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Novel Anionic Thermally Latent Initiating Systems: Controlled Anionic Polymerization of Glycidyl Phenyl Ether with Silylated Nucleophiles/Inorganic Fluoride Salts System

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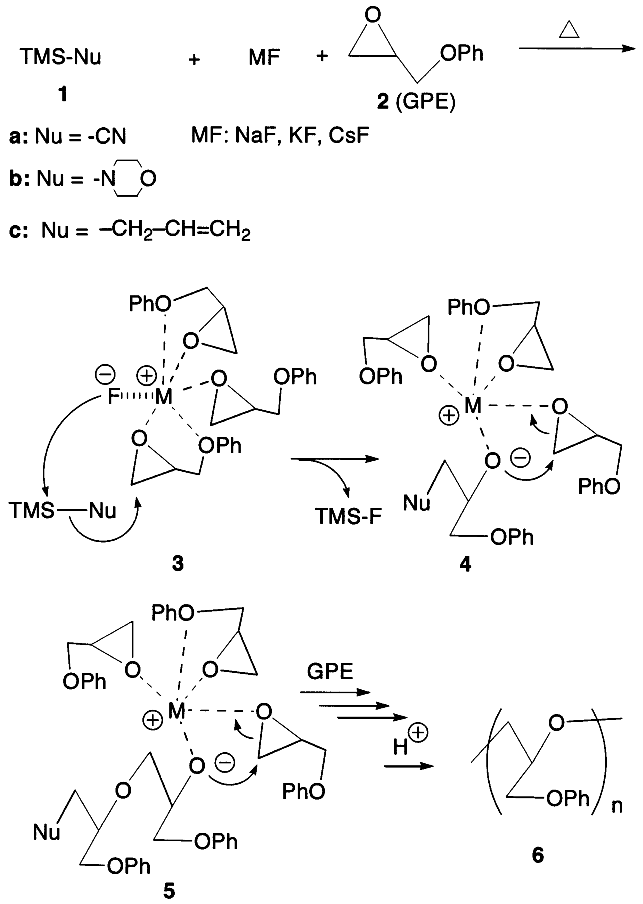
Introduction. For the past decades, numerous numbers of new *latent initiators*, which show no activity under normal polymerization conditions but release active species by external stimulation, such as heating and photoirradiation, have been widely developed, since latent initiators have attracted much attention in several industrial fields such as paints, inks, epoxy molding compounds, and photoresists.[1] For example, diaryliodonium and triarylsulfonium salts can generate active species by photoirradiation, which are useful as efficient initiators for epoxy resin.[1d,2] We have reported that several onium salts, such as benzylsulfonium,[3] pyridinium,[4] and phosphonium[5] salts, serve as thermally latent and photolatent initiators, releasing a benzyl cation or proton as an active species. Further, we have developed non-salt-type latent initiators such as N-substituted phthalimides,[6] aminimides,[7] carboxylic acid esters,[8] and sulfonic acid esters[9] to enhance the solubility of the initiators in monomers. Although a large number of cationic latent initiators have been reported, an *anionic* one has been rarely developed, despite an anionic polymerization being expected to show significant practical advantages.[10] The polymers synthesized by anionic polymerization generally have a narrow molecular weight distribution (M_w/M_n) and controlled their structures because the growing species should be relatively stable to prevent side reactions, such as chain transfer reaction or termination during the polymerization. Furthermore, the utilization of suitable conditions can allow living polymerization capable of affording polymers with strictly controlled chain architectures.

We describe herein anionic polymerization of glycidyl phenyl ether (**2**, GPE) with various trimethylsilylated nucleophiles **1** [TMS−Nu, **1a:** trimethylsilylnitrile (TMS−CN); **1b:** *N*-(trimethylsilyl)morpholine; **1c:** allyltrimethylsilane] in the presence of inorganic fluoride salts (MF: NaF, KF, CsF) as a novel anionic thermally latent initiating system (Scheme 1). Fluoride ion-mediated reactions of silylated nucleophiles are widely used in carbon−carbon bond formations under nearly neutral conditions, in which organic fluoride salts, such as tetrabutylammonium fluoride (TBAF) and tris(diethylamino)sulfonium difluorotrimethylsilicate (TSAF), are mostly employed as a fluoride ion source. More recently, we have reported that the KF/18-crown-6 system was also a useful fluoride ion source to promote desilylation of trimethylsilylated compounds efficiently.[11] Then, a fluoride ion may be expected to generate even from a simple inorganic fluoride salt (MF)/ether compound (such as epoxides) system: the dissociation of inorganic fluoride salts should be carried out at elevated temperature, presumably due to solvate by coordination of ether compounds to metal cation species (M^+).

Scheme 1



Results and Discussion. Table 1 shows the result of bulk polymerization of GPE (**2**) with TMS−CN (**1a**) as a silylated nucleophile in the presence of inorganic fluoride salts such as NaF, KF, and CsF. At first, the attempted polymerization with NaF did not proceed even at 150 °C for 24 h (run 1), but the second with KF produced a small amount of polymer (run 2). On the other hand, the polymerization in the presence of CsF took place at 150 °C for 3 h to yield the polymer with relatively narrower M_w/M_n quantitatively (run 3), and the conversion of GPE reached more than 40% even at 100 °C for 3 h, although no polymerization proceeded at room temperature over 2 weeks (runs 4 and 5). These results strongly suggest that the TMS−CN/CsF system efficiently serves as a new thermally latent initiator for the polymerization of GPE.[12]

Figure 1 shows the temperature−conversion curve in the bulk polymerization of GPE with TMS−CN (**1a**) in the presence of CsF. The polymerization of GPE with the **1a**/CsF system did not proceed below 80 °C, while the polymerization started above 80 °C and GPE was quantitatively polymerized at 120 °C.

The polymerization of THF with the **1a**/CsF system did not provide the corresponding polymer even at 65 °C for 1 week.[13] The result and the relatively narrow

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Table 1. Anionic Polymerizations of GPE (2) with TMS−CN (1a) in the Presence of Inorganic Fluoride Salts[a]

run	fluoride salts	temp (°C)	time (h)	conv[b] (%)	M_n (M_w/M_n)[c]
1	NaF	150	24	0	no polymerization
2	KF	150	24	10	1425 (1.02)
3	CsF	150	3	100	2530 (1.14)
4	CsF	100	3	41	2098 (1.08)
5	CsF	rt	>2 weeks	0	no polymerization

[a] Reaction conditions: to 1 mmol of GPE, 3 mol % of TMS−CN and 3 mol % of inorganic fluoride salts were used. [b] Determined by ^{1}H NMR. [c] Estimated by GPC based on polystyrene standard samples.

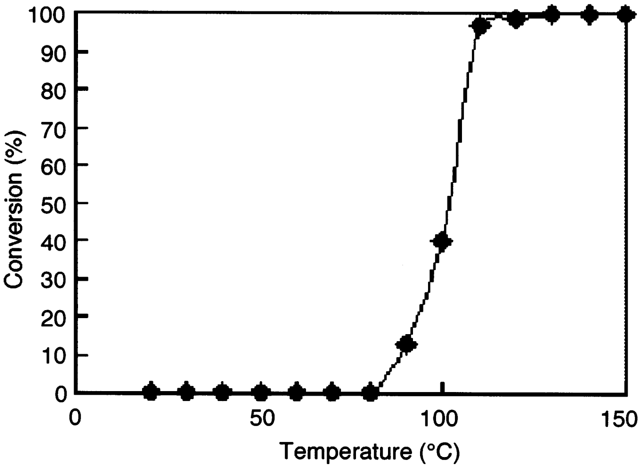

Figure 1. Relationship between the temperature and conversion for bulk polymerization of GPE with 3 mol % of TMS−CN (**1a**) in the presence of 3 mol % of CsF for 3 h.

M_w/M_n in the present polymerizations of GPE strongly suggest that in the present initiating system the anionic ring-opening polymerization should propagate via the nucleophilic attack of the C≡N anion to GPE. Hence, as we expected, the initially formed fluoride ion should efficiently combine with a Si atom on the TMS group of the silylated nucleophile (**1a**) at elevated temperature to generate the C≡N anion and trimethylsilyl fluoride (TMS−F) via desilylation of TMS−CN, followed by initiating the epoxy polymerization, as shown in Scheme 1. The growing species in the polymerization would be alkoxide anion **4**, which should exist with an ion-pair bond between the terminal alkoxide anion and the cesium cation coordinated by epoxy compounds **2**, to prevent side reactions such as chain transfer reaction or termination during the polymerization to give the polymers with broad M_w/M_n.

The above consideration of the present polymerization mechanism clearly suggests that the polymerization initiating temperature could be controlled on the basis of the bond energy between the trimethylsilyl group and the corresponding nucleophile moiety (TMS−Nu). Thus, in similar polymerizations, silylated nucleophiles with the higher bond dissociation energy between the trimethylsilyl group and the corresponding nucleophile (TMS−Nu) than that of TMS−CN would exhibit catalytic activity at higher temperatures. Then, we attempted similar polymerizations with silylated nucleophiles **1b** and **1c**, which have a higher bond dissociation energy than that of TMS−CN (**1a**) (vide infra) in the presence of CsF for 3 h at various temperature (Figure 2). These polymerizations with the **1b**/CsF and **1c**/CsF systems did not occur even at 120 °C, which is an adequate polymerization initiating temperature for the polymerization with the **1a**/CsF system, where the initiation of the polymerization was observed above 120 and 140 °C, respectively, and each conversion of GPE was quantitative at 150 and 200 °C. In addition, these polymers synthesized with **1b**/CsF and **1c**/CsF systems also exhibited a relatively narrow M_w/M_n (**1b**/CsF: 1.17−1.22; **1c**/CsF: 1.20−1.24).

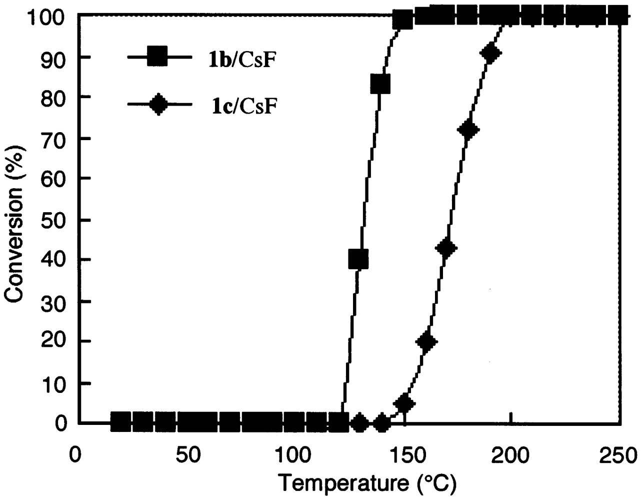

Figure 2. Relationship between the temperature and conversion for bulk polymerization of GPE with 3 mol % of silylated nucleophiles **1b** and **1c** in the presence of 3 mol % of CsF for 3 h.

Each bond dissociation energy between the trimethylsilyl group and the corresponding nucleophile moiety of silylated compounds **1a**−**c** (TMS−Nu) was investigated by density functional theory calculations (B3LYP/6-31G*), and the energy order was **1b** (227.55 kcal/mol) ≥ **1c** (220.32 kcal/mol) ≫ **1a** (200.00 kcal/mol). Thus, it was found that the above experimental results about the activity order for the present polymerization well agreed with the theory calculation ones when the energy gap was relatively large, e.g., **1a** ≫ **1b** and **1c**. In addition, the difference between the theoretical calculation results and the above experimental ones, in the polymerizations with silylated nucleophiles **1a** and **1b**, also suggested that the nucleophilic ability included electronic and steric factors. These additional factors are heavily involved in the initiating activity for the polymerization, to the dissociation energy factor, when the value of the bond dissociation energy was relatively close, e.g., **1b** ≥ **1c**. Hence, the theoretical calculation results and the experimental ones may suggest that the polymerization initiating temperature can be roughly controlled by estimation of the bond dissociation energy between the trimethylsilyl group and the corresponding nucleophile moiety (TMS−Nu).

After polymerization under the similar reaction conditions to run 3 in Table 1, additional GPE was charged, and the mixture was further polymerized for 3 h to yield the polymer with higher molecular weights (M_n = 2848) than the case of run 3 in Table 1, while maintaining the relatively narrow M_w/M_n (1.17). These results may suggest that terminal alkoxide anion **5** would be stable by coordination of cesium cation and that a living polymerization for GPE could be carried out by using the present novel thermally latent initiating system under appropriate conditions.

In summary, this work demonstrated that silylated nucleophiles **1**/CsF systems successfully serve as new thermally latent *anionic* initiating ones for polymerization of GPE, and the polymerization initiating temperature was found to be roughly controlled on the basis of the bond dissociation energy between the trimethylsilyl group and the corresponding nucleophile moiety (TMS−Nu).

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(13) Figure 1 shows that the present polymerization of GPE was carried out over 80 °C. However, similar polymerization also proceeds at 65 °C, although long polymerization time (ca. 24 h) was required.

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