show an increase in solubility with increasing polarity of solvent. All the initiators were found to be soluble in CH_3COCH_3, CH_3CN, DMF, THF and DMSO while partially soluble in $CHCl_3$ and MeOH. All initiators were insoluble in less-polar solvents such as toluene and diethyl ether. The solubility of initiators in epoxy monomers such as GPE, CHO, propylene oxide (PPO) and epichlorohydrine (ECH) were also examined. All these initiators have shown good solubility in GPE, PPO and ECH whereas partial solubility in CHO.

These solubility characteristics might indicate the use of phosphonium salts as latent cationic initiator in curing applications.

Conclusion

In the present study, novel thermo-latent initiators based on xanthenyl phosphonium salts were synthesized and their activity was studied with respect to effect of electronic and steric factors in cationic polymerization of epoxides. With GPE polymerization, the order of initiator activity was found as $I_H > I_{Cl} > I_{Me} > I_{OMe}$. The order of activity with CHO was as $I_{Cl} > I_H > I_{Me} > I_{OMe}$. This reveals that rate of CHO polymerization controlled by electronic factors, while in GPE; it is controlled by both steric and electronic factors. Therefore, the control of initiation can be achieved by changing the structural parameters. The solubility in GPE, thermal stability and resistance toward moisture might imply their worth as thermally latent initiator in cationic polymerization.

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

References

1. Lee H, Neville K (1967). Handbook of Epoxy Resins; McGraw-Hill, New York.
2. Mark HF, Gaylord NG, Bikajes NM (1968) Encyclopedia of Polymer Science and Technology; Eds. Interscience: New York 8:303.
3. Crivello JV, (1999) J Polym Sci Part A Polym Chem, 37:4241.
4. Yagci Y, Endo T (1997) Adv Polym Sci 127:59.
5. Yagci Y, Reetz I (1998) Prog Polym Sci 23:1485.
6. Gupta MK, Singh RP (2006) Macmol Symp 240:186.
7. Murai S, Nakano Y, Hayase S (2000) J Appl Polym Sci 80:181.
8. Park SJ, Heo GY (2005) Macromol Chem Phys 206:1134.
9. Hamazu F, Akashi S, Koizumi T, Takata T, Endo T (1991) J Polym Sci Polym Chem 29:1675.
10. Shimomura O, Sato T, Tomita I, Endo T (1998) Macromolecules 31:2013.
11. Shimomura O, Tomita I, Endo T (1998) Macromol. Rapid Commun 19:493.
12. Lee SB, Takata T, Endo T (1990) Macromolecules 23:431.
13. Lee SB, Takata T, Endo T (1991) Macromolecules 24:2689.
14. Nakano S, Endo T (1996) J Polym Sci Part A Polym Chem 34:475.
15. Nakano S, Endo T (1995) J Polym Sci Polym Chem 33:505.
16. Kim MS, Lee SB, Lee KB, Endo T (2005) J Appl Polym Sci 95:1439.
17. Takuma K, Takata T, Endo T (1993) Macromolecules 26:862.
18. Kim M, Sanda F, Endo T (2001) J Appl Polym Sci 81:2347.
19. Morikawa H, Sudo A, Nishida H, Endo T (2005) J Appl Polym Sci 96:72.
20. Kosolapoff GM, Maier L (1972) Organic Phosphorus Compounds Wiley-Interscience, New York.
21. Toneri T, Sanda F, Endo T (1998) J Polym Sci Part A Polym Chem 36:1957.
22. Toneri T, Watanabe K, Sanda F, Endo T (1999) Macromolecules 32:1293.
23. Toneri T, Sanda F, Endo T (2001) Macromolecules 34:1518.
24. Gupta MK, Singh RP (2007) J Appl Polym Sci Communicated.
25. Pellon RF, Carrasco R, Milian V, Rodes L (1995) Synth Commun 25:1077.
26. Pickert M, Frahm AW (1998) Arch Pharma Pharm Med Chem 331:177.
27. Hamanzu F, Akashi S, Koizumi T, Takata T, Endo T (1992) Macromol Chem Rapid Commun 13:203.
28. The δ value of xanthenyl methine proton in ^{1}H NMR spectra were observed with I_H I_{Cl}, I_{Me} and I_{OMe} at 7.01, 7.02, 6.94, and 6.70 ppm in DMSO-d_6, respectively.
29. The δ values of phosphine in ^{31}P NMR spectra were observed at 21.42 ppm with I_H, at 21.72 and 25.67 ppm with I_{Cl}, at 21.14 and 25.88 ppm with I_{Me} and at 20.99 and 25.67 ppm with I_{OMe}.
30. Ottar B (1947) Acta Chem Scand 1:283.