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# Novel Cationic Thermally Latent Initiators: Ring-Opening Polymerization of an Oxirane with Polyaniline Doped with a Perfluorosurfactant as a Novel Pseudo-Non-Salt-Type Initiator Showing a Color Changing before and after Initiation

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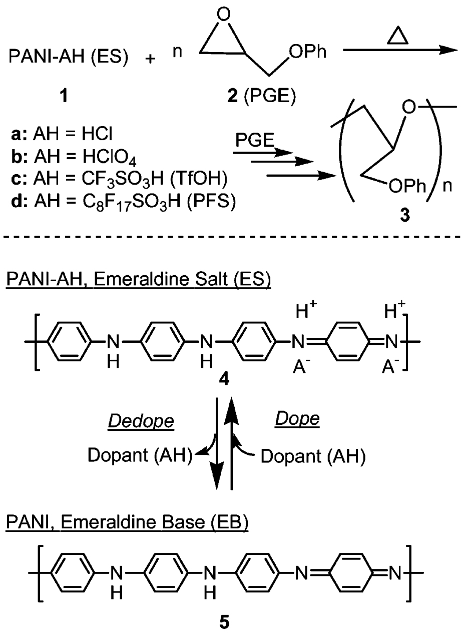
**Introduction.** Control of polymerization and the curing initiation process have been widely investigated in the fields of polymer science and technology,[1] and especially external stimulation-induced polymerizations are of quite interest due to control of the initiation step of polymerization. For the past decades, numerous numbers of new latent initiators, which show no activity under normal polymerization conditions but release active species by external stimulation such as heating or photoirradiation, have been widely developed since latent initiators are useful in several industrial fields such as paints, inks, epoxy molding compounds, and photoresists.[2−9] Development of an efficient latent initiator has been desirable for enhancement of both storage stability and handling, and Pappas et al.,[3] Crivello et al.,[4] Abu-Abdoun et al.,[5] Yagci et al.,[6] Toba et al.,[7] Li et al.,[8] and Endo et al.[9] have developed various onium salt-based cationic thermal and/or photolatent initiators, e.g., benzylsulfonium, benzylpyridinium, and benzylammonium salts with less nucleophilic counteranions like hexafluoroantimonate and hexafluorophosphonate for the polymerization of styrene and epoxides. In addition, the rate of polymerizations initiated by onium salts increases with decreasing nucleophilicity of their counteranion, e.g., $BF_4 < PF_6 < AsF_6 < SbF_6 < B(C_6F_5)_4$. However, their problems are low solubility in monomers and solvents and remaining of inorganic compounds in the resulting polymers. These problems may be overcome by developing non-salt-type initiators,[10] such as carboxylic acid esters, sulfonic acid esters, and phosphonic acid esters. We recently reported that phenols bearing trifluoromethyl or fluorine groups are a new class of non-salt-type initiators for cationic photopolymerization of an epoxide.[11]

We are interested in developing a "pseudo-non-salt-type initiator" whose stability can be visibly checked, since the preservation stabilities of non-salt-type latent initiators were generally more unstable than onium salts, presumably due to ready hydrolysis even by weak acid and/or base impurities. Furthermore, development of a (pseudo-) non-salt-type initiator that can be visibly judged its preservation stability by a color change should be practically useful.

Polyanilines have four different states along with different colors:[12] (a) leucoemeraldine base [fully reduced form (faint yellow color)], (b) emeraldine base [EB (PANI), half-oxidized form (blue color)], (c) conducting emeraldine salt [ES (PANI-AH), half-oxidized and protonated form (dark green color)], and (d) pernigraniline base [fully oxidized form, (purple color)].

Scheme 1



PANI-AH, which is the only conductive form, has onium salt units in the polymer chain and various PANI-AHs that have been recently developing by doping of anionic surfactants,[13] such as dodecylsulfonic acid, dodecylbenzenesulfonic acid, and bis(2-ethylhexyl)sulfosuccinic acid, are highly soluble in various solvents and miscible with a variety of organic compounds. The typical PANI-AH doped with HCl is insoluble in most solvents.

The approach with PANI-AH as a pseudo-non-salt-type (pseudo-homogeneous) latent initiator has not been reported, and then we investigated herein the ability for thermally latent initiator of PANI doped with a perfluorosurfactant, $C_8F_{17}SO_3H$ (PFS), which should generate a less nucleophilic counteranion after doping of the PANI. Then, the polymerization activity of PANI−PFS (**1d**) for a pseudo-non-salt-type thermally latent initiator was examined by using phenyl glycidyl ether (**2**, PGE) as a monomer (Scheme 1).[14] In addition, the similar polymerizations with several PANIs doped with several acids [PANI−AH; **1a**: PANI−HCl; **1b**: PANI−$HClO_4$; **1c**: PANI−TfOH (TfOH = $CF_3SO_3H$)] were also investigated as references.

**Results and Discussion.** Table 1 shows the result of bulk polymerization of PGE with 1 mol % of PANI-AH (ES, **1**) as a thermally latent initiator for 6 h.[15,16] PANI−HCl, which is a typical acid doped PANI, hardly initiated polymerization even at 150 °C (run 1). Meanwhile, similar polymerizations with PANI−$HClO_4$ and PANI−TfOH took place at 100 °C, but the conversion yields of the monomers and the $M_w$s (weight-average molecular weights) of the resulting products were extremely low (runs 2 and 3). The polymerization with PANI−PFS, which is readily miscible in PGE as if it is a homogeneous catalyst, efficiently propagated to give polymer **3** having relatively high molecular weight for a common polymerization of PGE ($M_w$ = ca. 2500), and the conversion of PGE reached quantitatively even at 100 °C (run 4). In addition, no polymerization proceeded at room temperature over 2 months (run 5), and in similar polymerizations with 0.5 and 0.1 mmol of PANI−PFS the conversions of PGE and/or the $M_w$s of the resulting products decreased under the same polymerization conditions (runs 6 and 7).[17] The above results strongly suggested that PANI−PFS

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**Table 1. Thermally Initiated Polymerizations of Phenyl Glycidyl Ether (PGE, 2) in the Presence of Acid-Doped Polyanilines (PANI–AH, 1a–d) for 6 h[a]**

| run | PANI–AH (ES, **1a**–**d**) | temp (°C) | conv[b] (%) | $M_w$ ($M_w/M_n$)[c] |
|---|---|---|---|---|
| 1 | PNAI–HCl (**1a**) | 150 | <5 | *d* |
| 2 | PANI–$HClO_4$ (**1b**) | 100 | 9 | *d* |
| 3 | PANI-TfOH (**1c**) | 100 | 38 | *d* |
| 4 | PANI–PFS (**1d**) | 100 | 100 | 2485 (1.67) |
| 5[e] | PANI–PFS (**1d**) | room temp | no polymerization | |
| 6[f] | PANI–PFS (**1d**) | 100 (0.5 mmol) | 91 | 2480 (1.67) |
| 7[g] | PANI–PFS (**1d**) | 100 (0.1 mmol) | 6 | 951 (1.26) |

[a] Reaction conditions: To 1 mmol of PGE, 1.0 mol % of PANI–AH was used. See ref 16. [b] Determined by $^1H$ NMR spectroscopy. [c] Estimated by gel permeation chromatography [eluent, tetrahydrofuran (THF)] based on polystyrene standard samples. $M_n$ and $M_w$ are mean number- and weight-average molecular weights, respectively. [d] Lower measuring limit ($M_w$: < 500). [e] Reaction time: over 2 months. [f] PANI–AH: 0.5 mol %. [g] PANI–AH: 0.1 mol %.

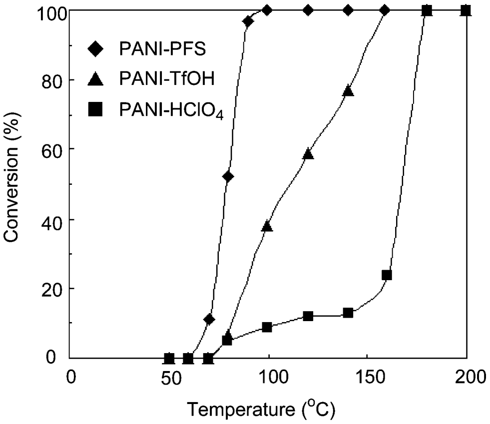

**Figure 1.** Relationship between the temperature and conversion for bulk polymerization of phenyl glycidyl ether (PGE) with 1 mol % of acid-doped polyanilines (PANI–AHs; **1b**: PANI–$HClO_4$; **1c**: PANI–TfOH; **1d**: PANI–PFS) for 6 h (see ref 16).

efficiently serves as a new thermally latent initiator for the polymerization of PGE.

Figure 1 shows the temperature–conversion curve in the bulk polymerization of PGE with PANI–AH, **1b**–**d**, for 6 h. The polymerization of PGE with PANI–$HClO_4$ did not proceed below 80 °C, but the polymerization started over 80 °C. Then, the PGE was quantitatively polymerized at 180 °C. The polymerization with PANI–TfOH was smoothly initiated over 80 °C, and the conversion of PGE reached more than 97% at 150 °C. On the other hand, the similar polymerizations with PANI–PFS quite readily propagated over 70 °C, and the conversion of PGE reached more than ca. 97% even at 90 °C. As a consequence, the activity order for a thermally latent initiator should be estimated as **1d** ≫ **1c** > **1b** ≫ **1a** on the basis of the relationship between the temperature and conversion. Incidentally, development of thermally latent initiators showing the activity for polymerization at "relatively mild temperature (<100 °C)" should be of interest, since high-temperature curing sometimes brings deterioration of electric properties in sealing system for an electronic device.

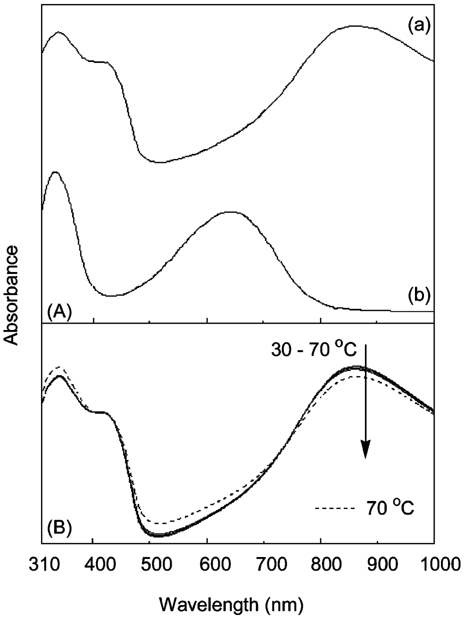

**Figure 2.** (A) UV/vis/near-IR spectra of acid-doped polyanilines **1d**/phenyl glycidyl ether (**2**) (PANI–PFS/PGE) solution (a) before and (b) after heating at 100 °C for 6 h. (B) UV/vis/near-IR spectra of PANI–PFS/PGE solution during heating from 30 °C up to 70 °C (heating rate: 10 °C/10 min).

Figure 2 indicates the ultraviolet/visible/near-infrared (UV/vis/near-IR) spectra of PANI–PFS/PGE solution before [(A)-a], during (B), and after heating [(A)-b]. Figure 2(A)-a shows the typical three absorption bands derived from the ES form (PANI–PFS) around 342, 424, and 865 nm. The absorption band around 342 nm should arise from $\pi-\pi^*$ electron transition within the benzenoid segment, and the absorption bands which have a local maximum around 424 and 865 nm should be related to doping level (the protonation of the polymer backbone) and formation of polaron, respectively. Meanwhile, Figure 2(A)-b indicates the typical two absorption bands derived from EB form around 335 and 642 nm, which should be assigned to the $\pi-\pi^*$ transition of the phenyl ring and to the "exciton" transition (n–$\pi^*$ transition), respectively, and it was clearly in agreement with the spectrum of NMP (*N*-methyl-2-pyrolidone) solution of the corresponding EB which was prepared by dedoping of PANI–PFS with 1 M KOH aqueous solution. These results strongly implied that PANI–PFS can be dedoped by heating at relatively mild temperature (~90 °C), as the result of which the polymerization of PGE undertook.[18] Thus, these results strongly suggested that the present initiator mediated the polymerization along with the color changing behavior.

The UV/vis/near-IR spectra at different temperatures from 30 up to 70 °C were measured as shown in Figure 2B,[19] in order to closely investigate the initiation step of the polymerization. Consequently, the spectra suggested that the ES form has begun to change at 70 °C, at which decrease of the typical absorption band based on the ES form around at 850 nm and increases of the typical absorption bands derived from the EB form around 330 and 600 nm were detected. This strongly supports initiation of the polymerization via the thermal redoping process of PANI–PFS.

In summary, this work demonstrated that PANI–PFS efficiently served as a pseudo-non-salt-type thermally latent initiator for polymerization of PGE even at relatively mild temperature (~90 °C). In addition, propagation of the polymerization or stability of the latent initiator (PANI–PFS) can be visibly checked simply by the color changing derived from dedoping from the ES form (dark green) to the EB form (blue). Further detailed investigations and applications for organic reactions are now in progress, and the results will be reported elsewhere.

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**Supporting Information Available:** UV/vis/near-IR spectra of **1b**−**d** (ES form) in *m*-cresol and dedoped **1b**−**d** (EB form) in NMP; IR spectra and TGA (thermogravimetric analysis) curves of **1a**−**d** (ES form). This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Mark, H. F., Gaylord, N. G., Bikales, N. M.; Eds.; *Encyclopedia of Polymer Science and Technology*, **1968**, *8*, 303; Interscience Publishers: New York, 1966; Vol. 4, p 528.

(2) For example: (a) Endo, T.; Sanda, F. *Macromol. Symp.* **1996**, *107*, 237−242. (b) Muizebelt, M. J. *J. Coat. Technol.* **1985**, *57*, 43−49. (c) Lee, H., Neville, K., Eds.; *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967. (d) Tanaka, Y., Mika, T. F., Eds.; *Epoxy Resins Chemistry and Technology*; Marcel Dekker: New York, 1973. (e) Senturia, S. D.; Sheppard Jr., N. F. *Epoxy Resins and Composites IV*; Springer-Verlag: Berlin, 1986.

(3) (a) Pappas, S. P. *J. Imaging Technol.* **1985**, *11*, 146−157. (b) Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Part A*: *Polym. Chem.* **1984**, *22*, 77−84.

(4) Review: Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241−4254.

(5) (a) Neckers, D. C.; Abu-Abdoun, I. I. *Macromolecules* **1984**, *17*, 2468−2473. (b) Abu-Abdoun, I. I.; Aale-Ali, *Eur. Polym. J.* **1992**, *28*, 73−78.

(6) (a) Yagci, Y.; Schnabel, W. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 133−143. (b) Yagci, Y.; Lukac, I.; Schnabel, W. *Polymer* **1993**, *34*, 1130−1133. (c) Yagci, Y.; Endo, T. *Adv. Polym. Sci.* **1997**, *127*, 59−86. (d) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485−1538. (e) Yagci, Y.; Reetz, I. *Macromol. Symp.* **1998**, *132*, 153−164. (f) Onen, A.; Arsu, N.; Yagcl, Y. *Angew. Makromol. Chem.* **1999**, *264*, 56−59.

(7) (a) Toba, Y.; Usui, Y.; Konishi, T.; Ito, O.; Uesugi, T. *Macromolecules* **1999**, *32*, 6545−6551. (b) Toba, Y.; Usui, Y.; Alam, M. M.; Ito, O. *Macromolecules* **1998**, *31*, 6022−6029. (c) Toba, Y.; Saito, M.; Usui, Y.; *Macromolecules* **1999**, *32*, 3209−3215.

(8) Li, H.; Ren, K.; Neckers, D. C. *Macromolecules* **2001**, *34*, 8637−8640.

(9) (a) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900−904. (b) Kikkawa, A.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1089−1095. (c) Park, J.; Kihara, N.; Ikeda, T.; Endo, T. *Macromolecules* **1997**, *30*, 3414−3416. (d) Uno, H.; Takata, T.; Endo, T. *Chem. Lett.* **1988**, 935−938. (e) Takahashi, E.; Sanda, F.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **2002**, *40*, 1037−1046. (f) Takuma, K.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 862−863. (g) Toneri, T.; Sanda, F.; Endo, T. *Macromolecules* **2001**, *34*, 1518−1521. (h) Hino, T.; Endo, T. *Macromolecules* **2003**, *36*, 4672−4674. (i) Hino, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2162−2165. (j) Hino, T.; Endo, T. *J. Polym. Sci., Part A*: *Polym. Chem.* **2004**, *42*, 2166−2170. (k) Hino, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5407−5412.

(10) (a) Lee S. D.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1041−1048. (b) Kim, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 3499−3501 and references cited therein.

(11) Hino, T.; Endo, T. *Macromolecules* **2004**, *37*, 1671−1673.

(12) Wallace, G. G.; Spinks, G. M.; Kane-Maguire, L. A. P.; Tesdale, P. R. *Conductive Electroactive Polymers*; Intelligent Materials Systems CRC Press: Boca Raton, FL, 2002.

(13) (a) Kuramoto, N.; Genies, E. M. *Synth. Met.* **1995**, *68*, 191−194. (b) Kuramoto, N.; Michaelson, J. C.; McEvoy, A. J.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1478−1480.

(14) The reasons that we employed PGE as an epoxide in the present study are as follows: (a) In general, some bifunctional epoxides such as bisphenol A diglycidyl ether are highly viscous oils, and then they are extremely intractable. (b) PGE can be regarded as a half unit for bisphenol A diglycidyl ether, which is widely used as an epoxide model monomer. (c) The polymerization system with PGE can be carried out at even higher temperature, due to its high boiling point.

(15) PANI−AHs were prepared according to the typical synthetic procedure yielding PANI−HCl by using ammonium persulphate (APS) as an initiator: MacDiarmid, A. G.; Chiange, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; Reidel: Dordrecht, Holland, 1987. Synthesis of PANI−PFS: Aniline (40 mmol) was dispersed in 250 mL of 1 N PFS aqueous solution. An APS (40 mmol) was dissolved in 50 mL of distilled water, and then the solution was added in a dropwise manner to the mixture containing aniline and the surfactant at 0−5 °C under constant stirring conditions. After complete addition of the oxidizing agent, the reaction mixture was stirred for 24 h. The resulting product was filtered and washed with deionized water until the filtrate was colorless, and then the obtained polymer (PANI−PFS) was dried under reduced pressure at 40 °C for 12 h.

(16) Typical polymerization procedure: A mixture of PGE (5 mmol) and reagent **1a** (0.05 mmol) as an initiator in an ampule tube was cooled, evacuated, and sealed off. The ampule was heated in an oil bath at set temperature for 6 h with stirring. After the reaction, the ampule was cooled immediately with liquid nitrogen, and the reaction was quenched with NEt$_3$/MeOH solution. After warming to room temperature, the conversion of PGE was estimated by the $^1$H nuclear magnetic resonance ($^1$H NMR) spectrum of the crude reaction mixture. The reaction mixture was dissolved into methylene dichloride (1 mL), and the resulting solution was filtrated and poured into *n*-hexane/ether (100 mL) to precipitate the polymer. After the *n*-hexane/ether layer was removed by decantation, the residual viscous polymer was collected and dried at 50 °C overnight under vacuum. The structure of the polymer was confirmed to be poly-PGE by $^1$H NMR and IR spectra. $^1$H NMR (CDCl$_3$) $\delta$ 7.36−6.85 (m, 5H, *Ph*), 4.48−3.47 (m, 5H, $CH_2$−CH−CH$_2$). IR (neat): 1599, 1495, 1292, 1217, 1173, 1040 cm$^{-1}$.

(17) Incidentally, the cationic polymerization of PGE had already been reported, and its end conversion was found to depend on the concentration of the initiator, such as SnCl$_4$. See: Matyjaszewski, K., Ed.; *Cationic Polymerization: Mechanism, Synthesis and Applications*; Marcel Dekker: New York, 1996. Kubisa, P.; Penczek, S. *Prog. Polym. Sci.* **1999**, *24*, 1409−1437.

(18) The UV/vis/near-IR spectrum of the NMP solution of PANI−PFS interestingly showed the absorption bands derived from the ES form presumably due to the highly fluoro-substituted dopant, while those of the other PANI−AHs were expectedly readily converted to the EB forms in NMP.

(19) The heating rate was carried out at 10 °C/10 min for reasons in the measurement.

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