Polymerization of Epoxide With Hydroxylamides as Thermally Latent Initiators

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ABSTRACT: A new class of thermally latent initiators for the ring-opening polymerization of epoxides has been developed. The latent initiators developed herein were the hydroxylamides **1a**, **1b**, and **1c**, which were synthesized from phthalide, 3-isochromanone, and *cis*-cyclohexahydrophthalide, respectively, by their ring-opening reactions with pyrrolidine. These hydroxylamides were designed so that their hydroxyl groups could attack the amide moiety intramolecularly upon heating, leading to ring closure and formation of the corresponding lactones while releasing pyrrolidine, the initiator for the anionic ring-opening polymerization of an epoxide. The temperatures at which this thermal dissociation occurred were strongly dependent on the hydroxylamide molecular structure. When using the hydroxylamides as thermally latent initiators, the polymerizations of bisphenol-A diglycidyl ether were investigated at various temperatures. This investigation clarified that the threshold temperature, that is, the temperature at which polymerization was initiated, increased in the order of **1a**, **1b**, and then **1c**. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

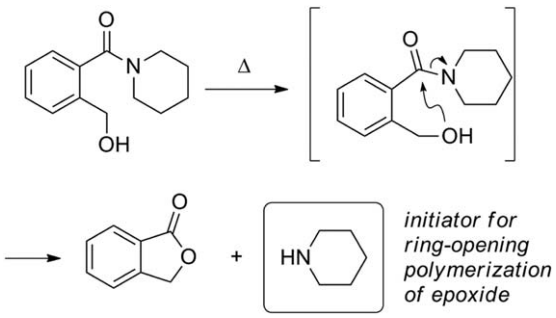
KEYWORDS: anionic polymerization; crosslinking; initiators; ring-opening polymerization

INTRODUCTION Epoxy resins have been widely used in coatings, paintings, and adhesive applications, because their curing reactions give materials with good mechanical strength and chemical resistance. The curing reactions of epoxy resins are performed by adding appropriately selected hardeners or initiators to the epoxide mixture. When the hardeners or initiators are highly active, they are used in a so-called "two-component system," where they are mixed with the epoxy resins immediately prior to the curing reactions. In contrast, "one-component systems" where the epoxy resins and initiators are premixed, and thus ready for use, are practically more appreciated. The initiators used therein must be "latent," which are carefully designed so that they can be premixed and stored stably; however, some external stimulation, such as irradiation and heating, is required to trigger their programmed dissociation into the corresponding fragments that can initiate the ring-opening polymerization of the epoxides. So far, various photo-latent[1–7] and thermally latent initiators for the ring-opening polymerization of epoxides have been developed, the latter of which involve diverse onium salts such as ammonium,[8,9] anilinium,[10] pyridinium,[11] pyradinium,[12,13] imidazolium,[14,15] phosphonium,[13,16,17] and sulfonium,[18,19] and iodonium[20] salts. In addition, the development of nonsalt type thermally latent initiators has been also an important research target because of their potentially low toxicity and high miscibility in epoxy resins. Such nonsalt type latent initiators involve cyanoacetamide,[21] aminimides,[22] phosphonic amide esters,[23] doped polyaniline,[24] and sulfonates.[25]

Previously, we have reported that a hydroxylamide could also serve as a thermally latent anionic initiator for the polymerization of epoxides.[26] As shown in Scheme 1, the species that initiated the polymerization was piperidine, released from the hydroxylamide by its thermally induced cyclization. The key point in the molecular design of this hydroxylamide-type latent initiator is the linking of the hydroxyl group and amide group by a tether containing a rigid *o*-phenylene moiety, so that the decrease in entropy upon reaction can be minimized. This design also allows for the formation of a thermodynamically stable five-membered lactone, of which formation is favorable from the viewpoint of enthalpy. Based on a similar concept, we have also developed phosphamide-type latent initiators.[23]

Our interests currently lie in expanding the scope of the abovementioned molecular design of hydroxylamides for developing a variety of initiators that can initiate the ring-opening polymerization of epoxides at various temperatures

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Release of an amine-type initiator by the thermally induced cyclization of hydroxylamide.

on demand. Herein we demonstrate the polymerization of bisphenol A diglycidyl ether (BADGE) using a series of hydroxylamides **1** that can be derived from pyrrolidine, a simple 5-membered cyclic amine, as thermally latent initiators (Scheme 2). Because there are a wide variety of 5-membered cyclic amines with a broad range of functional groups such as proline, a naturally occurring amino acid, by proving the usefulness of **1** as latent initiators, we aimed to broaden the range of structural diversity of hydroxyamide-type initiators.

EXPERIMENTAL

Materials

Pyrrolidine, BADGE, glycidyl phenyl ether (GPE), and methanol were purchased from Wako Pure Chemical Industries and were used as received. Phthalide, 3-isochromanone and *cis*-1,2-cyclohexanedicarboxylic anhydride were purchased from Tokyo Chemical Industry and used as received. The procedure for synthesizing *cis*-cyclohexahydrophthalide from *cis*-1,2-cyclohexanedicarboxylic anhydride is described in the Supporting Information.

Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL300 NMR spectrometer with tetramethylsilane as an internal standard. Viscosity was measured with a Brookfield viscometer (Model Cap 2000$^+$). Differential scanning calorimetry (DSC) measurements were performed on a SEIKO DSC6200. Thermogravimetry (TG) measurements were performed on a SEIKO EXSTAR6000.

Synthesis of Hydroxylamide 1a

To a solution of phthalide (1.34 g, 10.0 mmol) in methanol (10 mL), a solution of pyrrolidine (0.85 g, 12 mmol) in methanol (10 mL) was added at room temperature. The resulting solution was stirred at room temperature for 24 h, and then concentrated under reduced pressure. The resulting residue was dissolved in ether (50 mL) and washed three times with 0.1 M hydrochloric acid (50 mL). The ether solution was dried over $MgSO_4$ and then concentrated under reduced pressure. The resulting residue was fractionated using silica gel column chromatography with a 1:1 mixture of hexane and acetone as the eluent, to obtain **1a** as a colorless liquid (1.37 g, 6.67 mmol, 67% yield). ^{1}H NMR (300 MHz, in $CDCl_3$, δ in ppm) 7.44–7.32 (m, 4H), 4.53 (d, $J = 6.1$ Hz, 2H), 3.98 (br t, $J = 6.1$ Hz, 1H), 3.68 (t, $J = 7.0$ Hz, 2H), 3.34 (t, $J = 6.5$ Hz, 2H), 2.04–1.63 (4H, m); ^{13}C NMR (75.4 MHz, in $CDCl_3$, δ in ppm) 170.4, 139.2, 136.7, 130.0, 129.93, 127.7, 126.8, 64.15, 49.66, 46.08, 26.39, 24.72.

Synthesis of Hydroxylamide 1b

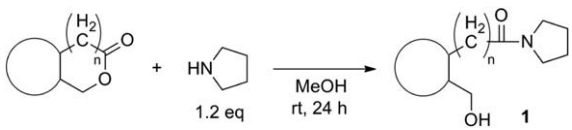
To a solution of 3-isochromanone (1.48 g, 10.0 mmol) in methanol (10 mL), a solution of pyrrolidine (0.85 g, 12 mmol) in methanol (10 mL) was added at room temperature. The resulting solution was stirred at room temperature for 24 h, and then concentrated under reduced pressure. The resulting residue was dissolved in ether (50 mL) and washed three times with 0.1 M hydrochloric acid (50 mL). The ether solution was dried over $MgSO_4$ and then concentrated under reduced pressure. The resulting residue was fractionated using silica gel column chromatography with a 1:10 mixture of hexane and ethyl acetate as the eluent, to obtain **1b** as a colorless liquid (1.10 g, 5.02 mmol, 50% yield). ^{1}H NMR (300 MHz, in $CDCl_3$, δ in ppm) 7.43–7.40 (m, 1H), 7.29–7.26 (m, 2H), 7.17–7.15 (m, 1H), 4.78 (t, $J = 6.1$ Hz, 1H), 4.61 (d, $J = 6.1$ Hz, 2H), 3.78 (s, 2H), 3.67 (t, $J = 6.8$ Hz, 2H), 3.48 (t, $J = 6.8$ Hz, 2H), 2.07–1.99 (m, 2H), 1.94–1.87 (m, 2H); ^{13}C NMR (75.4 MHz, in $CDCl_3$, δ in ppm) 170.2, 140.4, 139.8, 130.7, 130.4, 128.1, 127.6, 63.64, 47.32, 46.25, 38.86, 26.09, 24.28.

Synthesis of Hydroxylamide 1c

To a solution of *cis*-cyclohexahydrophthalide (1.40 g, 10.0 mmmol) in methanol (10 mL), a solution of pyrrolidine (0.85 g, 12 mmol) in methanol (10 mL) was added at room temperature. The resulting solution was stirred at room temperature for 24 h, and then concentrated under reduced pressure. The resulting residue was dissolved in ether (50 mL) and washed three times with 0.1 M hydrochloric acid (50 mL). The ether solution was dried over $MgSO_4$ and then concentrated under reduced pressure. The resulting residue was fractionated using silica gel column chromatography with a 100:1 mixture of chloroform and methanol as the eluent, to obtain **1c** as a white solid (1.03 g, 4.87 mmol, 49% yield). Mp 55–57 °C; ^{1}H NMR (300 MHz, in $CDCl_3$, δ in ppm) 4.20–4.00 (m, 1H), 3.69–3.85 (m, 1H), 3.38–3.64 (m, 5H), 2.77–2.66 (m, 1H), 2.11–1.74 (m, 8H), 1.65–1.23 (m, 5H); ^{13}C NMR (75.4 MHz, in $CDCl_3$, δ in ppm) 175.4, 63.25, 46.65, 45.88, 43.52, 38.83, 29.49, 26.11, 25.04, 24.77, 24.13, 22.02.

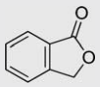
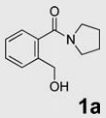
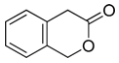
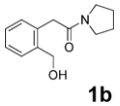
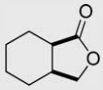
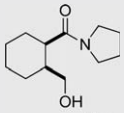
Thermal Dissociation of Hydroxylamides

Each of the hydroxylamides, **1a–1c**, was heated at various temperatures for 2 h in a glass bulb (bulb A) using a



SCHEME 2 Synthesis of hydroxylamides **1**.

TABLE 1 Chemical Structure and Reaction Outcomes of Hydroxylamides, 1, from the Corresponding Lactones

Entry	Lactone	Hydroxylamide	Yield/%	Properties
1		 **1a**	67	Liquid
2		 **1b**	50	Liquid
3		 **1c**	49	Solid, mp = 55–57 °C

Kugelrohr distillation apparatus. Bulb A was connected to a second bulb (bulb B) that was cooled with ice, into which the pyrrolidine formed by the thermal dissociation of the hydroxylamide was condensed. The residue in bulb A was analyzed by ^{1}H NMR spectroscopy to determine the conversion of the hydroxylamide into the corresponding lactone.

Polymerization of BADGE using Hydroxylamides

Typical procedures are given below for the polymerization using **1a**.

1. BADGE (1.36 g, 4.00 mmol) and hydroxylamide **1a** (164 mg, 0.799 mmol) were mixed and degassed at room temperature to obtain a homogeneous mixture.
2. Three small portions of the reaction mixture (~20 mg) were taken and put on a Brookfield viscometer and heated at 50, 100, and 150 °C to monitor the increase in viscosity of the mixture.
3. Several small portions of the mixture (~30 mg) were taken and heated using a DSC instrument in both dynamic mode (heating rate = 10 °C/min) and isothermal mode at several temperatures to obtain the corresponding heat evolution profiles. These experiments were performed under a flow of nitrogen.
4. The rest of the mixture was heated at 180 °C in an oven. The corresponding cured materials were analyzed by TGA and DSC in a dynamic mode (heating rate = 10 °C/min) under a flow of nitrogen.

MODEL POLYMERIZATIONS OF GPE AND HYDROXYLAMIDES

Typical Procedure

A mixture of GPE (150 mg, 1.00 mmol) and hydroxylamide **1a** (20.5 mg, 0.10 mmol) was heated at 180 °C for 2 h. After cooling, the mixture was dissolved in THF and analyzed by thin layer chromatography (TLC) to check for the presence of phthalide formed by the thermal dissociation of **1a**.

RESULTS AND DISCUSSION

Synthesis of Hydroxylamides

The hydroxylamides, **1**, were readily obtained by mixing the corresponding lactones and pyrrolidine in methanol at room

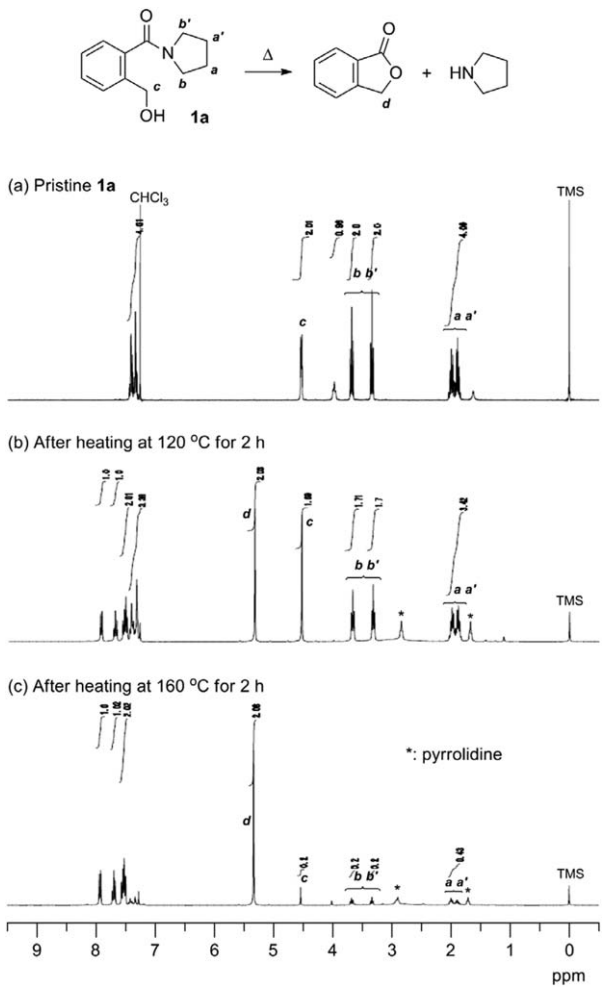


FIGURE 1 ^{1}H NMR spectroscopic monitoring of the thermal dissociation of **1a**.

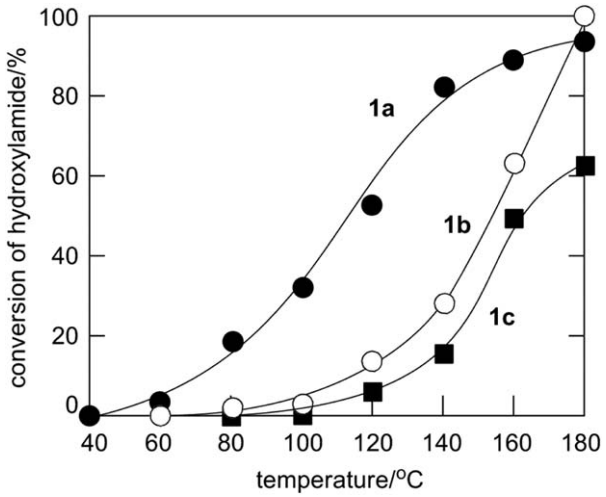


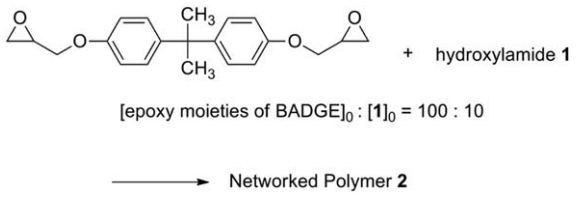
FIGURE 2 Temperature-dependences of the thermal dissociations of the hydroxylamides, **1**.

temperature (Scheme 2). The molecular structures of the lactones used, those of the resulting hydroxylamides, and the corresponding yields are shown in Table 1. All of the reaction products were isolated by column chromatography and their structures were confirmed by NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of **1a** are shown in Figures 1 and S1 (in Supporting Information), respectively. The NMR spectra of **1b** and those of **1c** are shown in Figures S2 and S3 (in Supporting Information), respectively.

Thermal Dissociation of Hydroxylamides

To investigate the thermal dissociation behaviors of the hydroxylamides, they were heated at different temperatures using a Kugelrohr distillation apparatus (Supporting Information Fig. S4). For example, hydroxylamide **1a** was placed in a glass bulb (bulb A) that could be heated in the oven of the apparatus to induce the thermal dissociation of **1a**. Bulb A was connected to another bulb (bulb B) outside of the oven, which was cooled to condense and collect the pyrrolidine formed by the thermal dissociation of **1a** that was distilled out from the bulb A. After heating at a certain temperature (40–180 °C) for 2 h, the remaining residue in bulb A was analyzed by ^{1}H NMR spectroscopy. Figure 1 shows three spectra: (a) the ^{1}H NMR spectrum of **1a**, (b) that of the residue after heating at 120 °C for 2 h, and (c) that of the residue after heating at 160 °C for 2 h.

In these spectra, the signal attributable to the methylene protons of **1a** and the singlet signal attributable to the methylene protons of phthalide appeared at 5.32 and 4.51 ppm, respectively, clarifying that **1a** underwent the desired thermal dissociation into phthalide and pyrrolidine, where the dissociation was promoted by raising the reaction temperature. Comparison of the intensities of these singlet signals attributable to the methylene protons allowed for calculation of the conversion of **1a** into phthalide by thermal dissociation. The conversions calculated in this way are plotted against temperature in Figure 2, which clarified the



SCHEME 3 Polymerization of BADGE using hydroxylamide **1** as a latent initiator.

dependence of the thermal dissociation of **1a** on temperature, where below 40 °C, the dissociation was negligible, at 60 °C, formation of a small amount of phthalide was observed, and above 160 °C, more than 80% of **1a** was transformed into the phthalide.

In a similar way, using the Kugelrohr distillation apparatus and ^{1}H NMR spectroscopy, the thermal dissociation behaviors of hydroxylamides **1b** and **1c** were investigated. For the calculation of the conversion of **1b** into 3-isochromanone, the corresponding signals at 5.25 and 4.56 ppm, respectively, attributable to the methylene group located between the aromatic group and the oxygen atom, were used. For the calculation of the conversion of **1c** into *cis*-cyclohexahydrophthalide, the corresponding signals at 4.21 and 4.11 ppm, respectively, attributable to the methylene group located between the cyclohexyl group and the oxygen atom, were used. Figure 2 shows the dependences of the degree of dissociation on temperature, where for the dissociation of **1b**, a higher temperature than that required for the dissociation of **1a** was necessary. Hydroxylamide **1c** was less labile than **1b**, however. It was stable below 100 °C, and its conversion into the corresponding lactone at 180 °C was only 60%.

In all cases, when the hydroxylamide underwent thermal dissociation to give the corresponding lactone, pyrrolidine was distilled and condensed into bulb B. The yields of pyrrolidine formed were much lower than those expected from the conversions of the hydroxylamides into the corresponding lactones, presumably due to the difficulties in the complete condensation of the formed pyrrolidine in bulb B as a result of its high volatility.

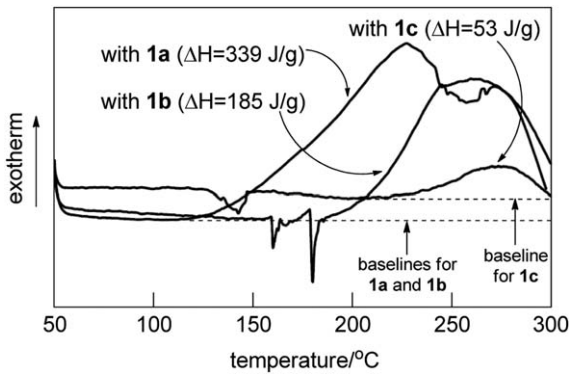


FIGURE 3 DSC-profiles of the hydroxylamides **1** measured using a dynamic scan mode.

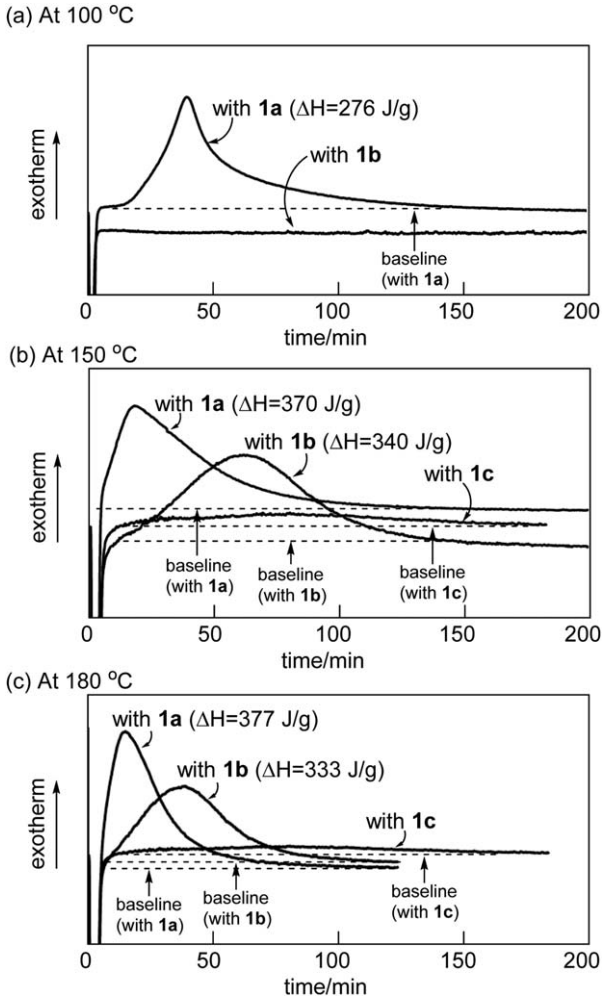


FIGURE 4 DSC-profiles of the hydroxylamides **1** measured using an isothermal scan mode.

Polymerization of Epoxide with Hydroxylamides as Thermally Latent Initiators

The performances of the three hydroxylamides as thermally latent initiators for the polymerizations of epoxides were evaluated by the following three methods employing BADGE as a monomer (Scheme 3): (1) a reaction mixture comprised of BADGE and hydroxylamide (10 mol % to epoxide moiety) was heated in a DSC instrument using a dynamic scan mode to investigate the temperature-dependence of reaction heat evolution; (2) the reaction mixture was heated in the DSC instrument using an isothermal mode to investigate the time-dependence of reaction heat evolution; and (3) the increase in viscosity caused by the polymerization at several temperatures was monitored by a viscometer.

Figure 3 shows the heat evolution profiles obtained from DSC analysis using a dynamic scan mode (25–300 °C at a heating rate of 5 °C/min under nitrogen). As the profiles show, the use of **1a** as a latent initiator resulted in the evolution of heat at the lowest temperature. By employing **1b**, the heat evolution peak shifted to a higher temperature, and in the case of **1c**, this temperature was even higher. These results implied that temperature required for the initiation of the polymerization could be tuned by changing the structure of the hydroxylamide initiator.

Figure 4 shows the heat evolution profiles obtained by the DSC analysis in an isothermal mode. The same reaction mixtures as those used for the abovementioned DSC analysis in a dynamic scan mode were heated at 100, 150, and 180 °C. When the reaction mixture containing **1a** was heated at 100 °C, the corresponding heat evolution started after 10 min and its peak was observed at 40 min, suggesting that **1a** dissociated efficiently and the resulting pyrrolidine formed initiated the polymerization reaction. In contrast, no heat evolutions were observed by heating the reaction mixtures containing **1b** and **1c** at 100 °C, suggesting that their dissociations were not efficient enough to release a sufficient amount of pyrrolidine. By elevating the temperature to 150

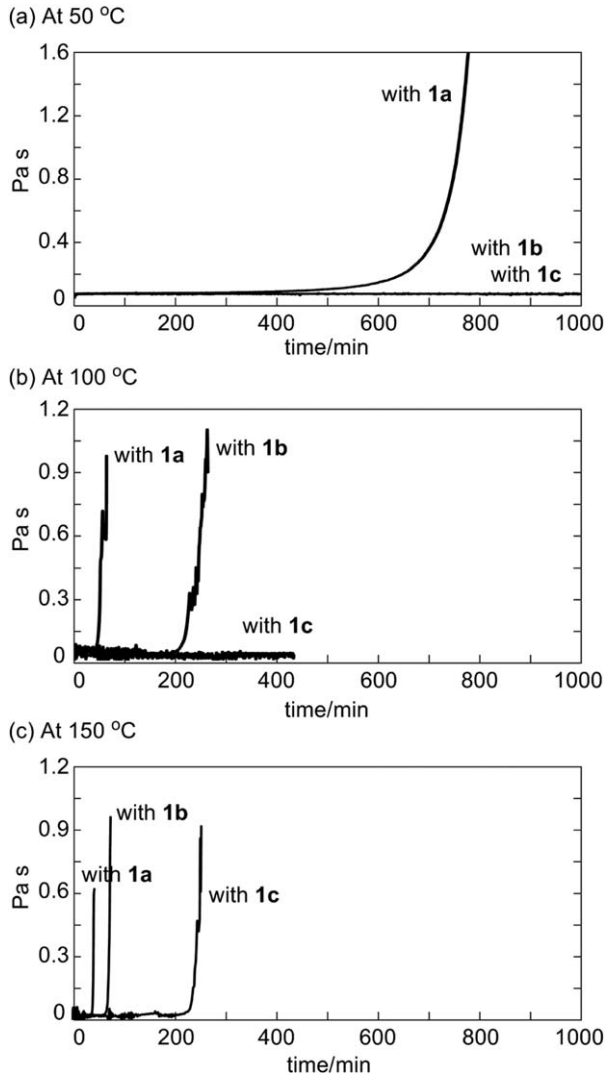


FIGURE 5 Time-viscosity relationships for the polymerizations at various temperatures of BADGE using **1** as a thermal-latent initiator.

TABLE 2 Thermal Properties of the Network Polymers Obtained by the Polymerization of BADGE with Hydroxylamide[a]

Entry	Hydroxylamide	Polymerization Time/min	T_g (°C)[b]	T_{d5} (°C)[c]	T_{d10} (°C)[c]
1	**1a**	40	87	350	365
2	**1b**	45	86	345	362
3	**1c**	90	61	324	354

[a] Conditions: [epoxy moieties of BADGE]$_0$:[hydroxylamide]$_0$ = 100:10; at 180 °C.

[b]Determined by DSC (heating rate 10 °C/min).
[c]Determined by TGA (heating rate 10 °C/min).

°C, a heat evolution peak appeared in the analysis of the reaction mixture that contained **1b**, and quite a broad and low heat evolution was observed in the analysis of the mixture containing **1c**. Even when the temperature was elevated to 180 °C, it was difficult to observe a clear heat evolution from the reaction mixture containing **1c**, while the polymerizations of the other reactions were accelerated significantly at this temperature.

Figure 5 shows the time-viscosity relationships for the reaction mixtures at 50, 100, and 150 °C. These relationships implied that (1) **1a** was the most labile hydroxylamide that induced polymerization at 50 °C, (2) **1b** was the second most labile hydroxylamide that induced polymerization at 100 °C, and (3) by elevating the reaction temperature to 150 °C, the most stable hydroxylamide **1c** induced the polymerization.

We attempted to investigate polymerization behaviors of BADGE using pristine pyrrolidine as an initiator by DSC analysis and viscosity measurement. However, the reaction was not controllable: As was expected from the intrinsic reactivity of pyrrolidine with epoxide, in some cases, exotherm took place immediately just after mixing, and the viscosity started to increase, leading to the unreproducible DSC and viscosity measurements.

Analyses of the Network Polymers Obtained by Polymerization of BADGE using Hydroxylamides as Latent Initiators

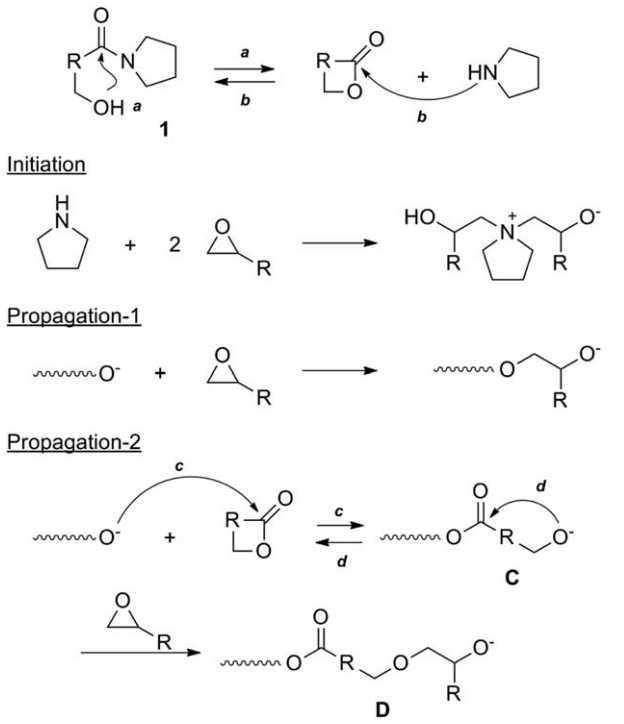
The reaction mixtures comprised of BADGE and hydroxylamide **1a** (10 mol % to epoxide moiety) were heated at 180 °C for 40 min. The other reaction mixtures containing **1b** and **1c** were heated at 180 °C for 45 and 90 min, respectively. IR analyses of the resulting network polymers revealed that the absorption at 916 cm^{-1}, attributable to the epoxy group of BADGE, disappeared, suggesting that the curing reactions were complete. The network polymers prepared were analyzed by DSC and

TG techniques to investigate their thermal properties, and the corresponding glass transition temperature (T_g) and temperatures for 5 and 10% weight loss (T_{d5} and T_{d10}) are listed in Table 2. The use of hydroxylamides **1a** and **1b** as latent initiators resulted in the formation of network polymers with similar T_g and T_d values. In contrast, the use of **1c** led to the significant deterioration of heat resistance, presumably due to incompletion polymerization.

Possible Mechanisms

The reaction pathways for epoxide polymerization that could be involved in the present system using hydroxylamides as latent initiators are shown in Scheme 4. The first process that occurs is the thermally induced dissociation of the hydroxylamide into the corresponding lactone and pyrrolidine.[26] The basic chemistry of this dissociation is the alcoholysis of the amide, which is generally disfavored due to the low nucleophilicity of alcohols, low electrophilicity of amides, and poor leaving ability of amines.

However, these unfavorable factors were overcome in the present system by the following two elements incorporated into the molecular design of the hydroxylamide initiator: the first being that the location of the hydroxyl group is at a suitable position for its intramolecular nucleophilic attack on



SCHEME 4 Possible reaction pathways involved in the present polymerization system using hydroxylamide **1** as a latent initiator.

the amide group, leading to the formation of a thermodynamically favored five- or six-membered lactone; the second point is that tethering the hydroxyl group and the amide group together using rigid moieties, such as *o*-phenylene and cyclohexyl groups, minimizes the conformational freedom of the molecule. The reason for the more labile nature of **1a** than **1b** was therefore related to the stability of the formed lactones, that is, five-membered rings are more stable, in general, than six-membered rings. However, the more labile nature of **1a** than **1c** was related to the rigidity of the tethers, that is, the *o*-phenylene tether is more rigid than the cyclohexyl tether. Once pyrrolidine was formed by the thermal dissociation of **1**, it initiated the polymerization of the epoxide. The propagating end in the polymerization of the epoxide was an alkoxide, and the counter cation was a quaternary ammonium.

In Scheme 4, "Propagation-2" involves the ring-opening reaction of the lactone by the terminal alkoxide. This reaction gave an alkoxide, C, which could react with the epoxide into a chain extended alkoxide, D. However, this propagation could be competed with by a back reaction to reform the alkoxide C and lactone. To clarify whether the lactones released from **1** participated in the polymerization or not, polymerization of GPE using **1** was performed at 180 °C. The resulting mixtures were analyzed by TLC. In these cases, phthalide and 3-isochromanone released from **1a** and **1b**, respectively, were not detected, implying that they underwent the ring-opening reaction and were incorporated into the resulting polymers. However, *cis*-hexahydrophthalide released from **1c** was clearly detected, implying that this sterically hindered lactone was less reactive in the anionic polymerization system.

CONCLUSIONS

We have demonstrated that three hydroxylamides, **1**, served as thermally latent initiators in the polymerization of the epoxide, bisphenol-A diglycidyl ether. The dissociation temperatures of these hydroxylamides depended on their structures, and thus the temperatures for carrying out the polymerizations of epoxide using **1** were tunable by the appropriate choice of initiator. The hydroxylamides could be synthesized easily from lactones and amines, and this simple, and thus versatile, synthesis promises a wide range of applications for these new types of latent initiators.

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