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Communications to the Editor

Cationic Photopolymerization of an Epoxide by Substituted Phenols as a Novel Nonsalt-Type Photolatent Initiator

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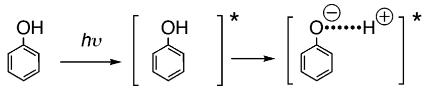
Introduction. Among *latent catalysts* which show activity only under appropriate external stimulation such as heating and photoirradiation, *latent initiators* have attracted considerable attention owing to control the initiation step of polymerization or curing and are utilized in the fields of adhesives, packings, and paints.[1] Development of an efficient latent initiator has been desirable for enhancement of both storage stability and handling, and Pappas et al.,[2] Crivello et al.,[3] Abu-Abdoun et al.,[4] Yagci et al.,[5] Toba et al.,[6] and Li et al.[7] have developed various onium salt-based cationic thermal and/or photolatent initiators. We have also reported that several onium salts, e.g., benzylsulfonium, benzylpyridinium, and benzylammonium salts, serve thermal and/or photolatent initiators for the polymerization of styrene and epoxides.[8] Such onium salts, however, have a limitation on industrial application because these salts have several problems: low solubility in monomers and solvents and remaining of inorganic compounds in the resulting polymers. Recently, considerable efforts have been made to overcome these problems by developing *nonsalt-type initiators*.[9] More recently, we have also reported N-substituted phthalimides, aminimides, carboxylic acid esters, sulfonic acid esters, and phosphonic acid esters as a nonsalt-type thermal latent initiator.[9d]

In the course of our study on the design and application of nonsalt-type latent initiators, we paid attention to phenols. Phenols are generally difficult to initiate polymerizations of epoxides even at elevated temperature, probably due to its insufficient acidity for polymerizations and relatively higher nucleophilicity of the dissociated phenoxide ion, which acts as a polymer termination. Indeed, treatment of epoxides with phenols only gave the ring-opened compounds or yielded the oligomers at best. On the other hand, acidity and basicity of organic compounds are well-known to undergo significant changes upon excitation to the excited states. For instance, pK_a of phenol is 10.0, while the excited-state pK_a is 3.6 in aqueous solution, presumably owing to promote the dissociation between the proton and phenoxide ion (eq 1).[10] In addition, nucleophilicity of phenoxide ion could decrease sterically and electronically by introduction of an adequate substituent(s) on its benzene ring, resulting in stabilization of the dissociation state. Then, these knowledge and considerations prompted us to investigate polymerizations with various phenols **2** as a new class of a nonsalt-type photoinitiator, in which glycidyl phenyl ether (**1**, GPE) was used as a monomer (Scheme 1).



(1)

Results and Discussion. Bulk photopolymerizations of GPE (**1**) were examined with 5 mol % of 2,6-di-*tert*-butylphenol (**2a**), 2,2-bis(4-hydroxy-(3,5-dimethylphenyl)propane (tetramethylbisphenol A) (**2b**), α,α′-bis(4-hydroxy-3,5-dimethylphenyl)-1,4-diisopropylbenzene (**2c**), 3,5-bis(trifluoromethyl)phenol (**2d**), 2,3-difluorophenol (**2e**), and pentafluorophenol (**2f**) at room temperature for 48 h, in which a 500 W high-pressure mercury lamp attached with a cold mirror which almost cut the light of wavelength excepted 250−500 nm was used as a light source (Table 1). The polymerizations with phenols **2** bearing bulky substituents at the *o*-positions of the aromatic group were first carried out. As a consequence, the reactions with phenol **2a** and even with phenols **2b**,**c**

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Scheme 1

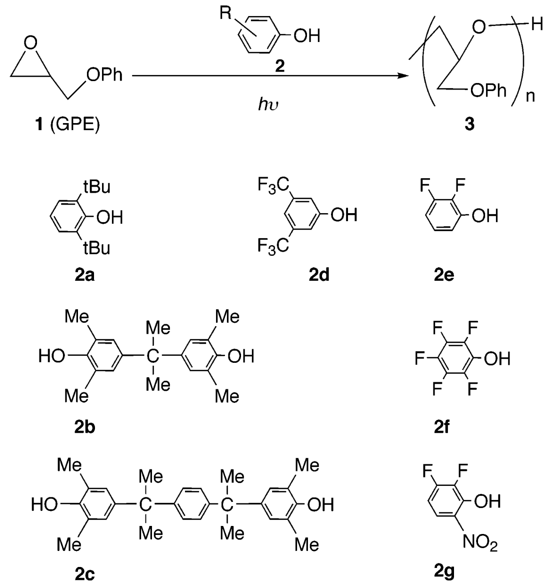


Table 1. Bulk Photoinitiated Polymerization of GPE with Substituted Phenols 2a−f at Room Temperature for 48 h[a]

run	substituted phenols	conv[b] (%)	M_n	M_w/M_n[c]
1	**2a**	no polymerization		
2	**2b**	no polymerization		
3	**2c**	no polymerization		
4	**2d**	66	2869	1.54
5	**2e**	74	3501	1.60
6	**2f**	70	3221	1.57

[a] Reaction conditions: To 1 mmol of GPE, 5 mol % of phenols **2** was used. [b] Determined by ^{1}H NMR. [c] Estimated by GPC based on polystyrene standard samples.

having two phenol units in the unimolecular did not gave the corresponding polymer **3**, in which monomer **1** was recovered almost quantitatively (runs 1−3). Next, the similar reaction with phenol **2d** bearing electron-withdrawing (EWD) groups, trifluoromethyl (CF_3) groups, on its benzene ring was carried out to yield polymer **3** with the number-average molecular weight (M_n) in good conversion (run 4). Furthermore, when similar polymerizations were attempted with fluorine (F)-substituted phenols **2e** and **2f**, each conversion of GPE and M_n slightly increased (runs 5 and 6). Therefore, introduction of such EWD groups might efficiently stabilize the dissociated phenoxide ion in excited state, resulting in propagation of the cationic ring-opening polymerization. On the other hand, no polymerization with phenols **2a**−**f** proceeded even at 100 °C for 24 h under room light, and accordingly the present polymerization was specifically carried out under photoirradiation. These results clearly indicate that suitable EWD groups substituted phenols **2d**−**f** serve as a new nonsalt-type photolatent initiator for the polymerization of an epoxide.

The photoinitiated bulk polymerizations were examined under different reaction times with the EWD groups substituted phenols **2d**−**f** and with 2,3-difluoro-6-nitrophenol (**2g**) which should be regarded as a phenol **2e** analogue, namely, a substituted phenol bearing a nitro group at the *o*-position of phenol **2e**. Figure 1 shows the time−conversion curve for the polymerizations of GPE with 10 mol % of phenols **2d**−**g** at room temperature. As a result, the polymerization with CF_3-substituted phenol **2d** were initiated after 3 h, and the conversion of GPE reached more than ca. 80% for 12 h. On the other hand, similar polymerizations with F-substituted phenols **2e** and **2f** smoothly propagated, and each conversion of GPE reached more than ca. 90% for 12 h. To our surprise, however, phenol **2g** did not initiate the polymerization even for 24 h, in which an almost quantitative yield of monomer **1** was recovered. In addition, the polymerization of GPE with phenol **2g** under room light also did not proceed even at 100 °C for 24 h. The activity order for a photolatent initiator should be estimated as **2f** $\approx$ **2e** $>$ **2d** $\gg$ **2g** on the basis of the relationship between the time and conversion.

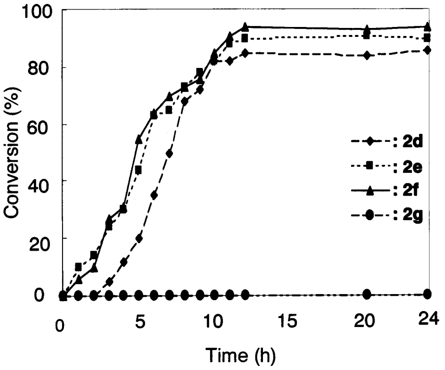
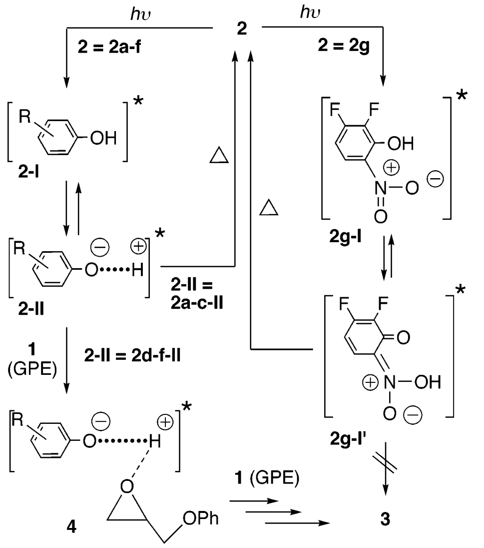


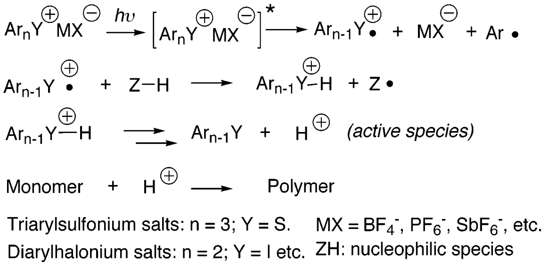
Figure 1. Relationship between the time and conversion for bulk photoinitiated polymerization of GPE with 10 mol % of phenols **2d**−**g** at room temperature.

The present polymerization may be speculated to proceed via a distinctly different mechanism from that with hitherto known photolatent initiators represented by onium salts, such as triarylsulfonium and diaryliodonium salts. Thus, an actual active species in the case of photopolymerization with hitherto known photolatent initiators is a chemical species in the ground state, which generated via photolysis of the excited initiator, ultimately.[11,12] On the other hand, in the present case with phenols **2d**−**f**, an excited species **2-II** (excited phenols **2d-f-II**) will be directly concerned to initiate the cationic polymerization via the corresponding intermediate **4**, as shown in Scheme 2. In addition, agreement between the ^{1}H NMR spectrum of the resulting poly(GPE) in the present polymerization and that in the similar reaction initiated by Lewis acid such as $BF_3{\cdot}OEt_2$, in which the actual active species is a proton generated via reaction of Lewis acid with residual moisture in the reaction system, supported that the present reaction should be initiated by a proton derived from the phenols.[13] Incidentally, no photodegradation product observed in the similar photoreaction of such phenol in the absence of monomer **1**. In the reactions with phenols **2a**−**c**, the polymerization activity of each excited phenols **2a**−**c-II** should be insufficient to lead the corresponding intermediates **4** yielding polymer **3**, presumably due to the above reason. Meanwhile, the unexpected result in the reaction with phenol **2g** is considered as follows. Thus, the excited phenol **2g-I** generated by UV irradiation to phenol **2g** should efficiently lead to intermediate **2g-I′** via excited-state intramolecular proton transfer between the phenol OH and the *o*-substituted NO_2 group (nitro−*aci*-nitro tautomerism, **2g-I** to **2g-I′**), resulting to prevent the polymerization.[14]

Scheme 2



Scheme 3



In summary, a new class of nonsalt-type cationic photolatent initiators directly showing the polymerization activity in the excited state was developed by use of excited phenols with suitable substitutions. Thus, phenols **2d**−**f** bearing CF$_3$ or F groups as the suitable substituent(s) were successfully found to act as a nonsalt-type photolatent initiator for cationic ring-opening polymerization of GPE, in which the activity order for a photolatent initiator should be estimated as **2f** ≈ **2e** > **2d**. Similar photopolymerizations with various substituted phenols including substituted naphthols are now in progress in order to improve the polymerization efficiency,[15] and the results will be published elsewhere.

References and Notes

(1) (a) Mark, H. F., Gaylord, N. G., Bikajes, N. M., Eds. *Encycl. Polym. Sci. Technol.* **1968**, *8*, 303; Interscience Publishers: New York, 1966; Vol. 4, p 528. (b) Muizebelt, M. J. *J. Coat. Technol.* **1985**, *57*, 43. (c) Sanda, F.; Endo, T. *Macromol. Symp.* **1996**, *107*, 237. (d) Lee, H., Neville, K., Eds. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1967. (e) Tanaka, Y., Mika, T. F., Eds. *Epoxy Resins Chemistry and Technology*; Marcel Dekker: New York, 1973. (f) Senturia, S. D.; Sheppard, N. F., Jr. In *Epoxy Resins and Composites IV*; Springer-Verlag: Berlin, 1986.

(2) (a) Pappas, S. P.; Hill, L. W. *J. Coat. Technol.* **1981**, *53*, 43. (b) Pappas, S. P. *High Solids Coat.* **1983**, *8*, 2.

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

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

(5) (a) Yagci, Y.; Schnabel, W. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 33. (b) Yagci, Y.; Lukac, I.; Schnabel, W. *Polymer* **1993**, *34*, 1130. (c) Yagci, Y.; Endo, T. *Adv. Polym. Sci.* **1996**, *78*, 61. (d) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485. (e) Yagci, Y. *Macromol. Symp.* **1998**, *134*, 177. (f) Onen, A.; Arsu, N.; Yagcl, Y. *Angew. Makromol. Chem.* **1999**, *264*, 56.

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

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

(8) Toneri, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1957 and references cited therein.

(9) (a) Reetz, M. T.; Hutte, S.; Goddard, R.; Miner, U. *J. Chem. Soc., Chem. Commun.* **1995**, 275. (b) Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1997**, *30*, 6695. (c) Baskaran, D.; Chakrapani, S.; Sivearam, S.; Hogen-Esch, T. E.; Muller, A. H. *Macromolecules* **1999**, *32*, 2865. (d) Kim, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 3499 and references cited therein.

(10) Gao, J.; Li, N.; Freindorf, M. *J. Am. Chem. Soc.* **1996**, *118*, 4912 and references cited therein.

(11) For examples: (a) Crivello, J. V.; Lam, J. H. *Macromolecules* **1977**, *10*, 1307. (b) Crivello, J. V.; Lam, J. H. *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *17*, 977. (c) Kevill, D. N.; Anderson, S. W.; Ismail, N. H. J. *J. Org. Chem.* **1996**, *61*, 7256.

(12) For instance, triarylsulfonium and diarylhaloniumiodonium salts initiate polymerizations under UV irradiation in the following manner. At first, onium salts (Ar$_n$Y$^+$MX$^-$) are excited by absorption of light, and then decay of the excited compounds occurs with the cleavage of a Ar−Y bond to give cation radical Ar$_{n-1}$Y$^{\bullet+}$, anion MX$^-$, and aryl radical Ar$^\bullet$. The cation radical will generally react with a nucleophilic species, Z−H, to generate cationic species [Ar$_{n-1}$Y−H]$^+$ and radical Z$^\bullet$, although it can react in a number of ways due to its high reactivity. Then the cationic species rapidly deprotonates to give the aromatic compound Ar$_{n-1}$Y and a proton, which should actually exist as a protonic acid in the reaction system. The protonic acid ultimately behaves as the predominant active species initiating cationic polymerizations (Scheme 3).

(13) The terminal end group of the resulting polymer is expected to be the corresponding substituted phenoxy group and/or hydroxyl one derived from (residual) moisture, but it was not clearly observed at this stage in the NMR measurement due to overlap of phenoxy unit based on poly(GPE).

(14) Excited-state intramolecular proton transfer is one of an important photochemical process, and many investigations have been widely carried out experimentally and theoretically: (a) Vargas, V.; Amigo, L. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1124. (b) Himo, F.; Noodleman, L.; Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Phys. Chem. A* **2002**, *106*, 8757. (c) Lukeman, M.; Wan, P. *J. Am. Chem. Soc.* **2002**, *124*, 9458 and references cited therein.

(15) The pK_a of β-naphthol is 9.2, while the excited-state pK_a is 2.8 in aqueous solution; see ref 10.

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