Novel Piperidinium Salts as Latent Initiators for Cationic Polymerization of Epoxide and Vinyl Ether

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ABSTRACT: Novel dibenzylpiperidinium salts with non-nucleophilic anions (DBPi-SbF$_6$, DBPi-PF$_6$) have been prepared as latent cationic initiators. Utility of these salts in the photo and thermal-induced cationic polymerizations of epoxide and vinyl ether monomer systems has been studied. The new initiator, DBPi-SbF$_6$ showed good solubility, high reactivity, and high thermal latency for polymerizations of epoxide and vinyl ether monomers with only 1 wt % of concentration. Cationic polymerization of vinyl ether monomer was significantly faster than epoxide monomer by the synthesized initiators. This article describes the synthesis, characterization, and activity of novel initiators. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1878–1883, 2009

Key words: dibenzylpiperidinium salts; cationic polymerization; latent initiators; epoxide; vinyl ether

INTRODUCTION

Photoinitiated polymerization is nowadays a well-accepted technology enabling a wide variety of applications in protective and decorative coatings, graphic arts, and electronic parts. Driving forces for this development are unique features of this technology, which allow the realization of significant economic and ecological advantages.[1–6] These include use of high solid content formulations with very low emission of volatile organic compounds, full control over the curing process resulting in reduced losses, high cure speed at low processing temperature allowing high productivity even with heat sensitive materials. The first introduced photoinitiator such as benzyl dimethyl ketal was used for polymerization of unsaturated polyesters with radical process. At the same time onium salt photoinitiators were developed, capable of producing strong Brdonsted acids such as HBF$_4$, HSbF$_6$, HAsF$_6$, and HPF$_6$ upon UV irradiation.[7,8] Thereby, these strong acids were subsequently capable of initiating the cationic polymerization of olefins, cyclic ethers, cyclic sulfides, lactones, and lactams. The cationic systems have not achieved the same industrial importance as the radically curing systems because it is difficult to develop cationic initiators possessing both high sensitivity and wide absorption wavelength range. For these reasons, the intense efforts are being directed toward improvement of the performance of cationic photopolymerizable systems.

The vinyl ethers and epoxide resins cured via a cationic mechanism are negligibly toxic, not inhibited by oxygen, exhibit relatively low viscosities, have low shrinkage during curing, and exhibit dark-curing behavior.[9–11] Epoxide resins are generally used in the electronics industry as molding and sealing compounds for electronic packaging due to their excellent insulating characteristics and thermal properties, good adhesion, outstanding chemical resistance, and no reaction byproducts that could cause void formation. The amine or anhydride is widely used as a curing agent, which is a prerequisite for the thermal curing of epoxide resins.[12,13] However, there are some problems such as toxicity of amine, the deterioration of electrical properties at high temperature and humidity in the case of epoxide/amine system, and high energy consumption resulting from the long curing time at high temperature in the case of epoxide/anhydride system. To overcome such problems, the latent cationic initiators for epoxide resins have been intensively studied to overcome the drawbacks of common curing agent systems.[14–16] The photoinitiated cationic polymerization of vinyl ethers has received attention as a new UV-curing system because it is more highly reactive than the epoxide resins.[17,18] Lapin and coworkers.[19,20] reported the photo-induced cationic polymerization of vinyl ether monomers and oligomers with

sulfonium salts. Crivello et al.[21–29] reported that tri-arylsulfonium salts and iodonium salts can serve as photo-induced cationic initiators in the polymerization of epoxide resins and vinyl ether monomers. Endo and coworkers[30–36] and Yagci and co-workers[37–39] have also reported several benzylsulfonium salts and benzylpyridinium salts as latent thermal and latent photo-induced cationic initiators for the polymerization of styrene, vinyl ethers, and epoxides. Ideally, latent initiators should be stable indefinitely below threshold temperature but generate the initiating species and polymerize rapidly without inhibition or retardation of polymerization above the temperature, indicating high latency of latent initiator. Initiators with high latency can enhance pot life and reduce the polymerization time of a monomer. The high latency is, therefore, important to establish further utilization of latent initiators in the industrial fields. Pappas and coworkers.[40,41] suggested that the larger activation energy for initiation of thermally latent initiators, e.g., benzylsulfonium or benzylpyridinium salts, might depend on the cleavage of the bond between a heteroatom and a carbon atom.

In our previous work, we reported novel sulfonium salts and their utility in cationic polymerization.[42] In this article, we report the synthesis of new *N*, *N*-dibenzylpiperidinium salts with different counter anions and their application as latent initiators for cationic polymerization (photo and thermal) of aliphatic epoxide and vinyl ether monomers.

EXPERIMENTAL

Materials

Commercially available reagent grade benzyl bromide, citric acid, and piperidine were purchased from Aldrich Chemical Co. Sodium hexafluoroantimonate ($NaSbF_6$), and potassium hexafluorophosphate (KPF_6) were purchased from TCI Korea. The epoxide and vinyl ether monomers used in this study were commercially available and used without further purification. 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (CHE) was obtained from Dow Chemical Co. (Cyracure UVR6110), and tri(ethylene glycol) divinyl ether (DVE3) was purchased from Aldrich Chemical Co. The chemical structures of CHE and DVE3 are shown in Figure 1.

Measurements

The ^1H and ^{13}C NMR spectra of the ammonium salts were taken with a Varian 200 Gemini Fourier transform 200-MHz spectrometer at room temperature in acetone-d_6 using tetramethylsilane as an internal standard. The UV absorption spectra of the cationic
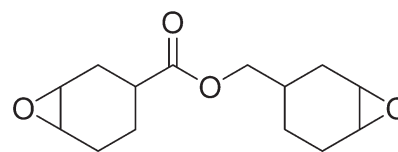
CHE: Cyracure UVR6110
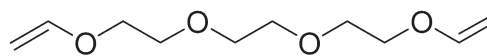
DVE3: Tri(ethylene glycol) divinyl ether

Figure 1 Commercially available epoxide (CHE) and divinyl ether (DVE3) monomers used in this study.

initiators were obtained using a Scinco *S*-4100 PDA UV-visible spectrophotometer (concentration of $10^{-3}M$ in acetonitrile). The IR spectra were recorded on a Nicolet 380 FTIR spectrometer using sandwiched KBr plate technique. Differential scanning calorimeter (DSC) measurements were carried out with TA 2910 instrument at a heating rate of 10°C/min under a flow of N_2 gas.

Photoreactive measurement

The irradiation source was a 500W deep UV lamp (mercury/xenon, UI-502Q, USHIO, Japan), which gave a UV intensity of 10 mW/cm^2 at 260 nm. The UV intensity was measured with an OAI Power Meter Model 206 of Optical Associates Inc. Samples of monomer containing 1 wt % cationic initiators were sandwiched in KBr plate. Two KBr plates were separated by a 12.5-μm thick polyimide frame as a spacer. To measure the photoreactivities of the cationic initiators, samples were irradiated with different time intervals, and the progress of reaction was followed by FTIR spectroscopy, which allows monitoring the decrease of the characteristic absorption bands $\sim$ 791 cm^{-1} for epoxide rings and $\sim$ 1620 cm^{-1} for vinyl ether double bonds. The degree of conversion was calculated from decrease in IR absorbance after a given exposure.[43]

Synthesis of *N*,*N*-Dibenzylpiperidinium Hexafluoroantimonate (DBPi-SbF$_6$)

To a stirred solution of benzyl bromide (21.1 g, 123.4 mmol) in methanol (40 mL), piperidine was gradually added (5.0 g, 58.7 mmol) under an ice bath, and then the mixture was stirred at room temperature for 48 h. After that, methanol was evaporated, and the residue was extracted twice with diethylether/distilled water (100 mL/100 mL). NaSbF$_6$ (18.8 g, 72.7 mmol) was added to the aqueous
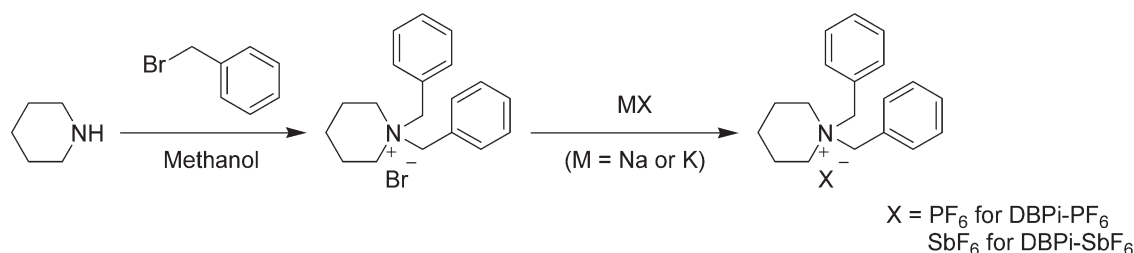
Scheme 1 Synthesis of dibenzylpiperidinium salts.

layer and stirred for 12 h. A precipitated salt was collected by filtration. The crude product was dissolved in methylene chloride, washed with 2 wt % aqueous citric acid solution and with distilled water. The organic layer was dried over anhydrous sodium sulfate and concentrated. Recrystallization of the salt from ethanol furnished pale yellow crystals, which were separated by filtration and dried in vacuum at room temperature.

Yield 48%. mp 164°C. IR (KBr, cm^{-1}) 3057, 2957, 1453, 1368, 1311, 1215, 1035, 923, 753, 701, 652. ^{1}H NMR (acetone-d$_6$, δ) 1.57–1.69 (m, 2H, piperidinium), 2.21–2.27 (m, 4H, piperidinium), 3.50 (t, 4H, piperidinium), 4.81 (s, 4H, benzyl), 7.53–7.68 (m, 10H, aromatic). ^{13}C NMR (acetone-d$_6$, δ) 20.39, 21.37, 56.90, 64.77, 128.21, 130.03, 131.41, 134.33. UV (10^{-3}M in acetonitrile) λ$_{max}$ = 263 nm.

Synthesis of N,N-Dibenzylpiperidinium Hexafluorophosphate (DBPi-PF$_6$)

The title compound was synthesized in a similar manner to the method of DBPi-SbF$_6$ by using KPF$_6$ instead of NaSbF$_6$.

Yield 64%. mp 188°C. IR (KBr, cm^{-1}) 3066, 2959, 1454, 1368, 1311, 1215, 1035, 923, 825, 751, 698. ^{1}H NMR (acetone-d$_6$, δ) 1.56–1.68 (m, 2H, piperidinium), 2.17–2.29 (m, 4H, piperidinium), 3.49 (t, 4H, piperidinium), 4.79 (s, 4H, benzyl), 7.53–7.68 (m, 10H, aromatic). ^{13}C NMR (acetone-d$_6$, δ) 20.34, 21.35, 56.83, 64.65, 128.23, 129.99, 131.36, 134.32. UV (10^{-3}M in acetonitrile) λ$_{max}$ = 263 nm.

RESULTS AND DISCUSSION

Synthesis of cationic initiators

Two dibenzylpiperidinium salts, DBPi-SbF$_6$ and DBPi-PF$_6$, were prepared by a reaction of piperidine with excess of benzyl bromide in methanol followed by exchange of counter anions with NaSbF$_6$ and KPF$_6$ in water. As shown in Scheme 1, the quaternization reaction of piperidine was sluggishly spending 48 h, even though the ring of piperidine is not conjugated, probably due to steric hindrance of the first N-substituted benzyl group. The resultant salts were hydrophobic and white crystalline compounds with sharp melting points. These salts are stable in the solid state and can be stored without decomposition in absence of light at room temperature. The characterization data is depicted in Table I.

DBPi-SbF$_6$ was soluble in CHE up to the concentration of 10 wt % but it has limited solubility in DVE3 just 3 wt % at room temperature. To the contrary, DBPi-PF$_6$ was poorly soluble ∼ 1 wt % in afore-mentioned monomers. Samples of monomer containing initiator showed no gelation, no change in viscosity as well as no change in the ability of thermal and photopolymerization after keeping at room temperature for more than 2 months.

Thermal polymerization

The thermal polymerizations of epoxide (CHE) and vinyl ether (DVE3) monomers by using the latent cationic initiators were examined with the DSC method. Thermal curing of CHE and DVE3 monomers were carried out with 1 wt % of initiators. Figure 2 shows that the temperature-conversion relationship in the thermal polymerization of CHE by DBPi-SbF$_6$ and DBPi-PF$_6$. Thermal polymerization of CHE by DBPi-SbF$_6$ was initiated above 190°C and preceded rapidly above the initiating temperature, whereas in the case of DBPi-PF$_6$, it was initiated above 230°C. On the other hand, temperature-conversion curves in Figure 3 for thermal polymerization of DVE3 by DBPi-SbF$_6$ and DBPi-PF$_6$ were initiated above 185°C and 208°C, respectively, revealing higher activity for thermal polymerization

TABLE I
Characteristics of Synthesized Piperidinium Salts

Salts	mp (°C)	λ$_{max}$ (nm)	Yield (%)	FTIR absorbance (cm^{-1})
DBPi-SbF$_6$	164	263	38	3057, 2957, 1453, 1215, 1035, 753, 652
DBPi-PF$_6$	188	263	64	3066, 2959, 1454, 1215, 1035, 825, 698
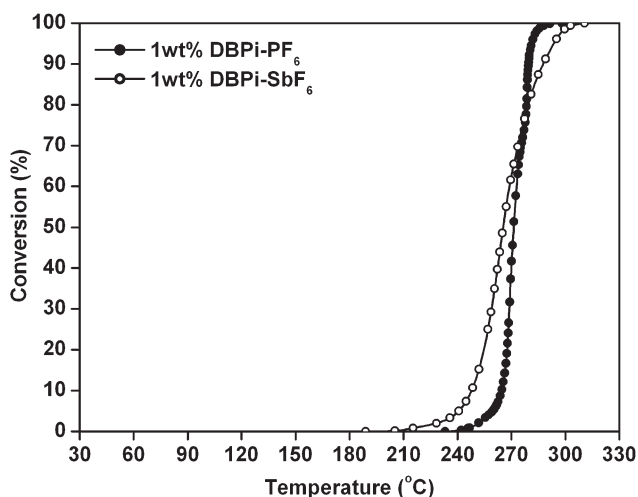
Figure 2 Temperature-conversion relationship in thermal polymerization of CHE monomer with 1 wt % initiator.

Figure 4 Time-conversion relationship of CHE and DVE3 monomer with 1 wt % DBPi-SbF$_6$ at isothermal condition.

than those of epoxide system with lower initiating temperatures. Thus, these results indicate that the ammonium salt initiator with SbF$_6$ counter anion is more reactive than with PF$_6$. The order of reactivity of the latent initiators, depending on the nature of the counter anions, was in good agreement with previously reported results in the similar reactions (SbF$_6^-$ > PF$_6^-$).[30]

Latent properties

The latent properties of the cationic initiator, DBPi-SbF$_6$ in the thermal polymerization of CHE and DVE3 were evaluated by the time-conversion relationship of monomer with 1wt% DBPi-SbF$_6$ at isothermal DSC. The conversion curves of CHE/DBPi-SbF$_6$ (1 wt %, open square) and DVE3/DBPi-SbF$_6$ (1 wt %, open circle) systems in Figure 4 showed
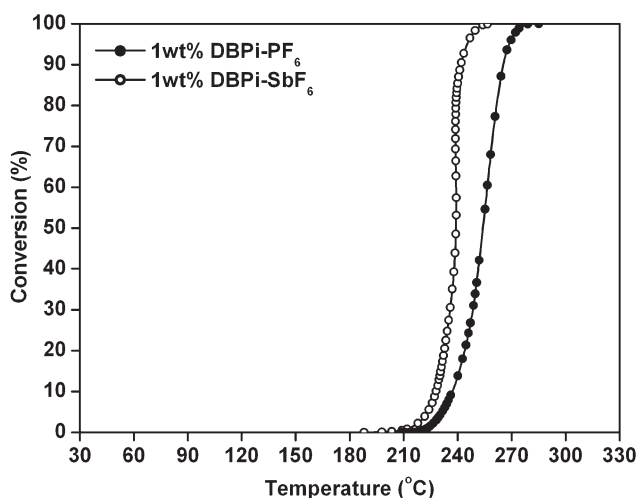
rapid change at 200°C, whereas no appreciable changes observed in the conversion curves at 100°C even after 60 min. It indicates that DBPi-SbF$_6$ is promising latent cationic initiator in curing of CHE and DVE3 monomers.

Photopolymerization

The UV spectra of the ammonium salts in acetonitrile exhibit the absorption maxima at 263 nm with absorption range of 230–300 nm and absorptivity of about 700 L/mol cm as shown in Figure 5. The photopolymerization of CHE and DVE3 monomers with synthesized salts (1 wt % of the monomer) was carried out by irradiation under deep UV lamp. The conversion was monitored by decrease of the IR spectral intensities of the corresponding functional group. The time-conversion relationship in the

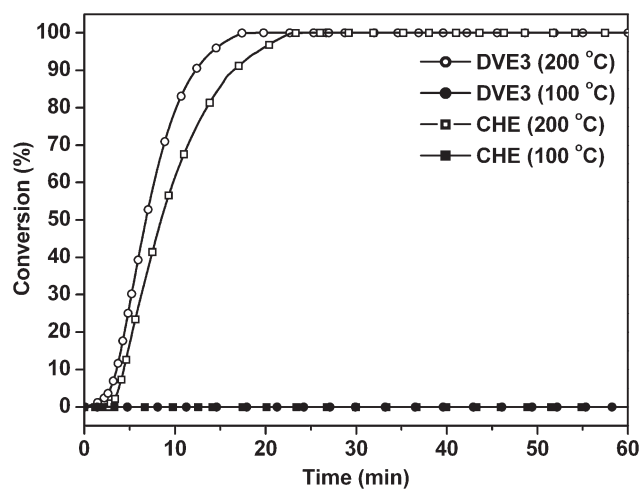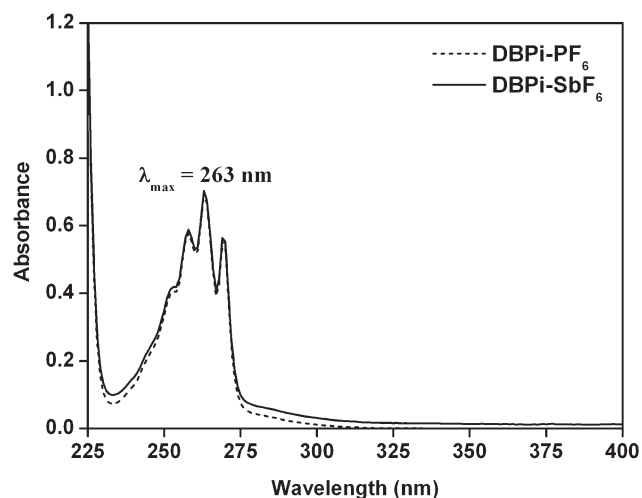**Figure 3** Temperature-conversion relationship in the thermal polymerization of DVE3 monomer with 1 wt % initiator.

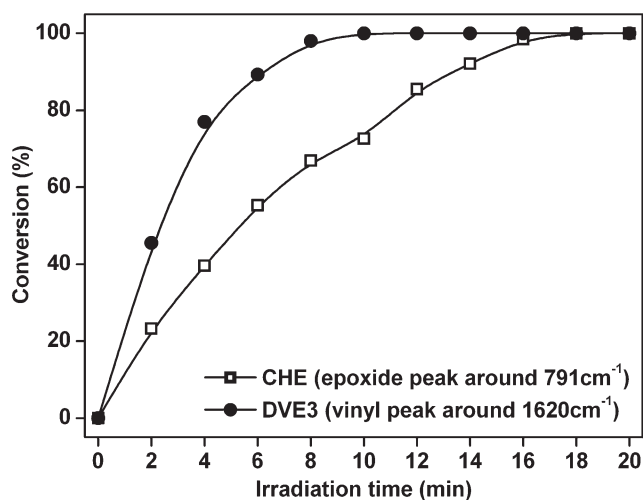**Figure 5** UV spectra of the piperidinium salts in acetonitrile.

Figure 6 Time-conversion relationship in the photopolymerization of CHE and DVE3 monomer with 1 wt % DBPi-SbF$_6$ at room temperature.

photopolymerization of the epoxide and vinyl ether monomers is shown in Figures 6 and 7, respectively. The conversion of DVE3 was much faster when compared with CHE monomer using ammonium salts and the initiator with SbF$_6$ counter anion is more reactive than PF$_6$. It is supposed that the initiating species in the thermal reaction are carbenium cations, which is the same as that in the photoreaction because almost the same effects have been observed in thermal and photoreactions.

CONCLUSIONS

Two dibenzylpiperidinium salts were prepared as latent cationic initiators, and their utility in cationic polymerizations of epoxide and vinyl ether monomers was verified as low as 1 wt % concentration.
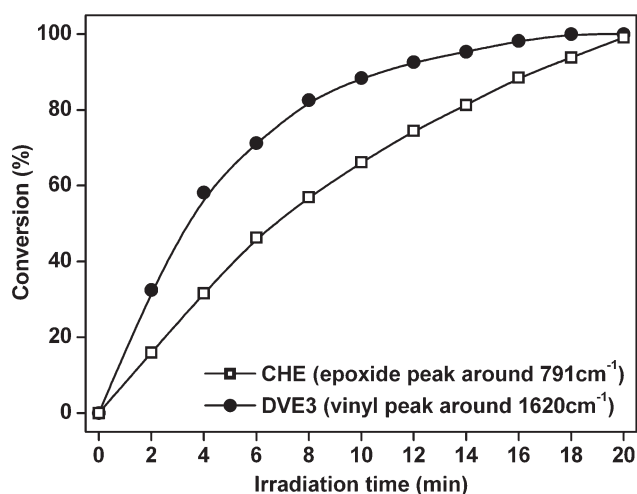

Figure 7 Time-conversion relationship in the photopolymerization of CHE and DVE3 monomer with 1 wt % DBPi-PF$_6$ at room temperature.

The piperidinium salt with SbF$_6$ counter anion showed higher activity than that with PF$_6$ counter anion in the polymerization. It has been found that the cationic photopolymerization of vinyl ether monomer was significantly faster when compared with epoxide monomer by the use of DBPi-SbF$_6$.

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