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S-Alkyldibenzothiophenium Salts as New Thermal Latent Cationic Initiators

Osamu Shimomura and Toshihiko Sato

General Sekiyu K.K., 6-1, Ukishima-cho, Kawasaki-ku, Kawasaki 210-8526, Japan

Ikuyoshi Tomita

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226−8503, Japan

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Various kinds of onium salts such as iodonium,[1,2] pyridinium,[3] phosponium,[4] and sulfonium[1,5,6] salts have been reported to serve as efficient thermal latent and photo latent cationic initiators. These onium salts reveal the initiation activity by means of the generation of a carbenium ion or a proton under external stimulations. Besides the cationic species, neutral components (e.g., sulfides from sulfonium salts) are produced, which, in some cases, have nucleophilic characters and hinder the polymerization. In the case of sulfides, the nucleophilicity is known to decrease in the order Me_2S > Ph_2S > phenoxathiin > dibenzothiophene > benzothiophene > thiophene.[7,8] Thermal-induced cationic polymerization with benzyl salts of aliphatic or aryl sulfide has been investigated in which some kinds of the salts possessing benzyl moieties were found to serve as efficient latent thermal initiators in the cationic polymerizations.[6] Since sulfonium salts derived from less nucleophilic sulfides such as dibenzothiophene are relatively rather unstable, a new thermal latent catalyst that reveals high initiation activity to the cationic polymerization might be designed simply by the alkylation of the sulfur atoms. Accordingly, we describe herein the possibility of dibenzothiophenium salts (**3a**−**d**) as the thermal latent catalyst in the cationic polymerization of glycidyl phenyl ether (**1**).

Although the bulk polymerization of glycidyl phenyl ether (**1**) by 5-methyldibenzothiophenium tetrafluoroborate[7] (**3a**, 1 mol %) did not take place at ambient temperature (25 °C), the reaction at 80 °C proceeded homogeneously in 83% conversion to give a polymer after 1 h (Scheme 1). Thus, the efficiency of **3a** and its *S*-octyl analogue (**3b**) were evaluated at various temperatures for 1 h (Figure 1a). The conversion of **1** increased as the polymerization temperature rose. In the case of **3a**, almost no polymerization took place at ambient temperature for 3 h, while **3b** converted 19% of **1** under the same conditions (Figure 1b). As expected, the order of the activity was found to be **3b** > **3a**, in accordance with the stability of dibenzothiophenium salts.[9] However, the *S*-methyl derivative (**3a**) is a better candidate for the construction of a latent initiator that does not reveal the activity at ambient temperature (but on heating).

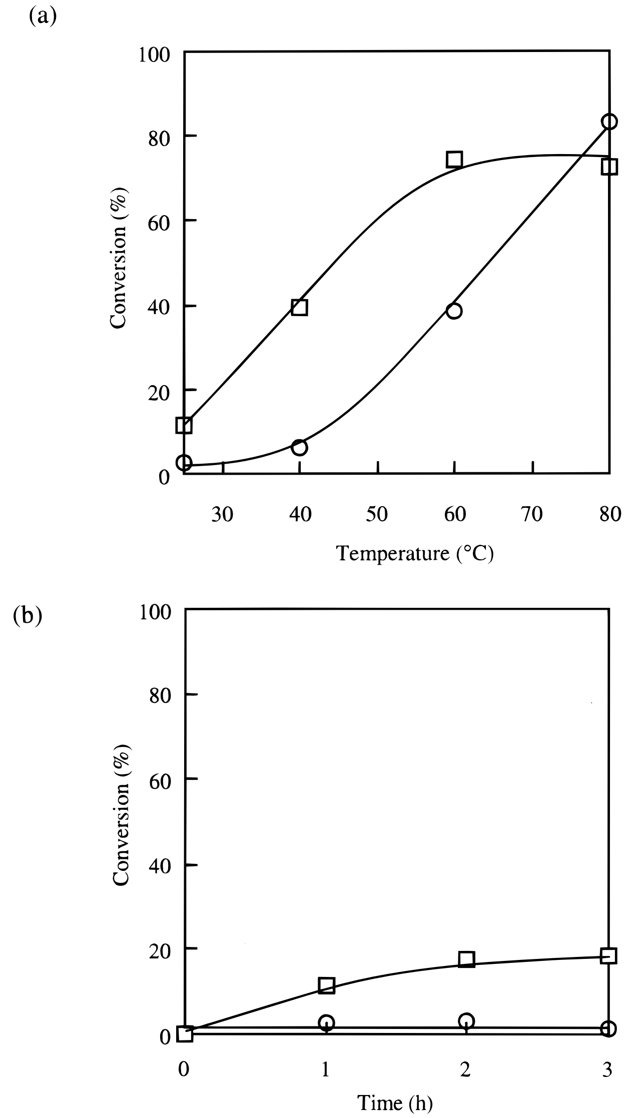
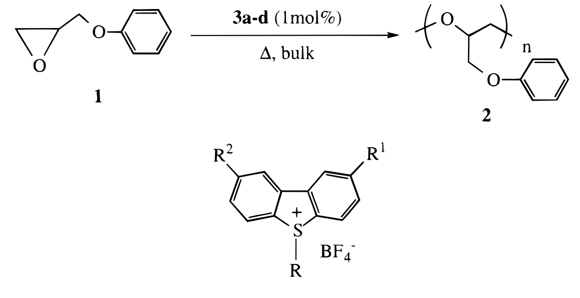


Figure 1. Temperature−conversion curves of **1** in the polymerization initiated with **3a** (○) and **3b** (□) at various temperatures for 1 h. (b) Time−conversion curves of **1** in the presence of **3a** (○) and **3b** (□) at ambient temperature (25 °C).

Scheme 1



3a : R = CH_3, R^1 = H, R^2 = H
3b : R = C_8H_{17}, R^1 = H, R^2 = H
3c : R = CH_3, R^1 = C_2H_5, R^2 = H
3d : R = CH_3, R^1 = C_2H_5, R^2 = C_2H_5

The latency of **3a** is still not enough; the slow conversion of **1** was observed at 12% on heating at 40 °C for 3 h (Figure 2a). It may be preferable to suppress

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* Author to whom all correspondence should be addressed.

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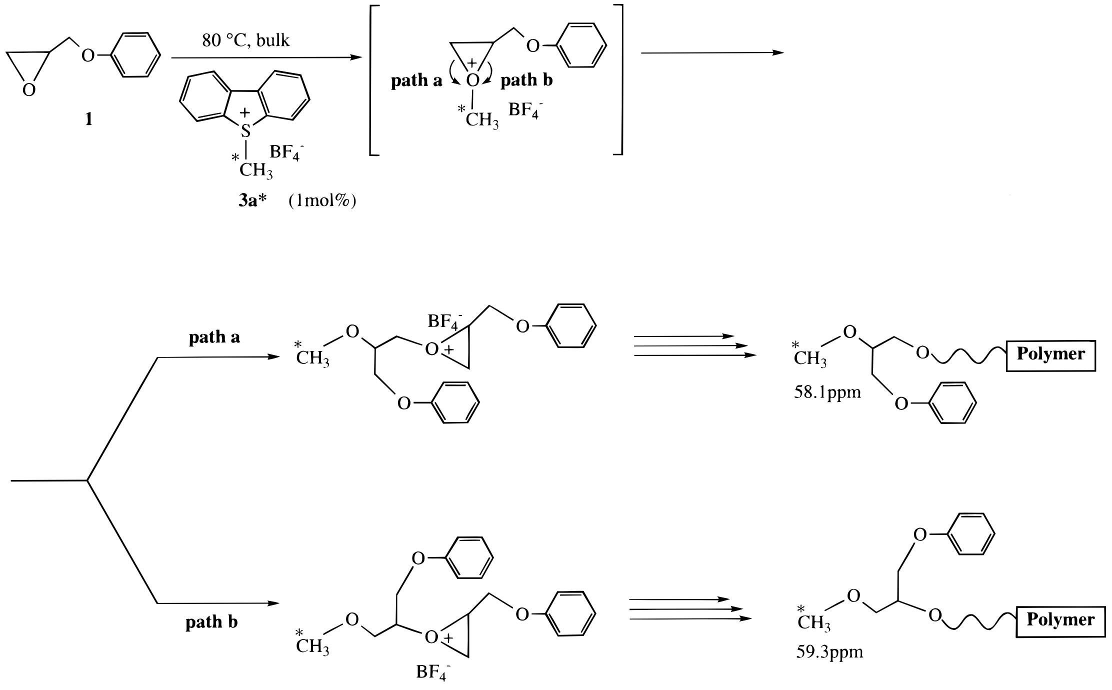
Scheme 2



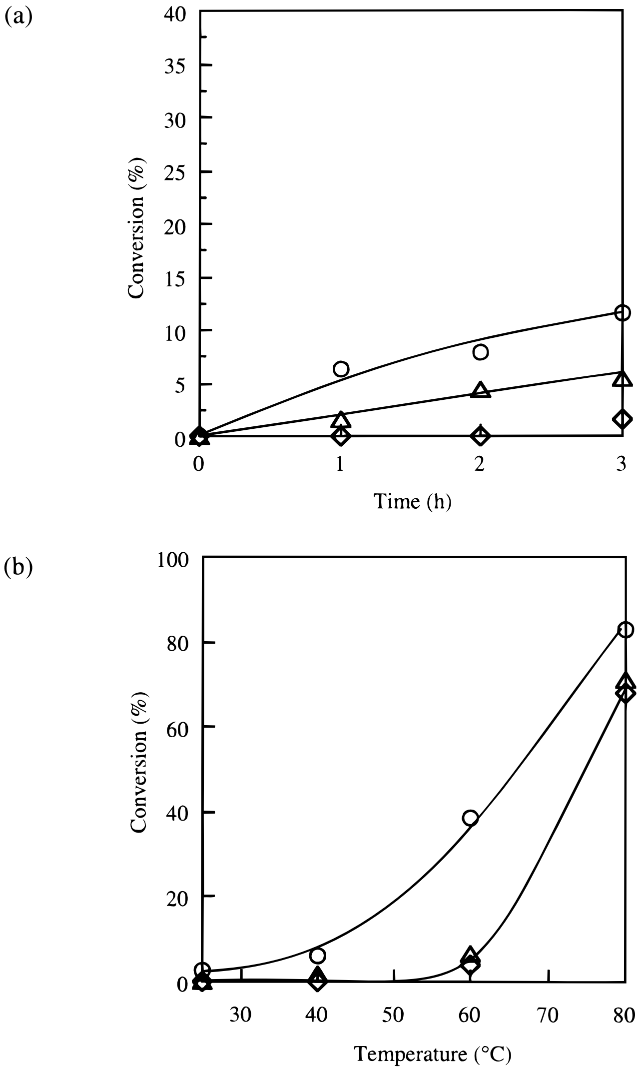


Figure 2. (a) Time−conversion curves of **1** in the presence of **3a** (○), **3c** (△), and **3d** (◇) at 40 °C. (b) Temperature−conversion curves of **1** in the polymerization initiated with **3a** (○), **3c** (△), and **3d** (◇) at various temperatures for 1 h.

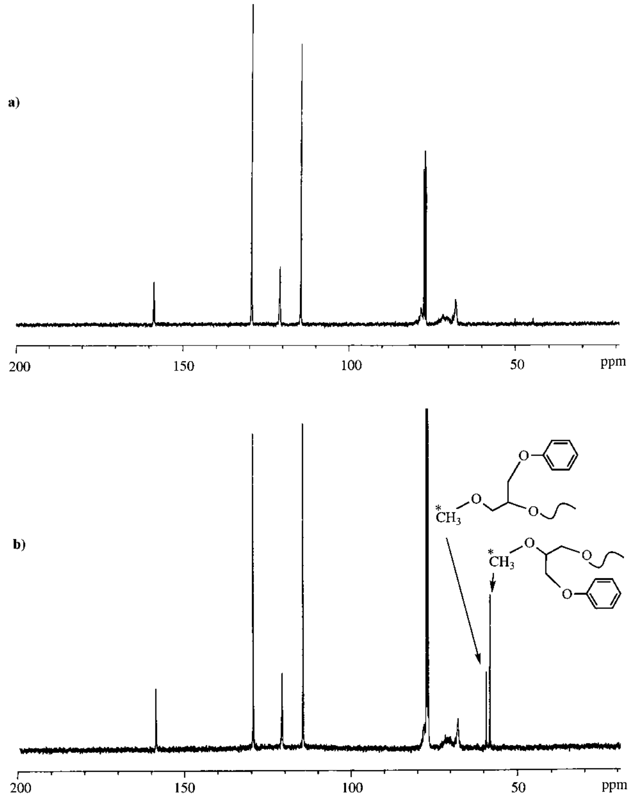


Figure 3. ^{13}C-NMR spectra of poly(glycidyl phenyl ether) initiated by **3a** (a) and **3a*** (b).

the activity of the catalyst for the application as a thermal latent initiator. Thus, dibenzothiophenium salts (**3c** and **3d**) in which alkyl groups were introduced on the aromatic rings were prepared and examined.[10] As shown in Figure 2a, the activities of dibenzothiophenium salts were apparently reduced at 40 °C as the number of the substituents increased. The order of the activities was found to be **3a** > **3c** (2-ethyl) > **3d** (2,8-diethyl), and no reaction proceeded in the case of **3d**. The results might indicate that the electron-donating substituent on the aromatic system raised the initiation temperature. Further, the catalytic activities of **3c** and **3d** were evaluated at various temperatures for 1 h (Figure 2b). A dramatic improvement of the latent properties was observed by the introduction of the ethyl groups, indicating that both **3c** and **3d** are promising thermal latent initiators.

To elucidate the nature of the initiating species generated from the *S*-alkyldibenzothiophenium salts, the bulk polymerization of **1** was carried out at 80 °C for 1 h using a ^{13}C-labeled *S*-methyl salt (**3a***, 1 mol %). From the ^{13}C NMR spectrum of the polymer isolated by reprecipitation with MeOH, two peaks attributable to the methoxy groups were observed at 58.1 and 59.3 ppm (Figure 3b).[11] Since the corresponding peaks were not present in the case of the polymer obtained by **3a** (Figure 3a), some of the initiating ends, at least, should have the methyl groups originated from *S*-methyl moieties. Accordingly, it may be supported that the *S*-methyldibenzothiophenium salt (**3a**) generates the methyl cation that attacks **1** to initiate the polymerization (Scheme 2). The formation of two kinds of the end-methoxy groups can be explained by the two paths for the ring-opening process.[12]

In summary, the dibenzothiophenium salts (**3a**−**3d**) were demonstrated as a new latent thermal initiating system. The detailed study on the effect of substituents on the salts and the application to other monomer systems are now in progress.

Supporting Information Available: Text giving synthetic details and spectral data (4 pages). Ordering and Internet access information is given on any current masthead page.

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(11) The assignment of methoxy groups was performed by referring to the ^{13}C NMR spectrum of a model compound, i.e., 1,2-dimethoxy-3-phenoxypropane, in which the signals of the methoxy groups were observed at 58.1 ppm ($-$CH-O-*C*H$_3$) and 59.3 ppm ($-$CH$_2$$-O-$*C*H$_3$).

(12) By the measurement of the NNE spectrum, the integral ratio of the two peaks at 58.1 and 59.3 ppm was estimated as 66:34, which might reflect on the selectivity in the ring-opening process (paths a and b in Scheme 2).

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