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Mechanistic Study of Ring-Opening Copolymerization of ϵ -Caprolactam with Epoxide: Development of Novel Thermosetting Epoxy Resin System

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ABSTRACT We investigated the mechanism of the ring-opening copolymerization of ϵ -caprolactam (ϵ -CL) with glycidyl phenyl ether (GPE) to afford poly(ϵ -CL-co-GPE) as a model reaction of the thermal curing of certain epoxy resins with ϵ -CL. The reaction of ϵ -CL and GPE proceeded efficiently in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 170 °C for 2 h. The monomer reactivities r_1 of ϵ -CL and r_2 of GPE calculated according to the Fineman-Ross method and the Kelen-Tüdös method were 0.58 and 5.52, respectively. These values indicate that poly(ϵ -CL-co-GPE) has a pseudo-block gradient copolymer. Based on these results, we examined the thermal curing reactions of certain epoxy resins with ϵ -CL. The corresponding novel cured products were obtained quantitatively, and each of them showed a high glass transition temperature and high thermal stability, presumably due at least in part to a pseudo-block gradient primary structure resembling that of poly(ϵ -CL-co-GPE).

KEYWORDS: ϵ -caprolactam; ring-opening copolymerization; Fineman-Ross method; Kelen-Tüdös method; thermal curing reactions

INTRODUCTION

Epoxides show higher reactivity than other cyclic ethers, due to their high strain energy (117 kJ/mol).^{1,2} Compounds bearing two or more epoxy groups polymerize readily to afford epoxy resins, which can be cross-linked (cured) to afford materials with excellent thermal stability, mechanical properties, adhesive performance, and chemical resistance. Indeed, epoxy thermo-setting systems are widely applied in various industrial fields.

Strategies for polymerization of epoxides are usually classified into two categories: ring-opening polymerization and polyaddition of epoxides. Ring-opening polymerization of epoxides proceeds smoothly with cationic initiators³, anionic initiators³, carboxylic anhydride⁴, and carbon dioxide⁵⁻⁶. Endo et al. reported that alternating ring-opening copolymerization of epoxides with lactone

proceeds using a catalyst.^{7,8} Polyaddition of epoxides with protonic reagents such as amines, alcohols, phenols, thiols, and carboxylic acid also proceeds smoothly.⁹⁻¹¹ Furthermore, Nishikubo et al. reported that polyaddition of epoxides with various aprotic reagents such as dichlorogermane,¹² aromatic dichloride,¹³ disulfonyl chloride,¹⁴ active esters,¹⁵⁻²² chloroacetoxyster,²³ triazine dichloride,²⁴ chloroformyl,²⁵ phosphonic dichloride,²⁶ dichlorophosphate,²⁶ and phosphonate²⁷ proceeds smoothly in the presence of a catalyst.

ϵ -Caprolactam (ϵ -CL) is a well-known starting material for the bulk synthesis of polyamide nylon-6 by ring-opening polymerization using organic bases as catalysts at elevated temperature. Thus, we expected that ring-opening copolymerization of epoxides and ϵ -CL would proceed to generate the corresponding poly(amide-ethers). Indeed, when we examined the reaction of ϵ -CL and 2,2-bis(4-

glycidylphenoxyphenyl)propane (BGP) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the corresponding thermally cured product was obtained quantitatively.²⁸ In this system, the cross-linked material showed a high glass transition temperature (T_g) and a high thermal decomposition temperature (T_d), i.e., $T_g = 211$ °C and $T_d = 360$ °C, respectively. However, the reaction mechanism was unclear.

Therefore, in this study, we examined the polymerization behavior of ϵ -CL and glycidyl phenyl ether (GPE) as a model reaction. Based on the results, thermal curing reactions of ϵ -CL and several epoxy resins were investigated.

EXPERIMENTAL

Materials

ϵ -Caprolactam (ϵ -CL), glycidyl phenyl ether (GPE), 2,2-bis(4-glycidylphenoxyphenyl)propane (BGP), 3,3',5,5'-tetramethyl-4,4'-diglycidylphenoxybiphenyl (TDP), *N,N*-diglycidyl-4-glycidylphenoxyaniline (DGA), *N,N*-dimethylaniline, aniline, melamine, imidazole, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were commercial products. 1-Methyl-2-pyrrolidinone (NMP), dimethyl formamide (DMF), dimethyl acetamide (DMAc), and dimethyl sulfoxide (DMSO) were dried over CaH_2 and purified by distillation before use.

Measurements

Infrared (IR) spectra were taken with a JASCO FT/IR4200. ^1H NMR spectra were recorded in $\text{DMSO}-d_6$ on JEOL Model ECS-400K (400 MHz for ^1H NMR) instruments, with Me_4Si (TMS) as an internal standard. The number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight / number-average molecular weight (M_w/M_n)] of the polymers were estimated by size exclusion chromatography (SEC) with a Tosoh HLC-8220 SEC instrument equipped with TSK gel columns (Tskgel Super AW3000 and AW2500 x 2) and with refractive-index and ultraviolet detectors, using LiBr and phosphoric acid solution in DMF

(20 mM) as an eluent. Calibration was done with narrow molecular weight polystyrene standards. Thermal analysis was performed on Shimadzu thermogravimetric analyzer (TGA) Model TGA-50/50H and differential scanning calorimeter (DSC) Model DSC60/60A. When the thermal decomposition temperature was measured by TGA, the sample was heated at 150 °C for 30 min to remove adsorbed H_2O and then cooled to room temperature under nitrogen. After that, the decomposition ratio of the products was measured, using a heating rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) was also determined at a heating rate of 10 °C/min under nitrogen. Matrix-assisted laser desorption ionization time-of flight mass spectroscopy (MALDI-TOF-MS) experiments were performed with an AXIMA-CFRplus (Shimadzu / Kratos) using dihydroxybenzoic acid as a matrix and chloroform as a solvent.

Polymerization of Glycidyl Phenyl Ether (GPE)

A mixture of GPE (1.50 g, 10 mmol) and DBU (0.15 g, 1.0 mmol) was stirred at 80 °C for 30 min in glass tube, and then heated at 170 °C for 2 h. The resulting residue was poured into a large amount of 1 N hydrochloric acid aqueous solution, and the precipitated solid was collected by filtration on a membrane filter (Millipore LAWPO 4700 pore size 0.45 μm), washed with water, and then dried *in vacuo* at room temperature for 24 h to afford a white solid. Yield = 1.46 g (97 %). $M_n = 830$ ($M_w/M_n = 1.18$).

Polymerization of ϵ -caprolactam (ϵ -CL)

Reaction of ϵ -CL (1.14 g, 10 mmol) and DBU (0.15 g, 1.0 mmol) was carried out in the same way as ring-opening polymerization of GPE. However, ϵ -CL was recovered quantitatively.

Polymerization of glycidyl phenyl ether (GPE) and ϵ -caprolactam (ϵ -CL).

A typical procedure for the reaction of GPE and ϵ -CL at the feed ratio of ϵ -CL /GPE = 1/1 was as follows. A mixture of GPE (1.50 g, 10 mmol), ϵ -CL (1.14 g, 10 mmol), and DBU (0.15 g, 1.0 mmol) was stirred at 80 °C for 30 min in glass tube, and then heated at 170 °C. After 2 h, the resulting residue was poured into a large amount of 1 N hydrochloric acid aqueous solution. The precipitated solid was collected by filtration on a membrane filter (Millipore LAWPO 4700 pore size 0.45 μ m), washed with water, and then dried *in vacuo* at room temperature for 24 h to afford a white solid. Yield = 2.24 g (85 %). $M_n = 1,040$ ($M_w/M_n = 1.07$). IR (film, cm^{-1}): 2937 (n CH_2), 1607 and 1506 (n C=C aromatic), 1128 and 1042 (n C-O-C). ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS) δ (ppm) : 1.46 ~ 1.57 (m, $-\text{CH}_2\text{-CH}_2\text{-CH}_2-$), 2.27 ~ 2.29 (m, $-\text{CH}_2\text{-C(O)-}$), 3.03, 3.05 (dd, $J = 6\text{Hz}$, $-\text{CH}_2\text{-NH-}$), 3.44 ~ 3.86 (m, $-\text{CH}_2\text{-O-}$, $>\text{CH-}$, $-\text{NH-}$), 5.14 (broad s, $-\text{OH}$), 6.90 ~ 7.30 (m, aromatic H), 7.39 (broad s, $-\text{NH-C(O)-}$).

Preparation of polymer by reaction of glycidyl phenyl ether (GPE) and ϵ -caprolactam (ϵ -CL) for measurement of MALDI-TOF mass spectra

The reaction of ϵ -CL (1.14 g, 10 mmol) and GPE (1.50 g, 10 mmol) in the presence of DBU (1.0 mmol) was performed at 170 °C for 2 h. The resulting residue was poured into a large amount of *n*-hexane to precipitate oligomer with $M_n = 250$ and $M_w/M_n = 1.91$. Its structure was confirmed by MALDI-TOF mass spectra.

Thermal curing reaction of ϵ -caprolactam (ϵ -CL) and 2,2-bis(4-glycidyloxyphenyl)propane (BGP)

A typical procedure for the reaction of ϵ -CL and BGP was as follows. A mixture of ϵ -CL (1.14 g, 10 mmol) and BGP (3.34 g, 10 mmol) (feed ratio of ϵ -CL/BGP = 10/10) in the presence of DBU was stirred at 80 °C for 30 min in a glass tube, and then heated at 170 °C. After 10 min, the

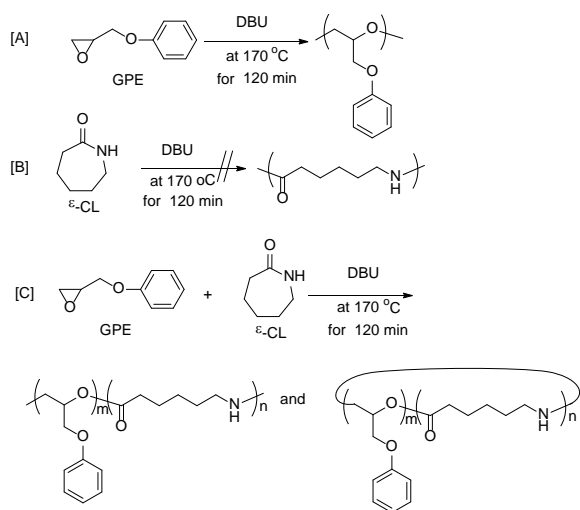
solution changed quantitatively to a cured product, which was difficult to remove from the glass tube (the tube had to be broken to obtain the product). In the case of the feed ratio of ϵ -CL/BGP = 10/2, a mixture of ϵ -CL (1.14 g, 10 mmol), BGP (0.67 g, 2 mmol), and DBU (0.15 g, 1.0 mmol) was treated in the same way as mentioned above. The resulting mixture was washed with DMF and methanol, and the cured material was obtained by filtration. Yield = 0.199 g (11 %).

RESULTS AND DISCUSSION

Ring-opening polymerization of glycidyl phenyl ether (GPE) and ϵ -caprolactam (ϵ -CL)

We expected that anionic-ring opening copolymerization of glycidyl phenyl ether (GPE) and ϵ -caprolactam (ϵ -CL) would afford the corresponding poly(amide-ether). First, the reaction of GPE was carried out in the presence of DBU in bulk at 170 °C for 2 h. The reaction mixture was poured into a large amount of 1 N hydrochloric acid aqueous solution to precipitate polyGPE with $M_n = 830$ and $M_w/M_n = 1.18$ in 97% yield (Scheme 1 [A]). ϵ -CL alone showed no reaction under the same conditions (Scheme 1 [B]). When the reaction of GPE and ϵ -CL was performed at an equimolar feed ratio under the same conditions, a polymer with $M_n = 1,040$ and $M_w/M_n = 1.07$ was obtained (Scheme 1 [C]). The structure of this polymer was confirmed by ^1H NMR, IR and MALDI TOF mass spectroscopy. In the ^1H NMR spectrum (Fig. 1), the signals at 1.46 ~ 1.57 ppm are assignable to methylene protons of polyamide formed by ring-opening polymerization of ϵ -CL. The signals at 2.27 ~ 2.28 ppm are assignable to methylene protons of $-\text{C(O)-CH}_2-$ and those at 3.03 ~ 3.05 ppm are assignable to methylene protons of $-\text{CH}_2\text{-NH-CH}_2-$. The signals at 3.44 ~ 3.86 ppm are assignable to methylene, methine, and secondary amine protons. Aromatic protons and hydroxyl protons were also seen at 6.90 - 7.30 ppm and at 5.2 ppm, respectively. From the integration ratios of aromatic protons

and methylene protons of polyamide, the unit ratio of ϵ -CL and GPE could be calculated to be 1 : 1. IR spectra also supported the structure of this polymer. Thus, the ring-opening copolymerization of ϵ -CL and GPE afforded poly(ϵ -CL-*co*-GPE) in 85% yield.



SCHEME 1 Reaction of GPE and ϵ -CL using DBU.

We next examined the structure of the end groups of the synthesized poly(ϵ -CL-*co*-GPE) by means of MALDI-TOF MS. After the reaction of

GPE and ϵ -CL as described above, the reaction mixture was poured into a large volume of hexane to precipitate a white solid, whose structure was confirmed by MALDI-TOF MS. As shown in Figure 2, parent peaks were observed at 1035.6 and 1053.6 corresponding to the mass of the linear polymer and the cyclic polymer obtained by ring-opening copolymerization of ϵ -CL and GPE. Furthermore, a mass difference pattern corresponding to the molecular weight of GPE monomer ($M = 150.07$) was seen. In the case of the linear polymer, hydroxyl and DBU moieties were confirmed to be the end groups. These results are consistent with formation of poly(ϵ -CL-*co*-GPE) as shown in Scheme 1 [C].

Next, we examined the bulk polymerization of ϵ -CL and GPE using various bases such as *N,N*-dimethylaniline, aniline, melamine, and imidazole at the ϵ -CL/GPE feed ratio of 1/1 at 170 °C. The conditions and results are summarized in Table 1. In the case of *N,N*-dimethylaniline and aniline, the corresponding oligomers with $M_n = 630$ and 650 were obtained, with the same ϵ -CL/GPE composition ratio of 3/7 (Runs 1 and 2 in Table 1). Furthermore, in the case of melamine, the polymer with $M_n = 660$ was obtained, with a ϵ -CL/GPE composition ratio of 4/6 (Run 3 in Table 1). When imidazole

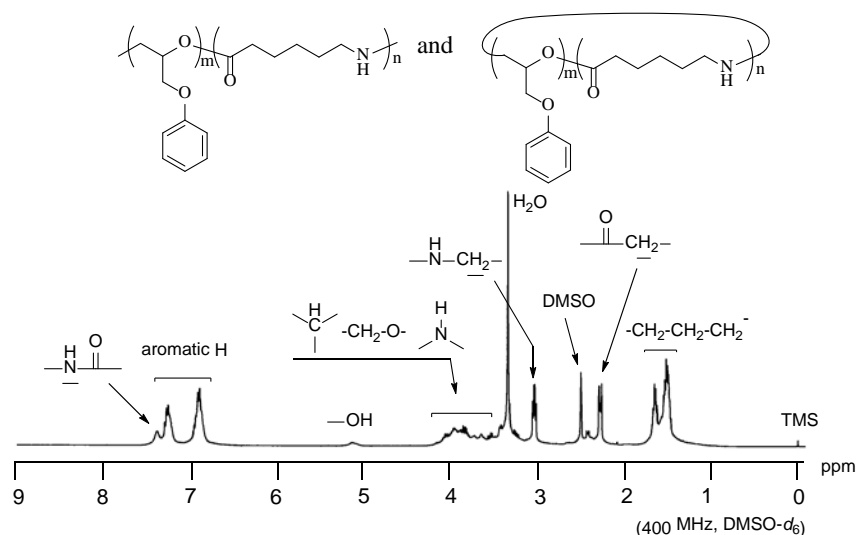


FIGURE 1 ^1H NMR spectrum of poly(ϵ -CL-*co*-GPE).

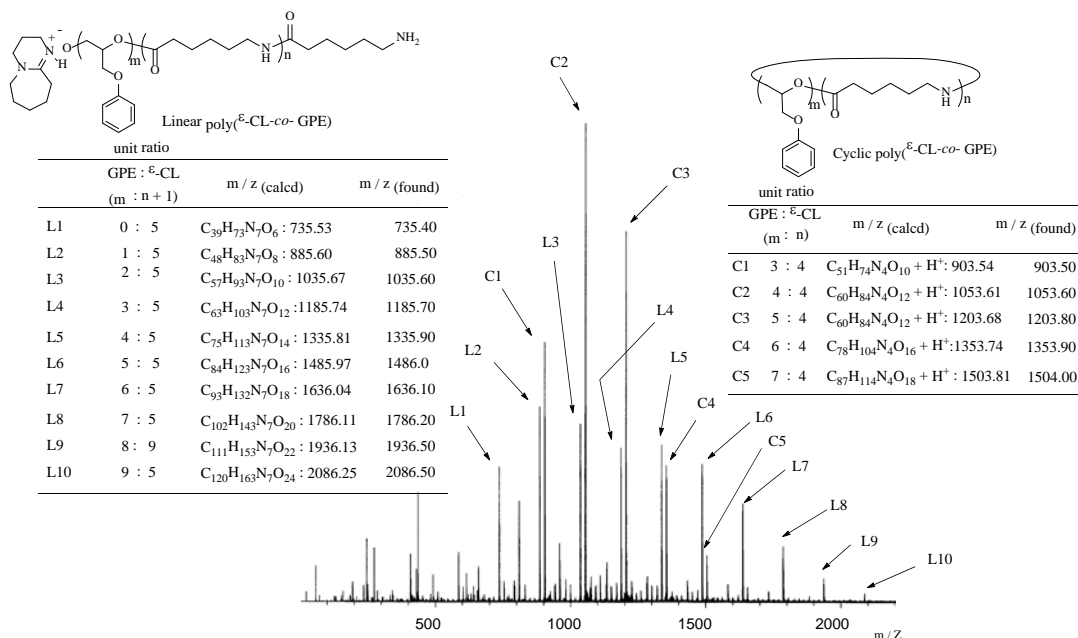


FIGURE 2 MALDI TOF Mass spectrum of poly(ϵ -CL-co-GPE).

or DBU was used in this polymerization, polymer with a composition ratio of ϵ -CL/GPE = 5/5 was obtained, with M_n = 940 or 1040, respectively (Runs 4 and 5 in Table 1).

Furthermore, a tendency of increasing glass

transition temperature (T_g), and thermal decomposition temperature (T_d) of the synthesized polymers was observed with increase of molecular weight (M_n) and yield. These results suggest that DBU is an appropriate base for this polymerization.

TABLE 1 Effect of various bases on the ring-opening copolymerization of ϵ -CL and GPE ^a

Run	Catalyst	Composition ratio ^b ϵ -CL : GPE	Yield ^c (%)	M_n^d (M_w/M_n)	T_g^e	$T_d^{f,i}$
1	<i>N,N</i> -Dimethylaniline	3 : 7	35	630 (1.06)	122	168
2	Aniline	3 : 7	58	650 (1.12)	124	165
3	Melamine	4 : 6	60	660 (1.01)	124	171
4	Imidazole	5 : 5	75	940 (1.13)	129	188
5	DBU	5 : 5	85	1040 (1.07)	130	218

^aConditions; ϵ -CL (10 mmol), GPE (10 mmol), catalyst (1.0 mmol), at 170 °C for 2 h. ^bCalculated by ¹H NMR. ^c Insoluble part in 1 N HCl aqueous solution. ^dEstimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). ^e T_g = glass transition temperature determined by DSC. ^f T_d^i = Initial thermal decomposition temperature determined by TGA.

The effect of solvents was investigated in this polymerization at 170 °C with DBU as a base for 2 h. As summarized in Table 2, polymers with lower molecular weight (M_n = 810, 830, and 890) were produced in DMAC, DMF and DMSO, respectively (Runs 1 ~ 3 in Table 2). In the case of NMP, a polymer with M_n = 1020 was obtained in 73% yield (Run 4 in Table 2). The ϵ -CL/GPE composition ratios of these polymers were 4/6 or 5/5. Bulk polymerization afforded a polymer with good

TABLE 2 Effect of solvents on the ring-opening copolymerization of ϵ -CL and GPE ^a

Run	Solvent	Composition ratio ^b ϵ -CL : GPE	Yield ^c (%)	M_n^d (M_w/M_n)	T_g^e	$T_d^{f,i}$
1	DMAC	4 : 6	61	810 (1.08)	126	208
2	DMF	5 : 5	76	830 (1.08)	131	214
3	DMSO	4 : 6	80	890 (1.13)	126	203
4	NMP	5 : 5	73	1020 (1.04)	128	201
5	- ^g	5 : 5	85	1040 (1.07)	130	218

^aConditions; ϵ -CL (10 mmol), GPE (10 mmol), catalyst (1.0 mmol), at 170 °C for 2 h. ^bCalculated by ¹H NMR. ^c Insoluble part in 1 N HCl aqueous solution. ^dEstimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). ^e T_g = glass transition temperature determined by DSC. ^f T_d^i = Initial thermal decomposition temperature determined by TGA. ^gBulk polymerization.

thermal properties and higher molecular weight in satisfactory yield (Run 5 in Table 2).

The effect of concentrations of DBU on this polymerization was examined under the same

TABLE 3 Effect of concentrations of DBU on the ring-opening copolymerization of ϵ -CL and GPE ^a

Run	DBU (mmol)	Composition ratio ^b ϵ -CL : GPE	Yield ^c (%)	M_n^d (M_w/M_n)	T_g^e	$T_d^{f,i}$
1	0.01	2 : 8	57	660 (1.20)	89	197
2	0.1	3 : 7	59	690 (1.31)	107	201
3	0.5	4 : 6	69	780 (1.12)	122	209
4	1.0	5 : 5	85	1040 (1.07)	132	218
5	2.0	4 : 6	84	940 (1.12)	129	212

^aConditions; ϵ -CL (10 mmol), GPE (10 mmol), DBU (0.01 ~ 2.0 mmol), at 170 °C for 2 h. ^bCalculated by ¹H NMR. ^c Insoluble part in 1 N HCl aqueous solution. ^dEstimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). ^e T_g = glass transition temperature determined by DSC. ^f T_d^i = Initial thermal decomposition temperature determined by TGA.

conditions as mentioned above previously. The reaction conditions and results are summarized in Table 3. The values of yields, M_n 's, T_g , and T_d^i of the obtained polymers increased slightly with the amount of DBU up to 1.0 mmol (Runs 1 ~ 4 in Table 3). In the case of 2.0 mmol of DBU, these values also decreased slightly (Run 5 in Table 3). By the consideration of the results on composition ratios of polymers, the copolymerization proceeded smoothly with 1.0 mmol of DBU. These indicate that the appropriate feed ratio of DBU/ ϵ -CL/GPE is to be 1/10/10.

The effect of reaction temperature was also examined in the range from 25 to 210 °C. Figure 3 illustrates the relationships among reaction temperature, yield, and molecular weight. At room temperature, the reaction did not proceed. Further, no remarkable difference in the yields of the obtained polymers was observed at above 60 °C. However, the value of M_n increased with increasing temperature up to 170 °C (M_n = 1040, yield = 85%), and then decreased gradually to 210 °C (M_n = 900, yield = 86%). Thus, the polymer might be decomposed at high reaction temperatures. We concluded that the optimum reaction temperature for this polymerization was 170 °C under these conditions.

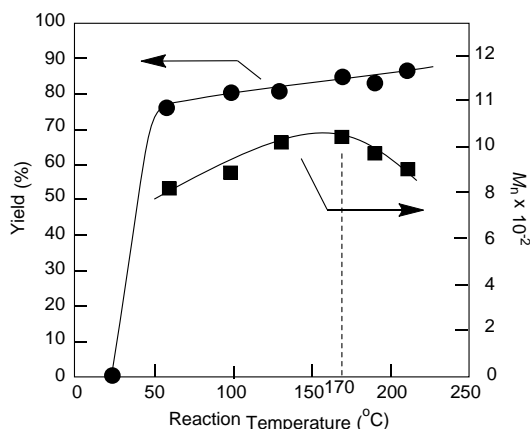


FIGURE 3 Effect of reaction temperature on the ring-opening copolymerization of ϵ -CL and GPE.

Effect of feed ratios of ϵ -CL and GPE at 170 °C for 2 h. The conditions and results are summarized in Table 4. ϵ -CL alone did not react, as mentioned above (Scheme 1[B]). The polymer yield increased with increasing feed

TABLE 4 Effect of feed ratio of ϵ -CL and GPE DBU on the ring-opening copolymerization ^a

Run	Feed ratio ϵ -CL : GPE	Composition ratio ^b ϵ -CL : GPE	Yield ^c (%)	M_n^d (M_w/M_n)	T_g^e	T_d^{if}
1	10 : 0	- ^g	- ^g	- ^g	- ^g	- ^g
2	9 : 1	8 : 2	20	440 (1.08)	107	201
3	7 : 3	7 : 3	52	660 (1.04)	122	209
4	5 : 5	5 : 5	85	1040 (1.07)	132	218
5	3 : 7	4 : 6	79	740 (1.09)	129	212
6	1 : 9	2 : 8	87	780 (1.18)	138	249
7	0 : 10	0 : 10	97	830 (1.18)	131	193

^aConditions; total amount of ϵ -CL and GPE = 20 mmol, DBU (1.0 mmol), at 170 °C for 2 h. ^bCalculated from ¹H NMR integration ratios. ^cInsoluble part in 1 N HCl aqueous solution. ^dEstimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). ^e T_g = glass transition temperature determined by DSC. ^f T_d^i = Initial thermal decomposition temperature determined by TGA. ^gCould not be determined.

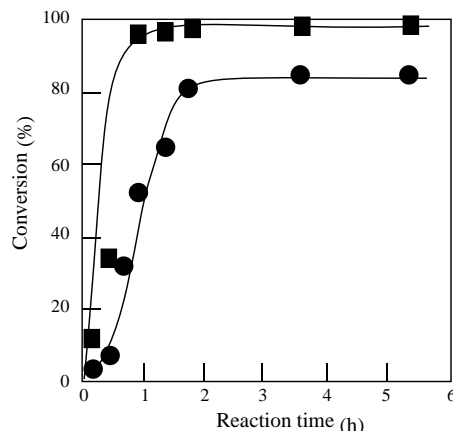


FIGURE 4 Time-course of the values of conversions of ϵ -CL and GPE in the ring-opening copolymerization. (■); GPE, (●); ϵ -CL.

ratio of GPE, but the highest molecular weight polymer was obtained at ϵ -CL/GPE = 5/5 (M_n = 1040, M_w/M_n = 1.07) (Run 4 in Table 4). As expected, the thermal stability of the polymer obtained at ϵ -CL/GPE = 1/9 was very different from that in the case of ϵ -CL/GPE = 0/10 (Runs 6 and 7 in Table 4). The highest molecular weight polymer was obtained at ϵ -CL/GPE = 5/5 (M_n = 1,040) (Run 4 in Table 4).

Furthermore, the time-course of the conversions of ϵ -CL and GPE in the ring-opening polymerization was examined using DBU in NMP at 170 °C. Conversion was calculated from the decrease of the integration ratios of the peaks at 7.39 ppm assignable to -NH- proton of ϵ -CL and at 2.70 ppm assignable to methylene protons of GPE. The results are shown in Figure 4. In the case of GPE, the conversion increased smoothly up to 95%.

However, ϵ -CL reacted slowly compared to GPE, and after 4 h, the conversion of ϵ -CL reached 85%.

TABLE 5 Parameters for calculation of monomer reactivity ratios of ϵ -CL and GPE. ^a

Run	Feed ratio ϵ -CL : GPE	$F = M_1/M_2^a$ (Monomer ratio)	$f = d[M_1] / d[M_2]^b$ (Polymer ratio)	Fineman-Ross		Kelen-Tüdös	
				$G = F(f-1)/f$	$F' = F^2/f$	$\eta = G / (\alpha+F)^c$	$\xi = F' / (\alpha+F')$
1	2 : 10	0.2	0.038	- 5.06	1.05	- 1.35	0.279
2	4 : 10	0.4	0.086	- 4.25	1.86	- 0.93	0.407
3	6 : 10	0.6	0.134	- 3.88	2.69	- 0.72	0.498
4	8 : 10	0.8	0.185	- 3.52	3.46	- 0.57	0.561
5	10 : 10	1.0	0.243	- 3.12	4.12	- 0.46	0.603
6	20 : 10	2.0	0.570	- 1.51	7.02	- 0.16	0.721

^a F ; feed molar ratio of ϵ -CL and GPE. ^b $f = d[M_1] / d[M_2] = m : n$ of poly(ϵ -CL-*co*-GPE_{*n*}); *m*: molar fraction of ϵ -CL in the copolymer, *n*: molar fraction of GPE in the copolymer, calculated from ¹H NMR integration ratios. ^c $\alpha = (F_{\max} \times F_{\min})^{1/2} = 2.71$

Next, the monomer reactivities of ϵ -CL and GPE were calculated by linearization²⁹ according to the Fineman-Ross method³⁰ and Kelen-Tüdös method,³¹ based on equations (1) and (2); r_1 and r_2 are molar ratios of ϵ -CL and GPE, respectively.

$$(1) F(f-1)/f = F^2/r_1 - r_2$$

$$(2) \eta = (r_1 + r_2/\alpha) \xi - r_2/\alpha$$

The parameters of the Fineman-Ross method and Kelen-Tüdös method are summarized in Table 5.

To keep conversion of the monomers below 10 %, the reaction of ϵ -CL and GPE at various feed ratios was carried out at 80 °C for 2 h using DBU in bulk. The composition ratios of the precipitated copolymers were determined by ¹H NMR spectroscopy, and the value of *f* in equation (1) was calculated. The results are summarized in Figure 5.

The correlation coefficients (R^2) of the Fineman-Ross method and Kelen-Tüdös method are 0.991 and 0.995, respectively. The values of r_1 and r_2 obtained from Fineman-Ross method are

0.57 and 5.48, and those from Kelen-Tüdös method are 0.59 and 5.56, respectively, which are in good agreement, and thus the average

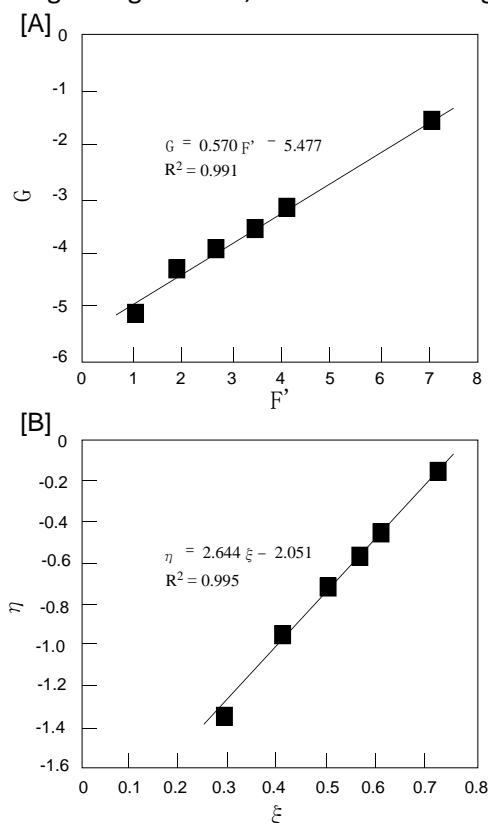
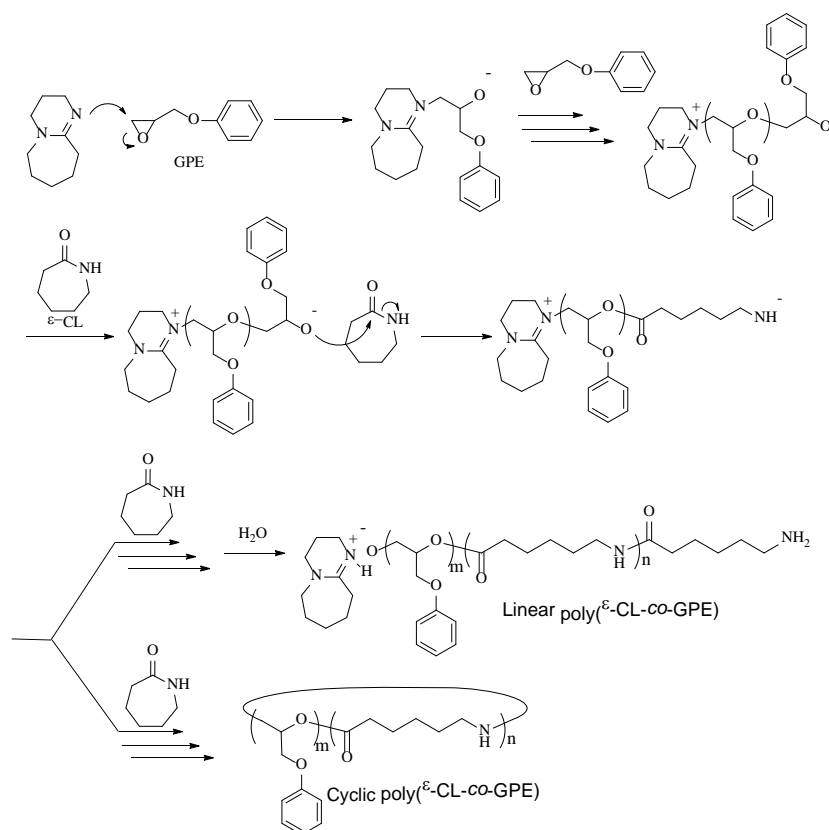


Figure 5. Calculation of molar ratios in the ring-opening copolymerization of ϵ -CL and GPE. The parameters G , F' , η , and ξ are summarized in Table 4. [A] Fineman-Ross method. [B] Kelen-Tüdös method.



SCHEME 2 Plausible mechanism on the reaction of GPE and $\epsilon\text{-CL}$ with DBU.

values of r_1 and r_2 are 0.58 and 5.52, respectively. That is, the molar ratio of GPE was much larger than that of $\epsilon\text{-CL}$. Schubert et al. reported the synthesis of a pseudo-block polymer by ring-opening copolymerization using 2-methyl-2-oxazoline and 2-phenyl-2-oxazoline, which the difference in their reactivity ratios were very large.^{32–34} This indicates that $\text{poly}(\epsilon\text{-CL-co-GPE})$ has a pseudo-block gradient copolymer constructed from $\text{poly}(\epsilon\text{-CL})$ and $\text{poly}(\text{GPE})$. These results are consistent with the reaction mechanism shown in Scheme 2. No polymer was obtained from $\epsilon\text{-CL}$ alone. Thus, the ring-opening polymerization starts with $\text{poly}(\text{GPE})$ formation, and then the end group alkoxide induces ring-opening reaction of $\epsilon\text{-CL}$ to afford an active end group -NH- , ultimately affording pseudo-block

gradient linear $\text{poly}(\text{GPE-co-}\epsilon\text{-CL})$ and cyclic $\text{poly}(\text{GPE-co-}\epsilon\text{-CL})$.

Epoxy thermo setting with $\epsilon\text{-CL}$

Based on the above findings, we examined the thermal curing reaction of 2,2-bis(4-glycidyloxyphenyl)propane (BGP) as an epoxy resin with $\epsilon\text{-CL}$ at various feed ratios using DBU in bulk at 170 °C (Scheme 3). The conditions and results are summarized in Table 6.

A mixture of $\epsilon\text{-CL}$ (1.14 g, 10 mmol) and BGP (3.34 g, 10 mmol) in the presence of DBU was stirred at 80 °C for 30 min in glass tube, and then heated at 170 °C. After 10 min, to a cured product was formed, which was difficult to remove from the glass tube (run 5 in Table 5).

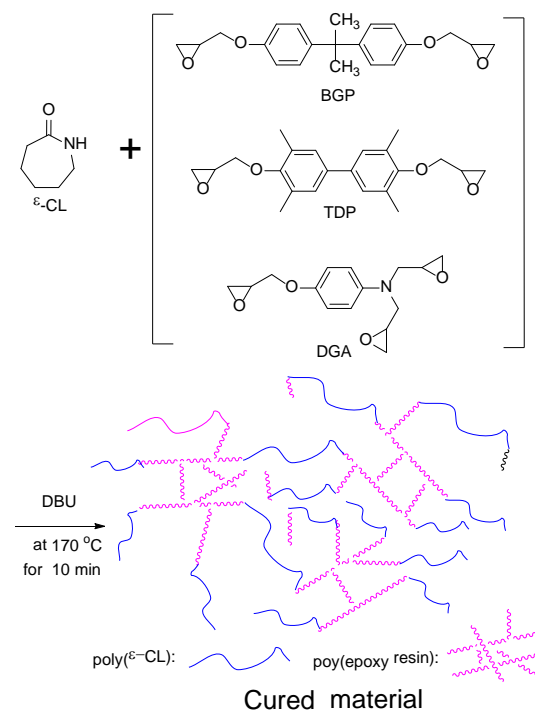
TABLE 6 Thermal curing reaction BGP, TDP, and DCA with ϵ -CL and GPE DBU on the ring-opening copolymerization^a

Run	Feed ratio (mmol)	Cured product ^b (%)	T_g ^c (°C)	T_d^i (°C)
1	ϵ -CL : BGP = 10 : 0	0	- ^e	- ^e
2	ϵ -CL : BGP = 10 : 2	11	72	114
3	ϵ -CL : BGP = 10 : 4	>99	131	323
4	ϵ -CL : BGP = 10 : 8	>99	133	321
5	ϵ -CL : BGP = 10 : 10	>99	211	360
6	ϵ -CL : BGP = 10 : 15	>99	182	328
7	ϵ -CL : BGP = 10 : 20	21	134	303
8	ϵ -CL : BGP = 0 : 10	>99	- ^f	283
9	ϵ -CL : TDP = 10 : 10 ^g	>99	206	338
10	ϵ -CL : DGA = 10 : 10 ^h	>99	209	328

^aReaction conditions; DBU (1 mmol), at 170 °C for 10 min. ^bDMF-insoluble material. ^c T_g ; glass transition temperature measured by DSC. ^d T_d^i ; initial thermal decomposition temperature measured by TGA. ^eCould not be determined. ^fCould not be observed.

^gReaction conditions; DBU(1 mmol), at 170 °C for 25 min.

^hReaction conditions; DBU(1 mmol), at 80 °C for 15 min.

**SCHEME 3** Thermal curing reaction of BGP, TDP, and DGA with ϵ -CL using DBU.

This suggested that the cured product, which was obtained in >99% yield, is strongly adhesive.

We then examined the reaction using various feeds ratios of ϵ -CL and BGP. In the absence of BGP, no cured product was obtained and only the starting material ϵ -CL was recovered (run 1 in Table 5). In the case of ϵ -CL/BGP = 10/2, the reaction product could be washed out with DMF and methanol, and the cured product was obtained in 11 % yield (run 2 in Table 5). The cured product was obtained in >99% yield at the feed ratios of ϵ -CL/BGP = 10/4, 10/8, 10/15, 0/10 (runs 3, 4, 6, and 8 in Table 5). However, in the case of ϵ -CL/BGP = 10/20, the cured product was obtained in only 21 % yield (run 7 in Table 1). The values of T_g were in the range between 72 and 211 °C and those of T_d^i were in the range between 114 and 360 °C. Both values depended on the feed ratio of ϵ -CL and BGP. In the case of ϵ -CL/BGP = 10/10, the cured product showed the highest T_g and T_d^i values of 211 and 360 °C, respectively. Thus, the formation and properties of the cured product are determined by the feed ratio of ϵ -CL and BGP. Furthermore, thermal curing reactions of 3,3',5,5'-tetramethyl-4,4'-diglycidyloxybiphenyl (TDP) and N,N-diglycidyl-4-glycidyloxyaniline (DGA) with ϵ -CL were examined at equimolar feed ratios under the above conditions (Scheme 3). TDP afforded the cured product within 25 min at 170 °C (Run 9 in Table 5). DGA afforded the cured product within 15 min at 80 °C (Run 10 in Table 5). The T_g and T_d^i values of these cured products were high, i.e., T_g = 206, 209 °C, and T_d^i = 338, 328 °C, respectively. It is particularly interesting that thermal curing reaction of DGA and ϵ -CL proceeded at such a low reaction temperature, affording a cured product with high thermal stability. This might be explained in terms of not only hydrogen bonding between the segments, but also a pseudo-block gradient

primary structure like that of poly(ϵ -CL-co-GPE) illustrated in Scheme 3.

CONCLUSIONS

Ring-opening copolymerization of ϵ -CL and GPE proceeded in the presence of DBU to afford poly(ϵ -CL-co-GPE) in high yield. The molar ratios r_1 of ϵ -CL and r_2 of GPE were determined to be $r_1 = 0.58$ and $r_2 = 5.52$ by the Fineman-Ross method and Kelen-Tüdös method. This indicates that poly(ϵ -CL-co-GPE) has a pseudo-block gradient copolymer like structure. Based on our studies of this reaction, thermal curing reactions of ϵ -CL with epoxy resins BGP, TDP, and DGA in the presence of DBU were performed at temperatures in the range between 80 and 170 °C, and the corresponding cured epoxy resins were formed quantitatively. The cured products showed high glass transition temperatures and high thermal stabilities, presumably in part because of a pseudo-block gradient primary structure resembling that of poly(ϵ -CL-co-GPE). This thermal curing system of ϵ -CL and epoxy resins provides a new class of poly(amide-ether) cured products with superior thermal properties. This thermosetting epoxy resin system is expected to be introduced commercially for various applications in the near future.

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GRAPHICAL ABSTRACT

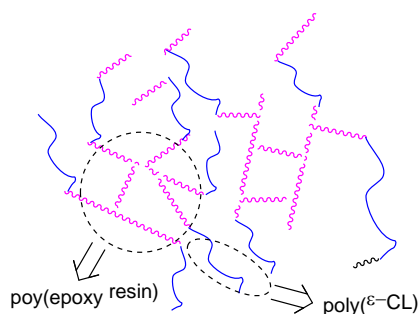
HIROTO KUDO, KENTARO BUYA

Mechanistic Study of Ring-Opening Copolymerization of ϵ -Caprolactam with Epoxide: Development of Novel Epoxy Thermosetting Resin System

TEXT: Ring-opening copolymerization of ϵ -caprolactam (ϵ -CL) with glycidyl phenyl ether (GPE) proceeded using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 170 °C, affording the corresponding poly(amide-ether). Evaluation of the monomer reactivities indicated that the synthesized poly(ϵ -CL-co-GPE) has a pseudo-block gradient copolymer. Based on this model reaction, we developed a new thermal curing system of epoxy resins with ϵ -CL, using DBU, to give the corresponding cured materials with high glass transition temperatures and high thermal stabilities.

GRAPHICAL ABSTRACT FIGURE ((Please provide a square image to be produced at 50 mm wide by 50 mm high. Please avoid graphs and other figures with fine detail due to the relatively small size of this image.))

GRAPHICAL ABSTRACT FIGURE



Cured Material containing
Pseudo-block Structure