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Synthesis of polycarbonate by melt self-polycondensation of 4,4′-isopropylidenedi(*p*-phenylene)bis(2,2,2-trichloroethyl) carbonate

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A facial synthesis of polycarbonate, which involves the self-polycondensation of 4,4'-isopropylidene-di(*p*-phenylene)bis(2,2,2-trichloroethyl) carbonate **3** in the presence of $Ti(O\text{-}iC_3H_7)_4$ has been developed. Polymerizations proceeded smoothly at 215–250°C under reduced pressure and produced aromatic polycarbonates with the weight-average molecular weights up to 39 000. Monomer **3** was easily obtained by transesterification of bis(2,2,2-trichloroethyl) carbonate with bisphenol A in the presence of 4-dimethylaminopyridine. Furthermore, the disproportionation reaction of various alkyl phenyl carbonates in the presence of $Ti(O\text{-}iC_3H_7)_4$ was studied in detail to demonstrate the feasibility of polycondensation. © 1997 Elsevier Science Ltd.

(Keywords: polycarbonate; melt self-polycondensation; transesterification)

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glass because of their good impact strength, heat resistance and transparency[1].

A number of synthetic routes for producing PCs have been described in the literature[2,3]. They can be prepared mainly in two ways, by interfacial polycondensation of diphenols with phosgene and melt polycondensation of diphenols with diaryl carbonate. The former method is currently employed almost exclusively for the production of PCs.

In recent years there has been increasing demands for a safer and environmentally favourable process to PCs, such as the process not requiring solvent and toxic phosgene[4]. Therefore, the transesterification process in the melt has been given more recognition because of no solvent (such as dichloromethane), no waste water, and no salt formation. But, diaryl carbonates are prepared by the reaction of phosgene and sodium phenolates. On the other hand, dimethyl carbonate (DMC) is readily obtained from oxidative carbonylation of methanol[5]. Several patents described the synthesis of PCs using DMC in place of diphenyl carbonate[6–8]. However, the reaction of aromatic diols with diaryl carbonates is thermodynamically favourable for polycarbonate synthesis whereas the reaction of aromatic diols with alkyl carbonates is thermodynamically unfavourable. So, the DMC method has not so far been shown to be practical for transesterification polymerization to PCs.

Alternative methods to prepare PCs using carbonate-ester interchange reaction of 4,4′-isopropylidene diphenol (Bisphenol-A, BPA) diacetate with DMC have been reported, where the unfavourable thermodynamical equilibrium can be offset by the use of BPA diacetate instead of BPA[9–11].

We were interested in the use of bis(2,2,2-trichloroethyl) carbonate in place of DMC because of a higher acidity (around $pK_a = 13$) of 2,2,2-trichloroethanol than that of methanol ($pK_a = 15$). Thus, the above thermodynamic problem in the formation of polycarbonate from BPA and DMC can be reduced. Furthermore, bis(2,2,2-trichloroethyl) carbonate would be produced from carbon monoxide and 2,2,2-trichloroethanol using a phosgene-free process.

We now report a successful synthesis of PC by melt self-polycondensation of 4,4′-isopropylidenedi(*p*-phenylene)bis(2,2,2-trichloroethyl) carbonate in the presence of $Ti(O\text{-}iC_3H_7)_4$.

EXPERIMENTAL

Materials

All reagents and solvents were obtained commercially and used as received.

Alkyl phenyl carbonates (**1**) were prepared by the reaction of phenol with methyl chloroformate or phenyl chloroformate with the corresponding alcohols in THF in the presence of triethylamine (TEA).

Methyl phenyl carbonate (**1a**): bp 132–133°C (5.2 mmHg). I.r. (NaCl): ν 1766 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 3.89 (*s*, 3H, CH_3), 7.13–7.36 ppm (*m*, 5H, Ar–H).

Isopropyl phenyl carbonate (**1b**): bp 45–46°C (0.15 mmHg). I.r. (NaCl): ν 1759 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 1.38 (*d*, 6H, CH_3), 4.98 (*m*, 1H, CH), 7.17–7.43 ppm (*m*, 5H, Ar–H).

Phenyl 2,2,2-trifluoroethyl carbonate (**1c**): bp 53–54°C

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(1.5 mmHg). I.r. (NaCl): ν 1782 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 4.55–4.63 (*q*, 2H, CH_2), 7.17–7.43 ppm (*m*, 5H, Ar–H).

Phenyl 2,2,2-trichloroethyl carbonate (**1d**): mp 33–34°C (from *n*-hexane). I.r. (NaCl): ν 1774 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 4.87 (*s*, 2H, CH_2), 7.21–7.44 ppm (*m*, 5H, Ar–H). Anal. Calcd for $C_9H_7O_3Cl_3$: C, 40.11%; H, 2.62%. Found: C, 40.30%; H, 2.78%.

Disproportionation reaction of alkyl phenyl carbonate in the presence of $Ti(O\text{-}iC_3H_7)_4$. Disproportionation reaction of alkyl phenyl carbonate in the presence of $Ti(O\text{-}iC_3H_7)_4$ (mole ratio = 1/0.012) was carried out at 150 and 170°C under argon. *p*-Dimethoxybenzene was used as an internal reference. The rate of disproportionation was followed by ^{1}H-n.m.r. spectroscopy or gas chromatography.

Bis(2,2,2-trichloroethyl) carbonate (**2**). To an ice-cooled solution of 2,2,2-trichloroethanol (7.6 ml, 0.079 mol) and trethylamine (49.1 ml, 0.354 mol) in THF (200 ml), 2,2,2-trichloroethyl chloroformate (15.8 ml, 0.118 mol) was added dropwise with stirring. Then, the mixture was stirred for 24 h at room temperature and triethylamine hydrochloride was filtered off. After removal of the solvent *in vacuo*, the residue was crystallized from *n*-hexane to give white needles. The yield was 22.4 g (88%): mp 87–89°C. I.r. (KBr): ν 1766 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 4.86 ppm (*s*, 4H, CH_2). Anal. Calcd for $C_5H_4O_3Cl_6$: C, 18.49%; H, 1.24%. Found: C, 18.67%; H, 1.31%.

4,4′-Isopropylidenedi(p-phenylene)bis(2,2,2-trichloroethyl) carbonate (**3**). In a polymerization tube equipped with a stirring bar and distillation column are placed BPA (0.15 g, 0.66 mmol), bis(2,2,2-trichloroethyl) carbonate (1.71 g, 5.27 mmol), and 4-dimethylaminopyridine (4.0 mg, 0.033 mmol). The mixture was heated at 160°C with stirring under argon for 30 min, under a vacuum of 100 mmHg for 1 h, 50 mmHg for 2 h, 30 mmHg for 2 h, and 1 mmHg for 10 min. The residue was crystallized from *n*-hexane to produce white needles. The yield was 0.344 g (90%): mp 101–103°C. I.r. (KBr): ν 1775 cm^{-1} (C=O). ^{1}H-n.m.r. ($CDCl_3$) δ: 1.68 (*s*, 6H, CH_3), 4.87 (*s*, 4H, CH_2), 7.11–7.27 ppm (*m*, 8H, Ar–H). Anal. Calcd for $C_{21}H_{18}O_6Cl_6$: C, 43.56%; H, 3.13%. Found: C, 43.75%; H, 3.25%.

Polymer synthesis. To a polymerization tube equipped with a stirring bar and a distillation column are introduced monomer (3.0 g, 5.18 mmol) and $Ti(O\text{-}iC_3H_7)_4$ (3.0 mg, 0.011 mmol) under a stream of argon. The mixture was heated at an atmospressure to 175°C for 15 min with stirring under argon, kept at this temperature for 2 h, and then raised to 215°C for 30 min. The polymerization tube is reduced to 0.1 mmHg or less while heating at 215°C for 2 h, rising up to 250°C for 30 min and then kept at this temperature for 3 h. The tube was removed from the oil bath, and cooled. The polymer was dissolved in dichloromethane, precipitated with methanol, filtered, and dried *in vacuo* at 80°C. The yield was 1.32 g (95%). I.r. (KBr): 1775 cm^{-1} (C=O). ^{13}C-n.m.r. (CDCl−3): 30.9 (C-1), 42.6 (C-2), 120.3 (C-4), 127.9 (C-5), 148.3 (C-6), 149.0 (C-7), 152.1 (C-8), $\bar{M}_n = 11\,000$, $\bar{M}_w = 39\,000$.

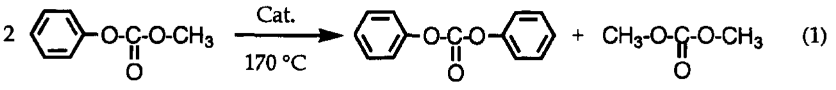
Measurements. *FT*i.r. spectra were measured on a Horiba FT-210 spectrophotometer. ^{1}H- and ^{13}C-n.m.r. spectra were recorded on a JEOL EX 270 spectrometer. Gas chromatograms were obtained by a Shimadzu GC-14A gas chromatograph with FID with a thermon-3000 glass column. Thermal analyses were performed on a Seiko SSS 5000 t.g.–d.t.a. 220 thermal analyzer at a heating rate of 10°C min^{-1} for thermogravimetry (t.g.). Molecular weights were determined by a gel permeation chromatograph (g.p.c.) with polystyrene calibration using JASCO HPLC equipped with Shodex KF-80M column at 40°C in THF.

RESULTS AND DISCUSSION

Model reaction

Prior to polymer synthesis, the model compound work was performed to determine which catalyst is effective for the disproportionation of alkyl phenyl carbonate and what kind of BPA dicarbonate is suitable as a polymer-forming monomer.

The disproportionation reaction of methyl phenyl carbonate **1a**, which yields diphenyl carbonate (DPC) and DMC, was investigated at 170°C in the presence of various metal alkoxides such as $Ti(O\text{-}iC_3H_7)_4$, $Pb(O\text{-}iC_3H_7)_2$, $Fe(OCH_3)_3$, $La(OCH_3)_3$, $Mn(OCH_3)_3$, $Co(OCH_3)_2$, $Ta(OCH_3)_5$, $Nb(OCH_3)_5$, and $Zr(OCH_3)_4$ [equation (1)].



$$2\ C_6H_5\text{-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-O-CH}_3 \xrightarrow[170\ ^\circ C]{\text{Cat.}} C_6H_5\text{-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-O-}C_6H_5 + CH_3\text{-O-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-O-CH}_3 \qquad (1)$$

1a **DPC** **DMC**

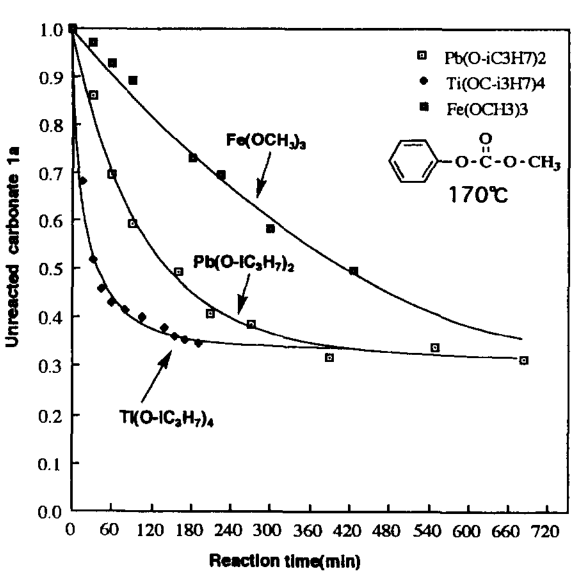


Figure 1 Disproportionation reaction of carbonate **1a** in the presence of 1.2 mol% $Ti(O\text{-}iC_3H_7)_4$, $Pb(O\text{-}iC_3H_7)_2$, $Fe(OCH_3)_3$ at 170°C under argon

These preliminary experiments indicated that Ti(O-iC$_3$H$_7$)$_4$, Pb(O-iC$_3$H$_7$)$_2$ and Fe(OCH$_3$)$_3$ were effective catalysts. Then, in order to determine which catalyst was the most effective, the course of disproportionation reaction was followed by ^{1}H-n.m.r. spectroscopy or gas chromatography in the presence of the above three catalysts. The results are shown in *Figure 1*. Among these catalysts, Ti(O-iC$_3$H$_7$)$_4$ gave the best results judging from the rate of disappearance of **1a**. Although the catalytic mechanism is not clear, the coordination of the carbonate group to the metal atom and the ligand exchange reaction of metal alkoxide with **1a**, followed by the nucleophilic attack of the metal phenolate to **1a**, may facilitate the disproportionation reaction.

The increasing reactivity of carboxylic acid derivatives toward nucleophiles may be roughly correlated with the order of increasing stability of the leaving group anion. Therefore, the reactivity of alkyl phenyl carbonates for disproportionation may depend on the acidity of alcohol moiety. So, various alkyl phenyl carbonates **1** such as **1a**, isopropyl phenyl carbonate **1b**, phenyl 2,2,2-trifluoroethyl carbonate **1c**, and phenyl 2,2,2-trichloroethyl carbonate **1d** were prepared from the reaction of phenol with methyl chloroformate or phenyl chloroformate with the corresponding alcohols in THF in the presence of TEA.

Figure 2 shows the course of disproportionation reaction of various alkyl phenyl carbonates **1** in the presence of 1.2 mol% of Ti(O-iC$_3$H$_7$)$_4$ at 150°C [equation (2)].

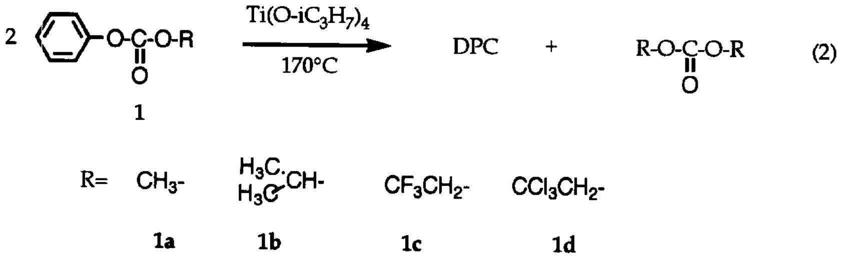
The concentrations of **1c** and **1d** decreased very rapidly compared with those of other **1**. The introduction of 2,2,2-trifluoroethyl and 2,2,2-trichloroethyl groups into carbonates is found to be effective to enhance the reactivity for disproportionation of **1**. This is probably because these alcohols have a higher acidity than other alcohols.

Monomer synthesis

Bis(2,2,2-trichloroethyl) carbonate (**2a**) and bis(2,2,2-trifluoroethyl) carbonate (**2b**) would be good candidates as dialkyl carbonates (**2**). We decided to synthesize carbonate **2a** on the basis of availability of starting reagents. Carbonate **2a** was prepared from 2,2,2-trichloroethanol and 2,2,2-trichloroethyl chloroformate in the presence of TEA in THF.

The reaction of BPA with DMC is thermodynamically unfavourable and requires long reaction time even in the presence of catalyst. On the other hand, the reactivity of carbonate **2a** toward nucleophiles may be higher than that of DMC because of high acidity of trichloroethanol.

Transesterification of aromatic carbonates are generally facilitated by the use of 4-dimethylaminopyridine (DAP). The effect is significant in the case of the reaction of phenol with bis(*o*-nitrophenyl) carbonate in which DAP acts as a nucleophilic catalyst[12]. Therefore, the synthesis of 4,4′-isopropylidenedi(*p*-phenylene)bis(2,2,2-trichloroethyl) carbonate (**3**) from BPA and **2a** carried out at 160°C in the presence of DAP under reduced pressure [equation (3)]



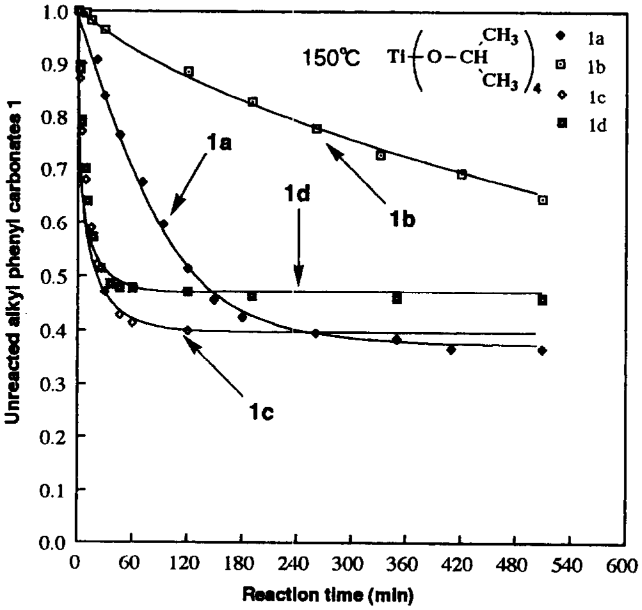


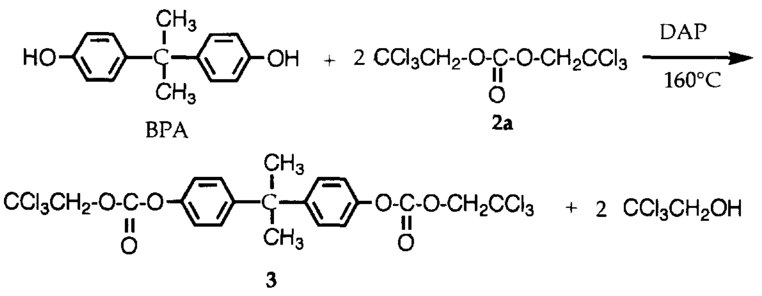
Figure 2 Disproportionation reaction of various alkyl phenyl carbonates 1 in the presence of 1.2 mol% Ti(O-iC$_3$H$_7$)$_4$ at 150°C under argon

The reaction proceeded smoothly and gave monomer **3** in excellent yield. The chemical structure of **3** was assigned on the basis of elemental analysis, i.r. and ^{1}H-n.m.r. spectroscopy. The i.r. spectrum of **3** had the characteristic C=O absorption at 1775 cm^{-1}. The ^{1}H-n.m.r. spectrum of **3** exhibited two singlet peaks at δ 1.68 (6H) and 4.87 (4H) for the methyl and methylene protons, and two doublet peaks (8H) at δ 7.11 and 7.27 for the aromatic protons.

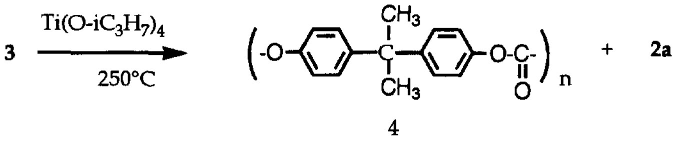
Polymer synthesis

Based on these results, the melt self-polycondensation of monomer **3** was performed under conditions similar to those for the disproportionation of **1**. Oligomer was prepared in the presence of Ti(O-iC$_3$H$_7$)$_4$ in the temperature range 175–200°C at the first stage, and then subjected to further polycondensation at 215–250°C under reduced pressure while carbonate **2a** was being distilled out. The polycarbonate (**4**) was dissolved in chloroform and purified by precipitation with methanol [equation (4)].

These results are summarized in *Table 1*. The polymerization at 250°C for 3 h in the presence of



(3)



(4)

Table 1 Synthesis of polycarbonate **4** by melt self-polycondensation of **3** in the presence of $Ti(O\text{-}iC_3H_7)_4$

Reaction conditions [a]				Polymer		
Temperature (°C)	Time (h)	Catalyst (mol%)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
215	2	1.3	90	6000	19000	3.2
250	1	0.51	90	9000	25000	2.8
250	3	0.21	95	11000	39000	3.5

[a] Polymerization condition: first stage, heating from room temperature to 175°C for 15 min, 175°C for 2 h, and heating from 175 to 215°C for 30 min, under argon

0.2 mol% of catalyst toward to monomer **3** at the second stage produced polymer **4** with $\bar{M}_n = 11\,000$ and $\bar{M}_w = 39\,000$, respectively, for standard polystyrene.

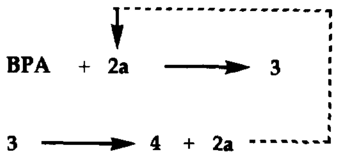
The polymer **4** (entry 3) was confirmed to be the corresponding polycarbonate by comparing its i.r. spectrum with those of model compounds. The i.r. spectrum exhibited characteristic absorptions at 1775 and 1230–1260 cm^{-1} due to C=O and C–O–C stretching, respectively. The most conclusive spectroscopic evidence for the proposed polycarbonate **4** was provided by ^{13}C-n.m.r. spectroscopy. A ^{13}C-n.m.r. spectrum of polymer **4** was identical to that of commercially produced polycarbonate.

The thermal stability of polymer **4** was examined by thermogravimetry (t.g.). The thermal stability of polymer **4** obtained (entry 3) is almost comparable to that of commercially produced polycarbonate. A 10% weight loss of polymer **4** was observed at 450°C in nitrogen.

CONCLUSION

Our studies demonstrate that polycarbonate with a high molecular weight can be readily obtained by melt self-polycondensation of 4,4′-isopropylidenedi(*p*-phenylene) bis(2,2,2-trichloroethyl) carbonate **3** in the presence of $Ti(O\text{-}iC_3H_7)_4$.

Furthermore, transesterification of bis(2,2,2-trichloroethyl) carbonate **2a** with BPA proceeded at 160°C in the presence of 4-dimethylaminolpyridine, giving monomer **3** in excellent yield. This method having the following synthetic cycle of polycarbonate [equation (5)] provides a potentially efficient route for the synthesis of aromatic polycarbonates from dialkyl carbonates and diphenols



(5)

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