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Synthesis and Properties of Poly(monocyclic orthocarbonate)s

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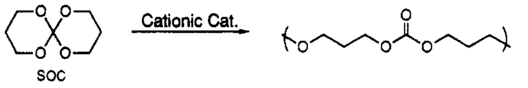
ABSTRACT: Aromatic poly(monocyclic orthocarbonate)s were synthesized by the reaction of 2,2-dichloro-1,3-benzodioxole (1) with various aromatic diphenols, and their properties were examined. Yields of the polymers were quantitative, independent of the structure of the diphenols. Number-average molecular weights ($\bar{M}_n$) ranged from 14 000 to 69 000 and increased with increasing nucleophilicity of the phenolic hydroxy group. Structural evidence for the poly(monocyclic orthocarbonate)s was obtained from its ^{1}H-NMR, ^{13}C-NMR, and IR spectra as well as elemental analysis. All polymers were amorphous and formed clear flexible films by casting from solution. The glass transition temperatures (T_g) of the polymers were in a range from 88 to 135 °C. The polymers lost 10% of their weight at around 340 °C under nitrogen. They were fairly stable toward electrophilic agents such as BF$_3$OEt$_2$, hydrogen chloride, or acetyl chloride in chlorobenzene at 100 °C for 12 h.

Introduction

Orthocarbonates are thermally stable and generally unreactive to alkali but quite susceptible toward electrophilic agents such as protonic and Lewis acids. This is the case even for spirocyclic derivatives such as spiroorthocarbonate (SOC). When aliphatic SOCs are treated with a cationic catalyst such as BF$_3$OEt$_2$, they readily undergo ring-opening isomerization polymerization to give poly(ether carbonate) efficiently (eq 1).[1,2] SOCs are interesting monomers showing expansion in volume on cationic ring-opening polymerization.[2] From our experiments, we have concluded that 2,2-spirobis(1,3-benzodioxole) (2) is only slightly reactive toward cationic catalysts, even under severe conditions,[3] although cationic polymerization of 2 with BF$_3$OEt$_2$ has been reported to give low molecular weight polymer.[4] Since 2 is easily prepared from catechol and 2,2-dichloro-1,3-benzodioxole (1) in quantitative yield (eq 2),[5] introduction of such structures into a polymer main chain can be expected to lead to a highly acid- and alkali-resistant polymer with good thermal stability. We have recently reported the first poly(spiroorthocarbonate) (3) which is prepared by the reaction of 2,2,6,6-tetrachlorobenzo[1,2-*d*:4,5-*d'*]bis[1,3]dioxole (4) with 1,2,4,5-tetrahydroxybenzene (5) (eq 3).[6] The polymer 3 is chemically and thermally stable and has a high crystallinity probably due to its high molecular symmetry. Thus, the introduction of the aromatic SOC structure into the polymer main chain produces a polymer with both novel structure and properties. Aromatic poly(orthocarbonate)s (6), which are prepared by the reaction of dichlorodiphenoxymethane with aromatic diphenols (eq 4), have already been prepared by Takekoshi. As expected from their structure, they are resistant to alkali but decompose under acidic conditions at elevated temperature.[7] Another possible aromatic poly(orthocarbonate) is poly(monocyclic orthocarbonate), e.g., eq 5, of which property would be interesting in comparison with those of 3 and 6.



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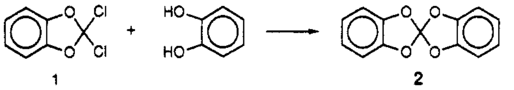

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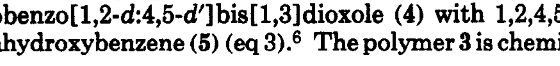

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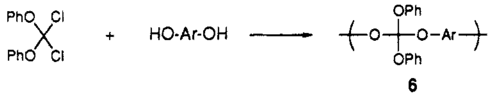

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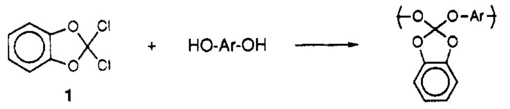

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Polymers bearing cyclic structures in the main chain generally have high melting points and T_g, because of their restricted rotation. Poly(vinylformal), which has five-membered acetal rings in the polymer main chain, is used as an adhesive for metals and molding materials[8] and actually possesses a much higher T_g and tenacity than the corresponding open-chain counterpart. Double-chain polymers with either ladder or spiro structures are theoretically more chemically and thermally stable than their open-chain counterparts.[9] Thus, the thermal and chemical stability of a polymer can be enhanced by introduction of the cyclic structure in the polymer main chain. Polycarbonate has excellent mechanical strength, high crystallinity, and shock- and thermal-resistant properties.[8] The poly(monocyclic orthocarbonate)s can be regarded as cyclic acetal derivatives of the polycarbonate. In this paper the synthesis and properties of a new class of aromatic poly(orthocarbonate)s, poly(monocyclic orthocarbonate)s, are described.

Results and Discussion

Model Study. To find proper conditions for the polycondensation and to examine the stability of the proposed aromatic poly(monocyclic orthocarbonate) in comparison with 3 and 6, a model study was carried out using three monocyclic orthocarbonates, 7–9. These compounds were prepared by reaction of 1 with phenol, *p*-cresol, or ethanol (eq 6) in refluxing ether, according to the reported procedure for 7[5] and 9.[10]

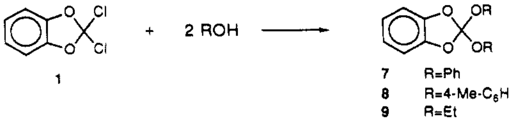

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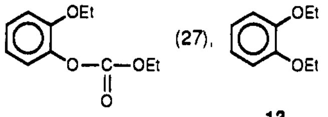
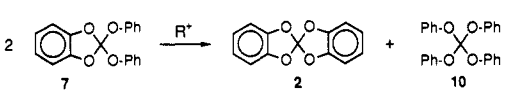
Table I
Reactions of 7–9 with Electrophilic Agents[a]

run	substrate	electrophilic agent (mol %)	recovery, %	product (yield, %)
1	7	CH_3COCl (10)	100	
2	7	HCl (2×10^4)[b]	56	catechol (20), phenol (12)
3	7	BF_3OEt_2 (10)	57	**2** (27), **10** (12)
4	8	BF_3OEt_2 (10)	56	**2** (32), **11** (7)
5	9	BF_3OEt_2 (10)	0	 **12** (27), **13** (10)

[a] The reaction was carried out in a sealed tube. Conditions: solvent, chlorobenzene (C = 1.0M); 100 °C; 12 h. [b] Gaseous HCl.

Compounds 7–9 reacted with a few electrophile agents at 100 °C in chlorobenzene (C = 1.0 M), and the results are shown in Table I. Inspection of the data of Table I suggests that aromatic monocyclic orthocarbonates such as **7** are very stable toward acetyl chloride (run 1), although the alkyl orthocarbonate rapidly reacts with it.[11] When 200 equiv of dry gaseous hydrogen chloride was passed through a solution of **7**, 44% of **7** was consumed to afford a mixture of catechol and phenol (run 2). Meanwhile, in the reaction of **7** with BF_3OEt_2 57% of **7** was recovered and 27% of **2** and 12% of tetraphenoxymethane (**10**) were isolated as products (run 3) (eq 7). Similarly, 56% of **8** was recovered and 32% of **2** and 7% of a tetraphenoxymethane derivative (**11**) were isolated as products (run 4) (eq 8). Formation of these products is presumably attributable to an acid-catalyzed acetal-exchange reaction. Meanwhile, yields of the obtained tetraphenoxymethane derivatives (**10** and **11**) were smaller than that of **2**, indicating the occurrence of some decomposition during the reaction. These results demonstrate that acyclic compounds (**10** and **11**) are less stable than the spirocyclic compound **2**.



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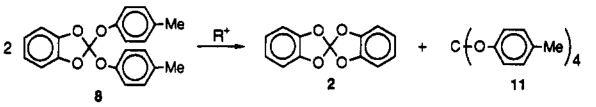
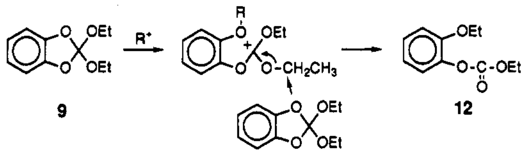


(8)

In contrast, diethyl-substituted monocyclic orthocarbonate **9** was extremely sensitive toward BF_3OEt_2 and was completely decomposed under the same conditions (run 5). Both ester (**12**) and ether (**13**) (Table I) were isolated as products by column chromatography and identified by their IR and NMR spectral data. These results clearly indicate that aromatic monocyclic orthocarbonate is more stable than an alkyl derivative toward electrophilic agents. The acid-labile nature of **9** can be elucidated by assuming that another monocyclic orthocarbonate molecule acting as a nucleophile can easily attack at the aliphatic carbon atom adjacent to oxygen of carbenium species first formed by the reaction of **9** with an electrophilic agent (eq 9). Therefore, such a nucleophilic reaction should be suppressed in the case of aromatic monocyclic orthocarbonate, owing to difficulty of nucleophilic substitution on an aromatic ring (eq 10). Thus, acid stability based on the aromatic group of a monocyclic orthocarbonate was confirmed. These results suggest that an aromatic diol should be used as the diol segment for the desired polycondensation.



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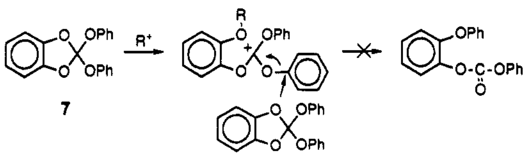
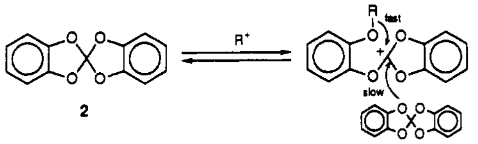


(10)

Spiroorthocarbonate **2** should be the most stable among the orthocarbonate derivatives **7**, **8**, **10**, and **11**, because it was obtained in a higher yield than those of the acyclic compounds (**10** and **11**) (Table I, runs 3 and 4) upon reaction of **7** and **8** with BF_3OEt_2. The acid-stable nature of **2** can be elucidated by assuming a proximity effect[12] (eq 11). Namely, the neighboring ether group (–OR) of a carbenium species formed by the initial reaction of **2** with an electrophilic agent (R^+) much more easily attacks the cationic center of the carbenium species than another spiroorthocarbonate molecule. On the other hand, acyclic orthocarbonate (**10**) would be more likely to undergo an intermolecular reaction (eq 12), because the concentration of **10** is much greater than that of the ether function (PhOR) and no proximity effect can be operative. Therefore, it is assumed that the proposed poly(monocyclic orthocarbonate)s should have medium stability toward electrophilic agents between those of **3** and **6**.



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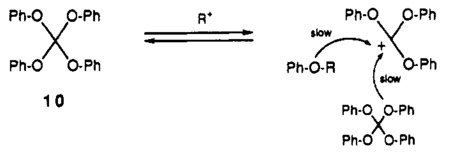

(12)

Synthesis of Polymer. Synthesis of poly(monocyclic orthocarbonate) (**14**) was achieved by the polycondensation of **1** with 4,4′-isopropylidenediphenol (**15**) under a nitrogen stream (eq 13). To find the optimum conditions, the following factors influencing the polymerization were

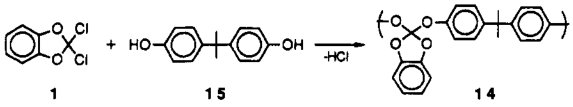

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Table II
Effect of Base on the Polycondensation of 1 with 15[a]

run	base	yield,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	2,6-lutidine	82	6000	4200	1.44
2	CH_3COONa	46	4000	3600	1.09
3	none[d]	100	14000	8700	1.56

[a] Conditions: benzene, 3.0 mL; monomer, 5 mmol; base, 10 mmol; 40 °C; 2.5 h. [b] Insoluble part in methanol. [c] Estimated by GPC (based on polystyrene standards; eluent, THF). [d] Under a nitrogen stream.

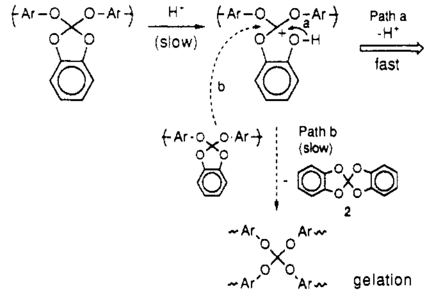
studied in detail: base, solvent, monomer concentration, and temperature, in terms of yield and molecular weight of the polymer. The results are summarized in Table II.

Quenching of hydrogen chloride produced during the polycondensation with bases such as triethylamine, pyridine, sodium hydroxide, sodium carbonate, and sodium acetate is limited by the fact that 1 readily reacts with various organic and inorganic bases.[10] A bulky amine, 2,6-lutidine, was used first, but the yield (82%) and molecular weight of 14 ($\bar{M}_n$ 4200) were not satisfactory. The reaction system became heterogeneous (2,6-lutidine hydrochloride) during the reaction, and consequently stirring of the mixture was very difficult, eventually causing low reaction efficiency (run 1). In the case of sodium acetate the yield of 14 was only 46% (run 2). The low yield is probably caused by the reaction of 1 with sodium acetate. Acetic acid, formed by the reaction of sodium acetate with hydrogen chloride generated, also might disturb the polycondensation because the reaction of 1 with acetic acid is known to occur.[10] When the removal of hydrogen chloride was achieved by passing nitrogen through the reaction mixture, both a quantitative yield and a higher molecular weight ($\bar{M}_n$ 8700) were attained (run 3).

Because of the model reaction of 1 with phenols proceeded efficiently in ether, the polycondensation of 1 with 15 was similarly carried out in ether. However, 14 gradually precipitated during the polymerization. Although 14 was obtained in quantitative yield, molecular weight was low ($\bar{M}_n$ 16 000) (Table III, run 1). To obtain a homogeneous polymerization system, the solubility of 14 was investigated. 14 was soluble in benzene, chloroform, tetrahydrofuran, dioxane, dimethylformamide, etc., but insoluble in methanol, ether, acetone, acetonitrile, hexane, dimethyl sulfoxide, etc. Meanwhile, 1 is so reactive that even at room temperature 1 reacts well with weak nucleophiles such as alcohol, amine, amide, ester, carboxylic acid, water, etc.[10] Thus, it concluded that the polymerization should be carried out in inert solvents which were capable of dissolving the polymer such as benzene.

First, the effect of solvent on the $\bar{M}_n$ and yield of the polymer was examined (Table III). More polar solvents such as chlorobenzene (dielectric constant, ϵ_r 5.71) and nitrobenzene (34.82) gave 14 with a higher molecular weight compared with less polar solvents such as benzene (2.28) and diphenyl ether (3.65). These results indicate that the $\bar{M}_n$ of 14 increases with increasing solvent polarity. The rate of the polymerization seemed to be faster in more polar solvents, which consequently causes efficient polycondensation. However, polycondensation in chlorobenzene gave the highest $\bar{M}_n$ (29 000) of the solvents tested. This would be difficult to remove hydrogen chloride from a high polar solvent such as nitrobenzene. Therefore, effects of temperature, concentration, and time were investigated in chlorobenzene.

The temperature and concentration affording the best results were the refluxing temperature of chlorobenzene and $C = 2.5$ M (run 7), respectively, as judged from Table III. In the reaction system with the highest concentration (run 6) the viscosity became too high and stirring of the mixture was impossible, eventually causing a low reaction efficiency. The required minimum reaction time was 3 h because the yield and the molecular weight of the polymer were changed little at more than 4 h (runs 7, 9, and 10). The key point of this polycondensation would be how to shift the equilibrium of polymerization–depolarization toward the polymer. To this end, the removal of hydrogen chloride generated during the polycondensation is important. The removal of hydrogen chloride was achieved by sparging with nitrogen gas during the polymerization. The removal of hydrogen chloride is also needed to suppress possible side reactions such as acid-catalyzed acetal-exchange leading to gelation. Takekoshi has reported that poly(orthocarbonate)s (6), synthesized by the polycondensation of dichlorodiphenoxymethane with diphenols, afforded an unstirrable gel without base at ambient temperature or below.[7] The acid-catalyzed acetal-exchange reaction would result in gelation, when the polycondensation is carried out under such acidic conditions. But in our system no gelation was observed in spite of similar acidic conditions, partly because of the efficient removal of hydrogen chloride generated in the system. This difference can also be explained by the proximity effect[12] which originated from the monocyclic orthocarbonate structure having an ortho-substituted benzene ring (eq 14), as discussed in the model study. As discussed above, the orthocarbonate ring of the polymer does not open to participate in the gelation via an acetal-exchange reaction along path b (eq 14). Or, even if the ring opens, the ring-closure reaction to the original orthocarbonate ring predominantes (path a). In fact, SOC 2 probably formed in the gelation was not detected in any polycondensation.



(14)

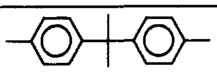
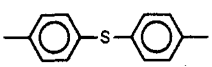
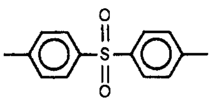
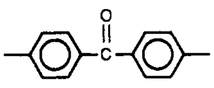
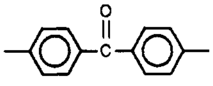
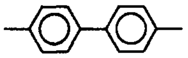
Under the above optimized conditions, high molecular weight poly(monocyclic orthocarbonate)s (**20**–**23**) were successfully prepared from 1 and a variety of bifunctional phenols (**16**–**19**) by removing gaseous hydrogen chloride with a nitrogen stream (Table IV). Poly(monocyclic orthocarbonate) having the highest molecular weight was obtained with 4,4′-thiodiphenol (**16**) which can be regarded as a diphenol of higher nucleophilicity. Diphenols bearing electron-withdrawing groups such as 4,4′-dihydroxydiphenyl sulfone (**17**) and 4,4′-dihydroxybenzophenone (**18**) gave corresponding polymers **21** and **22** with lower molecular weights. The molecular weight of the polymer seems to depend on the nucleophilicity of the phenolic hydroxy group. The rate of the polycondensation appeared to be larger with more nucleophilic diphenols, consequently leading to efficient polycondensation and thereby a higher molecular weight. **17** reacted with 1 to yield the corresponding polymer **21** with poor solubility presumably caused by the polar functional groups of **21**, which was gradually precipitated during the polycondensation. The obtained **21** was soluble in chloroform and dimethyl

Table III
Polycondensation of 1 with 15 under Various Conditions

run	solvent	[C], M	time, h	temp, °C	yield,[a] %	$\bar{M}_w$[b]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1[c]	ether	2.0	3.0	refl	100	32 000	16 000	1.98
2	benzene	3.3	2.5	40	100	14 000	8 700	1.56
3	Ph_2O	3.3	2.5	40	99	33 000	18 000	1.86
4	PhCl	3.3	2.5	40	100	62 000	29 000	2.13
5	$PhNO_2$	3.3	2.5	40	99	48 000	26 000	1.82
6	PhCl	3.3	2.5	refl	100	95 000	43 000	2.21
7	PhCl	2.5	2.5	refl	98	95 000	46 000	2.07
8	PhCl	2.0	2.5	refl	98	76 000	38 000	2.01
9	PhCl	2.5	3.0	refl	99	108 000	48 000	2.25
10	PhCl	2.5	4.0	refl	99	97 000	47 000	2.09

[a] Insoluble part in methanol. [b] Estimated by GPC (based on polystyrene standards; eluent, THF). [c] Polymer was gradually precipitated during the polymerization.

Table IV
Polycondensation of 1 with Various Diphenols[a]

run	diphenol		polymer	yield,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1		15	14	99	108 000	48 000	2.25
2		16	20	97	141 000	69 200	2.04
3[d]		17	21	100	e	e	e
4		18	22	98[f]	90 600	23 300	3.89
5[g]		18	22	95	56 400	14 000	4.03
6		19	23	97	92 100	37 900	2.43

[a] Conditions: solvent, chlorobenzene ([C] = 2.5 M); 3 h; reflux. [b] Insoluble part in methanol. [c] Estimated by GPC (based on polystyrene standards, eluent, tetrahydrofuran). [d] Heterogeneous reaction by gradual precipitation of the polymer formed. [e] Polymer insoluble in tetrahydrofuran. [f] Containing 6% gelled polymer. [g] [C] = 1.25 M.

sulfoxide but insoluble in tetrahydrofuran and dimethylformamide. In the polycondensation of 1 and 18 (run 4) a small amount of gelled polymer (6%) was formed. This gelled polymer may have resulted from the partial acid-catalyzed acetalization of the carbonyl group of 18 with the terminal hydroxy group of the produced 22 which could take place during the polycondensation, because the system was acidic. However, this gelation could be readily prevented by lowering the concentration (run 5).

Characterization of the Polymers. Most polymers derived from the various diphenols were soluble in common solvents (toluene, chloroform, tetrahydrofuran, and dimethylformamide) and formed clear and flexible films by casting from benzene solution. Infrared (IR) spectra of the poly(orthocarbonate)s were recorded from thin films. Neither carbonyl nor hydroxy absorptions appeared in the spectrum of 14 derived from 15. A few characteristic absorptions were observed at 1080–1230 (ether), 1490, and 1590 cm^{-1} (aromatic). ^{1}H-NMR spectra of the poly(monocyclic orthocarbonate)s were well consistent with their orthocarbonate structures. More concrete evidence for the orthocarbonate structure was obtained from their ^{13}C-NMR spectra. ^{13}C-NMR spectra of 14 and its model compound (7) are shown in Figures 1 and 2. Aromatic carbons derived from 1 were confirmed at 122.14 (a), 108.73 (b), and 145.38 (c) ppm which well agreed with 7. Other carbon signals derived from 15 were observed at 149.53 (e), 120.67 (f), 127.55 (g), 147.14 (h), 30.90 (i), and 42.30 (j) ppm. Signals of central orthocarbonate carbons of 7 and 14 were confirmed at 129.50 and 129.54 ppm, respectively, although their signal intensity was weak because they were quaternary carbons of which their relaxation time was longer than those of the other carbons. The corresponding orthocarbonate carbon signals of other poly(monocyclic orthocabonate)s (20–23) appeared at 128.86–129.37 ppm. The ^{13}C NMR chemical shifts of all the polymers are listed in Table V along with those calculated by additivity rules.[13] The observed chemical shifts fairly agreed with the calculated values.

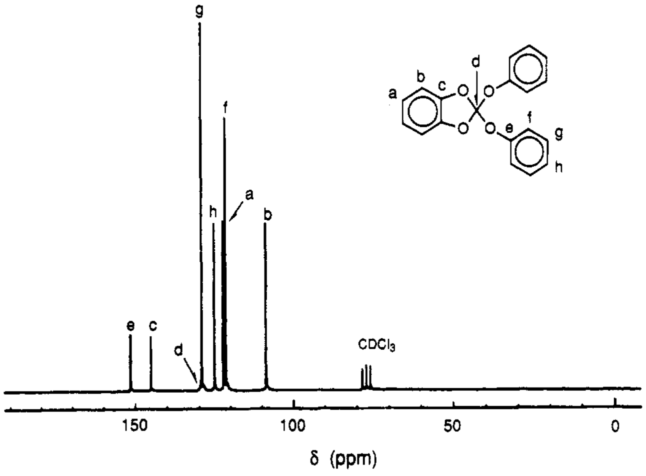
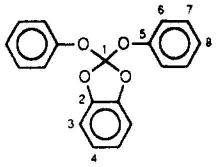
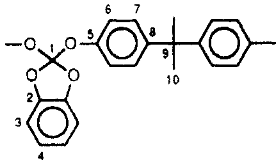
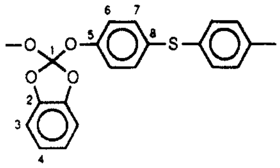
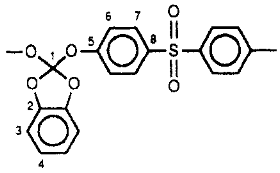
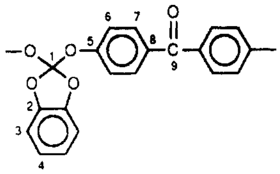
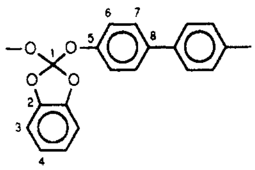


Figure 1. 25-MHz ^{13}C-NMR spectrum of 7 ($CDCl_3$ at 60 °C).

Table V
Observed and Calculated ^{13}C Chemical Shifts for Monocyclic Orthocarbonate 7 and Poly(monocyclic orthocarbonate)s[a,b]

compd		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	7	129.50	144.99 147.8[c]	108.59 108.8[c]	122.14 121.8[c]	151.33 155.4[d]	121.36 115.7[d]	129.15 129.9[d]	125.01 121.1[d]		
	14	129.54	145.38	108.73	122.14	149.53 (148.8)	120.67 (121.4)	127.55 (127.2)	147.14 (145.1)	42.30	30.90
	20	129.34	145.04	108.78	122.47	150.74 (149.8)	122.18 (122.0)	132.02 (131.7)	132.27 (132.3)		
	21	128.86	144.45	109.26	123.20	154.93 (156.4)	121.11 (122.2)	129.49 (127.8)	138.12 (137.3)		
	22	129.00	144.67	109.15	122.91	154.61 (155.0)	120.30 (121.1)	131.65 (130.8)	134.08 (134.3)	194.24	
	23	129.37	145.04	108.76	122.34	150.81 (150.2)	121.58 (121.8)	127.75 (128.1)	137.14 (138.1)		

[a] Condition: solvent, $CDCl_3$; temperature, 60 °C. [b] Chemical shifts in parentheses are calculated by additivity rules, corrected with new parameters determined by 7 ($C\alpha$ = +22.8, $C\beta$ = 7.1, $C\gamma$ = +0.7, $C\delta$ = −3.5). [c] Chemical shifts of 1,3-benzodioxole. [d] Chemical shifts of PhOH.

Table VI
Thermal Properties of Poly(monocyclic orthocarbonate)s

run	polymer	$\bar{M}_n$[a]	Tg,[b] °C	Td,[b,c] °C
1	**14**	48 000	106	345
2	**20**	69 200	78	340
3	**21**	*d*	148	320
4	**22**	14 000	114	325
5	**23**	37 900	129	340

[a] Estimated by GPC (based on polystyrene standards). [b] Heating rate, 10 °C/min. [c] 10% weight loss temperature in nitrogen. [d] $\bar{M}_n$ could not be estimated by GPC because **21** was insoluble in tetrahydrofuran.

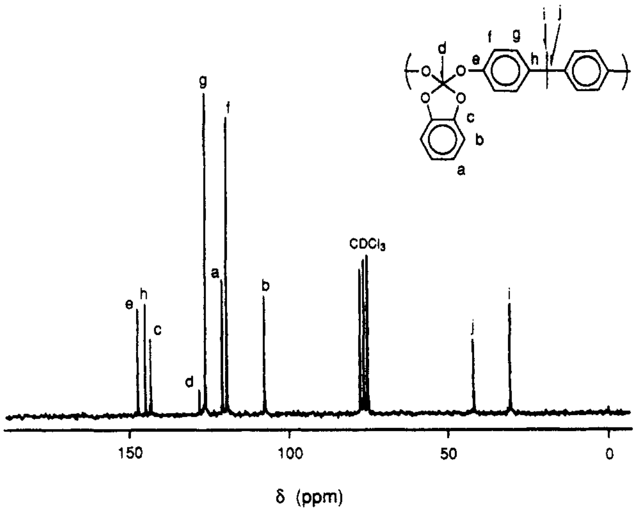


Figure 2. 25-MHz ^{13}C-NMR spectrum of **14** ($CDCl_3$ at 60 °C).

In addition to the spectral data, the data from elemental analyses were consistent with the proposed polymer structure. These results suggest that the polycondensation is quite clean.

Differential scanning calorimetry (DSC) of the poly(monocyclic orthocarbonate)s revealed no clear melting points, but the amorphous materials exhibited glass transition temperature (T_g) (Table VI). The T_g values were significantly lower than those of the corresponding linear polycarbonates. For example, the T_g of **14** was 110 °C, which was ca. 40 °C lower than that of the corresponding linear polycarbonate.[14] Apparently, the less polar orthocarbonate group provides weak intermolecular interaction, which undoubtedly results in the lowering of T_g in comparison with the polycarbonate which has a higher polarity and stronger interaction between polymer chains because of the presence of carbonyl groups. However, the T_g of poly(monocyclic orthocarbonate) (**14**) was higher than that of the corresponding poly(orthocarbonate) (**6**).[7] This observation can be explained by assuming that **14** is

Table VII
Reaction of Polymer 14 with Electrophilic Agents[a]

			recovered polymer[b]			
run	electrophilic agent (mol %)	temp, °C	yield, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	product[c] (%)
1		100	100	35000	2.28	
2	BF_3OEt_2 (10)	100	64[d]	5200	1.88	oligomer (23), **2** (18)
3	BF_3OEt_2 (10)	50	81[e]	8000[f]	4.75	oligomer (12), **2** (11)
4	BF_3OEt_2 (10)	rt	89[e]	9600[f]	7.88	oligomer (9), **2** (9)
5[g]	HCl (2 × 10^3)	100	87	6100	1.50	oligomer (12)
6[g]	HCl (2 × 10^3)	50	81	6700	1.42	oligomer (13)
7[g]	HCl (2 × 10^3)	rt	78	6300	1.41	oligomer (17)
8	CH_3COCl (10)	100	98	6400	1.57	oligomer (2)
9[h]	H_2O	100	100	35000	2.19	

[a] The reaction was carried out in a sealed tube. Conditions: chlorobenzene, $C = 0.5$ M; 12 h; $\bar{M}_n$ of polymer before treatment, 35 000. [b] Insoluble part in methanol. $\bar{M}_n$ was estimated by GPC. [c] Soluble part in methanol. [d] Containing 10% of gelled fraction. [e] Gelled polymer containing a small amount of soluble polymer in THF. [f] $\bar{M}_n$ value of a tetrahydrofuran-soluble polymer of a methanol-insoluble fraction. [g] The reaction was carried out under a nitrogen stream. [h] $C = 0.03$ M in dioxane:H_2O = 10:1 (v/v).

more rigid than **6** because of its monocyclic structure. Thermal stability of the poly(monocyclic orthocarbonate)s was evaluated by thermogravimetric analysis (TGA) under nitrogen. The decomposition temperatures were in the range of 320–345 °C (Table VI). These data seem to suggest that the decomposition temperatures of the polymers depend on the molecular weight rather than on the functional groups in the polymers. For example, the decomposition temperatures of **21** and **22** which had polar functional groups were substantially lower than those of **14** and **20** having less polar functional groups.

Stability. The stability of the obtained polymer toward electrophilic agents was tested using **14** ($\bar{M}_n$ 35 000) in chlorobenzene ($C = 0.5$ M) with the same electrophilic agents as those in the model study under the conditions shown in Table VII. Products from the methanol-soluble fraction obtained by the precipitation of the reaction mixture with methanol were isolated by column chromatography. The products were a mixture of the corresponding oligomers and **2**, as shown in Table VII. Although in the absence of an electrophilic agent no decomposition took place (run 1), some degradation occurred in the presence of electrophilic agents (BF_3OEt_2, hydrogen chloride, and acetyl chloride) to afford the recovered polymer with $\bar{M}_n$ 5200–9600 in 64–98% yield depending on the conditions (runs 2–8) along with the degradation products. Whenever BF_3OEt_2 was used, swellable gelled polymer was formed (runs 2–4). The yield of **14** recovered decreased as the reaction temperature was raising, and yields of oligomer and **2** increased accordingly. These results can be accounted for by assuming an occurrence of the acid-catalyzed degradation of the polymer main chain caused by an *inter*molecular acetal-exchange reaction. However, the IR spectrum of the gelled polymer was nearly the same as that of the original polymer **14**, and therefore the degree of gelation should be small. Thus, the monocyclic orthocarbonate structure of **14** undergoes some acetal-exchange reaction by the catalysis of a strong Lewis acid (see eq 14, path b).

Meanwhile, when a large excess of hydrogen chloride was passed through a chlorobenzene solution of the polymer, the yield of the polymer recovered increased with increasing reaction temperature (runs 5–7). Because the amount of hydrogen chloride incorporated in the solution decreases with increasing temperature, the polymer–monomer equilibrium shifts to the polymer side. When acetyl chloride was examined as an electrophilic agent, a polymer of lower molecular weight was recovered (run 8), along with a very small amount of oligomer (2%). Part of the polymer main chain is broken, probably by hydrogen chloride generated by thermal decomposition of acetyl chloride, rather than by acetyl chloride itself.[15] Polymer **14** was treated with excess H_2O in dioxane at 100 °C for 12 h, but no degradation was observed at all (run 9). Of the three poly(orthocarbonate)s (**3**, **6**, and **14**), poly(monocyclic orthocarbonate) (**14**) seems to have medium stability toward electrophilic agents. Poly(orthocarbonate) (**6**) is completely disintegrated by treatment with 140 °C steam for 1 h or 1 M HCl at 100 °C,[6] whereas no poly(spiroorthocarbonate) (**3**) is decomposed.

Conclusion

A variety of poly(monocyclic orthocarbonate)s were prepared by the reaction of 2,2-dichloro-1,3-benzodioxole (**1**) with diphenols in quantitative yields. These polymers had some chemical and thermal stability, film-forming nature, and relatively high glass transition temperature based on their cyclic structure.

Experimental Section

Materials. Acetyl chloride and BF_3OEt_2 were purified by distillation and stored under argon. Gaseous hydrogen chloride was generated by the reaction of sodium chloride with sulfuric acid (98%) at room temperature, which was dried by passing through concentrated sulfuric acid. 2,6-Lutidine from Tokyo Kasei Kogyo was purified by distillation after refluxing with calcium hydride for several hours. Commercial-grade anhydrous sodium acetate was dried under vacuum at 100 °C for 1 day before use. Dry ether, benzene, and diphenyl ether were obtained by distillation from the sodium benzophenone ketyl. Nitrobenzene and chlorobenzene were washed with concentrted sulfuric acid several times and with aqueous sodium carbonate, followed by drying with calcium chloride and distillating after refluxing with phosphorus pentoxide for several hours. Reagent-grade diphenols (**15**–**19**) from Tokyo Kasei Kogyo were purified by recrystallization from water.

Melting points were measured using a Yanaco mcro melting point apparatus. Thermal analyses were performed with a Shimazu DT-30 (TGA) and a Seiko DSC-200 (DSC). A 10% weight loss temperature by TGA in nitrogen was estimated at a heating rate of 10 °C/min. Glass transition temperatures (T_g) by DSC were taken as the inflection point on the trace. Gel permeation chromatography (GPC) was performed with a Toso GPC system CCP&8000 equipped with both ultraviolet (254 nm) and refractive index detectors and three consecutive linear gel columns, Toso TSK gels G2500H, G4000H, and G5000H at 35 °C (eluting solvent, commercial-grade tetrahydrofuran supplied by Mitsubishi Kasei Corp.; flow rate, 1.0 mL/min). Recycling preparative high-pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry Co., Ltd., LC-908 equipped with both ultraviolet (254 nm) and refractive index detectors and two consecutive linear gel column, JAIGELs 1H and 2H (eluting solvent, commercial-grade inhibitor-free tetrahydrofuran; flow rate, 3.8 mL/min). FT-IR spectra were obtained with a Jasco FT/IR-3 spectrometer. ^1H NMR and ^{13}C

NMR spectra were recorded on JEOL JNM-PMX60Si (^{1}H, 60 MHz), JNM-FX100 (^{13}C, 25 MHz), and JNM-EX90 (^{1}H, 90 MHz; ^{13}C, 22.5 MHz) spectrometers using TMS as an internal standard.

Synthesis of 2,2-Dichloro-1,3-benzodioxole (1). According to the method of Barger[16] and Yagupol'skii,[17], 1,3-benzodioxole (29.6 g, 0.24 mol) and phosphorus pentachloride (102.0 g, 0.48 mol) were mixed in a 200-mL round-bottomed flask under a nitrogen atmosphere and the mixture was heated at 90 °C. The orange mixture became homogeneous, and hydrogen chloride evolved vigorously. Then the mixture was further heated at refluxing temperature for 5 h. Phosphorus trichloride (bp 76 °C) was removed by distillation, and the residual mixture was distilled in vacuo to give a colorless oil. Yield: 40.8 g (89%). Bp: 95 °C (18 mmHg) [lit. [18]bp 82–89 °C 12 mmHg)]. The obtained product was further vacuum distilled two times and then stored under argon in a few sample tubes. IR (neat): 1477, 1238, 1064, 852, 736 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 6.93 (s, C_6H_4).

Synthesis of 2,2-Diphenoxy-1,3-benzodioxole (7).[5] A solution of 25.0 g (0.13 mol) of 1 in 100 mL of ether was stirred in a nitrogen-flowed 200-mL round-bottomed flask to which was added 24.6 g (0.26 mol) of phenol. The reaction flask was immersed in an oil bath, and the mixture was refluxed. During the reaction hydrogen chloride generated was removed by nitrogen flow. After 5 h, the reaction mixture was cooled to room temperature and concentrated by a rotary evaporator. Residual white solid crystal (39.4 g, 99%) was recrystallized from methanol. Mp: 102 °C (lit.[5] mp 100–102 °C). IR (KBr): 1593, 1483, 1255, 1219, 1176, 1161, 1145, 1138, 948, 763, 740, 690 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 6.75 (s, 4 H, C_6H_4), 7.17 (m, 10 H, C_6H_5). ^{13}C-NMR (25 MHz, $CDCl_3$): δ 108.59, 121.36, 122.14, 125.01, 129.15, 129.50, 144.99, 151.33.

Synthesis of 2,2-Bis(*p*-methylphenoxy)-1,3-benzodioxole (8). Compound 8 was prepared from 1 (2.5 g, 13 mmol) and *p*-cresol (2.8 g, 26 mmol) by a method similar to that of 7. The crude yield was 99%. Recrystallization from methanol gave white needles. Mp: 104–105 °C. IR (KBr): 3028, 2922, 1508, 1485, 1253, 1215, 1199, 1165, 1145, 1107, 945, 814, 751 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 2.23 (s, 6 H, CH_3), 6.70 (s, 4 H, C_6H_4), 7.70 (s, 8 H, C_6H_4). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.48; H, 5.44.

Synthesis of 2,2-Diethoxy-1,3-benzodioxole (9).[10] A solution of 10.1 g (0.22 mol) of ethanol and 24.3 g (0.24 mol) of triethylamine in 50 mL of absolute ether was added to a solution of 19.1 g (0.1 mol) of 1 in 20 mL of dried ether at 0 °C over a period of 1 h. After the addition, the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with additional ether and then washed with H_2O. The organic extract was dried over anhydrous $MgSO_4$ at room temperature overnight and evaporated. The obtained oily product was purified by distillation in vacuo (yield, 89%). Bp: 89 °C (3 mmHg) (lit.[10] bp 123 °C (15 mmHg)]. IR (neat): 3065, 2984, 2937, 2909, 1490, 1369, 1198, 1099, 1037, 938, 832, 778, 739 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 1.18 (t, J = 7 Hz, 6 H, CH_3), 3.73 (q, J = 7 Hz, 4 H, CH_2), 6.75 (s, 4 H, C_6H_4).

Synthesis of Polymer. Typical Procedure. Synthesis of 14. A solution of 0.9551 g (5.000 mmol) of 1 in 4.0 mL of absolute chlorobenzene was stirred in a nitrogen-flowed 25-mL round-bottomed flask to which was added 1.1415 g (5.000 mmol) of 15. The solution was stirred at refluxing temperature (132 °C). Hydrogen chloride generated during the reaction was removed by nitrogen flow. After 3 h, the resulting viscous mixture was cooled and diluted with 40 mL of tetrahydrofuran. This solution was added dropwise into 500 mL of methanol containing a small amount of triethylamine. The white fibrous polymer precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day. $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$): 48 000 (2.25). Yield: 99%. IR (film): 3061, 2966, 1508, 1485, 1253, 1228, 1172, 1128, 1101, 1076, 1014, 1003, 914, 833, 814, 798, 736, cm^{-1}. ^{1}H-NMR (90 MHz, $CDCl_3$): δ 1.56 (s, 6 H, CH_3), 6.70 (s, 4 H, C_6H_4), 6.97 (s, 8 H, C_6H_4). ^{13}C-NMR (25 MHz, $CDCl_3$): δ 30.90, 42.30, 108.73, 120.67, 122.14, 127.55, 129.54, 145.38, 147.14, 149.53. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.27; H, 5.16. Analytical and spectral data of other polymers are as follows.

Polymer 20. IR (film): 3112, 3067, 3039, 1590, 1484, 1251, 1225, 1162, 1125, 1080, 1013, 981, 915, 826, 798, 738 cm^{-1}. ^{1}H-NMR (60 MHz, DMSO-d_6): δ 6.87 (d, J = 4 Hz, 2 H, C_6H_2), 7.00 (d, J = 4 Hz, 2 H, C_6H_2), 7.20 (s, 8 H, C_6H_4). ^{13}C-NMR (25 MHz, $CDCl_3$): δ 108.78, 122.18, 122.47, 129.34, 132.02, 132.27, 145.04, 150.74). Anal. Calcd for $C_{19}H_{12}O_4S$: C, 67.85; H, 3.60; S, 9.53. Found: C, 67.82; H, 3.27; S, 9.26.

Polymer 21. IR (film): 3105, 3069, 3044, 1590, 1484, 1326, 1298, 1253, 1224, 1155, 1106, 1074, 837, 800, 741, cm^{-1}. ^{1}H-NMR (60 MHz, DMSO-d_6): δ 6.93 (d, J = 5 Hz, 2 H, C_6H_2), 7.07 (d, J = 5 Hz, 2 H, C_6H_2), 7.40 (d, J = 8 Hz, 4 H, C_6H_2), 7.92 (d, J = 8 Hz, 4 H, C_6H_2). ^{13}C-NMR (22.5 MHz, $CDCl_3$): δ 109.26, 121.11, 123.20, 128.86, 129.49, 138.12, 144.45, 154.93. Anal. Calcd for $C_{19}H_{12}O_6S$: C, 61.95; H, 3.28; S, 8.70. Found: C, 61.65; H, 3.26; S, 8.72.

Polymer 22. IR (film): 3153, 3110, 3068, 1660, 1602, 1502, 1485, 1307, 1277, 1224, 1161, 1110, 919, 771, 740, cm^{-1}. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 6.93 (s, 4 H, C_6H_4), 7.33 (d, J = 9 Hz, 4 H, C_6H_2), 7.77 (d, J = 9 Hz, 4 H, C_6H_2). ^{13}C-NMR (22.5 MHz, $CDCl_3$): δ 109.15, 120.30, 122.91, 129.00, 131.65, 134.08, 144.67, 154.61, 194.24. Anal. Calcd for $C_{20}H_{12}O_5$: C, 72.29; H, 3.59. Found: C, 72.46; H, 3.81.

Polymer 23. IR (film): 3089, 3065, 1605, 1486, 1254, 1225, 1160, 1120, 1005, 823, 815, 796, 739, 680 cm^{-1}. ^{1}H-NMR (60 MHz, $CDCl_3$): δ 6.85 (s, 4 H, C_6H_4), 7.23 (d, J = 9 Hz, 4 H, C_6H_2), 7.43 (d, J = 9 Hz, 4 H, C_6H_2). ^{13}C-NMR (25 MHz, $CDCl_3$): δ 108.76, 121.58, 122.34, 127.75, 129.37, 137.37, 145.04, 150.81. Anal. Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.98. Found: C, 75.28; H, 3.94.

Film Casting (General Procedure). A dried polymer sample (0.5 g) was dissolved in 5.0 mL of benzene to give a 10% (w/v) solution which was carefully spread to the glass plate. The film was allowed to dry slowly under a Petri dish for 1 day and then dried for 2 h in air at 50 °C. The dried film was released from the glass by soaking in water to give a colorless, transparent sample.

Stability. For Model Compound. Reaction of 7 with Acetyl Chloride. A mixture of 306 mg (1.0 mmol) of 7 and 7.11 μL (0.1 mmol) of acetyl chloride in 1.0 mL of chlorobenzene (C = 1.0 M) was heated in an evacuated sealed tube at 100 °C for 12 h. After cooling, the tube was opened, then a small amount of triethylamine was added to the reaction mixture, and the mixture was concentrated by a rotary evaporator. A residual white solid crystal (306.3 mg, 100%) was subjected to analyses by thin layer chromatography (20% (v/v) ethyl acetate in hexane, silica gel) and IR and ^{1}H NMR spectroscopy.

Reaction of 7 with Hydrogen Chloride. A solution of 306 mg (1.0 mmol) of 7 in 1.0 mL of chlorobenzene was stirred in a nitrogen-flowed 20-mL round-bottomed flask into which was bubbled 200 mmol of dry hydrogen chloride. The reaction flask was heated at 100 °C. After 12 h, the reaction mixture was cooled, a small amount of triethylamine was added, and the mixture was concentrated by a rotary evaporator. Isolation of the products was accomplished by column chromatography (20% ethyl acetate in hexane, silica gel). A total of 171.4 mg (56%) of starting material was recovered, and other isolated products were 22.0 mg (20%) of catechol and 22.6 mg (12%) of phenol.

Reaction of 7 with BF_3OEt_2. The reaction was carried out with 306 mg (1.0 mmol) of 7 and 12.3 μL (0.1 mmol) of BF_3OEt_2 in 1.0 mL of chlorobenzene by a method similar to that with acetyl chloride. After cooling, the tube was opened, then small amount of triethylamine was added to the reaction mixture, and the mixture was concentrated by in vacuo (5 mmHg, 12 h). Isolation of the products was accomplished by recycling preparative HPLC (eluent, THF). A total of 174.8 mg (57%) of starting material was recovered, and other isolated products were 30.8 mg (27%) of 2 and 23.4 mg (12%) of 10.

2. Mp: 109–110 °C (lit.[10] mp 107–109 °C). IR (KBr): ν_{Ar} 1480, ν_{CO} 1180, δ_{Ar} 750 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 6.90 (s, C_6H_4).

10. Mp: 96–97 °C (lit.[5] mp 97–98 °C). IR (KBr): ν_{Ar} 1589, 1488, ν_{CO} 1100, δ_{Ar} 755, 680 cm^{-1}. ^{1}H-NMR (60 MHz, CCl_4): δ 6.83–7.34 (m, C_6H_5).

Reaction of 8 with BF_3OEt_2. The reaction was carried out with 334 mg (1.0 mmol) of 8 and 12.3 μL (0.1 mmol) of BF_3OEt_2 in 1.0 mL of chlorobenzene by a method similar to that of 7 with BF_3OEt_2 as described above. A total of 187.1 mg (56%) of starting material was recovered, and other isolated products were 36.5 mg (32%) of 2 and 15.6 mg (7%) of 11.

11. Mp: 100–101 °C (lit.[19] mp 101 °C). IR (KBr): ν_{CH_3} 2922, ν_{Ar} 1507, ν_{CO}, 1095, δ_{Ar} 817 cm^{-1}. ^{1}H-NMR (60 MHz, CCl$_4$): δ 2.24 (s, CH$_3$, 3 H), 6.90 (s, C$_6$H$_4$, 4 H).

Reaction of 9 with BF$_3$OEt$_2$. The reaction was carried out with 210 mg (1.0 mmol) of **9** and 12.3 μL (0.1 mmol) of BF$_3$OEt$_2$ in 1.0 mL of chlorobenzene by a method similar to that above. Starting material was not recovered, and isolated products were 56.8 mg (27%) of **12** and 16.6 mg (10%) of **13**.

12. IR (neat): $\nu_{C{=}O}$ 1770 cm^{-1}. ^{1}H-NMR (60 MHz, CCl$_4$): δ 1.35 (t, J = 7 Hz, 3 H, OCH$_2$CH_3), 1.37 (t, J = 7 Hz, 3 H, OCOOCH$_2$CH_3), 4.03 (q, J = 7 Hz, 2 H, OCH$_2$), 4.23 (q, J = 7 Hz, 2 H, OCOOCH$_2$), 6.63–7.27 (m, 4 H, C$_6$H$_4$).

13. IR (neat): ν_{CO} 1220 cm^{-1}. ^{1}H-NMR (60 MHz, CCl$_4$): δ 1.36 (t, J = 7 Hz, 6 H, CH$_3$), 3.99 (q, J = 7 Hz, 4 H, CH$_2$), 6.72 (s, 4 H, C$_6$H$_4$).

For Polymer. Reaction of 14 with Acetyl Chloride. A mixture of 346 mg (1.0 mmol) of **14** and 7.11 μL (0.1 mmol) of acetyl chloride in 2.0 mL of chlorobenzene (C = 0.5 M) was heated in an evacuated sealed tube at 100 °C for 12 h. After cooling, the tube was opened, the reaction mixture was diluted with 4.0 mL of tetrahydrofuran, and a small amount of triethylamine was added. This solution was added dropwise into 200 mL of methanol. White fibrous polymer precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day. Yield of recovered **14**: 339.5 mg (98%). $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$): 6400 (1.57). A total of 7.0 mg (2%) of a methanol-soluble fraction was oligomeric product which was confirmed by IR, ^{1}H NMR, and GPC ($\bar{M}_n$ 1400).

Reaction of 14 with Hydrogen Chloride. A solution of 346 mg (1.0 mmol) of **14** in 2.0 mL of chlorobenzene was stirred in a nitrogen-flowed 20-mL round-bottomed flask into which was bubbled 20 equiv of dry hydrogen chloride. During the reaction, the flask was heated at a set temperature. After 12 h, the products were isolated by a method similar to that with acetyl chloride as described above. The yield of recovered **14** was in the range of 78–87% ($\bar{M}_n$ 6100–6700). A total of 12–17% of oligomer ($\bar{M}_n$ < 2000) was obtained as a methanol-soluble part.

Reaction of 14 with BF$_3$OEt$_2$. The reaction was carried out with 346 mg (1.0 mmol) of **14** and 12.3 μL (0.1 mmol) of BF$_3$OEt$_2$ in 2.0 mL of chlorobenzene by a method similar to that above. After cooling, the tube was opened and 4.0 mL of tetrahydrofuran and a small amount of triethylamine were added to the gelatinous reaction mixture. The resulting mixture was added dropwise into 200 mL of methanol. The white fibrous polymer precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day. The yield of methanol-insoluble polymer was 64–89%. The $\bar{M}_n$ of the tetrahydrofuran-soluble part extracted with a Soxhlet extractor was 5200–9600. The methanol-soluble fraction contained 9–23% of oligomer and 9–18% of **2** which was isolated by column chromatography (20% ethyl acetate in hexane, silica gel).

Stability toward H$_2$O. A solution of **14** (346 mg, 1.0 mmol) in a mixed solvent of H$_2$O (3.0 mL) and dioxane (30 mL) was refluxed at 100 °C for 12 h. After cooling, the reaction mixture was poured into 200 mL of methanol. The precipitated polymer was collected and dried in vacuo at 100 °C for 1day. **14** was quantitatively recovered, and GPC, IR, and ^{1}H NMR of the recovered polymer were the same as those of the starting polymer.

References and Notes

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Registry No. **1**, 2032-75-9; **7**, 111273-81-5; **8**, 144320-23-0; **9**, 96620-87-0; **14** (copolymer), 144320-24-1; **14** (SRU), 144320-29-6; **20** (copolymer), 144320-25-2; **20** (SRU), 144320-30-9; **21** (copolymer), 144320-26-3; **21** (SRU), 144320-31-0; **22** (copolymer), 144320-27-4; **22** (SRU), 144320-32-1; **23** (copolymer), 144320-28-5; **23** (SRU), 144320-33-2; AcCl, 75-36-5; HCl, 7647-01-0; BF$_3$(OEt$_2$), 109-63-7; PhOH, 108-95-2; p-CH$_3$C$_6$H$_4$OH, 106-44-5; EtOH, 64-17-5; 1,3-benzodioxole, 274-09-9.