Anionic Alternating Copolymerization of Epoxide and Six-Membered Lactone Bearing Naphthyl Moiety

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ABSTRACT: This article describes the anionic copolymerization of glycidyl phenyl ether (GPE) and 1,2-dihydro-3H-naphtho[2,1-*b*]pyran-3-one (DHNP), a six-membered aromatic lactone bearing naphthyl moiety. The copolymerization proceeded in a 1:1 alternating manner, to afford the corresponding polyester. The ester linkage in the main chain was cleavable by reduction with lithium aluminum hydride to give the corresponding diol that inherited the structure of the alternating sequence. The copolymerization ability of DHNP permitted its addition as a comonomer to an imidazole-initiated polymerization of bisphenol A diglycidyl ether. The resulting networked polymer, of which main chain was endowed with the DHNP-derived rigid naphthalene moieties, showed a higher glass transition temperature than that obtained similarly with using 3,4-dihydrocoumarin (DHCM) as a comonomer, an analogous aromatic lactone bearing phenylene moiety instead of naphthalene moiety of DHNP. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 619–624, 2011

KEYWORDS: anionic polymerization; copolymerization; polyesters; ring-opening polymerization

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INTRODUCTION Lactones have attracted considerable attention as monomers exhibiting a wide variety of polymerizability that can be tuned by choosing plural structural parameters such as ring-size, number of unsaturated bonds in the ring, substituents, and their positions.[1] So far, ring-opening polymerizations of simple aliphatic lactones have been the main focus in this area because of the flexible and biodegradable natures of the corresponding polymers.[2] In contrast, aromatic lactones have not been investigated fully despite their potentiality to afford the corresponding polymers endowed with high thermal stability and mechanical strength that can not be attained by aliphatic lactones.[3]

Previously, we have reported the first exploitation of 3,4-dihydrocoumarin (DHCM) as a monomer (Scheme 1).[4] This aromatic six-membered lactone has been out of the focuses in polymer chemistry, because it does not undergo anionic or cationic homopolymerization. However, we discovered that DHCM underwent 1:1 alternating anionic copolymerization with epoxide to afford the corresponding polyester successfully. This copolymerization ability of DHCM with epoxide allowed its use as a comonomer in the imidazole-initiated curing reaction of epoxy resins, which is widely applied to the bonding of electrodevices,[5] coatings,[6] structural adhesives,[7] and fabrication of nanocomposite materials.[8] By adding DHCM to this conventional curing system, the resulting cured materials gained remarkably improved thermal properties and adhesion strength.[4(a)] This finding of the successful copolymerization behavior of DHCM with epoxide has prompted us to develop its analogous systems based on designing new aromatic lactones.[9] The monomer highlighted in this article is 1,2-dihydro-3H-naphtho[2,1-*b*]pyran-3-one (DHNP), a six-membered aromatic lactone bearing naphthyl moiety, which can be easily synthesized by the cycloaddition reaction of 2-naphthol and acrylic acid. This lactone has been known as "Splitomicin," which is an inhibitor of Sir2p, an NAD$^+$-dependent Sir2 family deacetylase required for chromatin-dependent silencing in yeast.[10] What we expected to DHNP were (1) its copolymerization behavior with epoxide similar to that of DHCM and (2) enhancement of thermal stability of the corresponding copolymer because of incorporation of planar and rigid naphthalene moieties.[11]

EXPERIMENTAL

Materials

2-Naphthol, acrylic acid, 2-ethyl-4-methylimidazole (EMI), and solvents were purchased from Wako Pure Chemical Industries and were used as received. Amberyst® 15 (acidic ion exchange resin) and bisphenol A diglycidyl ether (Bis A-DGE) were purchased from Sigma-Aldrich, Japan.

Equipments and Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded with Lambda-300 (JEOL) with tetramethylsilane as an internal standard.

Additional Supporting Information may be found in the online version of this article. Correspondence to: T. Endo (E-mail: tendo@mol-eng.fuk.kindai.ac.jp)

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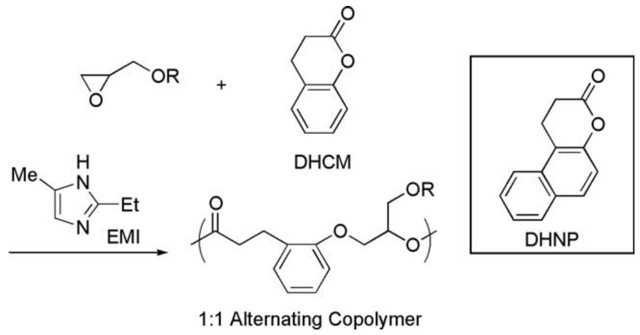


SCHEME 1 Anionic alternating copolymerization of epoxide and aromatic lactone.

Infrared (IR) spectra were obtained on a JASCO model FT-IR-460 plus. Number average molecular weight (M_n) and weight average molecular weight (M_w) were estimated from size exclusion chromatography, performed on a Tosoh model HLC-8120GPC equipped with Tosoh TSK gel-Super HM-H styrogel columns (6.0 mm ϕ × 15 cm), using tetrahydrofuran (THF) as an eluent at the flow rate of 0.6 mL min^{-1} after calibration with polystyrene standards. Gas chromatography (GC) was carried out with a Shimadzu gas chromatograph model GC-18A equipped with J&W Scientific DB-WAX-ETR 125-7332 (0.53 mm × 30 m) capillary column. Thermogravimetric analysis (TG), differential thermal analysis (DTA), and differential scanning calorimetric analysis (DSC) were performed with a Seiko Instruments model EXSTAR6000.

Synthesis of DHNP

DHNP was synthesized according to the reported method.[10] 2-Naphthol (4.43 g, 30.4 mmol) and Amberlyst 15® (3.0 g) were placed in a flask. Toluene (80 mL) and acrylic acid (4.42 g, 60.8 mmol) were added and heated with refluxing for 48 h. During the reaction, formed water was removed by azeotropic distillation. After cooling, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was passed through a thin layer of silica gel with using ethyl acetate/*n*-hexane (1/7 in v/v) as an eluent, and the eluted fractions were combined, concentrated under reduced pressure, and dried under vacuum to obtain DHNP (5.25 g; 87%): mp 48–49 °C; IR (KBr) 1769, 1515, 1077, 898, 811, 749; ^{1}H NMR ($CDCl_3$, δ) 2.88 (t, $J = 7.4$, 2H), 3.30 (t, $J = 7.4$, 2H), 7.20 (d, $J = 8.8$, 1H), 7.45 (d, $J = 7.5$, 1H), 7.55 (d, $J = 7.5$, 1H), 7.74 (d, $J = 8.8$, 1H), 7.84 (t, $J = 8.3$, 2H); ^{13}C NMR ($CDCl_3$, δ) 19.75, 28.47, 115.41, 117.29, 122.69, 125.04, 127.03, 128.62, 128.81, 130.69, 130.99, 149.49, 168.28.

Copolymerization of GPE and DHNP

Glycidyl phenyl ether (GPE; 751 mg, 5.00 mmol), DHNP (991 mg, 5.00 mmol), and EMI (11 mg, 0.10 mmol) were placed in a flask filled with argon gas. By stirring the mixture at room temperature, it became homogeneous. The resulting homogeneous mixture was heated at 120 °C for 1 h with stirring. After cooling to room temperature, the mixture was dissolved in THF (5 mL) and the resulting solution was poured into hexane (200 mL). After 1 h, the supernatant was removed by decantation, and the sedimentary gummy residue was dissolved in THF (5 mL) and the solution was dropped into diethyl ether (200 mL). The supernatant was removed by decantation, and the residue was dried under vacuum to afford copolymer **1** (1.45 g, 83%): $M_n = 2400$; $M_w = 4520$; IR (KBr) 1736, 1624, 1597, 808, 752, 692; ^{1}H NMR ($CDCl_3$, δ): 2.5–2.7 (broad, 2H), 3.1–3.4 (broad, 2H), 3.6–4.4 (broad, 4H), 5.0–5.6 (broad, 1H), 6.6–8.0 (broad m, 11H); ^{13}C NMR ($CDCl_3$, δ): 20.58, 33.87, 34.24, 65.66, 66.76, 67.08, 68.36, 68.78, 70.23, 70.56, 113.8, 114.4, 114.5, 121.0, 121.1, 121.2, 121.4, 121.6, 122.7, 122.8, 123.4, 126.5, 128.1, 128.2, 128.5, 129.2, 129.4, 132.5, 153.1, 153.2, 158.1, 158.2, 158.3, 172.6.

Reductive Cleavage of Copolymer 1

A solution of **1** (0.664 g; repeating unit 1.91 mmol) in THF (10 mL) was added to a suspension of $LiAlH_4$ (0.46 g) in THF (20 mL) at 0 °C, and then the mixture was stirred at room temperature. After 24 h, the mixture was poured into phosphate buffer (400 mL) at 0 °C, and then extracted with ethyl acetate (200 mL) three times. The organic layers were combined and washed with distilled water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was fractionated by column chromatography [silica gel, eluent = ethyl acetate/hexane (1/2 in v/v)] to obtain **2** (0.578 g, 1.64 mol, 86%): ^{1}H NMR (DMSO-d_6, δ) 1.65–1.80 (m, 2H), 3.09 (t, $J = 7.7$), 3.42–3.50 (m, 2H), 4.11–4.30 (m, 5H), 4.59 (t, $J = 5.1$, 1H), 5.49 (d, $J = 4.4$, 1H), 6.86–7.02 (m, 3H), 7.24–7.53 (m, 5H), 7.79 (d, $J = 9.0$, 1H), 7.85 (d, $J = 7.9$, 1H), 7.99 (d, $J = 8.6$, 1H); ^{13}C NMR (DMSO-d_6, δ) 21.05, 22.12, 60.69, 114.47, 114.76, 120.61, 123.06, 123.19, 123.40, 126.27, 127.45, 128.41, 128.91, 129.52, 132.49, 153.32, 158.58.

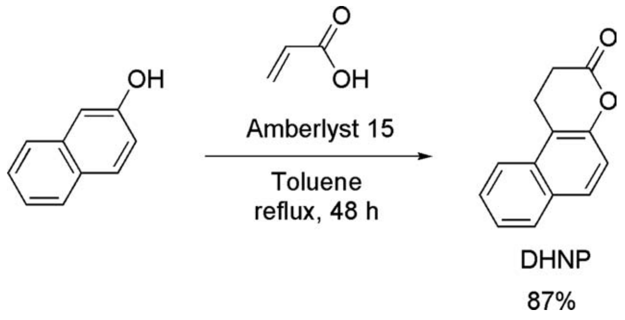
Copolymerization of Bis A-DGE and DHNP

Bis A-DGE (6.81 g, 20.0 mmol) and DHNP (1.40 g, 7.06 mmol) were mixed at 80 °C under vacuum to obtain a homogeneous mixture. To this mixture, EMI (259 mg, 2.35 mmol) was added at ambient temperature and stirred under vacuum to obtain the corresponding mixture. A small portion of the mixture (ca 10 mg) was taken and used for DSC analysis (30–200 °C with heating rate of 10 °C min^{-1}) to study the heat evolution behavior during the curing reaction. The rest was placed in a silicone vessel and heated at 100 °C for 1 h. The resulting cured material was analyzed by Fourier Transfer Infrared (FT-IR) to confirm the consumption of DHNP. Ten milligrams of the material was analyzed by DSC (30–200 °C with heating rate of 10 °C min^{-1}) to measure glass transition temperature (T_g). Five milligrams of the material was analyzed by TG/DTA (30–500 °C with heating rate of 10 °C min^{-1}) to study its thermal decomposition behavior and determine temperature for 10% weight loss (T_{d10}).

RESULTS AND DISCUSSION

Synthesis of DHNP

DHNP was synthesized from 2-naphthol in a straightforward manner (Scheme 2).[10] By heating 2-naphthol with acylic acid in the presence of Amberyst® 15, an acidic ion exchange resin, the cycloaddition reaction proceeded smoothly to

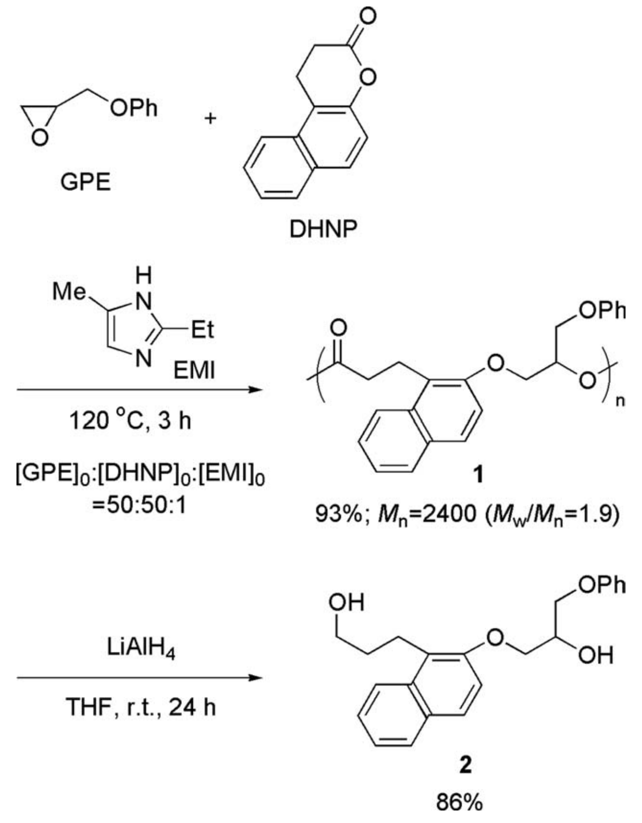


SCHEME 2 Synthesis of DHNP.

achieve the quantitative consumption of 2-naphthol. The reaction was free from side reaction, and thus removal of the solid catalyst by filtration and chromatography with a short silica gel column gave pure DHNP in a high yield. The spectroscopic features of DHNP involved the strong IR absorption at 1769 cm^{-1} and ^{13}C NMR signal at 168 ppm, which were attributable to the ester carbonyl group. The ^{1}H NMR and ^{13}C NMR spectra are shown in Figure S1 (in Supporting Information).

Copolymerization Behavior of DHNP and GPE

Before the investigation on the copolymerization, homopolymerization behavior of DHNP was studied. A bulk mixture of DHNP and EMI (1 mol %) was heated at 120 °C; however, no reaction took place. This robust nature was quite similar to that of DHCM, which did not undergo the homopolymerization at all.



SCHEME 3 Anionic alternating copolymerization of GPE and DHNP.

On the other hand, DHNP underwent the copolymerization with GPE successfully (Scheme 3). To an equimolar mixture of GPE and DHNP, EMI (1 mol % to the total amount of the two monomers) was added, and the resulting mixture was heated at 120 °C, with monitoring the progress of the copolymerization with GC. As shown in Figure 1, both the monomers were consumed almost in the same rate, implying the potential alternating character of the copolymerization to give the corresponding polyester **1**.

The formed polyester **1** was isolated as an ether-insoluble fraction in 83% yield. Its IR analysis revealed the formation of ester linkage by showing a strong absorption at 1735 cm^{-1} (Fig. 2). ^{13}C NMR analysis supported also the formation of ester linkage (Fig. 3). The signal for the ester carbonyl group appeared at different positions (173 ppm) to that for DHNP (168 ppm). In the region from 65 to 70 ppm, multiple signals appeared, although the ideal structure of the polymer **1** suggests there would be only three signals in this region. This multiplicity would be attributable to the presence of OH-terminated **1**. In the ^{1}H NMR spectrum of **1**, the two broad signals at around 2.6 and 3.3 ppm were attributable to the two methylene groups derived from DHNP (Fig. S2 in Supporting Information). In addition, there was a signal at 5.4 ppm, which was reasonably assigned to the methine proton locating on the carbon attached to the acyloxy group in the main chain. The presence of OH-terminated **1**, which was suggested by the ^{13}C NMR, was also confirmed by the signal at 5.2 ppm. These spectroscopic features of **1** were quite similar to those of the 1:1 alternating copolymer

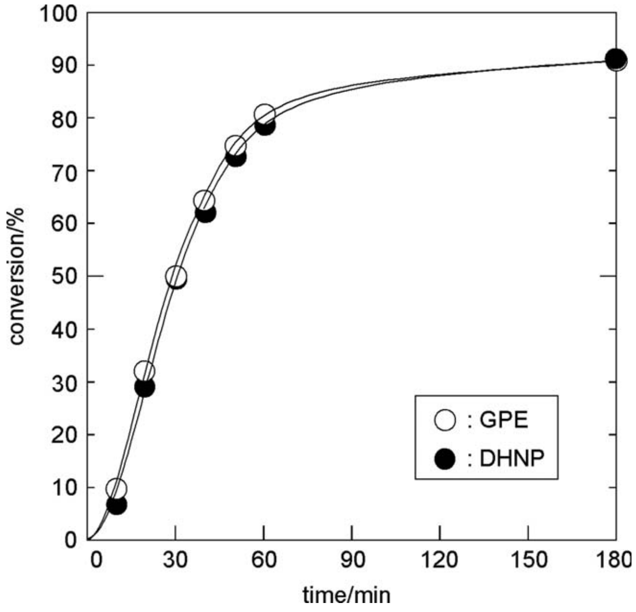


FIGURE 1 Time-conversion relationships for the copolymerization of DHNP and GPE ([GPE]$_0$:[DHNP]$_0$:[EMI]$_0$ = 50:50:1, at 120 °C).

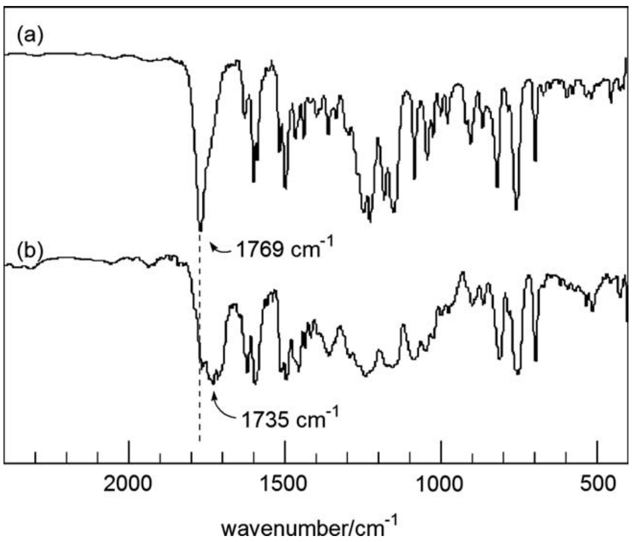


FIGURE 2 IR spectra of (a) a mixture of GPE, DHNP, and EMI (50:50:1) and (b) the corresponding alternating copolymer **1**.

of GPE and DHCM, suggesting the successful formation of the 1:1 GPE-DHNP alternating sequence.

The formation of the alternating structure of **1** was confirmed further by reductive scission of its polyester-type main chain (Scheme 3). By treatment of **1** with $LiAlH_4$, its ester linkages were cleaved readily to give the corresponding diol **2** as a sole product that was isolated by column chromatography in 86%. ^{1}H NMR and ^{13}C NMR analyses of the diol supported its structure derived from the repeating unit of polyester **1** formed by the 1:1 alternating copolymerization (Fig. S3 in Supporting Information).

Scheme 4 shows possible mechanism for the copolymerization. The initiation step would involve formation of a 2:1 adduct of epoxide and EMI, which has been reported for the imidazole-initiated anionic ring-opening polymerization of epoxide.[8] An alkoxide, thus, formed can react both with epoxide and DHNP; however, the intrinsic nature of the alkoxide would force it to choose DHNP rather than epoxide as a preferable monomer,[4(b)] leading to the formation of the corresponding naphthoxide. This "Step A" would be followed by "Step B," that is, nucleophilic attack of the naphthoxide to epoxide. In this step, the naphthoxide would not react with DHNP at all, but would react exclusively with epoxide to give the corresponding alkoxide. Alternation of Step A (= reaction of alkoxide with DHNP) and Step B (= reaction of naphthoxide with epoxide) can afford the alternating copolymer **1**.

Application of DHNP as a Comonomer to Epoxy-Imidazole Curing System

Based on the copolymerization ability of DHNP with GPE, we next focused on application of DHNP as a comonomer to the EMI-promoted curing reaction of epoxy resin. As shown in Scheme 4, the mechanism does not deny the possibility of formation of epoxide–epoxide sequence, and, therefore, copolymerizations with feed ratios ($[\text{epoxide}]_0/[\text{DHNP}]_0$) >1 would be performed successfully to give the corresponding copolymers rich in epoxide–epoxide sequence.[4(b)] In other words, a small amount of DHNP can be exploited as an additive to modify the conventional epoxy–imidazole curing system. As was described in Introduction, previously, a similar system was demonstrated with employing DHCM.[4(a)]

To confirm the feasibility of this concept, GPE, DHNP, and EMI were mixed in a feed ratio of 85:15:5 and the mixture

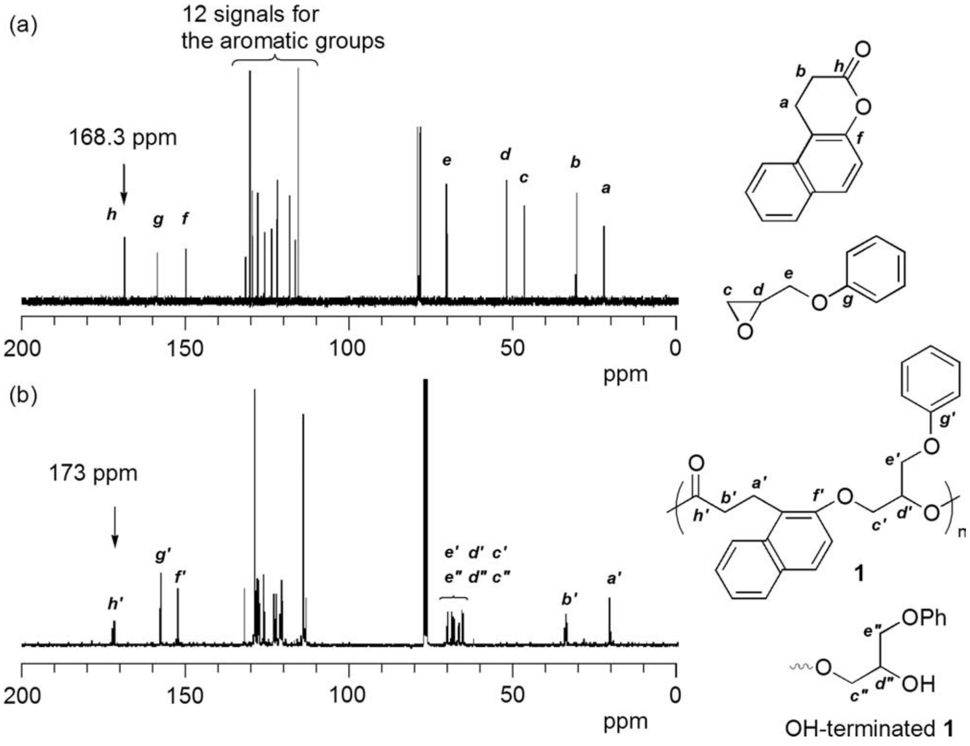
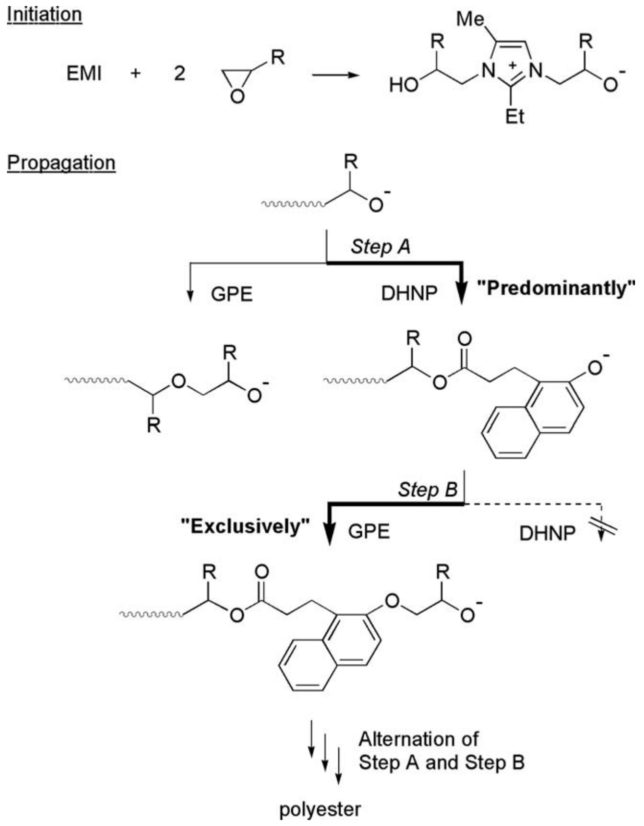


FIGURE 3 ^{13}C NMR spectra of (a) a mixture of GPE, DHNP, and EMI (50:50:1) and (b) the 1:1 alternating copolymer **1**.



SCHEME 4 Mechanism for the alternating copolymerization.

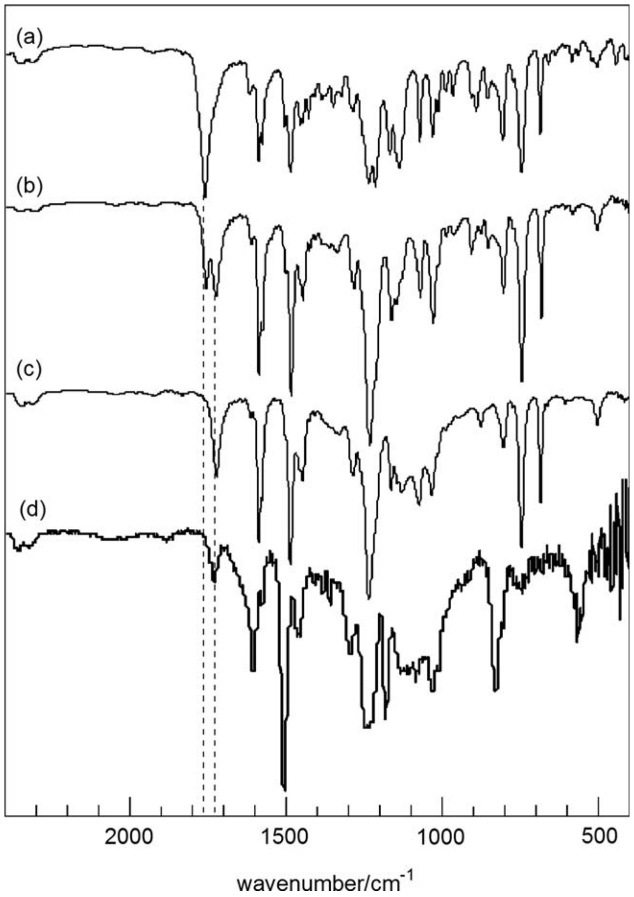
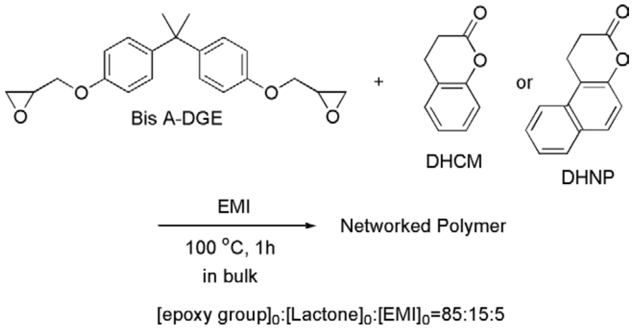


FIGURE 4 IR spectra of (a) a formulation composed of GPE, DHNP, and EMI (85:15:5), (b) a product obtained by heating the formulation for 30 min, (c) a product obtained by heating the formulation for 60 min, and (d) the product obtained by the copolymerization of Bis A-DGE and DHNP.

was heated at 100 °C for 1 h, with monitoring the progress of the copolymerization with IR. The set of these parameters is one of our standard ones.[4(a),9(a)] Figure 4(a) shows the IR spectrum of the mixture, which indicated the characteristic absorption of the carbonyl group of DHNP at 1769 cm^{-1}. After 30 min, a new absorption appeared at 1730 cm^{-1} [Fig. 4(b)], implying the formation of the corresponding copolymer having ester linkages in the main chain. After 1 h, DHNP was completely consumed, as confirmed by the corresponding spectum [Fig. 4(c)]. In addition, GC analysis of the resulting mixture revealed complete consumptions of both the monomers.

Based on the confirmation of the potential of DHNP as a new comonomer for the epoxy-imidazole system, we investigated its copolymerization with a bifunctional epoxide, Bis A-DGE (Scheme 5). Bis A-DGE, DHNP, and EMI were mixed in a feed ratio $[\text{epoxy moiety}]_0$:$[\text{DHNP}]_0$:$[\text{EMI}]_0 = 85{:}15{:}5$, and the resulting homogeneous mixture was heated at 100 °C for 1 h to obtain the corresponding networked polymer as a stiff solid, which was insoluble in any solvent. It was analyzed with IR to find that DHNP was successfully consumed and transformed into the corresponding ester linkages in the main chain [Fig. 4(d)]. The networked polymer was powdered and immersed in chloroform for 24 h; however, DHNP was not eluted at all to confirm its complete consumption.

In Table 1, some thermal properties of the obtained networked polymer are listed along with those of an analogous networked polymer obtained by using DHCM as a comonomer in place of DHNP for comparison.[4(a)] The temperatures of 10% weight loss (T_{d10}) of the networked polymers were comparable, as was expected from the similarity in the chemical bonds that consisted the main chain structures. On the other hand, the utilization of DHNP as a comonomer resulted in the higher glass transition (T_g) of the networked polymer than that obtained by using DHCM, presumably due



SCHEME 5 Copolymerizations of Bis A-DGE and lactones.

TABLE 1 Copolymerizations of Bis A-DGE and Aromatic Lactones

			Thermal Properties of the Networked Polymer	
Entry	Comonomer	Exothermal Peak Top Temperature of DSC Profile (°C)[a]	T_{d10} (°C)[b]	T_g (°C)[c]
1	DHCM	141	410	124
2	DHNP	146	409	135

[a] Measured by DSC in a dynamic scan mode (10 °C min^{-1}).
[b] Measured by TG/DTA.
[c] Measured by DSC.

to the higher rigidity of the DHNP-derived naphthyl moiety than the DHCM-derived phenylene moiety.

CONCLUSIONS

In summary, an aromatic six-membered lactone bearing naphthalene moiety (DHNP) was exploited as a new monomer that copolymerized with epoxide in an imidazole-initiated anionic system. The usefulness of this new lactone-type monomer was demonstrated by adding it to the conventional epoxy–imidazole curing system as a comonomer. The basic chemistry of the system was a copolymerization of a bisphenol A-derived bifunctional epoxide and DHNP, which permitted the incorporation of the DHNP-derived rigid naphthalene moieties into the main chain of the resulting networked polymer to achieve the higher glass transition temperature than that obtained similarly with using DHCM, an analogous aromatic lactone.

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