Synthesis of Poly(monocyclic orthocarbonate)s by Polycondensation with Silylated Diphenols

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ABSTRACT: Various poly(monocyclic orthocarbonate)s were synthesized by the polycondensation of 2,2-dichloro-1,3-benzodioxide (1) with a variety of silylated diphenols and their properties were examined. Polycondensation of 1 with silylated Bisphenol A (2) in bulk at room temperature proceeded under the catalysis of HCl or Bu_4NF to give high yields of the corresponding poly(monocyclic orthocarbonate) (10) but was very slow with catalysts such as Me_3SiCl, BF_3OEt_2, and CsF or without catalyst. In bulk polycondensation, 10 ($\bar{M}_n = 29100$) was obtained quantitatively when Bisphenol A (BPA) was used as catalyst, where a quantitative amount of Me_3SiCl was recovered as a byproduct. Solution polycondensation in chlorobenzene also proceeded efficiently at 60 °C to give 10 ($\bar{M}_n = 32400$) in 95% yield. The mechanism of the polycondensation is discussed. Several poly(monocyclic orthocarbonate)s were prepared in quantitative yield by the polycondensation of 1 with the corresponding silylated diphenols in the presence of BPA in chlorobenzene at 60 °C. Polycondensation of 1 with silylated alkyl diols afforded no corresponding poly(monocyclic orthocarbonate)s but instead complex mixtures including polymers having linear carbonate and/or ether functions. A little higher yield of 10 was attained in the polycondensation with an excess amount of 1. The molecular weight of 10 could be controlled by changing the amount of 4-*tert*-butylphenol instead of BPA to serve as both catalyst and terminator. The glass transition temperatures (T_g) of the polymers were in the range from 88 to 136 °C and were compared with those of the polymers derived from nonsilylated diphenols. The polymers lost 10% of their weights at temperatures ranging from 300 to 345 °C depending on their structures.

Introduction

Silylation is often utilized in conversion of nonvolatile materials to volatile materials for gas chromatographic and mass spectrometric analyses. In recent years, silylation has also been used in polymer synthesis to perform clean and selective polymerization under mild conditions as well as for ease of handling and purification of monomers. N-, O-, and S-silylated monomers such as diamine,[1] aminophenol,[2,3] diphenols,[4] mercaptophenol,[3a] dicarboxylic acid,[2] and hydroxy acid[5] are reported as one building block in a wide variety of polycondensations. These silylated monomers usually play a role as nucleophiles similar to the original nonsilylated monomers. Polycondensation with electrophiles such as acid chlorides and fluoroaromatics generally involves liberation of chloro- and fluorosilanes which are readily removable. Synthetic reactions utilizing the silylated monomers have the following advantageous aspects over the corresponding reactions with nonsilylated monomers:[1c,d] (i) easy purification of monomer by distillation, (ii) easy isolation or purification of the polymer formed, (iii) wide choice of solvents due to the enhanced solubility, (iv) polymerization under neutral conditions, and (v) recovery and recycling use of liberated silicon compounds.

Previously, we reported the high-yield synthesis of novel polymers, poly(monocyclic orthocarbonate)s, by the solution polycondensation of 2,2-dichloro-1,3-benzodioxole (1) with various diphenols (eq 1).[6] The polymers obtained were chemically and thermally more stable than the corresponding acyclic derivatives polyorthocarbonates.[7]

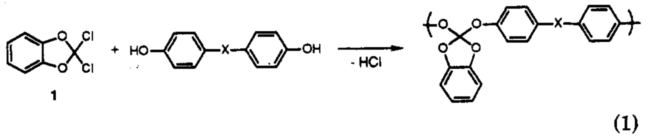

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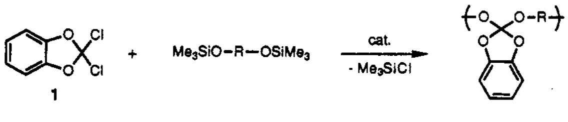
Table I. Effect of Catalyst on the Polycondensation of 2 and 1[a]

run	catalyst (mol %)	time, h	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]
1	none	10	0		
2	none	120	51	4400	1.38
3	Me_3SiCl (10)	10	0		
4	BF_3OEt_2 (5)	10	0		
5	CsF (5)[d]	10	0		
6	Bu_4NF (5)	10	78	5500	1.67
7	HCl[e]	24	94	6900	3.83
8	BPA (5)[f]	10	96[g]	27200	2.35

[a] The polycondensation was carried out using 5.00 mmol of each monomer in bulk at room temperature. [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on polystyrene standards). [d] Heterogeneous system. [e] A solution of HCl (gas, saturated at 20 °C) in PhCl was added. [f] 4.75 mmol of 2 and 0.25 mmol of Bisphenol A (BPA) were used. [g] 97% of Me_3SiCl was recovered.

If some silylated diphenols are available, the polycondensation can be employed more advantageously. For example, bulk polymerization can be attained, although it could not be accomplished in the polymerization of eq 1, because of the lower solubility of the diphenols and their high reactivity toward 1. Further, since a catalyst is generally required in the reaction of silylated diphenols, controlled polycondensation can be performed. Recently, we found that the polycondensation of 1 with silylated diphenols proceeds at room temperature in the presence of a catalyst to afford the corresponding poly(monocyclic orthocarbonate)s in high yield (eq 2). The present paper describes this polycondensation of 1 with the silylated diphenols in detail.



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Results and Discussion

1. Synthesis of Monomer. 1 was synthesized by the reaction of 1,3-benzodioxole with phosphorus pentachloride according to the reported method.[8] Silylated diphe-

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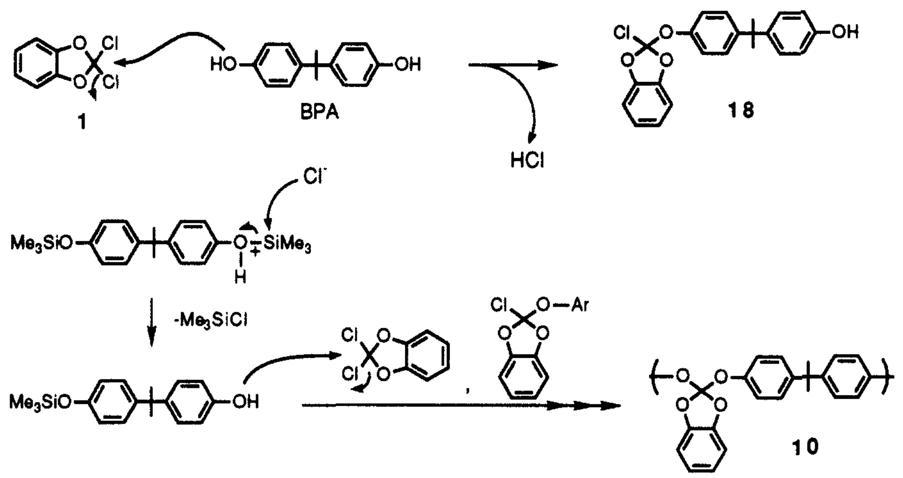
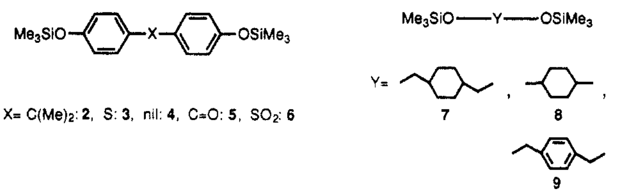
Scheme I

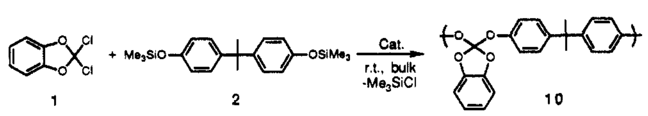


nols (2–6) and alkyl diols (7–9) were prepared by the reaction of the corresponding dihydroxy compounds with 1,1,1,3,3,3-hexamethyldisilazane. The silylation of the diphenols having electron-withdrawing groups such as carbonyl (5) and sulfonyl (6) groups was slow, and trimethylsilyl chloride (16 mol %) was used as a catalyst to accelerate the reaction. By the reaction at 140 °C for 10 h, 2–6 and 7–9 were obtained in quantitative yield. All the silylated diols could be simply purified by vacuum distillation. This easy purification is obviously due to the silylation.



2. Polymerization. As described in our previous paper,[6] it was difficult to carry out the bulk polycondensation of 1 with various diphenols. However, bulk polymerization could be carried out with the silylated diphenols, since they were freely miscible with 1. Reaction of silylated diphenol 2 with 1 proceeded slowly without catalyst at room temperature for 10 h, giving no methanol-insoluble polymer (Table I, run 1). Methanol-insoluble polymer ($\bar{M}_n$ = 4400) was obtained in a low yield in a prolonged reaction (run 2). Thus, the reactivity of 2 toward 1 is considerably lower than that of the corresponding nonsilylated diphenol which reacted spontaneously with 1 at room temperature without catalyst with liberation of HCl.[6]

(a) Effect of Catalyst. To accelerate the reaction, the effect of a catalyst on this polycondensation was investigated (eq 3). The results are summarized in Table I.



(3)

Tetra-*n*-butylammonium fluoride (Bu_4NF) and gaseous HCl accelerated the polycondensation to give the polymer in high yield (runs 6 and 7), although Me_3SiCl, BF_3OEt_2, and CsF were ineffective (runs 3–5). The molecular weight of the polymer (10) obtained was low (<7000). Use of Bisphenol A (BPA) was examined, because BPA can generate catalytic HCl in situ through fast reaction with 1. In the polycondensation, 0.95 equiv of 2 for each equivalent of 1 was used, since 5 mol % BPA was used. Therefore, BPA served not only as a catalyst but also as a monomer. Using BPA, high molecular weight polymer (10, $\bar{M}_n$ = 27200) was quantitatively obtained (run 8), and the molecular weight was much higher than that obtained using HCl or Bu_4NF as catalysts.

Table II. Polycondensation of 1 with 2 under Various Conditions[a]

run	BPA, mol %	solvent (mol/L)	temp, °C	time, h	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]
1	3	none	rt[d]	10	62	9400	1.68
2	5	none	rt	10	96	27200	2.35
3	7	none	rt	10	85	22000	1.88
4	5	none	0	2	4	2100	1.25
5	5	none	rt	2	75	6800	1.56
6	5	none	60	2	69	13500	2.11
7	5	none	rt	24	97	29100	2.60
8	5	PhCl (10)	rt	10	96	29000	2.99
9	5	PhCl (10)	60	10	95	32400	3.45
10	5	PhCl (10)	100	10	96	8900	2.68
11	5	PhCl (10)	rt	24	94	24000	3.16
12	5	PhCl (5)	rt	10	94	26700	3.08

[a] Conditions: 1 (5.0 mmol), 2 (4.75 mmol), BPA, (0.25 mmol). [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on polystyrene standards). [d] Room temperature.

Both chloride and fluoride anions catalyze the polycondensation by acceleration of O–Si bond cleavage by their nucleophilic attack at the silicon atom (Scheme I). It seems that the catalytic capacity of chloride is superior to that of fluoride in this polycondensation (Table I, runs 6 and 7). Presumably the O–Si bond cleavage is assisted by protonation of the oxygen atom as illustrated in Scheme I. HCl formed in situ by the reaction of BPA with 1 may catalyze more effectively than that added as catalyst, although the reason for this is not clear. The reaction of 1 with BPA is quite fast but the resulting monochloride (18, Scheme I) is more reactive than 1.[9] Undoubtedly, the polycondensation in the presence of BPA proceeds faster than that without BPA, at least in the initial stage.

(b) Structure of the Polymer and Mechanism of the Polymerization. The trimethylsilyl group as the polymer end group was confirmed in the ^{1}H NMR spectrum of the low molecular weight polymers (<6000, e.g., Table I, runs 2 and 6), and the ratio of the silyl group was correlated with their molecular weights measured by GPC. The IR, ^{1}H NMR, and ^{13}C NMR spectra of polymer 10 were the same as those previously reported,[6] and their elemental analysis data were in good agreement with the polymer structure. Scheme I indicates the mechanism of the polycondensation with BPA in which nucleophilic attack of Cl^- at the Si atom of 2 yields the corresponding

Table III. Synthesis of Various Poly(monocyclic orthocarbonate)s by the Polycondensation of 1 with Silylated Diphenols[a]

						elem anal. (%)					
						calcd			found		
run	silylated diphenol	polymer	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]	C	H	S	C	H	S
1	**2**	**10**	95	32400	3.45	76.29	5.24		76.04	5.22	
2	**3**	**11**	94	11800	5.06	67.85	3.60	9.53	67.95	3.60	9.01
3	**4**	**12**	93	3400	2.33	74.99	3.98		75.15	3.93	
4	**5**	**13**	74[d]	6900		72.29	3.59		72.56	3.80	
5	**6**	**14**	65	4300	2.06	61.95	3.28	8.70	61.71	3.31	8.32

[a] Conditions: 1 (5.0 mmol), 2–6 (4.75 mmol), BPA (0.25 mmol), chlorobenzene (1.0 mL), 60 °C, 10 h. [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on polystyrene standards). [d] Containing 7% of gelled polymer.

Scheme II

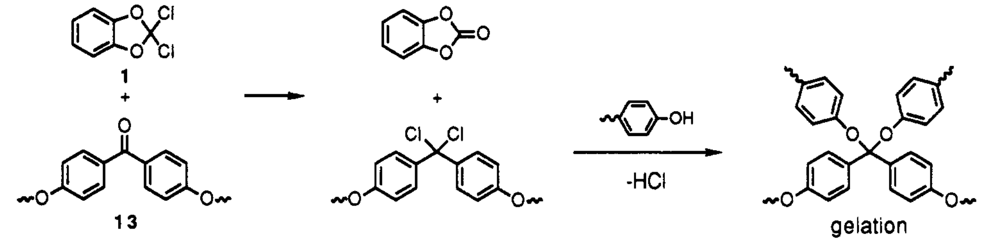


Table IV. Polycondensation of 1 with Silylated Aliphatic Diols[a]

run	silylated diol	polymer	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]	byproducts[d] (%)
1	**7**	**15**	16	3500	2.18	**20** (29), **21** (67)
2	**8**	**16**	25	740	1.06	**20** (59), **21** (10)
3	**9**	**17**	52	850	1.43	**20** (62), **21** (6)

[a] Conditions: 1 (5.0 mmol), 7–9 (4.75 mmol), BPA (0.25 mmol), chlorobenzene (1.0 mL), 60 °C, 10 h. [b] *n*-Hexane-insoluble polymer. [c] Estimated by GPC (based on polystyrene standards). [d] Determined by GC using authentic samples and an internal standard.

phenol that reacts with dichloride (**1**) or monochloride (**18**) to eventually afford poly(monocyclic orthocarbonate) (**10**). This mechanism is supported by the formation of Me_3SiCl, which was isolated in 97% yield after the polycondensation (run 8). The high yield recovery of Me_3SiCl suggests that the silyl moiety can be recycled.

(c) Polycondensation with Various Silylated Diols. The amount of the catalyst, temperature, concentration of monomer, and reaction time were examined to optimize the yield and molecular weight of the polymer. The results are summarized in Table II.

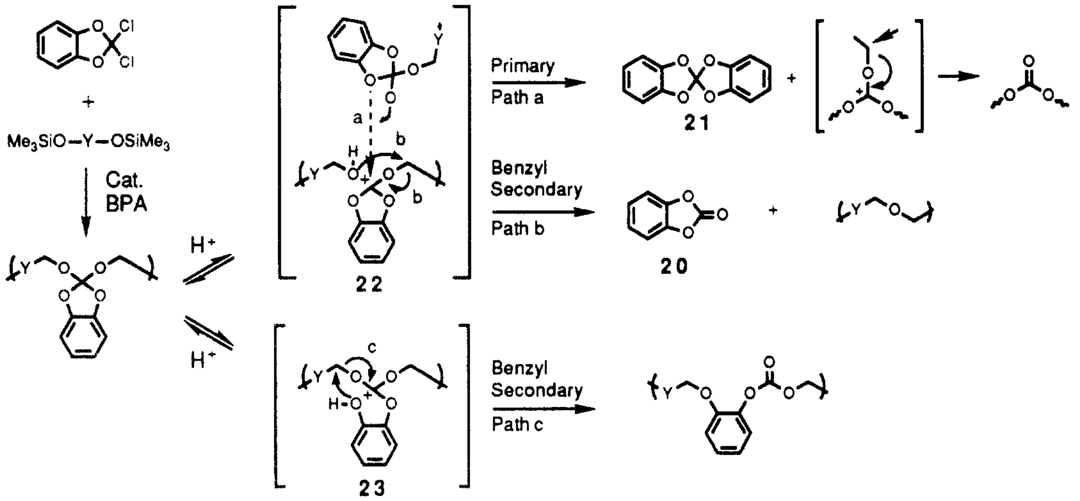
The bulk polycondensation using 5 mol % of BPA gave a yield and $\bar{M}_n$ higher than those with 3 and 7 mol % of BPA (runs 1–3). An increasing catalyst concentration accelerates the polycondensation. The lower yield and $\bar{M}_n$ in the case of 7 mol % of BPA can be accounted for by assuming that the polycondensation is in an equilibrium under the acidic condition, because it can be regarded as one of the acetal-forming reactions. The reaction was very slow at 0 °C (run 4). The $\bar{M}_n$ at 60 °C was higher than that at room temperature, but the yield was lower (runs 5 and 6). The highest yield and $\bar{M}_n$ were obtained at room temperature for 24 h using 5 mol % of BPA (run 7). To decrease the viscosity of the system, solution polycondensation was carried out. The highest $\bar{M}_n$ was obtained at 60 °C for 10 h using 5 mol % of BPA (run 9). At room temperature $\bar{M}_n$ was slightly lower than at 60 °C but did not increase on prolonged reaction time (runs 8 and 11). The $\bar{M}_n$ at 100 °C was much lower ($\bar{M}_n$ = 8900) (run 10). No effect of the monomer concentration was observed (run 12). In the solution polymerization, recovery of Me_3SiCl was readily performed, because it spontaneously separated as a supernatant from the reaction mixture. The polycondensation of **1** with the various silylated diphenols was carried out under the optimum conditions. As shown in Table III, various poly(monocyclic orthocarbonate)s (**10**–**14**) were prepared in high yield.

Except for silylated 4,4′-dihydroxybiphenyl (**4**), $\bar{M}_n$ and the yield of the corresponding poly(monocyclic orthocarbonate)s appear to depend on the nucleophilicity of the original phenols (runs 2, 4, and 5). The electron-releasing $>C(Me)_2$ and –S– groups of **2** and **3**, respectively, accelerate the rate of the polycondensation, whereas the electron-withdrawing >C(O) and $>SO_2$ groups of **5** and **6** retard it. In the case of **4**, polymer **12** was precipitated during the polycondensation, presumably due to the rigid structure of **12** formed. Therefore, the $\bar{M}_n$ of **12** was very low, although the yield of **12** was high (93%) (run 3). The polycondensation of **1** with **5** gave a polymer containing a small amount of gelled polymer (7%) (run 4). This gelation is probably due to a minor side reaction consisting of an intermolecular acetal formation by the reaction of terminal phenolic hydroxy moieties with the dichlorodiphenylmethane moiety which was formed by chlorination of the benzophenone moiety of **13** with **1** during the polycondensation. The chlorination of aromatic carbonyl compounds like benzophenone with **1** has been reported (Scheme II).[10]

The solubility of **14** was certainly enhanced by the addition of 5 mol % of BPA, probably because **14** had some irregular structure derived from the BPA unit. The GPC analysis of **14** could be carried out in THF solution, which was not possible with the polymer formed from nonsilylated 4,4′-dihydroxydiphenyl sulfone.[6]

The polycondensation with the silylated alkyl diols was attempted under similar conditions (solution polymerization in chlorobenzene at 60 °C for 10 h). The results are shown in Table IV. The polymerization of **1** with silylated 1,4-cyclohexanedimethanol (**7**) in the presence of 5 mol % of BPA afforded 16% of *n*-hexane-insoluble polymer which was not the desired poly(monocyclic orthocarbonate) but polycarbonate **15** containing little aromatic residues. From the *n*-hexane-soluble fraction, benzo-1,3-dioxol-2-one (**20**, 29%) and 2,3:7,8-dibenzo-1,4,6,9-tetraoxaspiro[4.4]nonane (**21**, 67%) were obtained as byproducts which were identified by GC using their authentic samples. The structure of **15** was suggested by its IR and ^1H NMR spectra in which the typical aliphatic polycarbonate absorption was observed at 1744 cm^{-1} in the IR and the corresponding proton signals could be assigned in the ^1H NMR (see

Scheme III



Experimental Section). When silylated 1,4-cyclohexanediol (**8**) and *p*-xylenediol (**9**) were used, a low molecular weight polymer structurally different from the desired poly(monocyclic orthocarbonate) was obtained along with a considerable amount of **20** and **21** in each case (runs 2 and 3). The polymer (**16**) obtained as the *n*-hexane-insoluble part from **8** had both carbonate and ether functions, while the IR spectra of the polymer (**17**) from **9** showed only ether functions. These products and the effect of the alkyl group can be explained by Scheme III.

Since the nucleophilic character of the aliphatic silyl ether (or alcohol) is higher than that of the aromatic one, it is conceivable that the corresponding poly(monocyclic orthocarbonate) would be formed in the initial stage. However, the polymer further reacts under the catalysis of hydrogen chloride to afford the final products depending on the structure of the diol segment. The initial protonation followed by C–O bond fission yields two kinds of stable carbenium ions (**22** and **23**). These ions are attacked by the ether oxygen of another molecule and/or isomerize intramolecularly. In the case of **7**, the initial cationic intermediate eventually gives polycarbonate and spiro compound **21** after successive acetal exchange reactions (path a). In contrast, in the cases of **8** and **9** the intramolecular reactions via paths b and c produce polyether and poly(ether–carbonate) along with **20**. The product distributions of these reactions suggest that path a predominates over paths b and c in the polymerization with **7**, while the opposite is true in the case of **8** and **9**. In particular, only path b seems to be operative in the case of **9**, since no carbonate function was present in the polymer obtained. This structure-dependent polymerization behavior might be explained by the different stabilities of the corresponding intermediary alkyl cations formed during the isomerizations via paths b and c. The secondary and benzyl carbocations for **8** and **9** are more stable than the primary carbocation for **7**. Further, in the case of **8** the initial protonation may take place on the oxygen adjacent to the aromatic ring (**23**) probably due to steric hindrance to finally give poly(ether–carbonate) through path c. This mechanism only deals with decomposition of the corresponding poly(monocyclic orthocarbonate) which would be formed initially, but the actual polymerization should be more complicated. It might be the case of the very low $\bar{M}_n$s of the polymers obtained (runs 2 and 3).

(d) Effect of Molar Ratio. Common polycondensations require exactly equal amounts of two monomers. However, we have recently demonstrated that the polycondensation of **1** with BPA proceeds efficiently when more than 1 equiv of **1** is used, because the reactivity of **1** is considerably lower than that of **18**.[9] Since the reactivity of **1** and **18** is not directly related to the silylation, a similar tendency should be observed. This was confirmed in the polycondensation of **2** with an excess amount (1.5 equiv) of **1** at 60 °C for 24 h in chlorobenzene. The yield of the polymer (**10**) was 91% and was the highest yield of the three experiments with different feed ratios, as shown in Table V. Although the effect of the feed ratio on the molecular weight was not large, the $\bar{M}_n$s of the polymers obtained were larger than the theoretical ones (runs 2 and 3) or the peak top molecular weight (M_{top}) of run 2 was comparable with that of run 1 when 1.5 or ca. 2.0 equiv of **1** was used toward **2** (Table V).

Table V. Effect of Molar Ratio of Reactants on the Polycondensation of 1 with 2[a]

run	ratio 1:2	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]	M_{top}[c]	$\bar{M}_n$[d] theor
1	50:50	73	6700	2.98	5500	∞
2	60:40	91	3900	1.76	5600	1384
3	66:34	83	2400	1.48	2700	779

[a] Conditions: 1 (3.0–9.0 mmol), 2 (4.75 mmol), BPA (0.25 mmol), chlorobenzene (1.0 mL), 60 °C, 24 h. [b] Methanol-insoluble polymer. [c] Peak top molecular weight estimated by GPC (based on polystyrene standards). [d] Theoretical $\bar{M}_n$. $\bar{M}_n(\text{theor}) = 346 \times [1 + (\bar{P} - 1)/2]$, $[\bar{P} = (1 + r)/(1 - r)$, $r = [1]/[2] + (\text{BPA})]$.

(e) Control of Molecular Weight. In the polycondensation mentioned above, BPA was used not only as a monomer but also as a catalyst which generated HCl. If a monofunctional phenol is used instead of BPA, it should serve as a terminator of the polycondensation. Therefore, the molecular weight of polymer obtained might be controlled by the amount of such a phenol added as a catalyst. 4-*tert*-Butylphenol (TBP) was chosen as a monofunctional phenol because of its high reactivity toward **1** and easy analysis by ^{1}H NMR. The results of the polycondensation of **1** with **2** in the presence of TBP (3–7 mol %) are shown in Table VI. As predicted, the $\bar{M}_n$ of the polymer (**10**) decreased with increasing TBP.

3. Thermal Properties of the Polymer. Differential scanning calorimetric (DSC) analysis of the polymers (**7**–**11**) revealed no clear melting point, but they exhibited clear glass transition temperatures (T_g) in the range 88–136 °C (Table VII). One T_g was observed in the DSC of each polymer (**11**–**14**). The T_g value seemed to increase with increasing polarity of the functional groups of the polymers. For example, the T_g of **10** was 31 °C lower than that of **14**. Apparently, the less polar isopropylidene

Table VI. Change of Molecular Weight by Addition of TBP in the Polycondensation of 2 with 1[a]

run	cat. (TBP), mol %	yield,[b] %	$\bar{M}_n$[b,c]	$\bar{M}_w/\bar{M}_n$[b,c]	$\bar{M}_n$[d] (by NMR)	M_n[e] (by calctn)
1	3	97	9300	2.14	12900	11619
2	5	94	7000	1.94	6900	7000
3	7	93	4300	2.48	5500	5021

[a] Conditions: TBP (0.3–0.7 mmol), 1 (5.0 mmol), 2 (4.65–4.85 mmol), bulk, room temperature, 3 days. [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on polystyrene standards). [d] $\bar{M}_n$ determined by ^{1}H NMR integral ratio of *tert*-butyl and isopropylidene groups. [e] Theoretical $\bar{M}_n$. $\bar{M}_n$(theor) = {[100 − [cat] (mol %)]/[cat.] (mol %)} × molecular weight of repeating unit (346.4) + 418.5.

Table VII. Thermal Properties of the Polymers[a]

run	polymer	$\bar{M}_n$[b]	T_g,[c] °C	T_d,[d] °C
1	**10**	32400 (48000)	105 (106)	345 (345)
2	**11**	11800 (69200)	88 (78)	330 (340)
3	**12**	3400 (37900)	110 (129)	300 (340)
4	**13**	6900 (14000)	113 (114)	315 (325)
5	**14**	4300 (—)	136 (148)	310 (320)

[a] All polymers were obtained in the presence of 5 mol % of BPA and contained the BPA unit (ca. 5 mol %). Data in parentheses are values for similar polymers obtained from nonsilylated diphenols. [b] Estimated by GPC (based on polystyrene standards). [c] Glass transition temperature. Heating rate 10 °C/min. [d] 10% weight loss temperature in N_2. Heating rate 10 °C/min.

moiety of **10** provides a weak intermolecular interaction which results in the lowering of T_g, in comparison with the sulfonyl moiety of **14**, which has a higher polarity and stronger interaction between the polymer chains, raising the T_g. The T_gs of the polymers were lower than those of the corresponding polymers obtained from nonsilylated diphenols except for that of **11**.[6] For example, the T_g of **14** was 136 °C, 12 °C lower than that of the corresponding polymer from the nonsilylated diphenol. In contrast, the T_g of **11** was 10 °C higher than that of the corresponding polymer from the nonsilylated diphenol. These results seem to be caused by the small amount of BPA segments incorporated in polymers **11**–**14**. Thus, the T_g of **10** does not depend on the use of the silylated monomer (run 1), in accordance with the lack of the corresponding structural change. Therefore, the enhancement of the T_g of **11** might be due to the contamination of the BPA unit, judging from the T_g values of **10** and **11**. In the case of **13** (run 4), a small difference in T_g between the two polymers would come partly from a large difference in $\bar{M}_n$.

The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA) under nitrogen. The decomposition temperatuers (T_d: 10% weight loss temperature) ranged from 300 to 345 °C (Table VII). These values were lower than the corresponding polymers prepared by the polycondensation with nonsilylated diphenols,[6] probably because of the lower molecular weights. Incorporation of 5 mol % of BPA unit in the polymers (**11**–**14**) does not seem to be directly related to T_d, consistent with the fact that the T_d of **10** (composed only of BPA units except for one unit) is the highest of all.

As mentioned in this paper, in light of the advantageous use of silylated monomers in polymerization, the polycondensation of 2,2-dichloro-1,3-benzodioxole (**1**) with bis(trimethylsiloxy)aryls to poly(monocyclic orthocarbonate)s was carried out. The polycondensation proceeded efficiently not only in solution but also in bulk in the presence of catalysts such as HCl, Bu_4NF, and BPA to yield quantitatively the corresponding poly(monocyclic orthocarbonate) (**10**). Furthermore, 4-*tert*-butylphenol (TBP), a monofunctional phenol, served not only as catalyst but also as a terminator controlling the $\bar{M}_n$ of the polymer. Thus, the use of the silylated diphenols had some advantages in this polycondensation such as easy purification and handling of monomers and polymers, enhanced solubility of monomers, and successful bulk polymerization.

Experimental Section

Materials and Measurements. The diphenols and alkyl diols used were reagent grade and were purified by recrystallization. Commercially available 1,1,1,3,3,3-hexamethyldisilazane, 1,3-benzodioxole, 4-*tert*-butylphenol, and tetra-*n*-butylammonium fluoride (1 mol/L in THF) were used without further purification. Me_3SiCl and BF_3OEt_2 were purified by distillation and stored under an argon atmosphere. Gaseous hydrogen chloride which was generated by the reaction of sodium chloride with sulfuric acid (98%) at room temperature was dried by passing through concentrated sulfuric acid and bubbled through chlorobenzene. Commercial grade cesium fluoride was dried under vacuum at 100 °C for 1 day before use. Chlorobenzene was washed with concentrated sulfuric acid several times and with aqueous sodium carbonate, followed by drying with calcium chloride and distilling after refluxing with phosphorus pentoxide for several hours.

Melting points were measured using a Yanaco micro melting point apparatus. Thermal analyses were performed with a Shimadzu DT-30 (TGA) and a Seiko DSC-200 (DSC). Decomposition temperatures (10% weight loss temperature) was estimated by TGA in nitrogen at a heating rate of 10 °C/min. Glass transition temperatures (T_g) were taken by DSC as the inflection point on the trace. Gel permeation chromatography (GPC) was performed with a Toso CCP&8000 GPC system equipped with both ultraviolet (254 nm) and refractive index detectors and three consecutive linear gel columns (Toyo Soda 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). FT-IR spectra were obtained with a JASCO FT/IR-3 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMN-PMX60Si (^{1}H, 60 MHz), JMN-FX100 (^{13}C, 25 MHz), and JMN–EX90 (^{1}H, 90 MHz; ^{13}C, 22.5 MHz) spectrometers using TMS as an internal standard.

Synthesis of Monomer. 2,2-Dichloro-1,3-benzodioxole (1). **1** was prepared according to the method of Barger[8a] and Yagupol'skii.[8b] 1,3-Benzodioxole (29.6 g, 0.24 mol) and phosphorus pentachloride (102 g, 0.48 mol) were mixed in a 200-mL round-bottomed flask under a nitrogen atmosphere. The mixture was heated to reflux for 5 h. The orange heterogeneous mixture became homogeneous, and hydrogen chloride was vigorously evolved. 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.[8c] bp 82–89 °C/12 mmHg). The product was further vacuum distilled two times and then stored under an argon atmosphere in a few ampule tubes.

IR (neat): 1477, 1238, 1064, 852, 736 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 6.93 (s, C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 109.67, 123.86, 128.44, 144.11.

Silylated Diols (2–9). Typical Procedure for Synthesis of 2. BPA (22.8 g, 0.1 mol) and 1,1,1,3,3,3-hexamethyldisilazane (21.0 g, 0.13 mol) were mixed in a 200-mL round-bottomed flask under a nitrogen atmosphere, and the mixture was heated at 140 °C for 10 h. Gaseous ammonia was vigorously evolved from the mixture. The reaction mixture was distilled in vacuo to give a colorless oil. Yield 35.7 g (95%), bp 164 °C/1.0 mmHg (lit.[11] bp 179–180 °C/1.5 mmHg).

IR (neat): 3036, 2964, 2903, 1608, 1508, 1265, 1253, 1176, 922, 844, 754 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 0.22 (s, 18H, $SiMe_3$), 1.57 (s, 6H, Me), 6.60 (d, J = 8 Hz, 4H, C_6H_4), 7.00 (d, J = 8 Hz, 4H, C_6H_4). ^{13}C NMR (25 MHz, $CDCl_3$): δ 0.26, 31.11, 41.64, 119.16, 127.62, 143.59, 152.83.

Other silylated diols were similarly prepared. Analytical and spectral data of them are as follows:

3: Yield 95%, bp 144–145 °C/0.09 mmHg (lit.[12] bp 120 °C/0.01 mmHg). IR (neat): 3059, 3030, 2960, 2900, 1591, 1490, 1253, 1165, 912, 844, 754 cm^{-1}. ^{1}H NMR (60 MHz, CCl_4): δ 0.23 (s, 18H, $SiMe_3$), 6.73 (d, J = 9 Hz, 4H, C_6H_4), 7.20 (d, J = 9 Hz, 4H, C_6H_4). ^{13}C NMR (25 MHz, $CDCl_3$): δ 0.09, 120.70, 128.14, 132.48, 154.43.

4: In the synthesis of **4** Me_3SiCl (16 mol %) as a catalyst was added to the reaction system. Yield 97%, bp 141 °C/0.2 mmHg, mp 67.5–68.5 °C (lit.[13] bp 166–167 °C/0.8 mmHg, mp 63–64 °C). IR (KBr): 3035, 2955, 2897, 1602, 1500, 1265, 1249, 1172, 938, 919, 841, 818, 750 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.28 (s, 18H, $SiMe_3$), 6.90 (d, J = 9 Hz, 4H, C_6H_4), 7.43 (d, J = 9 Hz, 4H, C_6H_4). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 0.24, 120.26, 127.70, 134.21, 154.32.

5 was synthesized by a method similar to the above. Yield 90%, bp 133–134 °C/0.05 mmHg. IR (neat): 3042, 2960, 2902, 1652, 1600, 1509, 1413, 1307, 1268, 1258, 1162, 910, 844, 775 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.30 (s, 18H, $SiMe_3$), 6.88 (d, J = 9 Hz, 4H, C_6H_4), 7.73 (d, J = 9 Hz, 4H, C_6H_4). ^{13}C NMR (25 MHz, $CDCl_3$): δ 0.00, 119.37, 130.98, 132.02, 158.99, 194.70. Anal. Calcd for $C_{19}H_{26}O_3Si_2$: C, 63.64; H, 7.31. Found: C, 63.76; H, 7.41.

6 was synthesized by a method similar to the above. Yield 89%, bp 217 °C/0.5 mmHg, mp 85.0–86.0 °C (lit.[12] mp 90 °C). IR (KBr): 3132, 2961, 2904, 1591, 1496, 1317, 1287, 1257, 1153, 1108, 907, 846, 760 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.28 (s, 18H, $SiMe_3$), 6.93 (d, J = 9 Hz, 4H, C_6H_4), 7.85 (d, J = 9 Hz, 4H, C_6H_4). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 0.07, 120.28, 129.46, 134.41, 159.38.

7: Yield 88%, bp 77–78 °C/0.07 mmHg (lit.[14] bp 141–142 °C/17 mmHg). IR (neat): 2954, 2915, 2854, 1450, 1249, 1247, 1114, 1078, 1027, 873, 838, 746 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.06 (s, 18H, $SiMe_3$), 0.87–1.82 (m, 10H, C_6H_{10}), 3.30 (dd, J = 5 Hz, 4H, OCH_2). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ −0.67, 25.28 (cis), 29.03, 37.73 (cis), 40.46, 65.52 (cis), 68.40.

8: Yield 68%, bp 51 °C/0.06 mmHg (cis–trans mixture), mp 52.5–53.5 (trans) (lit.[15] mp 53–54 °C), oil (cis). IR (neat): 2954, 2950, 2863, 1446, 1380, 1249, 1095, 1049, 1016, 983, 890, 838, 746 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.05 (s, 18H, $SiMe_3$), 1.10–1.93 (m, 8H, CH_2), 3.57 (m, 2H, OCH). ^{13}C NMR (22.5 MHz, $CDCl_3$): trans, δ 0.09, 33.33, 70.06; cis, δ −0.04, 30.87, 67.95.

9: Yield 91%, bp 88–90 °C/0.07 mmHg (lit.[14] bp 273 °C). IR (neat): 3054, 2956, 2898, 2863, 1513, 1461, 1423, 1373, 1251, 1213, 1083, 1020, 873, 840, 752 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ 0.08 (s, 18H, $SiMe_3$), 4.53 (s, 4H, OCH_2), 7.06 (s, 4H, C_6H_4). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ −0.56, 64.24, 126.23, 139.68.

Synthesis of Polymer by Bulk Polycondensation. General Procedure and Effect of Catalyst. A mixture of 0.955 g (5.00 mmol) of **1** and 1.86 g (5.00 mmol) of **2** was stirred in a flask under an argon atmosphere, to which 5 mol % (0.25 mmol) of a catalyst was added. When BPA (0.057 g, 0.25 mmol) was used as the catalyst, 4.75 mmol of **2** was used. The mixture was stirred at room temperature for 10–120 h. To the resulting mixture was added 40 mL of tetrahydrofuran (THF). This solution was poured into 500 mL of methanol containing a small amount of triethylamine to precipitate polymeric material. The white fibrous polymer that precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day. The results are summarized in Table I.

Solution Polycondensation. Typical Procedure for Synthesis of 10. A solution of 0.955 g (5.00 mmol) of **1** and 1.77 g (4.75 mmol) of **2** in 1.0 mL of absolute chlorobenzene was stirred in a flask under an argon atmosphere, to which 0.057 g (0.250 mmol) of BPA was added. The solution was stirred at 60 °C for 10 h. Me_3SiCl generated during the polycondensation was spontaneously separated from the polymer–chlorobenzene phase. After removal of Me_3SiCl, the polymer was dissolved in 40 mL of THF. This solution was poured into 500 mL of methanol containing a small amount of triethylamine. The white fibrous polymer that precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day. $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$): 32400 (3.45). Yield 95%.

IR (KBr): 2967, 1506, 1484, 1226, 1166, 1101, 1076, 1016, 1014, 833, 813, 736 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.55 (s, 6H, CH_3), 6.81 (s, 4H, C_6H_4), 7.04 (s, 8H, C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 30.83, 42.20, 108.74, 120.54, 122.15, 127.53, 129.35, 145.17, 147.06, 149.31. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.04; H, 5.22.

Other polymers were similarly prepared, and the results are summarized in Tables III and IV. Analytical and spectral data of the polymers are as follows:

11: IR (KBr): 1483, 1226, 1160, 1120, 1078, 1012, 981, 914, 811, 808, 736 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.56 (s, 0.37H, CH_3), 6.84 (s, 4H, C_6H_4), 7.14 (s, 8H, C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 108.81, 122.15, 122.47, 129.22, 132.00, 132.13, 144.91, 150.57. Anal. Calcd for $C_{19}H_{12}O_4S$: C, 67.85; H, 3.60; S, 9.53. Found: C, 67.95; H, 3.60; S, 9.01.

12: IR (KBr): 3039, 1484, 1253, 1224, 1162, 1124, 1004, 981, 916, 827, 823, 738 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.55 (s, 0.47H, CH_3), 6.85 (s, 4H, C_6H_4), 7.25 (d, J = 8.6 Hz, 4H, C_6H_2), 7.39 (d, J = 9.1 Hz, 4H, C_6H_2). ^{13}C-NMR (22.4 MHz, $CDCl_3$): δ 108.78, 121.61, 122.37, 127.75, 129.40, 137.16, 145.06, 150.83. Anal. Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.98. Found: C, 75.15; H, 3.93.

13: IR (KBr): 1658, 1600, 1502, 1484, 1411, 1307, 1276, 1224, 1159, 1108, 1016, 927, 771, 738 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.56 (s, 0.43H, CH_3), 6.94 (s, 4H, C_6H_4), 7.32 (d, J = 8.8 Hz, 4H, C_6H_2), 7.74 (d, J = 8.8 Hz, 4H, C_6H_2). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 109.15, 120.33, 122.91, 129.03, 131.65, 134.10, 144.69, 154.61, 194.24. Anal. Calcd for $C_{20}H_{12}O_5$: C, 72.29; H, 3.59. Found: C, 72.56; H, 3.80.

14: IR (KBr): 3066, 1589, 1483, 1326, 1297, 1224, 1155, 1105, 1012, 916, 835, 815, 811, 738 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.54 (s, 0.35H, CH_3), 6.92 (s, 4H, C_6H_4), 7.27 (d, J = 8.8 Hz, 4H, C_6H_2), 7.84 (d, J = 9.0 Hz, 4H, C_6H_2). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 109.33, 120.96, 123.26, 128.70, 129.48, 137.75, 144.30, 154.87. Anal. Calcd for $C_{19}H_{12}O_6S$: C, 61.95; H, 3.28; S, 8.70. Found: C, 61.71; H, 3.31; S, 8.32.

15: IR (neat): 3450, 2924, 2856, 1744, 1513, 1469, 1452, 1405, 1296, 1260, 952, 792 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.00–1.93 (m, 20H, CH_2), 3.43 (dd, J = 5 Hz, 2H, OCH_2), 4.00 (dd, J = 5 Hz, 6H, $OCOOCH_2$), 4.50 (br, 1.4H, unknown), 6.62–7.30 (m, 3H, Ar).

16: IR (neat): 3420, 2954, 2949, 1760, 1738, 1613, 1598, 1512, 1500, 1463, 1365, 1322, 1270, 1233, 1186, 1054, 940, 759, 744 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.30–2.12 (m, 6H, CH_2), 3.72 (br, 0.5H, CHOCH), 4.74 (br, 1H, CHOAr), 5.35 (br, 1H, CHOCOOAr), 6.58–7.17 (m, 3.6H, Ar).

17: IR (neat): 3420, 3057, 3028, 2922, 2888, 1450, 1415, 1268, 1212, 1181, 1084, 1074, 992, 832, 744, 700 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.54 (s, 3H, CH_3), 3.87 (br, 4.5H, unknown), 4.47 (s, 16H, $ArCH_2OCH_2Ar$), 4.93 (s, 7H, unknown), 5.13 (s, 20H, $ArCH_2OAr$), 6.57–7.27 (m, 70H, Ar).

Effect of Molar Ratio. The polycondensation was carried out with 5.0–9.0 mmol of **1**, 4.75 mmol of **2**, and 0.25 mmol of BPA in 1.0 mL of chlorobenzene at 60 °C for 24 h according to a procedure similar to that used for the solution polymerization. The resulting mixture was diluted with THF (50 mL). Unreacted **1**, when the excess of **1** was used, was confirmed by gas chromatography of this solution. The THF solution was worked up by a procedure similar to that used for the solution polymerization. The results are summarized in Table V.

Control of Molecular Weight. To a mixture of 0.955 g (5.00 mmol) of **1** and 1.73–1.80 g (4.65–4.85 mmol) of **2** was added 3–7 mol % (0.30–0.70 mmol) of 4-*tert*-butylphenol (TBP) under an argon atmosphere. The mixture was stirred at room temperature for 3 days. The resulting mixture was treated by a procedure similar to that used for the solution polymerization. The true $\bar{M}_n$ was estimated by the end group determination method using ^1H NMR. The results are summarized in Table VI.

^1H NMR (90 MHz, $CDCl_3$): 3 mol %, δ 1.26 (s, 0.50H, *t*-Bu), 1.55 (s, 6.0H, CMe_2), 6.81, 7.05 (s, 12.4H, Ar); 5 mol %, δ 1.26 (s, 0.97H, *t*-Bu), 1.55 (s, 6.0H, CMe_2), 6.81, 7.04 (s, 12.6H, Ar); 7 mol %, δ 1.26 (s, 1.22H, *t*-Bu), 1.55 (s, 6.0H, CMe_2), 6.82, 7.05 (s, 12.8H, Ar).

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