Synthesis of Bis(Cyclic Carbonate)s from Carbon Dioxide and Diglycidyl Ethers

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Abstract: Diglycidyl ether derivatives were synthesized from diols and epichlorohydrin using basic catalysts. Synthesis of bis(cyclic carbonate)s from the addition reaction of carbon dioxide with diglycidyl ether derivatives were performed in the presence of phase transfer catalyst (PTC). PTCs are more effective catalysts than alkali metal catalysts. The intrinsic activity of PTC in the reaction of carbon dioxide and diglycidyl ethers was found to follow the order of nucleophilicity of the anion (Cl\textsuperscript{-} > Br\textsuperscript{-} > I\textsuperscript{-}) in aprotic solvent such as N-methyl-2-pyrrolidone (NMP) in accord with the higher alkyl chain length (Oct\textsubscript{4} > Hex\textsubscript{4} > Bu\textsubscript{4} > Pr\textsubscript{4}). It was also found that the reactivity of carbon dioxide decreases as the aliphatic chain length of diglycidyl ether increases because of chain folding and the steric hindrance of methyl groups.

1. Introduction

Recently, attention has been paid to carbon dioxide as an inexpensive and infinite carbon resource [1]. Carbon dioxide fixation has, of course, received much attention from the viewpoint of preservation of the environment [1-6].

Due to their high polarity, coordination ability and reactivity, cyclic carbonates have been widely used for the optical, magnetical and electronic applications [7,8]. And the reaction of carbon dioxide with oxiranes to produce cyclic carbonate has been of interest as a useful method for the fixation of carbon dioxide by the chemical processes [7-9].

Generally, syntheses of cyclic carbonates from the reaction of carbon dioxide with oxiranes has been performed in the presence of Lewis acids, transition-metal complexes, or alkali metal compounds as catalysts under high pressure (> 20 atm) [2,4,5,11,12]. However, syntheses of cyclic carbonates from the reaction of carbon dioxide with oxiranes were performed in the reaction using phase transfer catalysts (PTC) such as quaternary ammonium salts [12-14]. This reaction gave bis(cyclic carbonate)s in high yield under atmospheric pressure at a relatively mild reaction temperature.

Various diglycidyl ether derivatives (Figure 1) were obtained by the reaction of diol (bisphenol A, bisphenol S) derivatives with epichlorohydrin using a basic catalyst (Scheme 1) [15,16]. And, the bis(cyclic carbonate)s were synthesized by the reaction of

\[ \text{H}_2\text{C} \quad \text{CHCH}_2\text{OH} \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{OCH}_2\text{CH} \quad \text{CH}_2 \]

**DGEBA (1A)**

\[ \text{H}_2\text{C} \quad \text{CHCH}_2\text{OS} \quad \text{O} \quad \text{OCH}_2\text{CH} \quad \text{CH}_2 \]

**DGEBS (2A)**

Figure 1. Structures of diglycidyl ether derivatives.

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prepared diglycidyl ether derivatives with carbon dioxide in the presence of a PTC under atmospheric pressure (Scheme 2) [13,17-20]. In these reactions, benzyltrimethylammonium chloride (BTMACl), benzyltrimethy lammonium bromide (BTMABr), tetra- butylammonium chloride (TBACL), tetrabutylammonium bromide (TBABr), and tetrabutylammonium iodide (TBAI) were used as a PTC. In order to compare the catalytic activity, alcoholic metal salts such as lithium chloride (LiCl), lithium bromide (LiBr), sodium chloride (NaCl), sodium bromide (NaBr), and sodium iodide (NaI) were adopted as catalysts. In this article, successful synthesis of a new functional monomer containing bis(cyclic carbonate) groups by the reaction of oxirane with carbon dioxide is presented. We investigated, in the reaction of carbon dioxide with oxirane, the role of anion and cation of PTC and the establishment of catalytic mechanism in the addition reaction of carbon dioxide using PTC.

2. Experimental

2.1. Materials

Bisphenol A and bisphenol S were obtained from Tokyo Kasei Kogyo Co. and used without purification. Epichlorohydrin and PTCs were purchased from Aldrich Co. and Fluka Co. Carbon dioxide was supplied from Acetylene Gas Co. and used without any further purification. Other chemicals were reagent grade and were used without further purification.

2.2. General Method

$^1$H- and $^{13}$C-NMR spectra were recorded on a Varian 300 UNITY plus 300 (300 MHz) using tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Mattson Polaris. Mass spectrometer analyses were carried out on a Kratos Model HV-3.

2.3. Synthesis of Diglycidyl Ether of Bisphenol A (DGEBA) (1A)

Into a reactor equipped with a thermometer, a mechanical stirrer, and a reflux condenser were charged 22.8 g (0.1 mol) of bisphenol A and 92.5 g (1 mol) of epichlorohydrin. The mixture was maintained at the temperature of 100 to 110 °C for 3 h while 20 g of 40% aqueous NaOH solution was added. After the reaction was complete, the hot solution was filtered to remove sodium chloride. The solution was evaporated to remove unreacted epichlorohydrin and dried in a vacuum oven at 60 °C for 24 h. The product (1A) was dissolved in chloroform and recrystallized from n-hexane. The structure of 1A is shown in Figure 1; yield 16.6 g (46%), m.p. 38-40 °C (m.p. 41-44 °C in [20]).

FT-IR(chloroform): 2968(C-H stretching), 1607(aromatic C-C), 1400(-CH$_3$ bending), 1210(C-O stretching), 915 cm$^{-1}$(epoxide C-O-C), $^1$H-NMR(300 MHz, DMSO-d$_6$): δ 1.5 (6H, C(CH$_3$)$_2$), 2.8-2.9 (4H, OCH$_2$CH$_2$O), 3.3 (quintet, 2H, OCH$_2$CH$_2$O), 4.2-3.7(d, 4H, OCH$_2$CH$_2$O), 41.1(C(CH$_3$)$_3$), 43.6 (OCH$_2$CH$_2$O), 49.6(OCH$_2$CH$_2$O), 68.8(OCH$_2$CH$_2$O), 113.8(CH aromatic), 127.3(CH aromatic), 142.8(C aromatic) 156.0(C aromatic); mass spec.(rel. intensity): 340(M$^+$, 68), 325(100), 297(4), 283(3), 254(8), 226(6), 191(42), 86(25), 57(75).

2.4. Synthesis of Diglycidyl Ether of Bisphenol S (DGEBS) (2A)

The same procedures described in the synthesis of 1A was followed except that 25.0 g (0.1 mol) of bisphenol S was adopted as a starting material. The product (2A) was recrystallized from acetone. The structure of 2A is shown in Figure 1; yield=18.3 g (50%), m.p.=158-160 °C (in [21] m.p.=158-161 °C).

FT-IR(chloroform): 3008(CH stretching), 1591(aromatic C-C), 1280(O=S=O asym. stretching), 1150(C-O stretching), 910 cm$^{-1}$(epoxide O=C-O); $^1$H-NMR(300 MHz, DMSO-d$_6$): δ 2.8-2.9 (4H, OCH$_2$CH$_2$O), 3.4(quintet, 2H, OCH$_2$CH$_2$O), 4.4-3.8(d, 4H, OCH$_2$CH$_2$O), 7.8-7.1(d, 8H, aromatic); $^{13}$C-NMR(300 MHz, CDCl$_3$): δ 43.6 (OCH$_2$CH$_2$O), 49.3(OCH$_2$CH$_2$O), 69.3(OCH$_2$CH$_2$O), 115.3 (CH aromatic), 129.2(CH aromatic), 133.7(C aromatic) 161.4(C aromatic); mass spec.(rel. intensity): 362(M$^+$, 95), 319(5), 305(15), 276(7), 248(8), 140(40), 64(30), 57(100).
2.5. Synthesis of bis(cyclic carbonate) of 1A with Carbon Dioxide (1B)

A solution of 16.6 g of 1A (0.05 mol) and 0.925 g of 10 mol % BTMACl in 25 mL N-methyl-pyrrolidone (NMP) was heated to 100 °C while stirring vigorously under a slow stream (20 mL/h) of carbon dioxide for 24 h. The reaction mixture was poured into acetone to remove impurities and catalyst, and insoluble materials were filtered off. After the filtrate was precipitated in H2O, the precipitate was collected and recrystallized from toluene. The product (1B) was dried in a vacuum oven for 24 h. The reaction path to the formation of 1B is shown in Scheme 1. 1B was obtained as a white powder; yield=20.3 g (95%), m.p. 163-168 °C.

FT-IR(Kbr): 3100(CH stretching), 1790(cyclic carbonate C=O), 1500(aromatic C=C), 1200 cm⁻¹(C-O stretching); ¹H-NMR(300 MHz, DMSO-d₆): δ 1.5(s, 6H, (C(CH₃)₂), 2.5(t, 4H, (OCH₂CH₂CH₂)), 3.3(quintet, 2H, (OCH₂CH₂CH₂)), 4.6-4.1(d, 4H, (OCH₂CH₂CH₂)), 7.1-6.8(8H, aromatic); ¹³C-NMR(300 MHz, DMSO-d₆): δ 30.6(C(CH₃)), 41.1(C(CH₂)), 65.9(OCH₂CH₂CH₂), 67.3(OCH₂CH₂CH₂), 74.7(OCH₂CH₂), 114.0(CH aromatic), 127.5(CH aromatic), 143.2(C aromatic), 154.1(C aromatic), 155.6(cyclic carbonate C=O); mass spec.(rel. intensity): 428(M⁺, 3), 384(25), 369(100), 340(5), 325(16), 126(15), 87(10), 44(20).

2.6. Synthesis of bis(cyclic carbonate) of 2A with Carbon Dioxide (2B)

Procedures as described in the synthesis of 1B with the exception that the reaction was carried out using 17.7 g (0.05 mol) of 2A and 30 mL of diethylene glycol dimethyl ether (diglyme) as a solvent. The product (2B) was recrystallized from acetone. The reaction path to the formation of 2B is shown in Scheme 1. 2B was obtained as a white powder; yield 16.63 g (74%), m.p. 200-210 °C.

FT-IR(Kbr): 2931(CH stretching), 1795(cyclic carbonate C=O), 1593(aromatic C=C), 1259(O=SO₂ asym. stretching), 1151 cm⁻¹(C-O stretching); ¹H-NMR(300 MHz, DMSO-d₆): δ 2.9-2.6(t, 4H, (OCH₂CH₂CH₂)), 3.3(quintet, 2H, (OCH₂CH₂CH₂)), 4.4-3.65(d, 4H, (OCH₂CH₂CH₂)), 7.8-7.1(8H, aromatic); ¹³C-NMR(300 MHz, DMSO-d₆): δ 65.8(OCH₂CH₂CH₂), 67.8(OCH₂CH₂CH₂), 74.4(OCH₂CH₂), 115.4(CH aromatic), 129.3(CH aromatic), 134.0(C aromatic) 154.6(C aromatic), 161.4(cyclic carbonate C=O); mass spec.(rel. intensity): 450(M⁺, 3), 406(5), 362(55), 248(10), 87(100), 64(85), 44(20).

2.7. Synthesis of bis(cyclic carbonate)s of DGBA Derivatives with Carbon Dioxide (Scheme 2)

Procedures as described in the synthesis of 2A with the exception that the reaction was carried out using five materials listed in Scheme 2. The results of IR spectra are shown in Figures 2-3. Figure 2 and Figure 3 show that the intensity cyclic carbonate peak

Figure 2. FT-IR spectra of momomers of 1B, 2EO, 5EO and 15EO.

Figure 3. FT-IR spectra of momomers of 1B, 1PO and 3.6PO.

(1790 cm⁻¹) decreases gradually as the increase of aliphatic chain length.

3. Results

3.1. Synthesis of Monomers (1A, 2A, 1B and 2B)

It was recently researched by the authors that the addition reaction of some of oxirane compound with carbon dioxide proceeds very smoothly to give the corresponding bis(cyclic carbonate) in high yield when catalyzed by quaternary ammonium salts under an atmospheric pressure.

First of all, we have generated several examples of
diglycidyl ether derivatives (1A and 2A) from various diols and epichlorohydrin. The reaction was carried out in the presence of basic catalysts. The \( ^1 \text{H-NMR}, ^{13} \text{C-NMR}, \) and FT-IR spectra of 1A and 2A thus obtained are in agreement with structures of 1A and 2A. The absorption peak at 915 cm\(^{-1}\) can be attributed to \( \nu_{\text{C=O}} \) in the oxirane ring.

Syntheses of 1B and 2B were performed by the reaction of prepared 1A and 2A with carbon dioxide, respectively, in the presence of quaternary ammonium salts i.e. BTMACl, BTMABr, TBAB etc. The addition reaction of 1A and 2A with carbon dioxide proceeded in high yields under atmospheric pressure. The IR spectra of 1B and 2B obtained were showed the absorption bands of \( \nu_{\text{C=O}} \) characteristic of the bis(cyclic carbonate)s at 1790 and 1795 cm\(^{-1}\), respectively.

3.2. Reaction Mechanism and Role of PTC

In the reaction of oxirane with carbon dioxide, the role of catalyst is very important. The mechanism of PTC-catalyzed reaction is shown in Figure 4. First, carbon dioxide in gas phase is adsorbed on liquid-gas interface contacting to organic phase. Then carbon dioxide is absorbed into organic phase containing PTC(Q\(^2\)X) and reactant(R). The nuclophilic anion of catalyst attacks oxirane ring. Complex compound(I) is formed, I and absorbed carbon dioxide react rapidly. Finally, cyclic carbonate is produced, catalyst is recycled.

3.3. Structure-Activity Relationship of the Catalyst

The reaction of 1A and carbon dioxide was carried out using quaternary ammonium salts (BTMACl, BTMABr, TBACl, TBABr, TBAL etc.) or alkali metal salts (LiCl, LiBr, NaCl, NaBr, NaI, etc.) as catalysts. The yields of 1B are listed in Table 1. Quaternary ammonium salts exhibited higher activity, while alkali metal salts were found to show only a very low activity.

In order to evaluate the role of the anion in the catalysts, a series of sodium and lithium compounds and the yields of 1B are listed in Table 1. Chloride was more active than bromide, also bromide was more active than iodide. It seems that high nucleophilicity of Cl\(^-\) in aprotic solvents enhanced the catalytic activity of quaternary ammonium chloride. It is apparent that the order of anion nucleophilicity is almost completely reversed on transfer from protic to aprotic solvents [22]. The traditional order of halide nucleophilicities, \( I^- > Br^- > Cl^- \), applies only when the nucleophile is deactivated through solvation by protic solvents, whereas the natural order, \( Cl^- > Br^- > I^- \) is observed in aprotic solvent such as NMP. The salt which has more nucleophilic anion has much activity in the reaction of oxirane and carbon dioxide under an atmospheric pressure in aprotic solvents, i.e. the order of activity of the salts is \( Cl^- > Br^- > I^- \).

Furthermore, the role of the catalyst cation is noticeable. For the effect of the cation part of the catalyst, five catalysts (tetrapropyl, tetrabutyl, tetrahexyl, tetraoctyl, and tetradecyl ammonium bromide) were used. The results were summarized in Table 2. The conversion of 1B increased as the increase of alkyl groups of catalysts, while in the case of Dod\(_3\)N\(^+\)Br\(^-\), the conversion decreased. It seems that the catalyst cation having large alkyl groups are easily dispersed in organic solvent because of the

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**Table 1. Yield of Cyclic Carbonates of Bisphenol A-co-EPCH with Various Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>12</td>
</tr>
<tr>
<td>LiBr</td>
<td>61</td>
</tr>
<tr>
<td>NaCl</td>
<td>41</td>
</tr>
<tr>
<td>NaBr</td>
<td>60</td>
</tr>
<tr>
<td>NaI</td>
<td>43</td>
</tr>
<tr>
<td>BTMACl</td>
<td>99.9</td>
</tr>
<tr>
<td>BTMABr</td>
<td>93</td>
</tr>
<tr>
<td>TBACl</td>
<td>99</td>
</tr>
<tr>
<td>TBABr</td>
<td>98</td>
</tr>
<tr>
<td>TBAI</td>
<td>82</td>
</tr>
</tbody>
</table>

Reaction condition: 0.1 mol of bisphenol A-co-EPCH, 10 mol % of catalyst, 50 mL of NMP, 100 °C, 1 atm, 24 h

*low solubility

**Table 2. Effect of Quaternary Ammonium Cation Structure on the Conversion of Bisphenol A-co-EPCH**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(_4)N(^+)Br(^-)</td>
<td>25.6</td>
</tr>
<tr>
<td>Bu(_4)N(^+)Br(^-)</td>
<td>40.0</td>
</tr>
<tr>
<td>Hex(_4)N(^+)Br(^-)</td>
<td>48.7</td>
</tr>
<tr>
<td>Oct(_4)N(^+)Br(^-)</td>
<td>56.7</td>
</tr>
<tr>
<td>Dod(_3)N(^+)Br(^-)</td>
<td>48.7</td>
</tr>
</tbody>
</table>

Reaction condition: 30 mmol of bisphenol A-co-EPCH, 5 mol % of catalyst, 50 mL of NMP, 80 °C, 1 atm, 6 h.

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lipophilicity of the cation. For example, although the distance (6.28 Å) between \((\text{C}_2\text{H}_5)\text{N}^+\) and \(\text{Br}^-\) is little difference the distance (2.85 Å) between \(\text{Na}^+\) and \(\text{Br}^-\), the difference of activity of anion and reactive rate is more affected. However, in the case of \(\text{Dod}_2\text{N}^+\text{Br}^-\), because of the high lipophilicity of the cation, to contact to the surface between aqueous and organic phase is very difficult for \(\text{Dod}_2\text{N}^+\text{Br}^-\) catalyst. So the phase transfer rate of anion is decreased, it is estimated the conversion of monomer is rather low (Table 2). Consequently, the order of activity of catalysts is \(\text{Oct}^+ > \text{Hex}^+ > \text{Bu}^+ > \text{Pr}^+\).

3.4. Effect of Aliphatic Chain Length of Monomer on the reactivity

The reactivity of oxirane with carbon dioxide was considerably affected by aliphatic chain length of monomer. The change of the IR spectra is shown in Figures 2-3. In Figure 2 and Figure 3, as the number of ethoxy groups of bisphenol A-co-epichlorohydrin (Scheme 2) is increased, \(\nu_{\text{CO}}\) of cyclic carbonate 1790 cm\(^{-1}\) is gradually decreased. As alkoy chains lengthen, addition of carbon dioxide is hindered because of chain folding or the fluidity of chains. Moreover, a monomer having propoxy groups is more difficult to add carbon dioxide since the steric hinderance of methyl groups is bulky. The reactivity of the addition reaction of carbon dioxide decreases as the aliphatic chain length of diglycidyl ether decreases.

4. Conclusions

Diglycidyl ether derivatives from diols (bisphenol A, bisphenol S) and epichlorohydrin were synthesized using basic catalysts. Bis(cyclic carbonate)s are unique compounds which have high polarity, high coordination ability and high reactivity. Synthesis of cyclic carbonates from the reaction of carbon dioxide with oxiranes were performed, the reaction used PTC. This reaction using PTC gave bis(cyclic carbonate)s in high yield under atmospheric pressure at a relatively mild reaction temperature.

The important results are as follows.

1) PTCs are more effective catalysts than alkali metal catalysts.

2) The salt which has more nucleophilic anion has much activity in the reaction of oxirane and carbon dioxide under an atmospheric pressure in aprotic solvent; the order of activity of the salts is \(\text{Cl}^- > \text{Br}^- > \Gamma\).

3) The intrinsic activity of \(\text{IB}^+\) increased with the increase of alkyl groups of catalysts (Oct\(^+\) > Hex\(^+\) > Bu\(^+\) > Pr\(^+\)).

4) The reactivity of carbon dioxide decreases as the aliphatic chain length of diglycidyl ether increases.

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References