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Synthesis of Poly[(*p*-xylylene carbonate)-*co*-(*p*-xylylene oxide)] with OH End Groups and Its Polyaddition with Diisocyanates

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ABSTRACT: Polycondensation of *p*-xylylene dibromide and M_2CO_3 (M = Li, Na, K, Rb, and Cs) catalyzed by CuI gives polymer **1** which contains the *p*-xylylene carbonate structural unit, $-CH_2C_6H_4CH_2O(C{=}O)O-$ (**a**), and the *p*-xylylene oxide unit, $-CH_2C_6H_4CH_2O-$ (**b**), randomly in the polymer chain. The use of Rb_2CO_3 and Cs_2CO_3 as the source of the carbonate group increases the yield of the polymer. Cu compounds including $[Cu(C{\equiv}CPh)(PPh_3)]_4$, $Cu(C{\equiv}CC_3H_7)$, CuBr, $CuBr_2$, and $CuBr_2(phen)_n$ (phen = 1,10-phenanthroline, n = 1,2) also catalyze the polycondensation to give a product rich in unit **a**. The polycondensation catalyzed by alkynylcopper(I) complexes with or without addition of 1,10-phenanthroline gives a polymer with a high content of unit **a** (>95%). Polymer **1** possesses CH_2OH terminal groups which are identified by ^1H and $^{13}C\{^1H\}$ NMR as well as by reaction with an alkyl isocyanate. Reactions of **1** with diisocyanates such as 4-methyl-1,3-benzenediisocyanate, *m*-xylylene diisocyanate, and 1,6-hexanediisocyanate cause the polyaddition of **1** to the N=C=O bonds resulting in new polymers containing the macromonomer units bonded through bisurethane groups.

Introduction

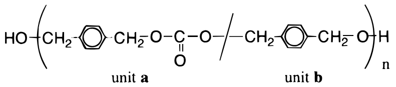
Ring opening polymerization of cyclic carbonates provides a useful synthetic method for various aromatic and aliphatic polycarbonates.[1−8] Preparation of polycarbonates from the polycondensation of cyclic monomers with CO_2 or CO_3^{2-} as a source of carbonate groups in the polymer produced also seems to be a promising phosgene free synthesis of polycarbonates. The latter type of polymerization is much less common than the ring opening polymerization of cyclic carbonates. Copolymerization of epoxides and carbon dioxide has been reported to proceed in an alternating fashion and to give aliphatic polymers containing carbonate groups in high density in the main chain.[9] Dehalogenative polycondensation of several organic dibromides and K_2CO_3 with the aid of crown ethers as the phase transfer catalyst gives the corresponding polycarbonate.[10] Recently we preliminarily reported that CuI catalyzes the polycondensation of *p*-xylylene dibromide with K_2CO_3 in polar solvents to give poly[(*p*-xylylene carbonate)-*co*-(*p*-xylylene oxide)].[11]

The last polymer is of interest because it arises from incorporating chemically different segments into polycarbonate chains. Modification of properties of polycarbonates by introducting the other structural units in the polymer chain[12−14] has been achieved by polycondensation of specially designed monomers.[15−19] Thus, we further investigated the synthesis of the poly(carbonate ether) and found the polymer structure containing CH_2OH terminal groups. In this paper we report the full details of the results on optimization of the polymerization conditions, the structure and properties of the polymer, and its use as a macromonomer having CH_2OH terminal groups.

Results and Discussion

Polycondensation of *p*-Xylylene Dibromide and M_2CO_3. Reaction of *p*-xylylene dibromide and K_2CO_3 in the presence of a CuI catalyst under CO_2 atmosphere gives polymer **1** as a colorless solid. The main chain of **1** contains the *p*-xylylene carbonate unit, $-CH_2C_6H_4CH_2O(C{=}O)O-$ (**a**), and the *p*-xylylene oxide unit, $-CH_2C_6H_4CH_2O-$ (**b**), randomly as shown in Chart 1.

Chart 1



NMR analyses of **1** show the presence of these structural units in the main chain. The ^1H NMR spectrum of **1** obtained from the reaction after 16 h gives rise to peaks at δ 5.14 and 4.50 whose positions agree well with those of the CH_2 hydrogens in dibenzyl carbonate and dibenzyl ether, respectively. The former peak is assigned to the CH_2 hydrogens of unit **a** and the latter to unit **b**. The ratio of the NMR peak areas indicates the molar ratio of **a** to **b** as 76:24. The ^{13}C NMR spectrum (Figure 1) exhibits peaks at δ 154.3, 72.3, and 68.1, which are assigned to the carbonyl carbon and CH_2 carbons of structural units **a** and **b**, respectively. Gel permeation chromatography (GPC) analysis shows molecular weights, M_n = 8100 and M_w = 9300, based on polystyrene standards.

Table 1 summarizes the results of polymerization under various conditions.[20] Polycondensation of *p*-xylylene dibromide with K_2CO_3, Na_2CO_3, and Li_2CO_3 (runs 1−6) requires excess carbonates because of their poor solubility in the organic solvent. Rb_2CO_3, having considerable solubility in the polar organic solvent,[21] undergoes smooth polycondensation with equimolar *p*-xylylene dibromide to give the polymer in 69% yield. The polymerization using K_2CO_3 under Ar (run 3) gives the product containing unit **b** as the major structural unit in 32% yield, while the reaction under CO_2 at 20 atm (run 4) affords results similar to those under atmospheric CO_2. The moderate to high yields of the polycondensation under several conditions indicate that the smooth reaction occurs similarly to the already reported phase transfer catalyst promoted condensation of organic chlorides with carbonate ion.[21,22]

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Table 1. Polycondensation of *p*-Xylylene Dibromide and Metal Carbonates Catalyzed by Cu Compounds[a]

run	catalyst	M_2CO_3	additive (mmol)	time (h)	yield[b] (%)	unit **a**:unit **b**[c]	$10^{-3}M_w$, $10^{-3}M_n$[d]
1	CuI	K_2CO_3		4	49	88:12	4.0, 2.5
2	CuI	K_2CO_3		16	45	76:24	9.3, 8.1
3[e]	CuI	K_2CO_3		24	32	38:62	8.1, 5.2
4[f]	CuI	K_2CO_3		24	70	83:17	9.4, 7.5
5	CuI	Li_2CO_3		20	4	42:58	6.0, 5.1
6	CuI	Na_2CO_3		4	38	83:17	2.7, 2.5 (1.9)
7	CuI	Rb_2CO_3		24	53	94:6	16.2, 10.1
8[g]	CuI	Rb_2CO_3		24	69	83:17	8.2, 6.2 (3.1)
9	CuI	Cs_2CO_3		24	72	87:13	8.4, 7.2
10	$[Cu(C\equiv CPh)(PPh_3)]_4$	K_2CO_3		10	73	95:5	11.3, 7.6 (4.4)
11	$[Cu(C\equiv CPh)(PPh_3)]_4$	K_2CO_3		70	81	86:14	16.6, 8.1
12	CuI	K_2CO_3	$PhC\equiv CH$ (2.5)	4	88	71:29	3.7, 1.3
13	CuI	K_2CO_3	$PhC\equiv CPh$ (2.5)	24	64	86:14	7.3, 5.4
14	$Cu(C\equiv CC_3H_7)$	K_2CO_3		4	16[i]	93:7	1.2, 1.2
15	$Cu(C\equiv CC_3H_7)$	K_2CO_3		10	52	77:23	8.2, 6.8
16	$Cu(C\equiv CC_3H_7)$	K_2CO_3		70	53	75:25	14.0, 11.4
17[h]	CuI	K_2CO_3	phen (0.4)	70	86	90:10	9.9, 5.4 (3.1)
18[h]	CuI	K_2CO_3	bpy (0.2)	24	23	83:17	8.9, 5.8 (1.9)
19[h]	CuI	K_2CO_3	tmeda (0.2)	24	10	83:17	11.9, 2.5 (1.9)
20	CuBr	K_2CO_3		24	58	87:13	15.0, 9.7 (6.4)
21	$CuBr_2$	K_2CO_3		24	64	82:18	10.9, 7.3 (6.2)
22	$CuBr_2$(phen)	K_2CO_3		24	51	83:17	8.7, 5.8 (1.9)
23	$CuBr_2(phen)_2$	K_2CO_3		24	43	76:24	18.7, 9.6
24	$[Cu(C\equiv CPh)(PPh_3)]_4$	K_2CO_3	phen (0.4)	70	57	97:3	10.1, 8.2 (5.1)
25	$Cu(C\equiv CC_3H_7)$	K_2CO_3	phen (0.4)	24	81	95:5	12.3, 8.8

[a] Reactions were carried out by heating a mixture of catalyst (0.1 mmol), *p*-xylylene dibromide (2.5 mmol), and metal carbonate (15 mmol) in NMP (5 mL) at 100 °C under CO_2 atmosphere (1 atm) unless otherwise stated. [b] Yields based on *p*-xylylene dibromide. [c] Determined by relative peak intensity of the ^1H NMR spectra. [d] Obtained by GPC using DMF containing 0.01 M LiBr as an eluent. The M_n values obtained from ^1H NMR peak area ratios are in parentheses. Some of the values may not be accurate due to an overlapping peak of the terminal group with that of the main chain. [e] Under Ar atmosphere. [f] Under CO_2 (20 atm). [g] 2.5 mmol of Rb_2CO_3 was used. [h] 7.5 mmol of K_2CO_3 was used. [i] The product contains monomer not separated from the product.

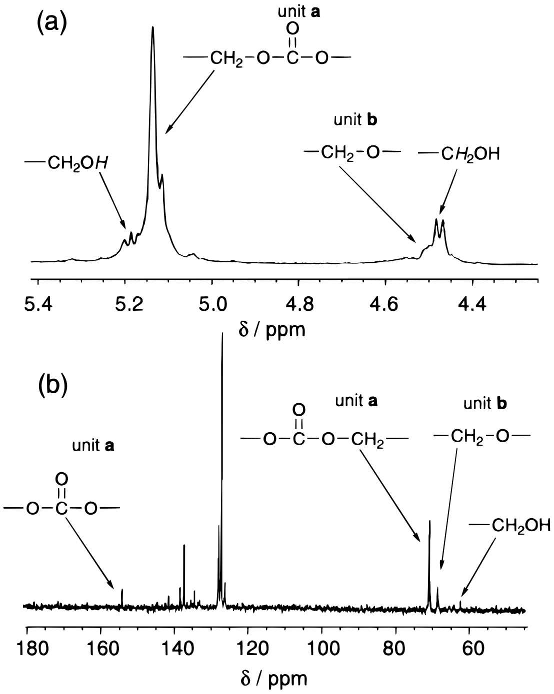


Figure 1. (a) ^1H (400 MHz) (CH_2 region) and (b) $^{13}C\{^1H\}$ (100 MHz) NMR spectra of **1** in DMSO-d_6.

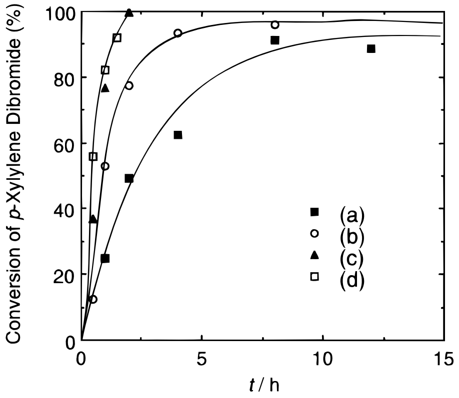


Figure 2. Profiles of polycondensation of *p*-xylylene dibromide with K_2CO_3 at 100 °C in NMP catalyzed by (a) CuI, (b) $Cu(C\equiv CC_3H_7)$, (c) $[Cu(C\equiv CPh)(PPh_3)]_4$, and (d) CuI + phen. Amounts of *p*-xylylene dibromides determined by GC were plotted using DMF as an internal standard.

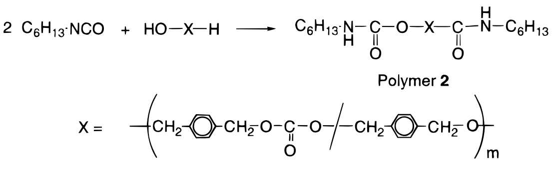
Use of $[Cu(C\equiv CPh)(PPh_3)]_4$ as the catalyst (runs 10 and 11) improves the yield of the product. Addition of a large excess of phenylacetylene to the CuI catalyzed polymerization (run 12) also increases the yield and the relative content of structural unit **a** compared with the reaction without the additive. Incorporation of alkyne into the polymer chain is not observed in the reaction, suggesting that the added alkyne serves as a ligand at the Cu center to promote the polymerization. Figure 2 compares the reaction profile of the polycondensation reactions catalyzed by CuI and by the alkynylcopper complexes. The rate of consumption of *p*-xylylene dibromide increases in the order: CuI, $Cu(C\equiv CC_3H_7)$, and $[Cu(C\equiv CPh)(PPh_3)]_4$. Addition of 1,10-phenanthroline (phen) to the CuI catalyzed reaction also enhances monomer consumption, as shown in Figure 2, and results in the formation of the polymer in high yields (run 17 in Table 1). CuI catalyzed reactions with addition of bpy (2,2′-bipyridine) and tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) afford the polymer in much lower yields (runs 18 and 19). Differences in the degree of promotion of polycondensation among the chelating diamines may be ascribed to the electron donating ability of the ligand in the order: phen > bpy > tmeda.[23] Monomer consumption of the $[Cu(C\equiv CPh)(PPh_3)]_4$ catalyzed polymerization is completed in 2 h

(Figure 2), while the results of polymerization for 10 and 70 h (runs 10 and 11 in Table 1) suggest further increases in the polymer yield and in molecular weights and decreases in the ratio of unit **a** in the polymer chain. A similar tendency is also observed in the products of the $Cu(C{\equiv}CC_3H_7)$ catalyzed polymerization for 4, 10, and 70 h (runs 14–16 in Table 1). All of these observations indicate that the conversion of *p*-xylylene dibromide at the initial period of the reaction is catalyzed more efficiently by the alkynylcopper complexes than by CuI and that gradual increase in the yields and molecular weights of the polymer in the reaction using the alkynylcopper catalyst continues after consumption of the monomer similarly to other polycondensation reactions.

Since polymerization reactions catalyzed by CuBr and by $CuBr_2$ afford similar results (runs 20 and 21), the catalytic activity does not vary depending on the initial Cu valency of the catalyst. Oxidative addition of an organic halide to a Cu(I) complex to afford a Cu(II) species[24] has been postulated in the living radical polymerization of methyl methacrylate (MMA).[25] Addition of 1,10-phenanthroline to the reaction mixture catalyzed by CuI or use of $CuBr_2(phen)_n$ ($n = 1, 2$) as the catalyst results in formation of a polymer with a high content of unit **a** in moderate to good yields (runs 17, 22, and 23).

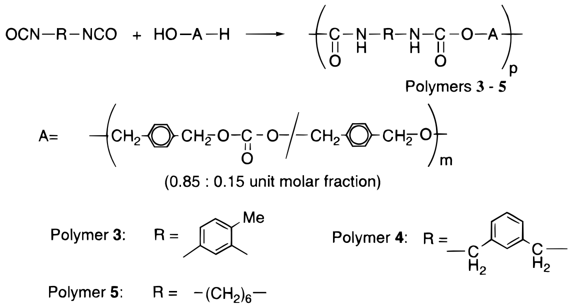
Characterization of Terminal Groups of 1. Oligomers obtained from the above polycondensation in a short period show a relatively sharp NMR peak at δ 4.72 due to CH_2Br hydrogens and an IR peak at 600 cm^{-1} that is assigned to the ν(C–Br) vibration. Polymer **1** obtained from the polycondensation after 4 h (run 1 in Table 1) does not give rise to the NMR peak corresponding to CH_2Br hydrogens, as shown in Figure 1a. The spectrum shows a small triplet at δ 5.18 and a doublet at δ 4.47, the latter of which overlaps with the broad peak due to the CH_2 hydrogens of unit **b**. These two signals are assigned to the OH and the CH_2 hydrogens of terminal CH_2OH groups because the addition of D_2O causes H–D scrambling between the OH hydrogens of terminal groups and added water, and turns the doublet to a singlet and removes the triplet. The $^{13}C\{^1H\}$ NMR spectrum of polymer **1** also shows a peak due to the CH_2 carbon of the terminal group at δ 62.0, which is at a position similar to the aliphatic carbon peak of *p*-xylylene glycol. Polymer **1**, when obtained from the reaction under different conditions, often does not show clear NMR signals of the terminal CH_2OH hydrogens, probably due to overlapping with the CH_2O hydrogen peak in the main chain and to relatively high molecular weights. These results indicate that the oligomer formed at the initial period of polymerization has CH_2Br terminal groups which undergo further polycondensation or are converted into CH_2OH terminal groups.

To confirm the presence of terminal CH_2OH groups in **1**, a reaction with an alkyl isocyanate was examined. Heating of an NMP (*N*-methylpyrrolidone) solution of a mixture of **1** and *n*-hexyl isocyanate results in formation of polymer **2** whose ends are capped with $-OCONHC_6H_{13}$ groups as shown in the following equation.



$$2\ C_6H_{13}NCO + HO{-}X{-}H \longrightarrow C_6H_{13}NH{-}C(=O){-}O{-}X{-}C(=O){-}NH{-}C_6H_{13}$$

Scheme 1. Polyaddition of 1 with Diisocyanate



The ^1H NMR spectrum of **2** gives rise to new peaks at δ 5.1, 1.3, and 0.9, which are assigned to the CH_2NHCO group, the other CH_2 hydrogens of the hexyl group, and CH_3 hydrogens, respectively.

The terminal CH_2OH group is not formed through degradation of the polymer because heating **1** in the presence of CuI does not cause a decrease in the molecular weights. The formation of terminal CH_2OH groups in the growing polymer chain during polycondensation can be accounted for by assuming hydrolysis of the C–Br bond[26] or decarboxylation of an intermediate alkyl carbonate complex, –OCOOCu.[27] The former mechanism seems to be less plausible since addition of a small amount of water to the polymerization mixture does not change the ratio between unit **a** and unit **b** significantly.

The CH_2OCH_2 linkage in polymer **1** is probably formed through condensation of CH_2OH and CH_2Br terminal groups on the basis of the following grounds. The reaction of *p*-xylylene dibromide with polymer **1** having CH_2OH end groups (units **a**:**b** = 97:3) in the presence of CuI in NMP gives polymer with a higher content of unit **b** (unit **a**:unit **b** = 87:13) and with higher molecular weight than the starting polymer. The increment of the content of unit **b** by increasing the reaction time also agrees with the observation that the CH_2OH terminal group of the growing polymer chain is responsible for formation of unit **b**.

Polyaddition of 1 with Diisocyanates. Terminal CH_2OH groups of **1** are expected to add to the N=C=O bonds of a diisocyanate to connect molecules of **1** through bisurethane groups. Scheme 1 shows the conceptually possible polyaddition reaction using **1** as the macromonomer.

Reaction of polymer **1** with 4-methyl-1,3-benzenediisocyanate proceeds smoothly at 100 °C to give a new polymer **3** as a light brown solid. The IR spectrum of **3** shows new peaks at 3324 and 1530 cm^{-1} which are assigned to the ν(NH) and ν(CN) vibrations of the urethane group. The ν(C=O) peak in the urethane linkage appears at 1740 cm^{-1} and overlaps in part with the corresponding peak of unit **a** in the polymer chain. Figure 3 shows the ^1H NMR spectrum containing a peak due to the NH hydrogen at δ 8.32 which is a reasonable position as the NH hydrogen of the urethane group. Peaks due to methyl hydrogens are also observed around δ 2.0. Comparison of GPC traces (Figure 4) of **3** and the parent polymer **1** clearly shows an increase in the molecular weight of the polycarbonate caused by polyaddition of the terminal OH groups to the diisocyanate. Polyaddition of **1** with *m*-xylylenediisocyanate also affords polymer **4** as shown in Scheme 1. The ^1H NMR spectrum of **4** shows peaks due to the above structural unit (**A**) derived from the macromonomer and

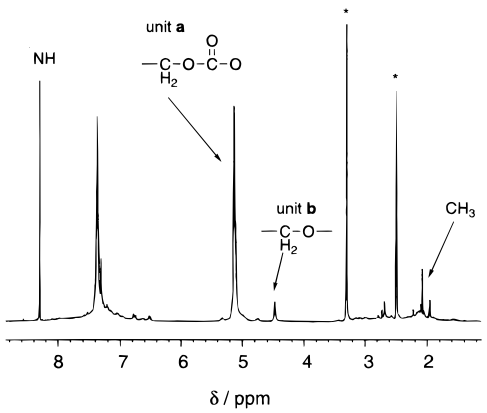


Figure 3. ^1H NMR spectrum of **3** at 400 MHz in DMSO-d_6. Peaks with an asterisk are due to the solvent and water contained in it.

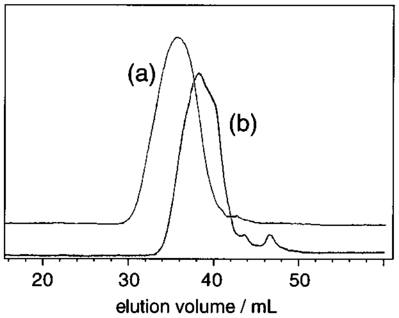


Figure 4. Comparison of the GPC chromatograms of (a) **3** (M_n = 15 600 and M_w = 28 800) and (b) **1** (M_n = 5900 and M_w = 9600) used as the starting material in the synthesis of **3**. Molecular weights are referred to a polystyrene standard.

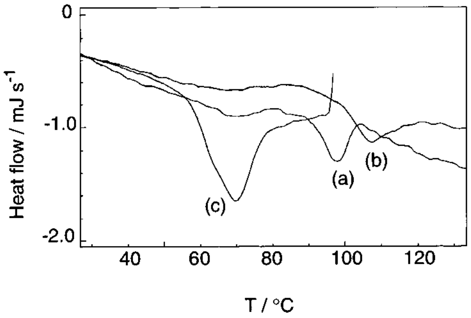


Figure 5. DSC scan of (a) **1** (M_n = 9200 and M_w = 13 700), (b) **3** (M_n = 18 000), and (c) **5** (M_n = 19 900) obtained at a heating rate of 10 °C min^{-1} under helium.

hydrogen peaks at δ 5.15 and δ 4.18 which are assigned to the CH_2 hydrogens of CH_2OCONH and CH_2NHCOO groups. Polyaddition of **1** to 1,6-hexanediisocyanate to lead to **5** does not occur at the above polymerization temperature. The desired product is obtained only by examining the polyaddition of **1** with low molecular weight to 1,6-hexanediisocyanate at an elevated temperature (150 °C); the product contains a major fraction with high molecular weight (M_n = 19 900) accompanied by a minor fraction with M_n = 3600.

Figure 5 shows the differential scanning calorimetry (DSC) curves of polymers **1**, **3** and **5**, showing the glass transition temperatures (T_g) at 92, 108, and 69 °C, respectively. Introduction of a rigid bisurethane unit, $-CONHC_6H_3(Me)NHCO-$, as well as increasing the molecular weight results in a higher T_g for **3** than **1**. Polymer **5** shows a lower T_g than the parent polymer **1** despite its higher molecular weight, indicating that the soft bisurethane unit, $-CONH(CH_2)_6NHCO-$, renders the polymer chain more flexible than **1**. The T_g of polycarbonates seem to be influenced largely by the structure of the diol moiety. The polycarbonate of a bisphenol A derivative has a T_g at 160 °C, while the T_g of alkylene polycarbonates with a highly flexible main chain structure ranges from −50 to +35 °C.[28]

Conclusion

Polycondensation of *p*-xylylene dibromide with M_2CO_3 in the presence of a Cu containing catalyst affords poly[(*p*-xylylene carbonate)-*co*-(*p*-xylylene oxide)]. Alkynylcopper complexes or a mixture of CuI and 1,10-phenanthroline effectively converts the monomer into the corresponding polymer. Since the terminal group in the growing polymer chain is converted from CH_2Br to CH_2OH during the polymerization, both the condensation of the CH_2Br group with CO_3^{2-} and that of the CH_2OH group with CO_3^{2-} occur under the reaction conditions. The terminal CH_2OH group of the polymer readily reacts with the N=C=O group of several organic diisocyanates. The resulting polymers have a unique structure containing macromonomer units bonded through aromatic or aliphatic bisurethane groups and show different values of T_g depending on the diisocyanate used.

Experimental Section

Materials and Measurements. All of the manipulation were performed under nitrogen using standard Schlenk techniques. NMP was dried over CaH_2 and distilled prior to use under nitrogen. $[Cu(C{\equiv}CPh)(PPh_3)]_4$, $Cu(C{\equiv}CC_3H_7)$,[29] $CuBr_2(phen)$, and $CuBr_2(phen)_2$[30] were prepared according to literature procedures. CuI (98%), Li_2CO_3 (99%), Na_2CO_3 (anhydrous), K_2CO_3 (anhydrous), Rb_2CO_3 (99%), and Cs_2CO_3 (99%) were purchased from Strem Chemicals Inc. and used as received. Organic chemicals are from a commercial source (Tokyo Kasei Co.) and used without further purification. GC measurement was carried out on a Shimadzu GC-8A equipped with a 2 m column packed with Silicone OV-1. IR and NMR spectra were recorded on a JASCO-IR 810 spectrophotometer and a JEOL EX-400 spectrometer, respectively. GPC analyses were carried out by a Toso HLC 8020 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), using a dimethylformamide (DMF) solution of LiBr (0.01 M) as the eluent with a flow rate of 1.0 mL min^{-1} and with RI and UV detectors. DSC analyses were performed on a Shimadzu DSC-50.

Polycondensation of *p*-Xylylene Dibromide and K_2CO_3 Catalyzed by CuI. To an NMP (5 mL) dispersion of a mixture of CuI (19 mg, 0.10 mmol) and K_2CO_3 (2.1 g, 15 mmol) was added *p*-xylylene dibromide (0.66 g, 2.5 mmol). The reaction mixture was stirred at 100 °C for 4 h under CO_2 atmosphere (1 atm). After removal of the insoluble material by filtration, the filtrate was evaporated under high vacuum to give a light brown solid. The solid was washed with methanol, ether, and aqueous EDTA (ethylenedimainetetraacetic acid) solution in this order to give **1** as a colorless solid (0.20 g, 48%). IR (KBr, cm^{-1}): 2964 (m), 2890 (w), 1738 (s), 1444 (m), 1383 (s), 1230 (s), 934 (s), 786 (s). ^1H NMR (400 MHz in dimethyl-d_6 sulfoxide (DMSO-d_6): δ 7.2−7.6 (m, C_6H_4), 5.18 (t, *J* = 5 Hz, $-CH_2OH$), 5.14 (s, $CH_2O(C{=}O)O$), 4.50 (s, CH_2OCH_2), 4.47 (d, *J* = 5 Hz, $-CH_2OH$). ^{13}C NMR (100 MHz in DMSO-d_6): δ 154.3 ($-O(C{=}O)O-$), 142.6, 138.0, 129.1, 128.0, 127.5, 127.4 (aromatic carbons), 72.3 (CH_2 of unit **a**), 68.1 (CH_2 of unit **b**), 62.0 ($-CH_2OH$).

Reactions of *p*-xylylene dibromide and Li_2CO_3, Na_2CO_3, Rb_2CO_3, and Cs_2CO_3 as well as those in the presence of phenylacetylene or diphenylacetylene were carried out in a similar manner.

Polycondensation of *p*-Xylylene Dibromide and K_2CO_3 Catalyzed by CuI in the Presence of 1,10-Phenanthroline. To an NMP (5 mL) dispersion of a mixture of CuI (19 mg, 0.10 mmol), K_2CO_3 (2.1 g, 15 mmol), and 1,10-phenanthroline (36 mg, 0.20 mmol) was added *p*-xylylene dibromide (0.66 g, 2.5 mmol). The reaction mixture was stirred at 100 °C for 4 h under CO_2 atmosphere (1 atm). The solution obtained from removal of the insoluble material by filtartion was gradually poured into aqueous EDTA solution (500 mL) to cause separation of a yellow solid, which was washed with methanol and ether to give **1** (0.29 g, 57%).

Polycondensation of *p*-Xylylene Dibromide and K_2CO_3 Catalyzed by $[Cu(C\equiv CPh)(PPh_3)]_4$. To an NMP (5 mL) dispersion of a mixture of $[Cu(C\equiv CPh)(PPh_3)]_4$ (45 mg, 0.10 mmol) and K_2CO_3 (2.1 g, 15 mmol) was added *p*-xylylene dibromide (0.66 g, 2.5 mmol). The reaction mixture was stirred at 100 °C for 4 h under CO_2 atmosphere (1 atm). The solution obtained from removal of the insoluble material by filtration was gradually poured into aqueous EDTA solution (500 mL) to give a yellow solid. The solid was washed with ether and dissolved in NMP (0.5 mL), which was precipitated from methanol to give **1** (0.30 g, 73%).

Reaction of 1 with *n*-Hexyl Isocyanate. A mixture of polymer **1** (0.15 g) and *n*-hexyl isocyanate (0.084 g) was dissolved in NMP (1 mL) with stirring at room temperature. After the reaction mixture was heated for 8 h at 100 °C, the solvent was evaporated to dryness under high vacuum. Washing the resulting solid repeatedly with MeOH affords an end-capped polymer **2** (0.080 g). ^1H NMR (90 MHz in DMSO-d_6): δ 7.4 (m, aromatic hydrogens), 5.2 (s, CH_2OCO), 5.1 (s, CH_2-NHCO), 4.6 (broad, CH_2O), 1.3 (broad, CH_2), 0.9 (t, CH_3).

Polyaddition of 1 with Diisocyanates. Polymer **1** used for polyaddition reaction with 4-methyl-1,3-benzenediisocyanate and with *m*-xylylenediisocyanate in the present study was prepared by polycondensation of *p*-xylylene dibromide (50 mmol) and K_2CO_3 (150 mmol) catalyzed by CuI (2.0 mmol) in the presence of phenanthroline (4.0 mmol) in NMP (50 mL) for 70 h at 100 °C. The molecular weights of the polymer were determined by GPC as $M_n = 9200$, $M_w = 13\,600$, respectively. $[\eta]_{inh} = 0.13$ dL g^{-1}. The ratio between structural units **a** and **b** is 85:15 from the ^1H NMR spectrum. Other macromonomer with lower molecular weights are prepared by variation of the polymerization conditions.

An NMP (1 mL) solution of **1** (88 mg, 0.11 mmol) and 4-methyl-1,3-benzenediisocyanate (20 μL, 0.14 mmol) was stirred at 100 °C for 18 h under nitrogen. After heating the solvent was evaporated under high vacuum to leave a brown solid, which was washed with methanol and dried in vacuo to give **3** as a light brown solid (73 mg, 68%). IR (KBr, cm^{-1}): 2950 (w), 1741 (s), 1705 (m), 1420 (w), 1384 (w), 1262 (s), 1230 (s). ^1H NMR (400 MHz in DMSO-d_6): δ 8.32 (NH), 7.3−7.5 (aromatic hydrogens), 5.10 ($CH_2O(C{=}O)O$), 4.55 (CH_2OCH_2), 2.05 and 1.95 (CH_3).

Polymer **4** was obtained similarly. IR data (KBr, cm^{-1}): 3324 (m), 3060 (w), 2964 (w), 2878 (w), 1740 (s), 1530 (m), 1258 (s), 1236 (s), 1090 (m). ^1H NMR (400 MHz in DMSO-d_6): δ 7.37 (aromatic), 5.15 (CH_2OCOO), 5.00 (CH_2OCONH), 4.48 (CH_2O), 4.18 (CH_2NHCOO). $^{13}C\{^1H\}$ NMR (100 MHz in DMSO-d_6): δ 158.3 (NHCOO), 154.6 (OCOO), 135.5, 133.6, 128.2, 126.4 (aromatic carbons), 68.6 (CH_2OCOO), 65.0 (CH_2-OCONH), 43.0 (CH_2NHCOO).

Preparation of **5** was carried out by a similar reaction of **1** having the molecular weight $M_n = 1800$, with 1,6-hexanediisocyanate at 150 °C. IR data (KBr, cm^{-1}): 3020 (w), 2932 (m), 2856 (m), 1743 (s), 1676 (s), 1451 (m), 1386 (m), 1260 (s), 1235 (s), 933 (m), 787 (m). ^1H NMR data (400 MHz in DMSO-d_6): δ 7.05−7.50 (aromatic hydrogens), 5.14 (s, CH_2OCOO), 4.99 (s, CH_2OCONH), 4.49 (s, CH_2O), 2.93 (s, CH_2NH), 1.31 and 1.21 (s, $(CH_2)_4$). $^{13}C\{^1H\}$ NMR (100 MHz in DMSO-d_6): δ 154.3 (OCOO), 135.5, 128.2, 128.1, 127.9, 127.5, 126.4 (aromatic carbons), 68.6 (CH_2OCOO), 64.5 (CH_2OCO), 62.5 (CH_2NH), 30.0, 29.3, 26.0, 25.9 ($(CH_2)_4$).

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(20) Previously we have reported the CuI catalyzed condensation of *p*-xylylene dibromide with K_2CO_3 to give the polymer containing units **a** and **b** in a 30:70 ratio.[11] The reaction was carried out by connecting the flask to a rubber balloon containing atmospheric pressure of CO_2. Further studies on the reaction have revealed that the reaction under CO_2 flow gives the polymer having unit **a** with higher content than the above closed reaction system. Polycondensation reactions in Table 1 were carried out under CO_2 flow.

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