Cationic Polymerization of Epoxide with Benzyl Phosphonium Salts as the Latent Thermal Initiator

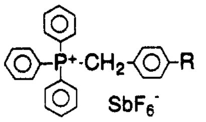
Keiichi Takuma, Toshikazu Takata, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received August 17, 1992
Revised Manuscript Received December 11, 1992

Introduction. Latent catalysts or initiators are utilized in various fields of materials such as adhesives, packings, and paints, since they can control the initiation step of polymerization and curing.[1-4] Especially, latent thermal initiators that induce polymerizations by heating as external stimulation are of extreme importance from the viewpoint of their wide variety of usage. Benzyl group-containing pyridinium[5-7] and sulfonium[8-18] salts with low nucleophilic counteranions have been reported as latent thermal initiators for cationic polymerizations of cyclic ethers and vinyl monomers. These initiators are characterized by easy synthesis and handling due to their highly reduced hygroscopicity and their stability toward air, moisture, and ordinary organic solvents. In our extensive studies, we have clarified the structure-activity relationship of these initiators and suggested that the benzyl cation is regarded as an actual initiation species formed via heterolytic cleavage of the C-N or C-S bond. Recently, we have found that 4-substituted benzyl triphenylphosphonium salts serve as thermally latent initiators for cationic polymerization of epoxide but induce cationic polymerization in a mechanism different from those with the sulfonium and pyridinium salts. This paper preliminarily describes the results of the cationic polymerizations with these phosphonium salts.

Results and Discussion. Benzyl group-substituted phosphonium salts (1-5) used in this study were prepared by the reaction of corresponding substituted and unsubstituted benzyl chlorides with triphenylphosphine followed by exchange of Cl^- with SbF_6^- by reaction with $KSbF_6$.[4]



1: R = NO_2
2: R = Cl
3: R = H
4: R = CH_3
5: R = OCH_3

Cationic ring-opening polymerization of glycidyl phenyl ether (GPE) with phosphonium salts (1-5) was carried out at temperatures ranging from 100 to 170 °C for 4 h. As shown in Figure 1, the polymerization of GPE took place above ca. 110 °C and the conversion of GPE reached more than 90% at 160 °C, indicating their thermal latency of the initiators. The number-average molecular weight of the obtained polymer was 1200-2500 (before precipitation). The order of the initiator activity was determined at a low conversion region of GPE in the temperature-conversion curves (Figure 1) and time-conversion curves for the initiators 1-3 (Figure 2) and is $NO_2 > Cl > H > CH_3 > CH_3O$. Namely, the polymerization was accelerated by introduction of an electron-withdrawing substituent on the benzyl group. The order of the activity was clearly reverse to those for the pyridinium and sulfonium salts,[6,8] in which the benzyl cation as the initiation species is stabilized by an electron-donating group in the para or meta position. An increase of the stabilization energy accelerates the elimination of the benzyl cation from the onium salts. However, this is not the case in this polymerization with the phosphonium salts. The initiation species in this polymerization should not be the benzyl cation but a proton liberated from the benzyl methylene, because ease of proton abstraction or acidity of the benzyl proton of the benzyl phosphonium salts increases with an increase of the electron-withdrawing capacity of the substituent of the benzyl group, i.e., stability of the corresponding benzyl phosphonium ylides. As shown in Table I, ¹H NMR chemical shifts of the benzyl proton of the phosphonium salts are actually correlated to their order of initiation ability.

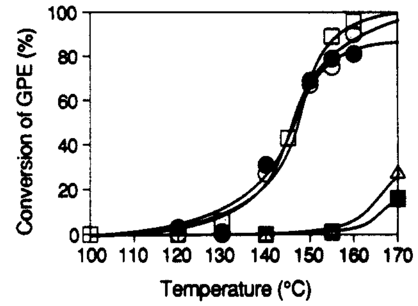


Figure 1. Temperature-conversion curves of bulk polymerization of GPE with 3 mol % initiator for 4 h: 1 (●), 2 (○), 3 (□), 4 (△), 5 (■).

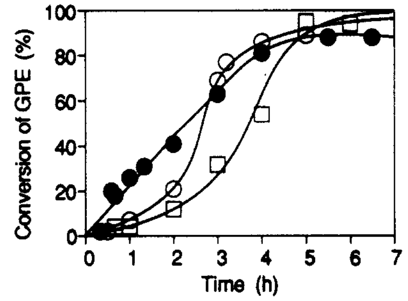


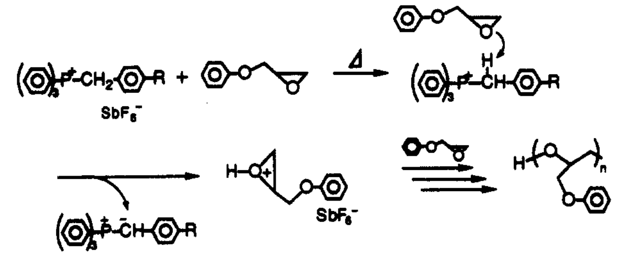
Figure 2. Time-conversion curves of bulk polymerization of GPE with 3 mol % initiator at 155 °C: 1 (●), 2 (○), 3 (□).

Table I
¹H NMR Chemical Shift of Benzyl Protons of the Phosphonium Salts

	phosphonium salt				
	1	2	3	4	5
R	NO_2	Cl	H	CH_3	CH_3O
δ/ppm[a]	5.29	5.10	5.05	5.01	4.98

[a] Solvent: acetone-d_6. Concentration: 1.0 mol/L.

Scheme I



Consequently, the polymerization of GPE with 1-5 is initiated unambiguously by a proton, which is abstracted presumably by GPE from the benzyl position of the initiator benzyl phosphonium salt (Scheme I).

If this initiation mechanism is actually operative, the phosphonium salt is converted to the corresponding phosphonium ylide. Although the ylide has not enough stability under the polymerization conditions, it can be

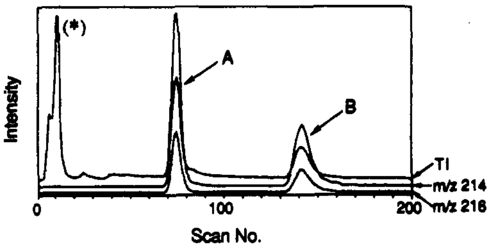


Figure 3. GC-MS chromatogram of the low molecular weight fraction (TI: total ion). GC conditions: column, SE-30 (2 m); carrier gas, He; column temperature, 230 °C. The first peak (*) was identified as a mixture of monomer and solvent ($CDCl_3$).

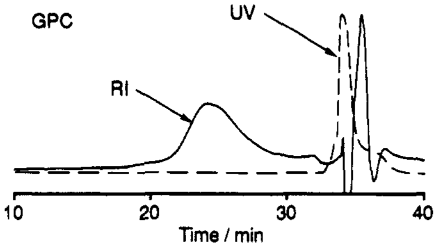


Figure 4. GPC chromatogram of a polymerization mixture of CHO obtained by the polymerization with 10 mol % initiator (1) at 80 °C for 5 h: UV (254 nm) and RI detection.

easily derived to the corresponding olefin by the Wittig reaction with a carbonyl compound. In fact, 4-chlorobenzyl triphenylphosphonium chloride was converted to 4-chlorostilbene (yield 93%) by a typical reaction procedure with 1.2 equiv of benzaldehyde. Then, the polymerization of GPE with phosphonium salt 2 was employed at 150 °C in the presence of benzaldehyde. Low molecular weight product separated with a preparative GPC from the reaction mixture was analyzed by GC-MS and ^1H NMR. The ^1H NMR spectrum of the product showed a doublet signal at δ 6.6 ppm ($CDCl_3$) that corresponds to olefinic protons of *cis*-4-chlorostilbene. Further, in the GC-MS analysis of the product, each mass chromatogram at m/z 214 and 216 showed two peaks of A and B (Figure 3). The mass spectrum (electron impact) of either peak A or B exhibited four strong signals at m/z 178 (M − HCl), 179 (M − Cl), 214 (M^+), and 216 (M + 2) that undoubtedly correspond to 4-chlorostilbene. These results indicate the formation of both *cis*- and *trans*-4-chlorostilbenes in this polymerization.[19] Accordingly, the predicted formation of the phosphonium ylides during the polymerization is proven by the above results.

On the other hand, if the initiation species is a proton, the obtained polymer should incorporate no moiety of the initiator. In fact, a GPC chromatogram of the polymer obtained by the polymerization of cyclohexene oxide with phosphonium salt 1 at 80 °C for 5 h showed an absence of the benzyl group.[20] Namely, the GPC chromatogram by RI detection had a peak corresponding to poly(cyclohexene oxide) at 24.1 min ($\bar{M}_n$ 7700), whereas that by UV detection showed no peak in the same area (Figure 4). Therefore, there was no aromatic group in the poly(cyclohexene oxide). This GPC characteristic is different from those in the cases of the sulfonium and pyridinium salts: the benzyl group is included in the polymers formed by the polymerization of these salts.[6,8] Probably, this difference comes from the pronounced stability of the corresponding phosphonium ylide compared with that of sulfonium and pyridinium ylides.

Thus, this work demonstrated that benzyl group-containing phosphonium salts serve as latent thermal initiators capable of initiating cationic polymerization where the benzyl proton is the actual initiation species.

References and Notes

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(19) Compounds corresponding to peaks A and B were tentatively identified as *cis*- and *trans*-chlorostilbenes, respectively.
(20) Conversion of monomer: 92% (estimated by ^1H NMR), $\bar{M}_n$ = 7700, and $\bar{M}_w/\bar{M}_n$ = 4.23 (determined by GPC, based on polystyrene standards).