A Novel Synthesis of Poly(carbonate)s by the Polyaddition of Bis(epoxide)s with Diphenyl Carbonate

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ABSTRACT: The synthesis of poly(carbonate)s with phenoxymethyl groups in their side chains by a polyaddition of bisphenol A diglycidyl ether (**4a**) with diphenyl carbonate (**2**) using quaternary onium salts or crown ether complexes as catalysts is described. When the polyaddition was performed with the catalyst containing Cl^- as a counteranion such as tetrabutylammonium chloride, tetrabutylphosphonium chloride, or 18-crown-6/KCl without solvent at 100 °C for 48 h, the corresponding poly(carbonate) with high molecular weight (M_n = 20 000−34 000) was successfully obtained. ^{1}H NMR and ^{13}C NMR spectra of the resulting polymer indicated that the reaction proceeded regioselectively at the epoxy groups of **4a** to give the polycarbonate with pendant phenoxy groups. The polyaddition of various bis(epoxide)s with **2** also proceeded in bulk to provide the corresponding poly(carbonate)s with high molecular weight in good yield.

Introduction

Poly(aryl carbonate) with the bisphenol A (BPA) skeleton has been widely used as an engineering thermoplastic. The polymer is ordinarily synthesized by the polycondensation[1,2] of BPA with phosgene or diphenyl carbonate. The same poly(aryl carbonate) can also be synthesized by the ring-opening polymerization[3] of the corresponding cyclic oligomeric carbonates synthesized by the condensation reaction of BPA with BPA−bis(chloroformate). Recently, Brunelle et al.[4] reported, in detail, the synthesis of BPA cyclic oligomeric carbonates and their successful ring-opening polymerization with anionic catalysts to produce high molecular weight poly(aryl carbonate).

Poly(aryl carbonate)s or poly(alkyl carbonate)s have been synthesized by different methods. For example, Inoue et al.[5] have reported the successful synthesis of high molecular weight poly(alkyl carbonate)s by the alternating ring-opening copolymerization of epoxides with carbon dioxide using appropriate anionic catalysts. This type of poly(alkyl carbonate) has been of great interest as a biodegradable polymer. Kricheldorf et al.[6] have reported the cationic ring-opening polymerization of 5,5-dimethyl-1,3-dioxane-2-one to give the corresponding poly(alkyl carbonate). Endo et al.[7] reported anionic or cationic ring-opening polymerizations of various cyclic carbonates from the viewpoint of volume expansion of the monomers upon polymerization. Recently, they also reported the synthesis of optically active poly(aryl carbonate)s[8] by anionic ring-opening polymerization of the corresponding aromatic cyclic carbonates containing optically active binaphthyl groups. Soga et al.[9] have also reported the synthesis of other poly(alkyl carbonate)s by the polycondensation of bis(alkyl halide)s with potassium phenoxide in the presence of carbon dioxide or with potassium carbonate using 18-crown-6 as a phase transfer catalyst.

Nishikubo et al.[10,11] found that polyfunctional carbonates could be used as a cross-linking reagent for epoxy resins, as were polyfunctional aryl esters, to obtain high-performance thermosetting resins. Other research groups also reported[12,13] the thermal curing reaction of epoxy resins using poly(aryl carbonate)s containing reactive ester linkages. The chemical modification of poly(aryl carbonate) by reaction with epoxy compounds containing trimethoxy silyl ether groups using appropriate quaternary onium salts was also reported,[14] although the degree of insertion was relatively low (25−34%).

Our research group[15] recently reported new addition reactions of epoxides with acyl chlorides or active carboxylic acid derivatives having good leaving groups such as PhS^- and PhO^-. These reactions proceeded regioselectively to give the corresponding addition products when suitable quaternary onium salts or crown ether complexes were used as catalysts under mild conditions. This reaction system could be applied widely to polymer syntheses. The first application of this reaction system is the chemical modification of polymers with pendant epoxide groups[16] and the chemical modification of polymers with pendant active ester groups.[17] These are useful method for the synthesis of various kinds of functional polymers. The second application of this approach is the novel synthesis of poly(ester)s[18] with pendant phenoxy groups or chloromethyl groups by the polyaddition of bis(epoxide)s with active di(ester)s or di(acyl chloride)s, respectively. This is a new synthetic method of polyesters, which are generally prepared by conventional polycondensation or ring-opening polymerization of lactones. The third application of this reaction system is a thermal curing reaction of epoxy resins[19] with polyfunctional active esters such as certain esters of phenolic resins or with polyfunctional alkyl aryl carbonates. This reaction system has been of great interest as a new thermal curing system to obtain high-performance epoxy resins with high hydrophobicity.

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In a series of research on new polymer synthesis based on the polyaddition of bis(epoxide)s with active di(ester)s or active dichlorides, we found that poly(aryl carbonate)s with pendant chloromethyl groups were successfully synthesized by polyaddition[20] of bis(epoxide)s with 2,2′-bis[(4-chloroformyl)oxyphenyl]propane using suitable quaternary onium salts or crown ether complexes as catalysts. To our knowledge, this is the first example of the polycarbonate synthesis by polyaddition of two kinds of difunctional monomers. Since the polyaddition systems produce no waste byproducts, it has a synthetic advantage in polymer chemistry and industry from the viewpoint of atom economy,[21] as proposed by Trost.

In light of these results, the authors designed a new reaction for the synthesis of polycarbonates by polyaddition of bis(epoxide)s with diphenyl carbonate under mild reaction conditions. In this paper, we report on the synthesis of poly(carbonate)s by the polyaddition of bis(epoxide)s with diphenyl carbonate using certain quaternary onium salts or crown ether complexes as catalysts. The reaction behavior of the polyaddition was also investigated.

Experimental Section

Materials. Solvents were dried using Na metal wire, P_2O_5, or CaH_2 and purified in the usual way before use. Phenyl glycidyl ether (**1**) was purified by distillation under reduced pressure. Diphenyl carbonate (**2**) was recrystallized twice from anhydrous ethanol. Commercial bisphenol A diglycidyl ether (**4a**), 4,4′-bisphenyl glycidyl ether (**4b**), and 3,3′,5,5′-tetramethyl-4,4′-biphenyl diglycidyl ether (**4c**) were recrystallized four times from methanol/ethyl methyl ketone (4/1), isobutyl methyl ketone, and the mixed solvent of isobutyl methyl ketone/ methyl ethyl ketone (3/1), respectively. Ethylene glycol diglycidyl ether (**4d**) was purified by distillation under reduced pressure. Tetrabutylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylphosphonium bromide (TBPB), tetrabutylphosphonium chloride (TBPC), tetraphenylphosphonium bromide (TPPB), tetraphenylphosphonium chloride (TPPC), 18-crown-6 (18-C-6), potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI) were used without further purification.

Measurement. Infrared (IR) spectra were measured on a Jasco model IR-700 and FT/IR-5300 spectrometers. The ^{1}H NMR (200 MHz) and the ^{13}C NMR (50 MHz) spectra were recorded on a JEOL model JNM FX-200 instrument in $CDCl_3$ using Me_4Si (TMS) as an internal standard. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with a Tosoh model HLC-8020 GPC equipped with a refractive index detector using two TSK gel G1000H columns (eluent: THF, calibrated using narrow molecular weight polystyrenes as standards). Glass transition temperatures T_g's of the polymers were measured on a Perkin-Elmer differential scanning calorimeter model DSC Station 4 at a heating rate at 10 °C /min.

Addition Reaction of 1 with 2. The addition reaction of **1** (0.601 g, 4.0 mmol) with **2** (0.428 g, 4.0 mmol) was performed using TBAC (0.022 g, 0.08 mmol) as the catalyst in bulk at 100 °C for 24 h in a sealed tube with stirring. The reaction mixture was diluted with ethyl acetate, washed thrice with minimal amounts of water to remove TBPC, and dried by stirring with $MgSO_4$. The $MgSO_4$ was filtered off, and then the solvent was evaporated in vacuo. The product was purified by silica gel column chromatography using chloroform as the eluent. The isolated yield of product **3** was 1.008 g (98%). IR (KBr, cm^{-1}): 1751 (ν C═O, carbonate), 1598 and 1499 (ν C═C, aromatic), 1272 and 1079 (ν C−O−C, ether), and 1235 and 1173 (ν O−C−O, carbonate). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 4.29 (d, J = 5.37 Hz, 8.0H, CH_2), 5.38−5.43 (m, 2.0H, C*H*), and 6.88−7.29 (m, 20H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 65.9 (*C*H$_2$), 74.7 (*C*H), 114.6, 121.3, 129.5, and 158.2 (aromatic C), and 154.1 (*C*═O). Melting point: 100.2−101.2 °C. Anal. Calcd for $C_{31}H_{30}O_7$: C, 72.36%; H, 5.88%. Found: C, 72.39%; H, 6.00%.

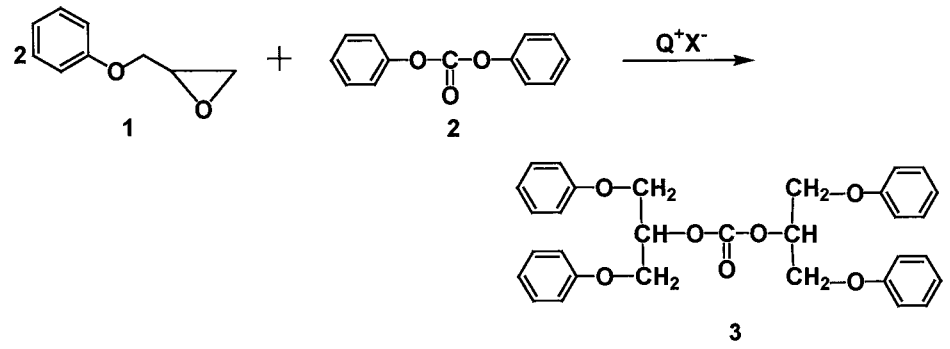
Typical Procedure for the Synthesis of Polymer 5a by Polyaddition of 4a with 2. A typical procedure for polyaddition of **4a** with **2** was as follows: **4a** (0.341 g, 1.0 mmol), **2** (0.214 g, 1.0 mmol), and TBPC (0.012 g, 0.04 mmol) were placed in a glass tube in a drybox, after which the tube was evacuated and then sealed using a gas torch. The reaction was performed at 100 °C for 48 h in the sealed tube under stirring; the solution was then diluted with 3 mL of chloroform and poured into 100 mL of methanol to precipitate the polymer. The resulting polymer was reprecipitated twice from chloroform into excess methanol and dried in vacuo. The yield of resulting polymer **5a** was 0.540 g (98%). The number-average molecular weight (M_n) of the polymer determined by GPC was 28 300 (M_w/M_n = 1.89). IR (film, cm^{-1}): 1749 (ν C═O, carbonate), 1598 and 1496 (ν C═C, aromatic), 1272 and 1079 (ν C−O−C, ether), and 1235 and 1182 (ν O−C−O, carbonate). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.59 (bs, 6.0H, CH_3), 4.07−4.44 (m, 8.0H, CH_2), 5.23−5.53 (m, 2.0H, C*H*), and 6.72−7.31 (m, 18H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 31.0 (*C*H$_3$), 41.7 (Ar−*C*−Ar), 65.8 (Ar−O−*C*H$_2$), 74.6 (*C*H), 114.0, 114.6, 121.3, 127.8, 129.5, 143.7, 156.1, and 158.2 (aromatic C), and 154.1 (C═O). Anal. Calcd for $C_{34}H_{34}O_7$: C, 72.64%; H, 5.51%. Found: C, 72.86%; H, 5.45%.

Synthesis of Polymer 5b by Polyaddition of 4b with 2. Polymer **5b** was synthesized by the polyaddition of **4b** (0.298 g, 1.0 mmol) with **2** (0.214 g, 1.0 mmol) using TBPC (0.012 g, 0.04 mmol) as a catalyst at 100 °C for 48 h in a sealed tube under stirring. The final yield of polymer **5b** was 0.510 g (99%). The M_n of polymer **5b** determined by GPC was 13 800 (M_w/M_n = 3.47). IR (film, cm^{-1}): 1748 (ν C═O, carbonate), 1598 and 1495 (ν C═C, aromatic), 1268 and 1079 (ν C−O−C, ether), and 1232 and 1173 (ν O−C−O, carbonate). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 4.05−4.45 (m, 8.0H, CH_2), 5.12−5.67 (m, 2.0H, C*H*), and 6.81−7.45 (m, 18H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 65.8 and 66.1 (Ar−O−*C*H$_2$), 74.7 (*C*H), 114.6, 115.0, 121.3, 127.7, 129.5, 133.8, 157.4, and 158.2 (aromatic C), and 154.1 (C═O). Anal. Calcd for $C_{31}H_{28}O_7$: C, 72.64%; H, 5.51%. Found: C, 72.86%; H, 5.45%.

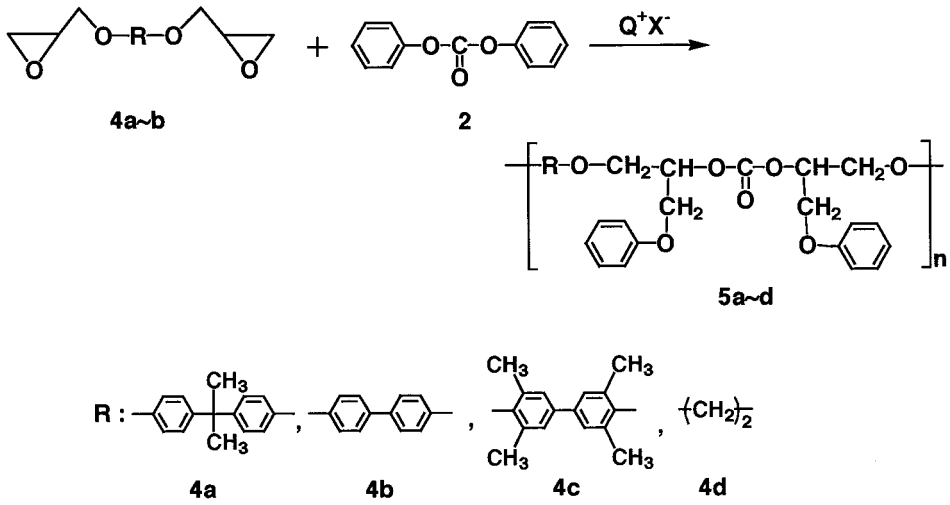
Synthesis of Polymer 5c by Polyaddition of 4c with 2. The polyaddition of **4c** (0.354 g, 1.0 mmol) with **2** (0.214 g, 1.0 mmol) was carried out in the presence of TBPC (0.012 g, 0.04 mmol) at 100 °C for 96 h in a sealed tube under stirring to obtain the corresponding poly(alkyl carbonate) **5c**. The final yield of polymer **5c** was 0.560 g (99%). The M_n of polymer **5c** determined by GPC was 24 300 (M_w/M_n = 3.00). IR (film, cm^{-1}): 1747 (ν C═O, carbonate), 1597 and 1494 (ν C═C, aromatic), 1263 and 1079 (ν C−O−C, ether), and 1236 and 1173 (ν O−C−O, carbonate). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 2.30 (bs, 12.0H, CH_3), 3.96−4.52 (m, 8.0H, CH_2), 5.12−5.70 (m, 2.0H, C*H*), and 6.84−7.40 (m, 14H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 16.2(*C*H$_3$), 65.6 and 69.5 (Ar−O−*C*H$_2$), 75.3 (*C*H), 114.6, 121.3, 126.2, 127.5, 129.5, 130.9, 136.8, and 158.2 (aromatic C), and 154.3 (C═O). Anal. Calcd for $C_{35}H_{36}O_7$: C, 73.97%; H, 6.38%. Found: C, 74.21%; H, 6.42%.

Synthesis of Polymer 5d by Polyaddition of 4d with 2. When **4d** (0.174 g, 1.0 mmol), **2** (0.214 g, 1.0 mmol), and TBPC (0.012 g, 0.04 mmol) as a catalyst were stirred at 100 °C for 96 h in a sealed tube, polymer **5d** was obtained. The final yield of polymer **5d** was 0.380 g (97%). The M_n of polymer **5d** determined by GPC was 10 100 (M_w/M_n = 1.62). IR (film, cm^{-1}): 1746 (ν C═O, carbonate), 1597 and 1494 (ν C═C, aromatic), 1268 and 1077 (ν C−O−C, ether), and 1236 and 1172 (ν O−C−O, carbonate). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 3.50−3.84 (m, 8.0H, CH−CH_2−O−CH_2CH_2−O−CH_2−CH), 3.96−4.18 (m, 4.0H, Ar−O−CH_2), 4.88−5.32 (m, 2.0H, C*H*), and 6.75−7.38 (m, 10H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 66.0 and 69.2 (*C*H$_2$CH_2−O−*C*H$_2$−CH), 70.9 (Ar−O−*C*H$_2$), 75.1 (*C*H), 114.6, 121.2, 129.5, and 158.3 (aromatic C), and 154.2 (C═O). Anal. Calcd for $C_{21}H_{24}O_7$: C, 64.94%; H, 6.23%. Found: C, 64.97%; H, 6.07%.

Scheme 1



Scheme 2



Results and Discussion

The addition reaction of **1** with **2** without solvent was examined as a model reaction for the polyaddition of bis(epoxide)s with **2**. Although the reaction without catalysts did not occur at all, the reaction proceeded using TBPC as a catalyst at 100 °C in bulk for 24 h to provide the corresponding addition product **3** in 98% yield. The structure of **3** was well confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of **3** showed absorption peaks at 1751 cm^{-1} due to the C═O stretching of the carbonate linkage, 1598 cm^{-1} due to the C═C stretching of aromatic groups, 1272 and 1079 cm^{-1} due to the C−O−C stretching of the ether linkage, and 1235 and 1173 cm^{-1} due to the O−C−O stretching of the carbonate linkage. In the ^{1}H NMR spectrum of **3**, the corresponding proton signals were observed at 4.29 ppm for the methylene protons, 5.38−5.43 ppm for the methine protons, and 6.88−7.29 ppm for the aromatic protons. The intensity ratios of methylene, methine protons, and aromatic protons agreed reasonably with the calculated values. In the ^{13}C NMR spectrum of adduct **3**, the expected signals were also observed at 65.86 ppm for the methylene carbon atom, 74.65 ppm for the methine carbon atom, and 154.13 ppm for the C═O carbon atom of the carbonate group as one signal, respectively. This means that the reaction of **1** with **2** proceeded regioselectively, that is, β-scission of the epoxide group of **1** occurred selectively, to give the corresponding carbonate **3** as shown in Scheme 1.

On the basis of the results of model reactions, the polyaddition of **4a** with **2** using 2 mol % of TBPC was carried out at 100 °C for 48 h without solvent. The polymer **5a** with M_n = 28 000 was obtained in 98% yield. No reaction occurred without catalysts under the same conditions. The IR spectrum of **5a** showed absorption peaks consistent with the expected structure. In the ^{1}H NMR spectrum of the polymer, the corresponding proton signals were observed with reasonable intensity ratios, at 1.59 ppm for the methyl protons, 4.07−4.44 ppm for the methylene protons, 5.23−5.53 ppm for the methine protons, and 6.72−7.31 ppm for the aromatic protons. The ^{13}C NMR spectrum of the polymer showed the corresponding carbon signals such as methyl, methylene, methine, and aromatic groups. Furthermore, the signal of the C═O carbon atom for the carbonate group was observed at 154.10 ppm as one signal. These results indicate that the reaction of **4a** with **2** proceeded regioselectively to give the corresponding poly(carbonate) **5a** as shown in Scheme 2.

The effect of catalysts on the reaction of **4a** with **2** was examined in bulk at 100 °C for 48 h. As summarized in Table 1, when the reaction was carried out with 2 mol % of certain onium salts such as TBAC, TBAB, TBAI, TBPC, TBPB, TPPC, and TPPB, poly(carbonate) **5a** was obtained in quantitative yields. In particular, when the polyaddition was carried out using TBAC or TBPC, polymer **5a** with higher molecular weights than that obtained using other onium salts was obtained. The polyaddition also proceeded smoothly using certain crown ether complexes such as 18-C-6/KCl, 18-C-6/KBr, and 18-C-6/KI, and polymer **5a** with the highest molecular weights (M_n = 34 000) was obtained when 2 mol % of 18-C-6/KCl was used as catalyst. These results show that TBAC, TBPC, and 18-C-6/KCl, all containing

Table 1. Effect of Catalyst on the Polyaddition of 4a with 2[a]

run no.	catalyst	yield[b]/%	$M_n \times 10^{-4}$ [c]	M_w/M_n [c]
1	none	0		
2	TBAC	100	1.78	2.06
3	TBAB	100	1.11	1.73
4	TBAI	99	0.52	1.46
5	TBPC	98	2.83	1.89
6	TBPB	98	0.37	4.52
7	TPPC	99	0.74	1.47
8	TPPB	98	0.43	1.39
9	18-C-6/KCl	99	3.44	1.73
10	18-C-6/KBr	99	2.06	1.78
11	18-C-6/KI	99	0.69	1.38

[a] The reaction was carried out with **4a** (1 mmol) and **2** (1 mmol) using 2 mol % of catalyst in bulk at 100 °C for 48 h. [b] Insoluble parts in methanol. [c] Estimated by GPC (THF) based on polystyrene standards.

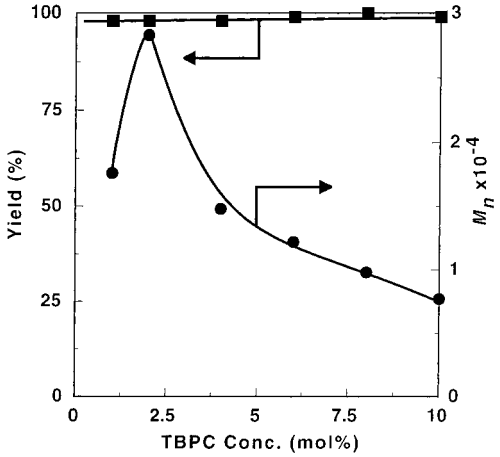


Figure 1. Effect of TBPC concentration on the polyaddition of **4a** (1 mmol) with **2** (1 mmol) in bulk at 100 °C: (■) yield; (●) M_n.

Cl^- as a counteranion, have higher catalytic activity than the catalysts containing Br^- or I^- as counteranions.

The effect of the catalyst concentration on the polyaddition of **4a** with **2** was examined using TBPC as the catalyst in bulk at 100 °C for 48 h. As shown in Figure 1, the M_n of obtained polymer **5a** increased from 1 to 2 mol % with catalyst concentration. On the other hand, the M_n decreased when the reaction was carried out using over 3 mol % of TBPC. It seems that the rate of polyaddition of **4a** with **2** increased with catalyst concentration; however, the M_n of polymer decreased gradually as catalyst concentrations increased, and this may be caused by the side reactions. The IR spectrum of **5a** from this polyaddition using 10 mol % of TBPC showed an absorption peak at 1749 cm^{-1} for the C=O stretching of carbonate linkages and a small shoulder at about 1800 cm^{-1} for the C=O stretching of the cyclic carbonate. This result suggested that the polyaddition of **4a** with **2** using 10 mol % of the catalyst underwent a side reaction, i.e., ring closure to produce a cyclic carbonate.

The effect of reaction time on the polyaddition of **4a** with **2** was investigated using 2 mol % of TBPC as the catalyst in bulk at 100 °C. As shown in Figure 2, although polymer **5a** was obtained in quantitative yield at all times, the number-average molecular weight of the obtained polymer increased with reaction time. The polymer **5a** with M_n of 30 000 was

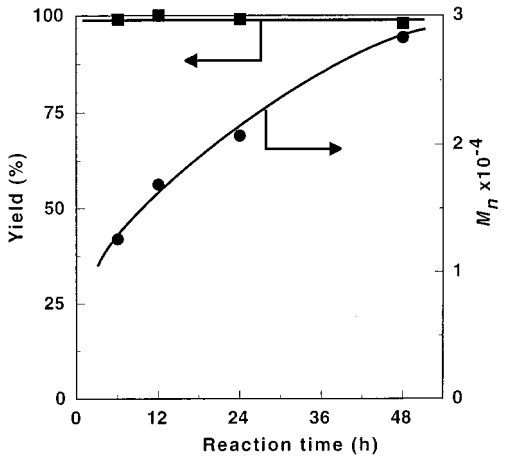


Figure 2. Effect of the reaction time on the polyaddition of **4a** (1 mmol) with **2** (1 mmol) in bulk using TBPC (2 mol %) at 100 °C: (■) yield; (●) M_n.

obtained by the reaction at 48 h. This means that the reaction proceeded by a step-growth polymerization mode.

The mechanism of the reaction of bis(epoxide)s with **2** can be considered according to the previously proposed mechanism[15c] for the reaction of epoxides with carboxylic acid esters using quaternary onium salts by our research group. Epoxide undergoes anionic polymerization using suitable initiators, in which alcholate of epoxide is an active species at the polymer terminal. At first, we found that the polymerization of epoxide using tetrabutylammonium chloride or bromide without solvent at 100 °C did not occur at all. This means that the alcholate of epoxide did not form during the reaction. Therefore, the mechanism of the reaction of epoxide with diphenyl carbonate using quaternary onium salts is shown in Scheme 3. The counteranion of the catalyst interacts with the β-carbon of the epoxide to provide an activated epoxide. The activated epoxide reacts with diphenyl carbonate to form tetrahedral intermediate **I**, and then **I** is transformed to produce the corresponding addition product releasing the catalyst. In the proposed mechanism, the catalytic activity of catalyst seems to depend on the balance of nucleophilicity and the leaving ability of the counteranion of the quaternary onium salts. The regioselectivity of the reaction could be ascribed to steric hindrance due to the substituent at the α-carbon atom of the epoxide and tetrabutylonium salts, which are relatively large.

On the basis of the obtained information for the polyaddition of **4a** with **2**, the synthesis of various poly(carbonate)s was performed by the polyaddition of bis(epoxide)s **4a**−**d** with **2** using 2 mol % of TBPC as the catalyst in bulk at 100 °C. As shown in Table 2, the reactions with **4a** and **4c** proceeded smoothly, and poly(carbonate)s **5a** and **5c** with high molecular weights were obtained. In the case of the reaction with **4b** and **4d**, the reaction proceeded more efficiently in chlorobenzene than in bulk to produce the corresponding polymers with high or moderate molecular weight. In the bulk polymerization of **4b** and **4d** with **2**, the decreased miscibility of the monomers with the produced oligomers at 100 °C may affect the reaction. The IR, ^1H NMR, and ^{13}C NMR data of the obtained polymers proved that the polyaddition of bis(epoxide)s with **2** proceeded regiose-

Scheme 3

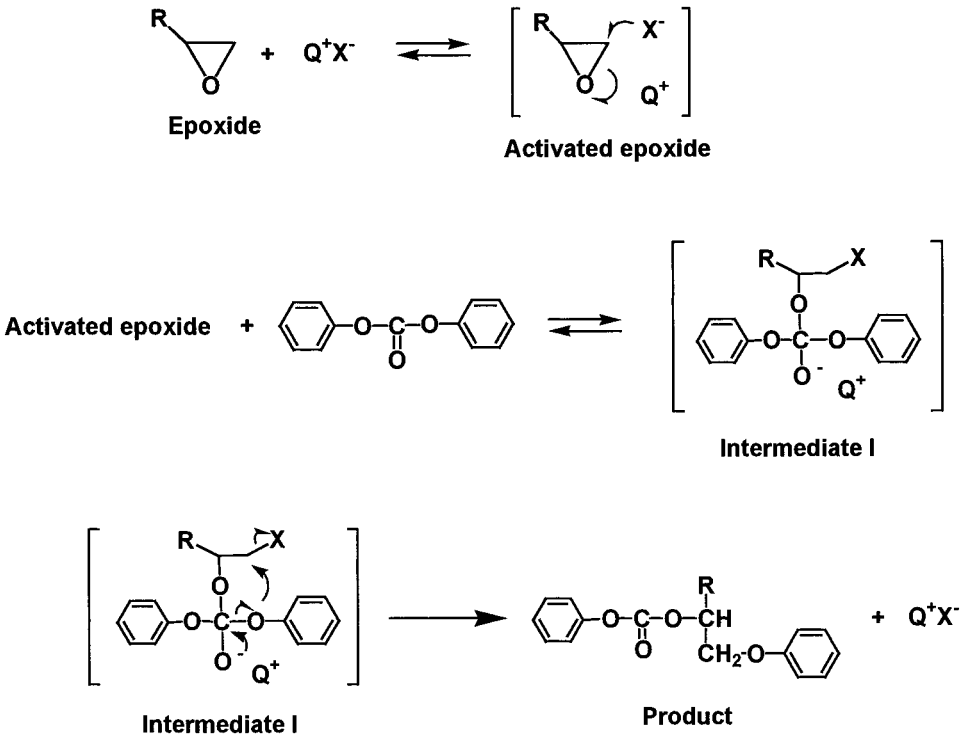


Table 2. Polyaddition of Bis(epoxide)s with 2[a]

run no.	bis(epoxide)	solvent	time /h	yield[b]/%	$M_n \times 10^{-4}$ [c]	M_w/M_n [c]	T_g/°C
20	**4a**	none	48	98	2.83	1.89	64
21	**4b**	none	48	100	1.38	3.47	69
22	**4c**	none	96	99	2.43	2.00	83
23	**4d**	none	96	95	1.01	1.35	
24	**4a**	chlorobenzene	48	93	1.96	1.68	64
25	**4b**	chlorobenzene	48	93	2.65	2.65	69
26	**4c**	chlorobenzene	96	99	1.58	1.58	83
27	**4d**	chlorobenzene	96	97	1.54	1.54	

[a] The reaction was carried out with **4a**−**d** (1 mmol) and **2** (1 mmol) using 2 mol % of TBPC in chlorobenzene (1.0 mol/L) or bulk at 100 °C. [b] Insoluble parts in methanol. [c] Estimated by GPC (THF) based on polystyrene standards.

lectively to give the corresponding poly(carbonate)s **5a**−**d** with pendant phenoxymethyl groups as shown in Scheme 2. The T_g of the obtained polymers was measured by DSC. The T_g's of polymer **5a**, **5b**, and **5c** were 64, 69, and 83 °C, respectively. However, polymer **5d** was a viscous liquid like at room temperature. The T_g's of these polymers were relatively low because the resulting polymers had flexible carbonate linkages in their main chains.

In conclusion, poly(carbonate)s with high molecular weights were successfully synthesized by the polyaddition of bis(epoxide)s with **2** using quaternary onium salts or crown ether complexes. The polyaddition was efficiently catalyzed by catalysts containing chloride as the counteranions. It was found that the polyaddition proceeded regioselectively at the epoxy rings of the bis(epoxide)s even in bulk to produce the corresponding poly(carbonate)s with pendant phenoxymethyl groups. The polyaddition will be classified as a new polymer synthesis of polycarbonates.

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