Macromolecules **2000,** *33,* 7737−7742

A Novel Synthesis of Reactive Polycarbonates with Pendant Chloromethyl Groups by the Polyaddition of Bis(epoxide)s with 2,2′-Bis[(4-chloroformyl)oxyphenyl]propane

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Received January 26, 2000; Revised Manuscript Received August 8, 2000

ABSTRACT: The polyaddition of bisphenol A diglycidyl ether (**4a**) with 2,2′-bis[(4-chloroformyl)oxyphenyl]-propane (**5**) was examined using quaternary onium salts as catalysts. When the polyaddition was performed using catalysts containing Br^- as a counteranion such as tetraphenylphosphonium bromide in chlorobenzene at 100 °C for 48 h, the corresponding poly(alkyl aryl carbonate) with high molecular weight ($M_n = 59\,000$) was obtained. It was found from the ^1H NMR and ^{13}C NMR spectra of the obtained polymer that the reaction proceeded regioselectively at the epoxy group of **4a** to provide the polycarbonate with pendant chloromethyl groups. The polyaddition of various bis(epoxide)s with **5** also proceeded smoothly to give the corresponding poly(carbonate)s with high molecular weight in good yields. The chemical modification of the obtained poly(carbonate)s with pendant chloromethyl groups by the phase-transfer method was also investigated using nucleophiles such as potassium thiocyanate and potassium 3-phenyl-2,5-norbornadienecarboxylate.

Introduction

Poly(aryl carbonate) has been synthesized by the polycondensation[1,2] of bis(phenol) with phosgene or diphenyl carbonate and has been widely used as engineering thermoplastics. Many polycarbonates with different polymer skeletons have also been synthesized by other methods. For example, poly(alkyl carbonate)s were synthesized by the alternating ring-opening copolymerization[3] of oxiranes with carbon dioxide. Poly(alkyl carbonate)s were also synthesized by polycondensation[4] of bis(alkyl halide)s with potassium phenoxide in the presence of carbon dioxide or with potassium carbonate using 18-crown-6. In addition, cationic ring-opening polymerization of 5,5-dimethyl-1,3-dioxane-2-one[5] and anionic or cationic ring-opening polymerizations of various cyclic carbonates[6] provide corresponding poly(alkyl carbonate)s or poly(aryl carbonate)s, respectively.

Ring-opening polymerizations without harmful waste byproducts have a synthetic advantage on the synthesis of polycarbonates from the viewpoint of Atom Economy, which was proposed by Trost.[7] Although the polyaddition to produce polycarbonates seems to be a useful synthetic method, no paper on the synthesis of polycarbonates by polyaddition has been reported to our knowledge.

Meanwhile, Nishibuko et al.[8] have found that the polyaddition of bis(epoxide)s with diacyl chlorides provided the corresponding high molecular weight polyesters with reactive pendant chloromethyl groups that were produced simultaneously with the formation of polymer backbone. The reaction system is a new method for the synthesis of reactive polymers with pendant chloromethyl groups. Reactive polymers containing pendant chloromethyl groups have been synthesized ordinarily by selective polymerizations[9] of the corresponding monomers having chloromethyl groups such as (*p*-chloromethyl)styrene, 2-chloroethyl vinyl ether, and epichlorohydrin and by chemical modifications of polymers[10] such as polystyrene with chloromethyl methyl ether using appropriate catalyst to produce chloromethylated polystyrene. Our reaction system can also be extended to new syntheses of reactive poly(silyl ether)s,[11] polyphosphonates,[12] and polysulsonates[13] containing reactive chloromethyl groups in their side chains by polyaddition of bis(epoxide)s with dichlorosilanes, phosphonic dichlorides, and disulfonyl chlorides.

Few papers for the synthesis of reactive poly(carbonate)s have been reported so far. Endo et al.[14] reported the synthesis of poly(alkyl carbonate) with an unsaturated reactive C═C bond by the cationic ring-opening polymerization of 5-methylene-1,3-dioxane-2-one. They also reported[15] the synthesis of poly(alkyl carbonate) with norbornene structure by the anionic ring-opening polymerization of the corresponding cyclic carbonate monomer. Although polymers with pendant chloromethyl groups are one of the most useful starting materials for the synthesis of certain functional polymers, the polycarbonates with pendant chloromethyl groups have never been reported.

Given this background, the authors investigated the synthesis of new reactive poly(alkyl aryl carbonate)s with pendant chloromethyl groups by the polyaddition of bis(epoxide)s with 2,2′-bis[(4-chloroformyl)oxyphenyl]-propane (BCPP) and the chemical modification of the resulting polymers.

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**) (Tokyo Chemical Industry: TCI) was purified by distillation under reduced pressure. Phenyl chloroformate (**2**) (TCI) was used without further purification. Commercial bisphenols A diglycidyl ether (**4a**) (TCI), 4,4′-biphenyl glycidyl ether (**4b**) (Yuka Shell Epoxy), and 3,3′,5,5′-tetramethyl-4,4′-biphenyl diglycidyl ether (**4c**) (Yuka Shell Epoxy) were recrys-

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10.1021/ma000134x CCC: $19.00

tallized four times from the mixed solvent of 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**) (TCI) was purified by distillation under reduced pressure. 2,2′-Bis[(4-chloroformyl)oxyphenyl]propane (**5**) (TCI) was recrystallized twice from anhydrous *n*-hexane. Tetrabutylammonium bromide (TBAB) (Kanto Chemical) was recrystallized twice from ethyl acetate. Tetrabutylammonium chloride (TBAC) (Aldrich), tetrabutylammonium iodide (TBAI) (TCI), tetrabutylammonium acetate (TBAAc) (Aldrich), tetrabutylphosphonium bromide (TBPB) (TCI), tetrabutylphosphonium chloride (TBPC) (TCI), tetraphenylphosphonium bromide (TPPB) (TCI), and tetraphenylphosphonium chloride (TPPC) (TCI) were used without further purification.

Measurement. Infrared (IR) spectra were measured on a Jasco Models 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 Joel 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 the use of a Tosoh model HLC-8020 GPC equipped with a refractive index detector using 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** (0.626 g; 4.0 mmol) was performed using TBPC (0.024 g; 0.08 mmol) as a catalyst in chlorobenzene (4 mL) at 80 °C for 24 h in a sealed tube under stirring. The reaction mixture was diluted with ethyl acetate, washed thrice with minimal amount of water to remove TBPC, and dried using $MgSO_4$ overnight under stirring. The $MgSO_4$ was filtered off, and then the solvent was evaporated in vacuo. The obtained product was purified by separate GPC using THF as the eluent. Isolated yield of product **3** was 1.092 g (89%). IR (KBr, cm^{-1}): 1763 (ν C=O, carbonate), 1596 and 1493 (ν C=C, aromatic), 1235 (ν O−C−O, carbonate), 1173 (ν C−O−C, ether), and 719 (ν C−Cl, chloromethyl). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 3.79−3.99 (m, 2.0H, CH_2Cl), 4.20−4.35 (m, 2.0H, OCH_2), 5.30−5.56 (m, 1.0H, C*H*), and 6.65−7.48 (m, 10.0H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 42.03 (*C*H$_2$Cl), 65.69 (O*C*H$_2$), 75.57 (*C*H), 114.59, 120.86, 121.59, 126.21, 129.49, 129.58, 150.90, and 157.99 (aromatic C), and 152.91 (*C*=O). Melting point: 59.0−59.8 °C.

Typical Procedure for the Synthesis of Polymer 6a by Polyaddition of 4a with 5. A typical procedure for polyaddition of **4a** with **5** was as follows: **4a** (0.341 g; 1.0 mmol), **5** (0.353 g; 1.0 mmol), TPPB (0.017 g, 0.04 mmol), and chlorobenzene (1 mL) were charged into 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 24 h in the sealed tube under stirring, and then the solution was 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 **6a** was 0.680 g (99%). The number-average molecular weight (M_n) of the polymer determined by GPC was 47 300 (M_w/M_n = 3.88). IR (film, cm^{-1}): 1761 (ν C=O, carbonate), 1605 and 1508 (ν C=C, aromatic), 1184 (ν O−C−O, carbonate), 1193 and 708 (ν C−Cl, chloromethyl), and 1081 (ν C−O−C, ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.44−1.79 (m, 12.0H, CH_3), 3.68−4.07 (m, 4.0H, CH_2Cl), 4.07−4.40 (m, 4.0H, OCH_2), 4.98−5.51 (m, 2.0H, C*H*), and 6.72−7.32 (m, 16.0H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 30.98 and 30.96 (*C*H$_3$), 41.75 and 42.51 (Ar-*C*-Ar), 42.06 (*C*H$_2$Cl), 65.72 (Ar−O-*C*H$_2$), 75.60 (*C*H), 114.04, 120.31, 127.85, 143.97, 148.23, 148.90, 148.96, and 155.89 (aromatic C), and 153.03 (C=O). Anal. Calcd for $C_{38}H_{38}O_8Cl_2$: C, 65.80%; H, 5.52%. Found: C, 65.52%; H, 5.25%.

Synthesis of Polymer 6b by Polyaddition of 4b with 5. Polymer **6b** was synthesized by the polyaddition of **4b** (0.298 g; 1.0 mmol) with **5** (0.353 g; 1.0 mmol) using TPPB (0.017 g, 0.04 mmol) as a catalyst in chlorobenzene (1 mL) at 100 °C for 6 h in a sealed tube under stirring. The final yield of polymer **6b** was 0.610 g (98%). The M_n of polymer **6b** determined by GPC was 17 600 (M_w/M_n = 4.71). IR (film, cm^{-1}): 1761 (ν C=O, carbonate), 1605 and 1498 (ν C=C, aromatic), 1230 and 1174 (ν O−C−O, carbonate), 1195 and 710 (ν C−Cl, chloromethyl), and 1082 (ν C−O−C, ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.66 (bs, 6.0H, CH_3), 3.71−4.10 (m, 4.0H, CH_2Cl), 4.10−4.28 (m, 4.0H, OCH_2), 5.06−5.56 (m, 2.0H, C*H*), and 6.91−7.53 (m, 16.0H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 30.86 (CH_3), 42.02 (CH_2Cl), 42.51 (Ar−*C*−Ar), 65.93 (Ar−O−*C*H$_2$), 75.57 (*C*H), 114.96, 120.31, 120.43, 127.91, 134.18, 148.26, 148.90, and 157.29 (aromatic C), and 153.03 (C=O). Anal. Calcd for $C_{35}H_{32}O_8Cl_2$: C, 64.52%; H, 4.95%. Found: C, 64.79%; H, 4.87%.

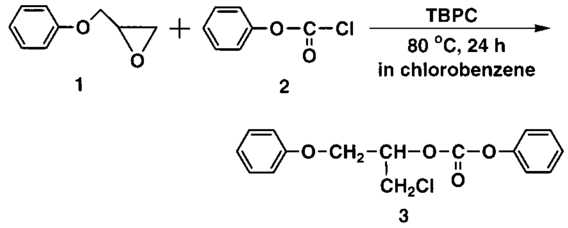
Synthesis of Polymer 6c by Polyaddition of 4c with 5. The polyaddition of **4c** (0.354 g; 1.0 mmol) with **5** (0.353 g; 1.0 mmol) was carried out in the presence of TPPB (0.017 g, 0.04 mmol) at 100 °C for 6 h in chlorobenzene (1 mL) to obtain corresponding poly(alkyl carbonate) **6c**. The final yield of polymer **6c** was 0.700 g (99%). The M_n of polymer **6c** determined by GPC was 17 100 (M_w/M_n = 1.64). IR (film, cm^{-1}): 1762 (ν C=O, carbonate), 1589 and 1505 (ν C=C, aromatic), 1255 and 1195 (ν O−C−O, carbonate), 1190 and 705 (ν C−Cl, chloromethyl), and 1082 (ν C−O−C, ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.66 (bs, 6.0H, CH_3), 2.35 (bs, 12.0H, CH_3), 3.85−4.21 (m, 8.0H, CH_2), 5.10−5.40 (m, 2.0H, C*H*), and 7.04−7.32 (m, 12.0H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 3.17 and 17.76 (*C*H$_3$), 28.71 (*C*H$_2$Cl), 29.38 (Ar−*C*−Ar), 65.85 (Ar−O−*C*H$_2$), 75.50 (*C*H), 107.24, 114.44, 114.78, 117.76, 123.75, 135.12, 135.79, and 140.99 (aromatic C), and 139.99 (C=O). Anal. Calcd for $C_{39}H_{40}O_8Cl_2$: C, 66.20%; H, 5.70%. Found: C, 65.94%; H, 5.62%.

Synthesis of Polymer 6d by Polyaddition of 4d with 5. When **4d** (0.174 g; 1.0 mmol), **5** (0.353 g; 1.0 mmol), chlorobenzene (1 mL), and TPPB (0.012 g, 0.04 mmol) as a catalyst were stirred at 100 °C for 24 h in a sealed tube, polymer **6d** was obtained. The final yield of polymer **6d** was 0.520 g (99%). The M_n of polymer **6d** determined by GPC was 15 900 (M_w/M_n = 2.58). IR (film, cm^{-1}): 1762 (ν C=O, carbonate), 1593 and 1505 (ν C=C, aromatic), 1250 and 1175 (ν O−C−O, carbonate), 1190 and 708 (ν C−Cl, chloromethyl), and 1082 (ν C−O−C, ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.68 (bs, 6.0H, CH_3), 3.54−4.04 (m, 12.0H, CH_2), 4.82−5.30 (m, 2.0H, C*H*), and 6.99−7.34 (m, 8.0H, aromatic H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm): 30.86 (*C*H$_3$), 42.21 (*C*H$_2$Cl), 69.15 (O−*C*H$_2$*C*H$_2$−O), 70.95 (O−*C*H$_2$−CH), 76.15 (*C*H), 120.31, 127.85, 148.17, and 148.90 (aromatic C), and 153.06 (C=O). Anal. Calcd for $C_{25}H_{28}O_8Cl_2$: C, 56.94%; H, 5.35%. Found: C, 56.99%; H, 5.28%.

Polymer Reaction of 6a with Potassium Thiocyanate (KSCN). The NMP solution (1.4 mL) containing polymer **6a** (0.25 g, 0.650 mmol of chloromethyl group, M_n = 39 000, M_w/M_n = 2.83), KSCN (0.077 g, 0.715 mmol), and TBAB (0.026 g, 0.080 mmol) was heated at 70 °C for 60 h. Then the reaction mixture was diluted with 30 mL of chloroform and washed thrice with minimal amount of water to remove TBAB and dried using $MgSO_4$ under stirring overnight. The solution was poured into *n*-hexane to precipitate the polymer. The resulting polymer was reprecipitated twice from chloroform into excess *n*-hexane and dried in vacuo. The yield of polymer **7a** was 0.261 g. The degree of substitution of chloromethyl groups was 43%. IR (film, cm^{-1}): 2158 (ν C≡N), 1762 (ν C=O, carbonate), 1606, 1508 (ν C=C, aromatic), 1240 (ν O−C−O, carbonate), and 1082 (ν C−O−C, ether), 710 (ν C−Cl ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.46−1.81 (m, 12.0H, CH_3), 3.72−4.07 (m, 2.3H, CH_2Cl), 4.07−4.43 (m, 4.0H, O−CH_2−CH−), 5.05−5.50 (m, 2.0H, −C*H*−), 6.67−7.33 (m, 16.0H, aromatic H).

Polymer Reaction of 6a with Potassium 3-Phenyl-2,5-norbornadienecarboxylate (KNBD). The reaction was carried out using KNBD (0.179 g, 0.715 mmol) as did the reaction with KSCN.

Scheme 1



The yield of polymer **7b** was 0.400 g. The degree of substitution of chloromethyl groups was 97%. IR (film, cm^{-1}): 1758 (ν C=O, carbonate), 1699(ν C=O, ester), 1606 and 1508 (ν C=C, aromatic), 1231 and 1184 (ν O−C−O, carbonate), and 1080 (ν C−O−C, ether). ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 1.41−1.78 (m, 12.0H, CH_3), 1.98−2.28 (m, 3.9H, CH_2 of NBD), 3.68−4.16 (m, 7.9H, CH_2OCO and C*H* of NBD), 4.22−4.55 (m, 4.0H, OCH_2), 5.04−5.30 (m, 2.0H, C*H*), and 6.64−7.53 (m, 30.0H, aromatic H and C*H*=C*H* of NBD).

Results and Discussion

The addition reaction of **1** with **2** was carried out as a model reaction for the polyaddition of the bis(epoxide) with the bis(chloroformate). The reaction proceeded very smoothly using 2 mol % of TBPC as a catalyst in chlorobenzene at 80 °C for 24 h. Conversions of **1** and **2**, which were estimated by GLC, were both 100%. The isolated yield of adduct **3** was 89%. The structure of the obtained product was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of adduct **3** showed absorption peaks consistent with the expected structure. In the ^{1}H NMR of adduct **3**, the corresponding proton signals were observed at 3.79−3.99 ppm due to the chloromethyl protons, at 4.20−4.35 ppm due to the methylene protons, at 5.03−5.56 ppm due to the methine protons, and at 6.65−7.48 ppm due to the aromatic protons. The intensity ratios of chloromethyl, methylene, methine protons, and aromatic protons completely agreed with the expected values. In the ^{13}C NMR spectrum of adduct **3**, the corresponding signals were observed at 42.03 ppm due to the chloromethyl carbon, at 65.69 ppm due to the methylene carbon, at 75.57 ppm due to the methine carbon, and at 152.91 ppm due to the C=O carbon of the alkyl−aryl carbonate group as one signal. This means that the addition reaction of epoxide and chloroformyl group proceeded chemoselectively and regioselectively to give the corresponding alkyl−aryl carbonate **3** as shown in Scheme 1. On the basis of the above result, the polyaddition of **4a** with **5** using 2 mol % of TPPB was carried out at 100 °C for 24 h in chlorobenzene. As a result, the polymer **6a** with M_n = 47 300 was obtained in 99% yield. The structure of the polymer **6a** was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of the obtained polymer showed absorption peaks consistent with the expected structure. In the ^{1}H NMR of the polymer, the corresponding proton signals were observed with reasonable intensity ratios, at 1.44−1.79 ppm due to the methyl protons, at 3.68−4.07 ppm due to the chloromethyl protons, at 4.07−4.40 ppm due to the methylene protons, at 4.98−5.51 ppm due to the methine protons, and at 6.72−7.32 ppm due to the aromatic protons. The ^{13}C NMR spectrum of the polymer showed the corresponding carbon signals such as methyl, chloromethyl, methylene, methine, and aromatic groups. Furthermore, the signal of the C=O carbon due to the carbonate group was obseved at 153.03 ppm as one signal. These results demonstrate that the reaction of **4a** with **5** proceeded chemoselectively and regioselectively to give the corresponding poly(alkyl aryl carbonate) **6a** with pendant chloromethyl groups as shown in Scheme 2. The effect of catalyst on the reaction of **4a** with **5** was examined in chlorobenzene at 100 °C for 24 h. In this reaction system, 2 mol % of quaternary onium salts was used as catalysts (Table 1). Each reaction proceeded smoothly, and soluble and high molecular weight poly(alkyl aryl carbonate) **6a** with pendant chloromethyl groups was obtained. When the polyaddition of **4a** with **5** was carried out using catalysts containing Br^- as a counteranion, the obtained polymer **6a** had higher molecular weights than those produced by using other catalysts. In particular, polymer **6a** with the highest molecular weight (M_n = 47 300) was synthesized when TPPB was used as the catalyst. The nucleophilicity of the counteranion of the quaternary onium salts seemed to be very important for the catalytic activity in this polyaddition. The catalytic activity of the quaternary onium salts increased in the following order of their counteranion, $Ac^- < I^- = Cl^- < Br^-$ as a counteranion. These results suggest that the quaternary onium salts with Br^- as a counteranion are the preferred catalysts for the synthesis of the reactive poly(alkyl aryl carbonate)s having a pendant chloromethyl group.

Scheme 2

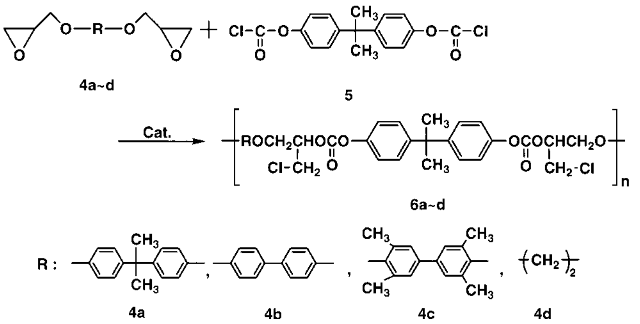


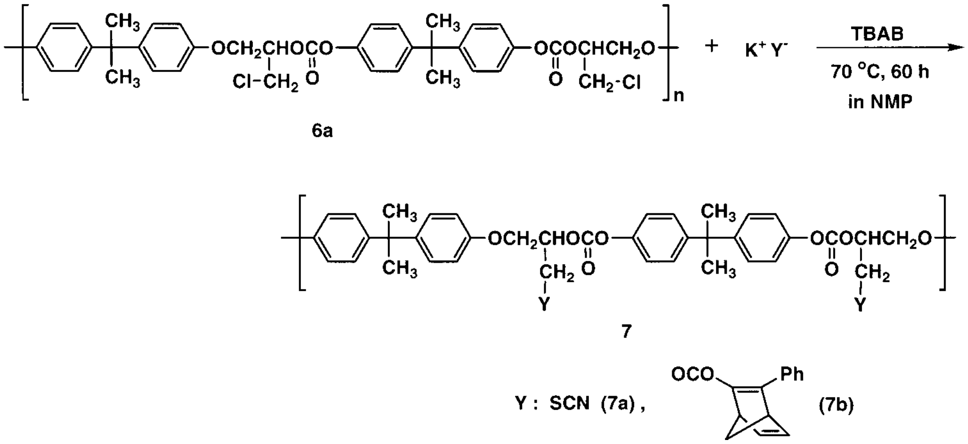
Table 1. Effect of Catalyst on the Polyaddition of 4a with 5[a]

catalyst	yield (%)[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]
TBAAc	99	2.34	4.13
TBAC	99	3.49	4.09
TBAB	98	3.96	4.60
TBAI	99	3.29	2.92
TBPC	98	1.37	2.36
TBPB	98	2.06	2.13
TPPC	99	4.27	3.26
TPPB	99	4.73	3.88

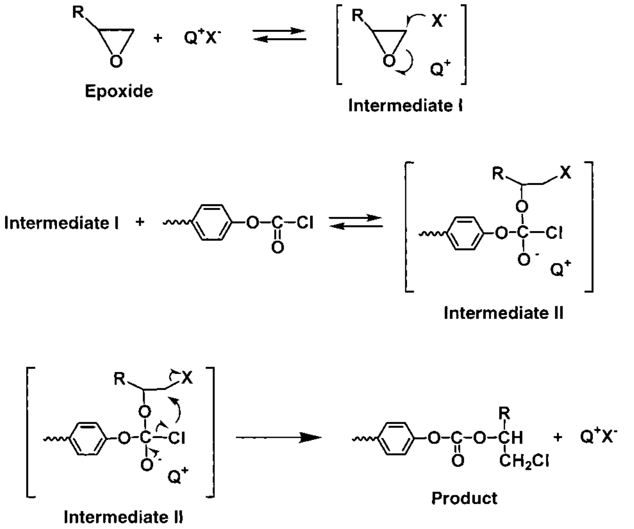
[a] The reaction was carried out with **4a** (1 mmol) and **5** (1 mmol) using 2 mol % of catalyst in chlorobenzene (1.0 mol/L) at 100 °C for 24 h. [b] Insoluble parts in methanol. [c] Estimated by GPC (THF) based on polystyrene standards.

Nishikubo and Kameyama previously proposed a mechanism of the reaction of epoxides with acyl chlorides and active carboxylic esters[16] catalyzed by quaternary onium salts. In the report, it was demonstrated that the reaction rates were depend on the leaving ability of the active esters as the following order $Cl^- > PhS^- > PhO^-$, etc. It was also reported that the reaction mechanism of bis(epoxide)s with diaryl phosphates[17] could be understood similarly to that of the reaction of epoxides with active carboxylic esters. The reaction mechanism of bis(epoxide)s with the bis(chloroformate) **5** is considered on the basis of the reported ones (Scheme 4). The counteranion of the used catalyst interacts with

Scheme 3



Scheme 4



β-carbon of epoxide to produce active intermediate **I**. The intermediate **I** reacts with chloroformate to form tetrahedral intermediate **II**, and then **II** transformed to provide the corresponding addition product releasing the used catalyst. In the proposed mechanism, the catalytic activity of catalysts seems to depend on the balance of nucleophilicity and the leaving ability of the counteranions of quaternary onium salts. The regioselectivity of the reaction would be ascribed to steric hindrances of the substituent at the α-carbon of the epoxide. Concerning the decomposition mode of intermediate II to the product, that is to say, chemoselectivity of chloroformate would be explained on the basis of the leaving ability of Cl^- and PhO^- as well as the reaction of epoxide with carboxylic acid esters.

The effect of reaction time on the polyaddition of **4a** with **5** was investigated in chlorobenzene at 100 °C using 2 mol % of TPPB as a catalyst. As shown in Figure 1, polymer **6a** was obtained in quantitative yield at all times, and the number-average molecular weight of polymer **6a** increased with reaction time. Then, polymer **6a** with $M_n = 59\,000$ was obtained after 48 h of reaction.

The reaction of **4a** with **5** was conducted using 2 mol % of TPPB as a catalyst in chlorobenzene at various temperatures for 24 h. The results are shown in Figure 2. The number-average molecular weight of polymer **6a** increased with reaction temperature. When the reaction was carried out at 120 °C, M_n of the polymer reached 48 000.

The effect of reaction solvent on the polyaddition of **4a** with **5** was examined at 100 °C for 24 h (Table 2). The reaction using 2 mol % of TBPB without solvents yielded the polymer **6a** with $M_n = 25\,300$. Although, when TPPB was used as the catalyst under the same conditions, the obtained polymers were not soluble in organic solvents such as chloroform, THF, DMF, and acetone. This result means that the cross-linked polymer was obtained when the reaction of **4a** and **5** was carried out in bulk using catalysts with high catalytic activity such as TPPB. The cross-linking reaction may occur by the insertion reaction of terminal epoxide groups into aryl carbonate linkage in the polymer main chain. On the other hand, when the reaction was carried out using TPPB as the catalyst in organic solvents, soluble polymers with high molecular weights were obtained in good yields. In particular, polymer **6a** with the highest molecular weight was synthesized using chlorobenzene as a solvent.

On the basis of the obtained information for the polyaddition of **4a** with **5**, various poly(alkyl aryl carbonate)s were synthesized by the polyaddition of certain bis(epoxide)s with **5** using 2 mol % of TPPB in chlorobenzene at 100 °C (Table 3). The polyaddition of **4b** with **5** gave the polymer **6b** with $M_n = 17\,600$. When the polyaddition of **4c** with **5** was carried out under similar conditions, polymer **6c** with $M_n = 17\,100$ was obtained in good yield. On the other hand, the polyaddition of **4d** with **5** produced polymer **6d** with $M_n = 15\,900$. The IR, ^{1}H NMR, and ^{13}C NMR data of the obtained polymers proved that the polyaddition of various bis(epoxide)s with **5** proceeded chemoselectively and regioselectively to give the corresponding poly(alkyl aryl carbonate)s **6b**−**d** with pendant chloromethyl groups as shown in Scheme 2. However, when the reaction of **4b** or **4c** with **5** was carried out for over 6 h, no soluble polymers were obtained. This result means that polymers **6b** and **6c** with the bis(phenyl) skeleton in the polymer main chain showed lower solubility than polymer **6a** with the bisphenol A skeleton and polymer **6d** with the ethylene skeleton. The T_g's of the obtained polymers were evaluated by DSC. The T_g's of polymers **6a**, **6b**, and **6c** were 104, 107, and 119 °C, respectively. Polymer **6d** was a viscous liquidlike substance at room temperature.

To estimate the usefulness of poly(alkyl carbonate)s with pendant chloromethyl groups as reactive polymers, the chemical modification of poly(alkyl aryl carbonate) **6a** was investigated. According to the general chemical modification of pendant chloromethyl groups with nu-

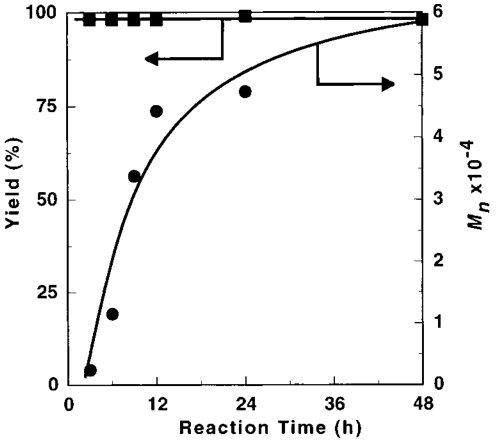


Figure 1. Effect of the reaction time on the polyaddition of **4a** (1 mmol) with **5** (1 mmol) in chlorobenzene (1.0 mol/L) using TPPB (2 mol %) at 100 °C: (■) yield; (●) M_n.

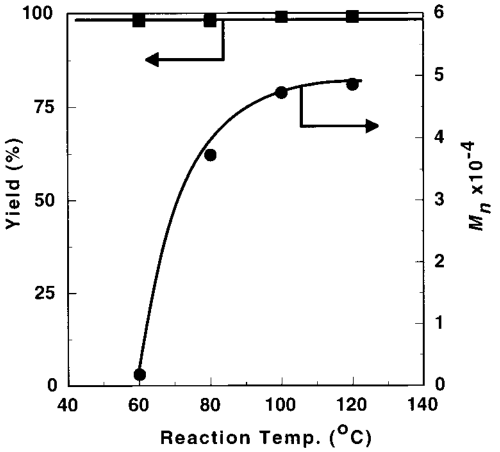


Figure 2. Effect of the reaction temperature on the polyaddition of **4a** (1 mmol) with **5** (1 mmol) in chlorobenzene (1.0 mol/L) using TPPB (2 mol %) for 24 h: (■) yield; (●) M_n.

Table 2. Effect of Solvent on the Polyaddition of 4a with 5[a]

solvent	catalyst	yield (%)[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]
none	TBPB	100	2.53	3.43
none	TPPB	99		
toluene	TPPB	99	0.93	1.49
chlorobenzene	TPPB	99	4.73	3.88
o-dichlorobenzene	TPPB	98	3.76	3.03
anisole	TPPB	100	3.34	3.37

[a] The reaction was carried out with **4a** (1 mmol) and **5** (1 mmol) using 2 mol % of catalyst in bulk or solvent (1.0 mol/L) at 100 °C for 24 h. [b] Insoluble parts in methanol. [c] Estimated by GPC (THF) based on polystyrene standards.

Table 3. Polyaddition of Bis(epoxide)s with 5[a]

bis(epoxide)	time (h)	yield (%)[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]	T_g (°C)
4a	24	99	4.73	3.88	104
4b	6	98	1.76	4.71	107
4c	6	99	1.71	1.64	109
4d	24	99	1.59	2.58	

[a] The reaction was carried out with **4a**−**d** (1 mmol) and **5** (1 mmol) using 2 mol % of TPPB in chlorobenzene (1.0 mol/L) at 100 °C. [b] Insoluble parts in methanol. [c] Estimated by GPC (THF) based on polystyrene standards.

cleophilic reagents using phase-transfer catalysts (PTC),[18] the reaction of **6a** with 1.1 equiv of potassium thiocyanate (KSCN) or 3-phenyl-2,5-norbornadienecarboxylate (KNBD) was carried out using 12 mol % of TBAB (Scheme 3) in NMP at 70 °C for 60 h. In the case of the reaction with KSCN, a polymer (**7a**) with pendant thiocyanate groups was obtained, and the degree of substitution (DS) of the chloromethyl groups was 43%, which was evaluated by ^{1}H NMR. The M_n of **7a** was estimated by GPC to be 41 000. The structure of **7a** was confirmed by IR and ^{1}H NMR spectra. Thus, it was suggested that the reactive poly(carbonate) could be chemically modified by KSCN with moderate conversion without a cleavage of the polymer main chain. In the case of the reaction of **6a** with KNBD, a polymer having pendant NBD moiety with DS of 97% was obtained. The structure of **7b** was confirmed by IR and ^{1}H NMR spectra. The ^{1}H NMR spectrum showed signals corresponding to the expected structure; in particular, methylene protons due to the NBD moiety were observed from 1.98 to 2.28 ppm with the intensity ratio as 3.9 H. The M_n of **7b** was 4000, which was relatively lower than that (M_n = 39 000) of the starting **6a**. This means that cleavage of the polymer main chain by the excess used KNBD would occur during the reaction. These mean that the reactive polycarbonate **6a** can modified with soft nucleophiles such as thiolates.

In conclusion, the present study demonstrated the synthesis of high molecular weight poly(alkyl aryl carbonate)s by the polyaddition of bis(epoxide)s with **5** using quaternary onium salts. It was found that the polyaddition proceeded regioselectively at the epoxy ring to provide the polycarbonates with reactive chloromethyl groups in the side chains. The polyaddition proceeded efficiently by quaternary onium bromides containing Br$^-$ as the counteranion in chlorobenzene to produce high molecular weight polymers. The polyaddition is a useful synthetic method to prepare polycarbonates without waste byproducts.

Acknowledgment. This work was supported by the Original Industrial Technology R & D Promotion Program (No. 8A-045-1) from the New Energy and Industrial Technology Development Organization (NEDO) of Japan, which is gratefully acknowledged.

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MA000134X