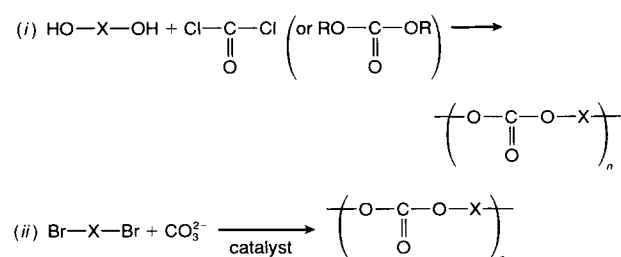


# Copper(I) Iodide Catalyzed Polycondensation of *p*-Xylylene Dibromide and Potassium Carbonate to Give Poly[(*p*-xylylene carbonate)-co-(*p*-xylylene oxide)]

**Keywords:** copper(I) iodide • *p*-xylylene dibromide • potassium carbonate • poly[(*p*-xylylene carbonate)-co-(*p*-xylylene oxide)]

## INTRODUCTION

Polycondensation of diols with phosgene or carbonic diester is commonly used in synthesis of various poly(carbonate)s [path (i) in Scheme 1].<sup>1</sup> Polycondensation of organic dihalides with carbonate anion would provide a preparation method of poly(carbonate) based on another concept [path (ii) in Scheme 1].



Scheme 1.

Soga and co-workers have previously reported synthesis of several poly(carbonate)s from crown ether assisted reaction of organic dibromide and  $\text{K}_2\text{CO}_3$  from an alternative reaction of organic dibromide, potassium salt of cresol, and  $\text{CO}_2$ .<sup>2,3</sup> Polycondensation of dipotassium diphenoxides,  $\alpha,\omega$ -dihalo compounds, and  $\text{CO}_2$  promoted by crown ether also gives the corresponding poly(carbonate)s.<sup>4</sup> Some copper compounds that catalyze condensation of organic halides and alkoxide ions to cause C—O bond formation<sup>5</sup> could also promote reaction (ii) involving dehalogenative coupling of organic dihalides and carbonic ion as a crucial step. Thus we examined CuI catalyzed polycondensation of *p*-xylylene dibromide and  $\text{K}_2\text{CO}_3$  in the presence of  $\text{CO}_2$ , and revealed that the reaction gives the polymer containing not only poly(carbonate) unit but also poly(ether) unit whose ratio in the polymer chain varies depending on preparation conditions. The reaction would provide a useful preparation method of this type copolymer that could not be obtained from alternative polymerization reaction. Here we report preparation and characterization of the above polymer.

## EXPERIMENTAL

### Measurements

IR spectra were recorded on a JASCO-IR 810 spectrometer.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a JEOL JNM-EX-400 spectrometer. Elemental analyses were carried out by Yanagimoto Type MT-2 CHN autocorder. GPC analyses were carried out on a Toso HLC 8020 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using an *N,N*-dimethylformamide (DMF) solution of LiBr (0.01M) as the eluent, a flow rate of 1.0 mL/min, and RI and UV detectors. DSC analyses were carried out on a Shimadzu DSC-50.

### Materials

*N*-methyl-2-pyrrolidone (NMP) was distilled prior to use and stored under nitrogen. CuI,  $\text{K}_2\text{CO}_3$ , and organic substrates were purchased and used without further purification.

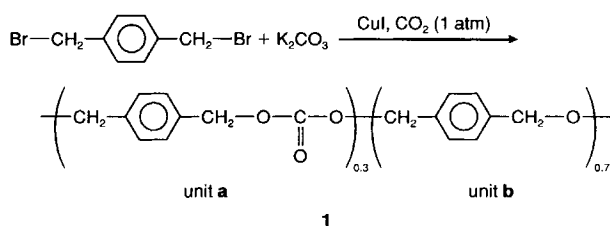
### Polymerization

A typical experimental procedure is as follows. To an NMP (5 mL) solution of CuI (19 mg, 0.10 mmol) and  $\text{K}_2\text{CO}_3$  (2.1 g, 15 mmol) was added *p*-xylylene dibromide (0.66 g, 2.5 mmol) under nitrogen at room temperature.  $\text{CO}_2$  was introduced to the resulting solution by connecting the reaction system with a rubber balloon containing 1 atm of  $\text{CO}_2$  (ca. 80 mmol). The reaction mixture was heated at 100°C for 4 h, and then the solvent was removed by evaporation under high vacuum. The resulting yellow paste was washed with methanol and acetone, and was reprecipitated by pouring it into  $\text{Et}_2\text{O}$  (ca. 100 mL) with stirring. The light yellow solid product was washed with distilled water and methanol several times and dried in vacuo to give **1** (0.15 g, 45%). Preparation of the polymers **2–5** was carried out in a similar manner.  $^1\text{H}$ -NMR (**1**, 400 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  4.5 (br,  $\text{CH}_2\text{—O}$ ), 5.1 [br,  $\text{CH}_2\text{—O—(C=O)—O}$ ], 4.55 (s,  $\text{CH}_2\text{Br}$ ), 7.2–7.6 (br,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (**1**, 100 MHz in  $\text{DMSO}-d_6$ ):  $\delta$  154.3 [ $\text{O—(C=O)—O}$ ], 141.7, 137.5, 134.5, 128.1, 127.4, 126.3, 71.1 ( $\text{CH}_2\text{—O—}$ ), 68.8 [ $\text{CH}_2\text{—O—(C=O)—O}$ ]. IR (**1**, KBr): 3022, 2852, 1737, 1253, 1078, 810  $\text{cm}^{-1}$ .

ANAL. Calcd for  $[1, \{C_9H_8O_3(C_6H_8O)_{2.3}\}_{5.2}(C_8H_8OBr)]$ : C, 67.3%, H, 5.4%. Found: C, 67.6%, H, 5.8%.  $M_w = 10,300$  ( $M_w/M_n = 4.1$ , by GPC in DMF vs. polystyrene standard).  $[\eta]_{inh} = 0.09$  (DMSO, 30°C).

## RESULTS AND DISCUSSION

Reaction of *p*-xylylene dibromide with potassium carbonate in the presence of CuI under CO<sub>2</sub> atmosphere gives polymer **1** as a light yellow solid. Analytical and spectroscopic results of **1** shown below indicate the structure containing a unit with carbonate group,  $[CH_2-C_6H_4-CH_2-O-(C=O)-O]$  (**a**) and that with ethereal group,  $[CH_2-C_6H_4-CH_2-O]$  (**b**), in a ratio of 0.3 : 0.7 in the main chain (Scheme 2).



Scheme 2.

The IR spectrum of the polymer **1** shows  $\nu(C=O)$  peak due to unit **a** at  $1737\text{ cm}^{-1}$  and  $\nu(C-O)$  peaks due to units **a** and **b** at  $1253$  and  $1078\text{ cm}^{-1}$ , respectively. Figure 1 shows the <sup>1</sup>H-NMR spectrum giving rise to methylene hydrogens of units **a** and **b** at 5.1 and 4.5 ppm, respectively. The peak area ratio indicates that the polymer contains units **a** and **b** in a 0.3 : 0.7 ratio. A small peak at 4.55 ppm

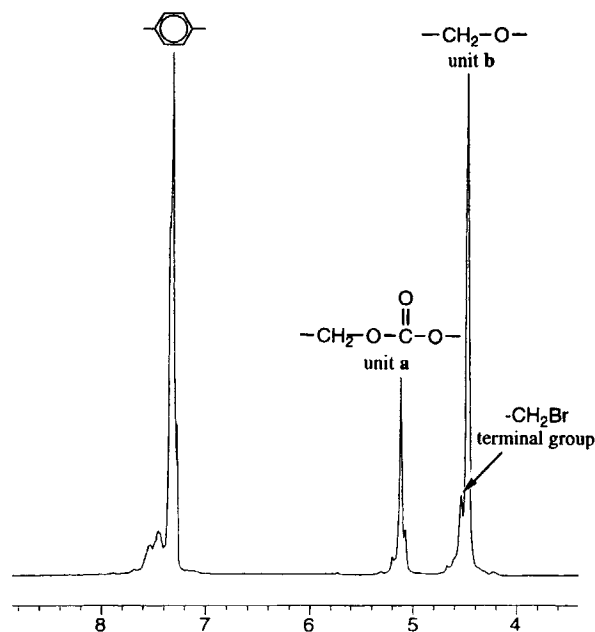


Figure 1. <sup>1</sup>H-NMR spectrum of polymer **1** (400 MHz in DMSO-*d*<sub>6</sub>).

is assigned to CH<sub>2</sub>Br group of terminal group (O—CH<sub>2</sub>—C<sub>6</sub>H<sub>4</sub>—CH<sub>2</sub>Br) of the polymer since the peak position agrees well with that of *p*-xylylene dibromide. Phenyl hydrogen peak of the polymer chain appear at 7.3 ppm, while hydrogens of aromatic ring in the terminal group is observed at 7.4–7.6 ppm. A small peak at 4.55 ppm is assigned to CH<sub>2</sub>Br group of terminal group (O—CH<sub>2</sub>—C<sub>6</sub>H<sub>4</sub>—CH<sub>2</sub>Br) of the polymer since the peak position agrees well with that of *p*-xylylene dibromide. Figure 2 shows <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of polymer **1**. Methylene carbons of units **a** and **b** appear at 68.8 and 71.1 ppm, respectively. The peak at 154.3 ppm due to carbonyl carbon strongly indicates the presence of carbonate group in the polymer chain. The <sup>1</sup>H—<sup>13</sup>C COSY NMR spectrum is consistent with the above assignment of the <sup>1</sup>H and <sup>13</sup>C-NMR signals. The polymer **1** with an inherent viscosity,  $[\eta]_{inh}$ , of  $0.09\text{ dL g}^{-1}$  in DMSO at 30°C gives a GPC trace showing  $M_w$  of 10,300 ( $M_w/M_n = 4.1$ ).

Table I summarizes results of polymerization of *p*-xylylene dibromide and K<sub>2</sub>CO<sub>3</sub> under various conditions. The reactions in the absence of K<sub>2</sub>CO<sub>3</sub> (run 6) or CO<sub>2</sub> (run 7) give no polymerization product. The reaction without CuI catalyst gives a small amounts (<3%) of the product with low molecular weight ( $M_w = 1200$ ). Addition of 1-hexyne and phenylacetylene to the reaction mixture gives rise to formation of analogous polymers **2** and **3** with higher content of unit **a** than **1**. The <sup>1</sup>H-NMR spectra of **2** and **3** show the absence of hexyl or phenyl group, suggesting that the alkyne is not incorporated in the polymer chain or as the end group. Use of Na<sub>2</sub>CO<sub>3</sub> (run 4) or [CuI(bpy)]<sub>2</sub> (bpy = 2,2'-bipyridine) catalyst (run 5) causes increase in the content of unit **a** in the polymer chain although the yields are lowered (38 and 16%, respectively). Partial formation of poly(ether) unit during the polymerization is not due to decarboxylation of initially formed poly(carbonate)s since heating dibenzyl carbonate with CuI does not promote decarboxylation to the corresponding ether. Scheme 3 shows a possible route to CH<sub>2</sub>—O—CH<sub>2</sub> bond formation involving decarboxylation of alkyl carbonato ligand bonded to the Cu center to give alkoxide ligand which undergoes further reaction with organic dibromide. Facile decarboxylation from alkyl carbonate complex<sup>6</sup> as well as C—O bond formation from

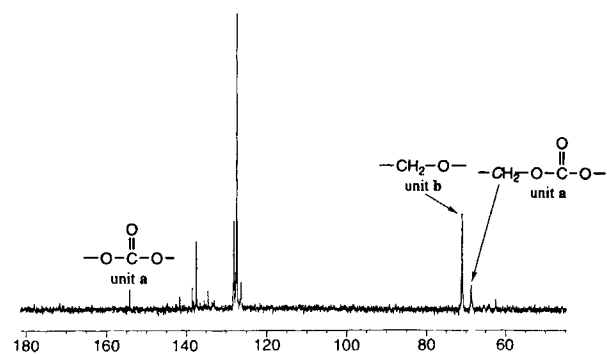


Figure 2. <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of polymer **1** (100 MHz in DMSO-*d*<sub>6</sub>).

**Table I.** Polycondensation of *p*-Xylylene Dibromide and Potassium Carbonate under Various Conditions<sup>a</sup>

Run	Conditions			Yield (%)	Product		
	Br—CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> —Br (mmol)	K <sub>2</sub> CO <sub>3</sub> (mmol)	CO <sub>2</sub> (mmol)		Polymer	Unit a : Unit b <sup>b</sup>	M <sub>w</sub> (M <sub>w</sub> /M <sub>n</sub> ) <sup>c</sup> (×10 <sup>-3</sup> )
1	2.5	15	80	45	<b>1</b>	0.3 : 0.7	10.3 (4.1)
2 <sup>d</sup>	2.5	15	80	73	<b>2</b>	0.6 : 0.4	6.0 (1.3)
3 <sup>e</sup>	2.5	15	80	57	<b>3</b>	0.6 : 0.4	3.7 (2.0)
4 <sup>f</sup>	2.5	15	80	38	<b>4</b>	0.8 : 0.2	1.7 (3.4)
5 <sup>g</sup>	2.5	15	80	16	<b>5</b>	0.7 : 0.3	5.2 (3.0)
6	2.5	0	80	0	—	—	—
7	2.5	15	0	0	—	—	—
8 <sup>h</sup>	2.5	15	80	< 3	—	0.6 : 0.4	1.2 (2.5)

<sup>a</sup> Reactions were carried out using CuI (0.1 mmol), *p*-xylylene dibromide (2.5 mmol), and potassium carbonate in NMP (5 mL) at 100°C for 4 h under carbon dioxide atmosphere.

<sup>b</sup> Determined by relative peak intensity in <sup>1</sup>H NMR spectrum. See text.

<sup>c</sup> Obtained by GPC using DMF containing 0.01M LiBr as an eluent.

<sup>d</sup> 1.0 mmol of 1-hexyne was added.

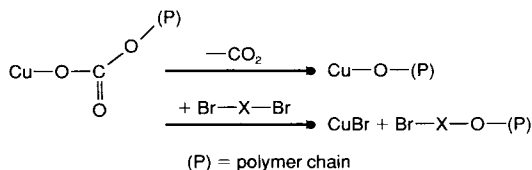
<sup>e</sup> 2.5 mmol of phenylacetylene was added.

<sup>f</sup> Na<sub>2</sub>CO<sub>3</sub> was used instead of K<sub>2</sub>CO<sub>3</sub>.

<sup>g</sup> [CuI(bpy)]<sub>2</sub> (0.1 mmol) was used instead of CuI.

<sup>h</sup> Without catalyst.

the reaction of alkoxide copper species with organic halides<sup>7</sup> have been previously reported.

**Scheme 3.**

In summary, CuI catalyzes polycondensation of *p*-xylylene dibromide and K<sub>2</sub>CO<sub>3</sub> in the presence of CO<sub>2</sub> to give a novel polymer containing *p*-xylylene ether unit in the main chain. The polymerization requires the presence of K<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub> as the source of carbonate group of the polymer chain.

The authors are grateful to financial support by a Grant-in-Aid for Scientific Research on Priority Areas "Activation of Small Molecules" (No. 05225208) from the Ministry of Education, Science, Culture, and Sports of Japan.

## REFERENCES AND NOTES

- (a) H. Schnell, in *Polymer Reviews, Vol. 9: Chemistry and Physics of Polycarbonate*, Wiley, New York, 1964; (b) M. J. Marks and J. K. Sekinger, *Polymer*, **36**, 209 (1995); (c) M. M. Deshpande, A. S. Jadhav, A. A. Gunari, J. C. Sehra, and S. Sivaram, *J. Polym. Sci. Part A: Polym. Chem.*, **33**, 701 (1995); (d) P. Tundo, F. Trotta, G. Moraglio, and F. Ligorati, *Ind. Eng. Chem. Res.*, **27**(9), 1565 (1988).
- (a) K. Soga, S. Hosoda, and S. Ikeda, *J. Polym. Sci. Polym. Lett. Ed.*, **15**, 611 (1977); (b) K. Soga, Y.

Toshida, S. Hosoda, and S. Ikeda, *Makromol. Chem.*, **178**, 2747 (1977); (c) K. Soga, Y. Toshida, S. Hosoda, and S. Ikeda, *Makromol. Chem.*, **179**, 2379 (1978); (d) K. Soga, S. Hosoda, and S. Ikeda, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 517 (1979).

- Y. Zhong, X. Fu, and L. Zhong, *Ziangan Daxue Ziran Kexue Xuebao* (Chinese), **29** (1986); *Chem. Abstr.*, **106**, 50693f (1987).
- G. Rokicki, W. Kuran, and J. Kielkiewicz, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 967 (1982).
- (a) F. Ullmann, *Chem. Ber.*, **36**, 2382 (1903); (b) F. Ullmann and C. Schlaepfer, *Chem. Ber.*, **37**, 2001 (1904). (c) H. Weingarten, *J. Org. Chem.*, **29**, 3624 (1964); (d) T. Yamamoto, and Y. Kurata, *Can. J. Chem.*, **61**, 86 (1973).
- (a) T. Tsuda, S. Sanada, K. Ueda, and T. Saegusa, *Inorg. Chem.*, **15**, 2329 (1976). (b) T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, **102**, 431 (1980).
- T. Kawaki and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **45**, 1499 (1972).

ISAO YAMAGUCHI  
KOHTARO OSAKADA\*  
TAKAKAZU YAMAMOTO

Research Laboratory of Resources Utilization  
Tokyo Institute of Technology  
4259 Nagatsuta, Midori-ku,  
Yokohama 226, Japan

Received August 7, 1995  
Accepted January 31, 1996

\* To whom all correspondence should be addressed.