

NOTES

Direct Polycondensation of Carbon Dioxide with Various Diols Using the Triphenylphosphine/Bromotrichloromethane/*N*-Cyclohexyl-*N*',*N*',*N*'',*N*'''-tetramethylguanidine System as Condensing Agent

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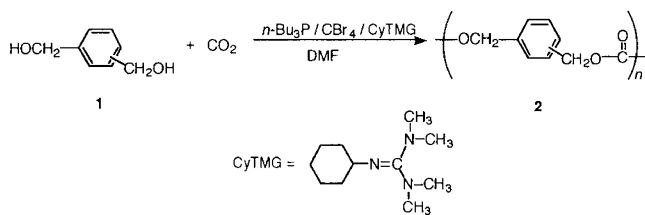
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Polycarbonate, a fundamental polymer in the field of materials science, is generally prepared by polycondensation of a dihydroxy compound such as bisphenol A with phosgene, a highly toxic agent.¹ Since aliphatic polycarbonates have been prepared by reaction of CO₂ with epoxides,^{2,3} the development of new synthetic methods for polycarbonates using CO₂ has attracted increasing interest from viewpoints not only of new polymerization reaction, but also of the potential carbon source as well as environmental aspects. The new polycondensation reaction of CO₂ with *p*- and *m*-xylylene glycols (**1**) using tributylphosphine/*N*-cyclohexyl-*N*',*N*',*N*'',*N*'''-tetramethylguanidine (CyTMG)/tetrabromomethane system as condensing agent (Scheme 1) was discovered and is the first direct synthesis of polycarbonates from CO₂ and diols.⁴ The scope and limitations of the direct condensation reaction of CO₂ with various alcohols for the formation of dialkyl carbonates using the condensing agent were surveyed.⁵ The above condensing agent was not effective for the polycondensation of CO₂ with other diol compounds such as di(ethylene glycol) (**3**), probably due to the lower reactivity of the hydroxy groups compared with the benzylic hydroxy groups of **1**.

Attempt has been made to develop a new condensing agent generally applicable to the direct synthesis of polycarbonates from CO₂ and diols. This paper reports that a combination of triphenylphosphine, bromotrichloromethane, and CyTMG works well as a condensing agent for the polycondensation of CO₂ with various diols, giving rise to the corresponding polycarbonates. Di(ethylene glycol) (**3**), tri(ethylene glycol) (**5a**), and 1,6-hexanediol (**5b**) were used as diol monomers. Polymeric diols, *i.e.*, poly(ethylene glycol)s (**5c**) with different molecular weights were used to be polycondensed with CO₂.



Scheme 1.

EXPERIMENTAL

Materials

Carbon dioxide from a gas cylinder was dried through a silica gel tube. Di(ethylene glycol) (**3**), tri(ethylene glycol) (**5a**), 1,6-hexanediol (**5b**), and solvents were purified by distillation. CyTMG was prepared according to the literature.^{6,7} Other reagents were used without further purification.

Polymerization

A typical example is as follows (entry 9 in Table I). To a solution of **3** (0.0531 g, 0.50 mmol), CyTMG (0.197 g, 1.0 mmol), and triphenylphosphine (0.197 g, 0.75 mmol) in chloroform (0.50 mL) were added CO₂ at room temperature with stirring. After 15 min, bromotrichloromethane (0.396 g, 2.0 mmol) was added to the mixture and the solution was stirred for 1 h. The reaction mixture was diluted with chloroform and washed with 0.50 mol L⁻¹ hydrochloric acid twice, 1.0 mol L⁻¹ NaOH aqueous solution twice, and water 10 times. The chloroform layer was dried sodium sulfate, filtered, and evaporated. After residual material was placed in refluxed petroleum ether for 3 h, petroleum ether was removed by decantation. These procedures were carried out 3 times and the insoluble product was dried *in vacuo* to give polycarbonate **4** (0.0336 g, 0.29 mmol) in 58.9% yield.

Measurements

¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury 200 spectrometer. IR spectra were recorded on a HORIBA FT-200 spectrometer. GPC was performed using a Shimadzu LC-6A with RI detector under the following conditions; Tosoh TSKgel G 2500 H_{XL} column, with DMF containing 0.02 mol L⁻¹ of lithium chloride as the eluent, at a flow rate of 1.0 mL min⁻¹. A calibration curve was obtained using polystyrene standards.

RESULTS AND DISCUSSION

Polycondensation of CO₂ with Di(ethylene glycol) (3)

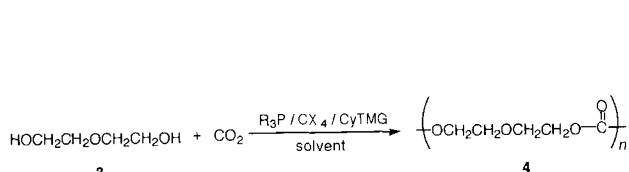
When direct polycondensation of CO₂ with **3** was carried out using a condensing agent consisting of tributylphosphine, tetrabromomethane, and CyTMG in DMF under conditions similar to those in the direct polycondensation of CO₂ with **1** as previously described,⁴ the po-

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Table I. Polycondensation of CO₂ with di(ethylene glycol) (**3**) using R₃P/CX₄/CyTMG system as a condensing agent^a

| Entry | R ₃ P | CX ₄ | Solvent | Molar ratio ^b | Yield ^c | M _n ^d |
|-------|-----------------------------|--------------------|-------------------|--------------------------|--------------------|-----------------------------|
| | | | | | % | |
| 1 | <i>n</i> -Bu ₃ P | CBr ₄ | DMF | 1.0 : 1.5 : 2.0 : 2.0 | 0 | — |
| 2 | Ph ₃ P | CBr ₄ | DMF | 1.0 : 1.5 : 2.0 : 2.0 | 0 | — |
| 3 | <i>n</i> -Bu ₃ P | CBrCl ₃ | DMF | 1.0 : 1.5 : 2.0 : 2.0 | 4.5 | 3000 |
| 4 | Ph ₃ P | CBrCl ₃ | DMF | 1.0 : 1.5 : 2.0 : 2.0 | 10.9 | 5200 |
| 5 | Ph ₃ P | CBrCl ₃ | Toluene | 1.0 : 1.5 : 2.0 : 2.0 | 31.5 | 4900 |
| 6 | Ph ₃ P | CBrCl ₃ | CHCl ₃ | 1.0 : 1.5 : 2.0 : 2.0 | 35.2 | 5100 |
| 7 | Ph ₃ P | CBrCl ₃ | CHCl ₃ | 1.0 : 2.0 : 2.0 : 2.0 | 24.0 | 5800 |
| 8 | Ph ₃ P | CBrCl ₃ | CHCl ₃ | 1.0 : 3.0 : 2.0 : 2.0 | 34.7 | 5200 |
| 9 | Ph ₃ P | CBrCl ₃ | CHCl ₃ | 1.0 : 1.5 : 4.0 : 2.0 | 58.9 | 4700 |
| 10 | Ph ₃ P | CBrCl ₃ | CHCl ₃ | 1.0 : 1.5 : 20.0 : 2.0 | 34.5 | 4000 |

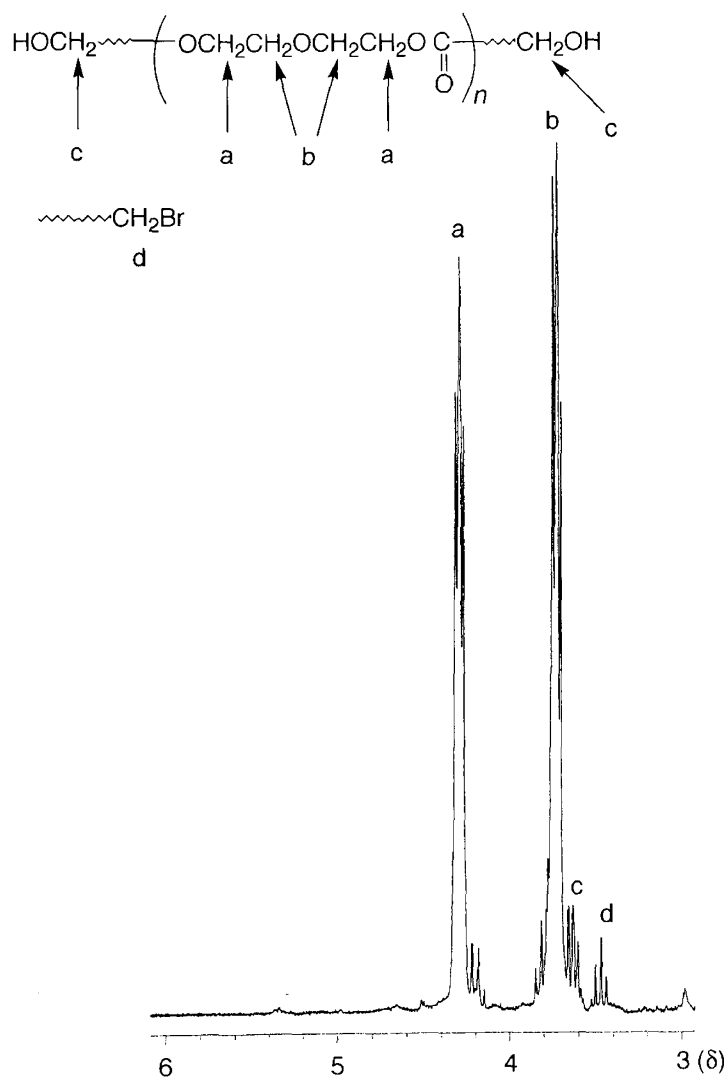
^a At room temperature for 1 h. ^b [3] : [R₃P] : [CX₄] : [CyTMG]. ^c Part insoluble in petroleum ether. ^d Determined by GPC with DMF as eluent.

**Scheme 2.**

lymerization did not proceed at all (entry 1 in Table I). When other reagents were used as condensing agents (Table I, Scheme 2), a combination of triphenylphosphine/bromotrichloromethane/CyTMG effectively produced a polycarbonate (entries 4–10). Although tributylphosphine combined with bromotrichloromethane and CyTMG gave the polycarbonate, the yield was lower than using triphenylphosphine (entry 3). The yield was higher when the reaction was carried out in chloroform solvent, compared with other solvents such as DMF (entries 4–6).

Optimum molar proportions of triphenylphosphine, bromotrichloromethane, and CyTMG were examined at room temperature for 1 h to give polycarbonate in higher yield. When the molar proportions of **3**, triphenylphosphine, bromotrichloromethane, and CyTMG were 1.0 : 1.5 : 4.0 : 2.0, the yield of polycarbonate was highest (58.9%, entry 9). When a larger amount of condensing agent was used, the yields decreased in all cases (entries 8 and 10). Molecular weight values determined by GPC analyses with *N,N*-dimethyl formamide (DMF) as eluent were not effected remarkably by changing the reaction conditions, and were around 3000–6000, probably due to loss of oligomeric products with lower molecular weights during precipitation into petroleum ether.

The structure of the isolated polymer was determined by ¹H NMR, ¹³C NMR, and IR spectra. Figure 1 shows the ¹H NMR spectrum of the isolated polymer in CDCl₃. Two triplet-like peaks at δ 3.73 and 4.29 are ascribed to methylene protons of CH₂OCH₂ and CH₂OC=O, respectively, supporting the structure of polycarbonate **4**. A small triplet peak centered at δ 3.63 due to the terminal methylene groups CH₂OH appeared. The other structure of the terminal group formed by termination (*vide infra*) and thus the peak ascribable to CH₂Br appeared at δ 3.46. From the integrated ratio of the terminal methylene peaks with the CH₂OC=O peak, molecular weight was calculated to be *ca.* 2000 (entry 9 in Table I). *M_n* of the same polymer estimated by GPC with polystyrene standards was 4700. These data indicate that GPC may

**Figure 1.** ¹H NMR spectrum of polycarbonate **4** in CDCl₃.

be overestimated in comparison with actual *M_n*. The ¹³C NMR spectrum (Figure 2) of the same sample shows a peak at δ 66.7 due to CH₂OC=O, a peak at δ 68.6 due to CH₂OCH₂, and a peak at δ 154.8 due to C=O of the carbonate. The IR spectrum of the product displayed strong absorptions at 1745 and 1263 cm⁻¹ attributable to stretching of the carbonyl and oxycarbonyl groups of the linear carbonate linkage. All the above spectroscopic data support polycarbonate structure **4**.

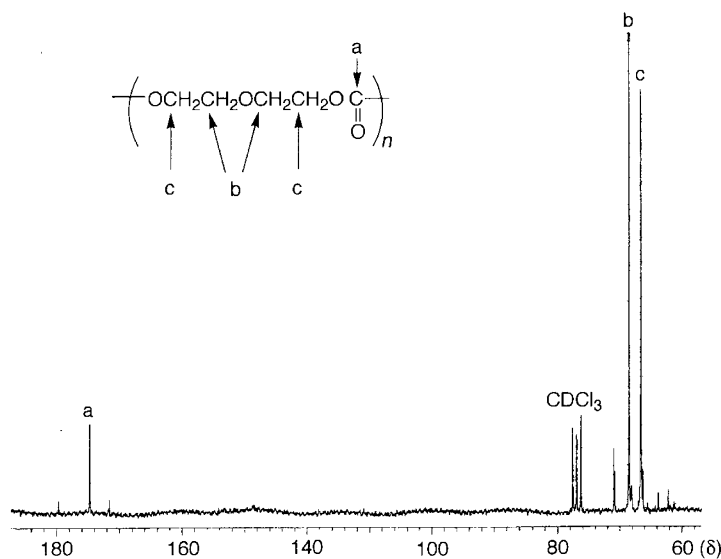


Figure 2. ^{13}C NMR spectrum of polycarbonate **4** in CDCl_3 .

Table II. Polycondensation of CO_2 with various diols using $\text{Ph}_3\text{P}/\text{CBrCl}_3/\text{CyTMG}$ system as a condensing agent^a

| Entry | Diol | Time | Yield ^b | M_n^c | DP ^d |
|-------|--|------|--------------------|---------|-----------------|
| | | h | % | | |
| 1 | Di(ethylene glycol) | 1 | 58.9 | 4700 | 35.6 |
| 2 | Tri(ethylene glycol) | 5 | 48.3 | 4900 | 27.8 |
| 3 | 1,6-Hexanediol | 15 | 8.8 | 5500 | 38.1 |
| 4 | Poly(ethylene glycol) | 15 | 75.1 | 6600 | 15.5 |
| 5 | Poly(ethylene glycol) ($M_n = 400$) | 15 | 71.6 | 6300 | 6.1 |

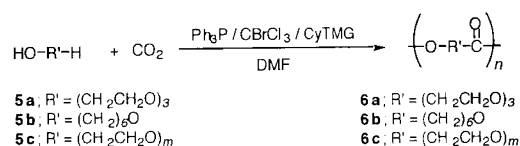
^a At room temperature in chloroform solvent. [diol] : [R_3P] : [CX_4] : [CyTMG] = 1.0 : 1.5 : 4.0 : 2.0. ^b Part insoluble in petroleum ether. ^c Determined by GPC with DMF as eluent. ^d DP = degree of polymerization determined by GPC.

Table III. ^1H NMR, ^{13}C NMR, and IR data of polycarbonates **6a–6c**

| | |
|-----------|--|
| 6a | ^1H NMR (CDCl_3) δ 3.65–3.82 (m, CH_2OCH_2 , 8H), 4.28 (t, $\text{CH}_2\text{OC}=\text{O}$, 4H) ^{13}C NMR (CDCl_3) δ 66.7 ($\text{CH}_2\text{OC}=\text{O}$), 68.6 ($\text{CH}_2\text{CH}_2\text{OC}=\text{O}$), 70.2 ($\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 154.8 (C=O) IR (NaCl) 1743 (C=O), 1263 cm^{-1} (O–C=O) |
| 6b | ^1H NMR (CDCl_3) δ 1.22–1.72 (br m, C– CH_2 –C, 8H), 4.09 (t, $\text{CH}_2\text{OC}=\text{O}$, 4H) ^{13}C NMR (CDCl_3) δ 25.3, 28.6 (C– CH_2 –C), 67.7 ($\text{CH}_2\text{OC}=\text{O}$), 155.3 (C=O) IR (NaCl) 1741 (C=O), 1259 cm^{-1} (O–C=O) |
| 6c | ^1H NMR (CDCl_3) δ 3.65–3.74 (m, CH_2OCH_2), 4.28 (t, $\text{CH}_2\text{OC}=\text{O}$) ^{13}C NMR (CDCl_3) δ 65.8 ($\text{CH}_2\text{OC}=\text{O}$), 67.7 ($\text{CH}_2\text{CH}_2\text{OC}=\text{O}$), 69.3 ($\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 153.9 (C=O) IR (NaCl) 1745 (C=O), 1265 cm^{-1} (O–C=O) |

Polycondensation of CO_2 with Other Diols

The polycondensation of CO_2 with other diols was carried out using a condensing agent consisting of triphenylphosphine, bromotrichloromethane, and CyTMG in chloroform at room temperature (Scheme 3). The diols used were tri(ethylene glycol) (**5a**) and 1,6-hexanediol (**5b**), as well as polymeric diols of poly(ethylene glycol)s (**5c**, molecular weights = 400, 1000). The polymerization results are shown in Table II. The analytical data of the products in Table III support the structures of the polycarbonates **6a–6c**. When the polycondensation of CO_2 with **5a** was carried out, longer reaction time was required (5 h) to produce the corresponding polycarbonate



Scheme 3.

6a (entry 2), probably because of lower reactivity of **5a** compared with **3**. Although the reaction of CO_2 with **5b** proceeded in ca. 60% monomer conversion, as determined by ^1H NMR of the reaction mixture, isolated yield of the polycarbonate **6b** was low (8.8%, entry 3), due to

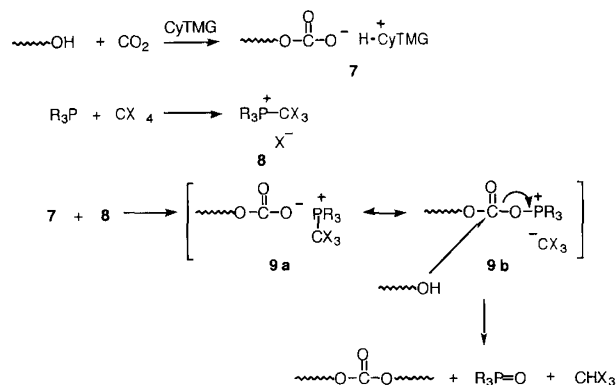
the product polycarbonate **6b** having very high solubility in various organic solvents, and therefore, the relatively lower molecular weight polymers were lost during isolation. Polymeric diols **5c** with different molecular weights were polycondensed with CO₂ to afford chain extension products **6c** by carbonate linkages (entries 4 and 5). DPs of polymers were not high, because of low reactivity of hydroxy groups in the polymeric monomers. The values may contain some error on using polystyrene standards.

Mechanism of Polycondensation

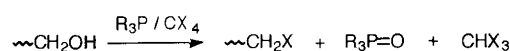
The mechanism for this polycondensation is shown in Scheme 3, as also described previously.⁴ The first step is the formation of carbonate anion **7** by reaction of a hydroxy group with CO₂ in the presence of CyTMG. Reaction of trisubstituted phosphine with tetrahalomethane takes place to form phosphonium halide **8**. An ion-exchange reaction between these two species **7** and **8** occurs, giving rise to phosphonium intermediate **9a**, which is in equilibrium with **9b**. A phosphoniumoxy group in **9b** is a leaving group; the nature of anion **7** can be changed from nucleophile to electrophile by conversion into **9b** having this leaving group. Therefore, nucleophilic attack of the hydroxy group in the monomer and/or propagating end onto the carbonyl carbon of **9b** may occur, followed by Arbuzov-type reaction to lead to a carbonate group, phosphine oxide and haloform. For termination, the halogenation of the -CH₂OH group may produce the terminal group -CH₂X as shown in Scheme 5, because the R₃P/CX₄ system has been used for preparation of alkyl halides from alcohols.⁸ The ¹H NMR spectrum of the polymer in Figure 1 shows a peak assignable to this terminal group at δ 3.46. This -CH₂X group does not react with carbonate anion such as **7** to form carbonate linkage under the polymerization conditions, because higher temperatures such as 80°C were required for the production of carbonate compounds by the condensation of alcohols, alkyl halides, with CO₂.^{9,10} In the polymerization mechanism, the last nucleophilic substitution is probably rate-controlling step. Therefore, the reactivity of the hydroxy group strongly affects the polymerization results. In the polycondensation here, longer reaction times were required compared to those in the previous polycondensation using monomer **1**, because of the lower reactivity of the hydroxy groups in the monomers **3** and **5a–5c** than that of the benzylic one. Hence, stable intermediates are necessary for the propagation in the present polymerization. Intermediate **9** produced from the combination of triphenylphosphine with bromotrichloromethane is probably more stable than intermediates from other phosphines and tetrahalomethanes.

CONCLUSIONS

When the polycondensation of CO₂ with **3** was carried out using various reagents as condensing agents and sol-



Scheme 4.



Scheme 5.

vents, the reaction proceeded well using the triphenylphosphine/bromotrichloromethane/CyTMG system as condensing agent in chloroform solvent to produce polycarbonate **4**. Molecular weights determined by GPC with DMF were around 3000–6000. Other diols **5a–5b**, as well as polymeric diols **5c** were polycondensed with CO₂ under conditions the same as above to give the corresponding polycarbonates **6a–6c**. The mechanism shown in Scheme 4 is proposed to explain the present polycondensation.

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