(39) Yank tested with Scotch tape.

(40) The elemental analysis of the PAP film (oxidized form) indicated that the molar ratios of C, H, and N are 6.0, 3.8, and 0.76, respectively. It seems likely that this result does not necessarily support III as a possible structure of PAP, but taking into account that imino groups (=NH) of III are partially hydrolyzed to produce aromatic keto groups,[41] one can speculate some reasonable structures the molar ratios of C, H, and N of which are in fair agreement with those calculated based on the elemental analysis data.

(41) Snead, W. K.; Remick, A. E. *J. Am. Chem. Soc.* **1957**, *79*, 6121, and references therein.

New Aspect of Cationic Ring-Opening Polymerization of Seven-Membered Spiroorthocarbonates: Synthesis and Polymerization of Substituted 1,6,8,13-Tetraoxaspiro[6.6]tridecanes

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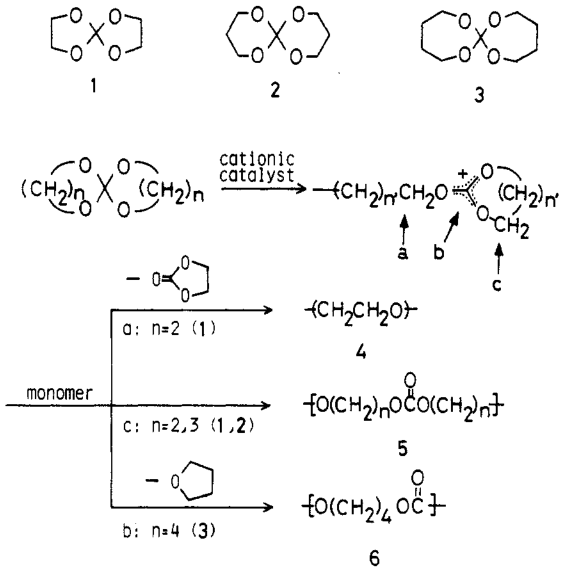
ABSTRACT: Two new spirocyclic monomers, spiroorthocarbonates (SOCs, 7 and 8) having spiro[6.6]tridecane skeletons, were synthesized and their polymerization behavior was studied under cationic conditions. By cationic ring-opening polymerization, SOCs 7 and 8 afforded clearly structure-different polymers, polycarbonate 9 and poly(ether–carbonate) 12, respectively, depending on the structure of SOC, but independent of solvent (chlorobenzene, ethylene dichloride, nitrobenzene), catalyst (BF_3OEt_2, $Ph_3C^+BF_4^-$, $PhCH_2S^+CH_2CH_2CH_2CH_2$ SbF_6^-), and temperature (from room temperature to 120 and 150 °C). On the basis of the difference of the structures between the SOCs, the results suggested two distinguishable polymerization courses controlled presumably by the electrophilicity of the reaction site of the propagating cationic species or the leaving ability of the eliminated moiety.

Introduction

Spiroorthocarbonate (SOC) is a useful monomer which shows expansion in volume on polymerization[1–5] and its application to new materials has recently become important. In 1973, Sakai et al. first studied the cationic ring-opening polymerization of three types of SOCs (**1**, **2**, and **3**) catalyzed by boron trifluoride etherate.[6] From the structure of the products, they proposed three modes of ring-opening polymerization of the SOCs in terms of the attacking sites of monomer toward cationic propagating species, as shown in Scheme I. SOC **2** having two six-membered rings effectively gives poly(ether–carbonate) alternative copolymer **5** ($n = 3$), while SOC **1** having two five-membered rings mainly affords polyether **4** [poly(ethylene oxide)] with a loss of ethylene carbonate. As for SOC **3**, polycarbonate **6** is obtained with complete elimination of tetrahydrofuran. From the viewpoint of material science, it is rather difficult to use SOCs other than **2** for expanding materials, if Sakai's polymerization map (Scheme I) is always operative.

Bailey et al.[7] and we[8–11] have already studied syntheses and cationic ring-opening polymerization of various derivatives of **2**, suggesting their utility as new monomers,[1–5] promising no shrinkage. During the course of the study, we have also prepared **3** and reexamined its reactivity, and have noticed higher sensitivity of **3** than **2** toward cationic species. Since low cationic polymerizability of SOC **2** has caused an emerging problem in designing the materials, it is of great significance in material science if a monomer can be obtained that not only retains the same skeleton as **3** but also undertakes cationic ring-opening polymerization without any elimination of tetrahydrofuran derivative. In this situation we have continued detailed investigations on the synthesis and the polymerization behavior of derivatives of **3**, so as to obtain the basis of the molecular designing of the better SOC monomers. Thus, from the results of the polymerizations of two SOC monomers bearing fused-ring systems based on the structure **3** (i.e., SOCs **7** and **8**), we have obtained important mechanistic information of the polymerization of SOCs. This paper reports these results.

Scheme I



Experimental Section

Both ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating in the pulsed FT modes, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C, unless otherwise stated. FT-IR specta were obtained with a JASCO FT/IR-3 at 25 °C. Mass spectra were taken at 25 °C with a Hitachi M-80 spectrometer equipped with a data processing system at an ionizing potential of 70 eV. Molecular weight and its distribution (MWD; $\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent, flow rate 1.0

Table I
Physical and Spectral Data of Monomers 7 and 8

						elem anal.	
monomer, mp	IR,[a] cm^{-1}	^{1}H NMR, δ[b]	^{13}C NMR, δ[c]	MS, m/z		found	calcd
7, $C_{18}H_{28}O_4$ (296), 186–9 °C (*n*-hexane-CH_2Cl_2)	2938, 2916, 2854, 1454, 1157, 1149, 1139, 1118, 1095	3.73 (br s, 8 H, OCH_2), 2.11–0.95 (br, 20 H)	123.2 (s), 66.1 (t), 38.8 (d), 26.9 (t), 24.1 (t), 24.0 (t)	296 (M^+, 0.15%), 171 ($[M - 125]^+$, 99%), 109 (C_8H_{13}, 100%), 95 ($C_7H_{11}^+$, 21%), 81 ($C_6H_9^+$, 31%)	H C	9.63 68.59	9.53 68.87
8, $C_{17}H_{16}O_4$ (284), 261–3 °C, (*m*-xylene)	3067, 3028, 2976, 2932, 2881, 1498, 1446, 1211, 1161, 1141, 1118, 1103, 991, 972, 784	4.93 (s, 8 H, OCH_2), 7.16 (s, 8 H, Ar)	124.0 (s), 65.6 (t), 137.0 (s), 127.4 (d), 126.6 (d)	284 (M^+, 1.5%), 165 ($[M - 119]^+$, 6%), 119 ($[M - 165]^+$, 59%), 104 ($C_8H_8^+$, 100%), 91 ($C_7H_7^+$, 75%)	H C	5.58 71.66	5.67 71.82

[a] KBr. [b] In $CDCl_3$ for 7 and in dimethyl-d_6 sulfoxide at 120 °C for 8. [c] In $CDCl_3$ for 7 and in dimethyl-d_6 sulfoxide at 80 °C for 8; s, singlet; d, doublet; t, triplet.

Table II
Cationic Polymerization of 7

						polym yield, %[d]			
run	[C][a]	solv[b]	cat (mol %)[c]	temp, °C	time	insol	sol[e]	$\bar{M}_n$ (M^*)[f]	$\bar{M}_w/\bar{M}_n$
1	3.9	CB	L (3)	120	100 min	34 (60)	15 (26)	5700 (5700)	1.14
2	3.7	CB	L (3)	120	80 min	30 (52)		6200 (8200)	1.44
3	3.0	CB	T (3)	120	60 min	28 (49)	29 (51)	3600 (4000)	1.55
4	3.3	CB	T (3)	80	60 min	32 (56)	25 (44)	4100 (4600)	1.53
5	3.2	CB	T (5)	RT[h]	24 h	34 (60)	21 (40)[g]	3900 (4600)	1.57
6	3.4	CB	B (20)	80	60 min	20 (35)	37 (65)	4900 (6200)	1.39
7	3.4	CB	B (3)	RT	24 h	31 (54)	24 (43)[g]	9300 (18400)	1.88
8	3.0	DCE	B (3)	RT	24 h	33 (58)[i]	23 (41)[i]	8700 (11900)	1.33
9	3.0	DCE	T (3)	RT	24 h	33 (58)	23 (42)[g]	3800 (4800)	1.70
10	3.0	NB	B (3)	RT	24 h	29 (50)	28 (50)	7300 (18000)	2.17

[a] Concentration of the monomer, mol/L. [b] CB, chlorobenzene; DCE, ethylene dichloride; NB, nitrobenzene. [c] L, thermal latent catalyst $\mathrm{PhCH_2}\overline{\mathrm{S^+CH_2CH_2CH_2CH_2}}\ \mathrm{SbF_6^-}$ (11); B, BF_3OEt_2; T, $Ph_3C^+BF_4^-$. [d] Absolute yields of insoluble and soluble parts in methanol. Yield in parentheses is based on theoretical yield of polycarbonate 9 (maximum yield of 9 is 57% based on the monomer). [e] Soluble part was the polymer with lower molecular weight, showing the same ^{1}H NMR spectrum as that of insoluble part, in each case. [f] GPC data for the insoluble part, estimated by polystyrene. M^* means molecular weight value at peak top in GPC chart. [g] Small amount of the monomer was recovered. [h] Room temperature, ca. 15–20 °C. [i] Yields of soluble and insoluble parts in *n*-hexane.

mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Solvents were distilled after the removal of water by usual methods and stocked over molecular sieves (4A). Catalyst BF_3OEt_2 and $Ph_3C^+BF_4^-$ were used as received (extra pure grade reagent, Tokyo Kasei Kogyo). Benzylsulfonium salt 11 was prepared according to our previous report.[12]

Synthesis of Monomer 7. Solid hexahydrophthalic anhydride (61.6 g, 0.40 mol) was added gradually to a suspension of lithium aluminum hydride ($LiAlH_4$, 18.2 g, 0.48 mol) in dry ether (1.0 L) at room temperature, so as to keep refluxing. After the addition, the mixture was stirred at room temperature overnight and refluxed for a few hours. Saturated aqueous sodium sulfate (100–150 mL) was carefully introduced from a dropping funnel until the white mixture was solidified. The resulting white mass was filtered off and washed with ether and THF. The combined filtrate was dried over anhydrous magnesium sulfate, evaporated and distilled, bp 108–115 °C/1.1 mmHg; yield 40.7 g (71%). ^{1}H NMR ($CDCl_3$) δ 4.56 (s, 2 H), 3.90–3.28 (m, 4 H), 2.13–1.00 (m, 10 H).

According to our previous report,[13] to a mixture of the diol as colorless viscous oil (4.77 g, 33 mmol) and tetramethyl orthocarbonate (2.25 g, 16.7 mmol) in dry benzene (10 mL) was added anhydrous *p*-toluenesulfonic acid (30 mg) in one portion at room temperature. After a few minutes a white precipitate appeared and then a few drops of triethylamine was added to the mixture. Immediately thereafter, methanol, dimethyl carbonate, and the solvent were removed in vacuo at room temperature. The residual white solid was recrystallized from *n*-hexane–methylene dichloride or *n*-hexane–ether; yield 3.23 g (60%).

Synthesis of Monomer 8. To a suspension of $LiAlH_4$ (18.0 g, 0.44 mol) in dry ether was added solid phthalic anhydride (59.2 g, 0.40 mol) in several portions at room temperature, maintaining ether reflux. The addition of all the anhydride was followed by stirring the mixture overnight and subsequent refluxing for several hours. Careful addition of 100–150 mL of saturated aqueous sodium sulfate resulted in forming a white mass. The mixture was filtered off and washed with THF, and the combined filtrate was dried over anhydrous magnesium sulfate. Evaporation afforded a colorless oil (53.2 g, crude yield 96%) which soldified by allowing it to stand and was recrystallized from benzene–THF. Repeated recrystallization yielded pure diol, 32.6 g (59%), mp 62–63 °C (lit.[14] 65–66.5 °C).

According to our reported method,[13] 1,2-benzenedimethanol (purity 90–95%, 2.76 g, 20 mmol) and tetramethyl orthocarbonate (1.36 g, 10 mmol) were heated at 100–120 °C in the presence of *p*-toluenesulfonic acid (anhydrous, 20 mg) in dry *m*-xylene (10 mL), while collecting methanol formed. After most of the theoretical amount of methanol (1.28 g) was collected (usually it took 2–4 h), the mixture was cooled whereupon the white crystals were precipitated. Triethylamine (0.1 mL) was added and the precipitate was collected by filtration, washed 3 times with *m*-xylene, and dried; colorless crystals, yield 1.68 g (59%). This yield, however, is not optimized.

Physical and spectral data for 7 and 8 are listed in Table I.

Polymerization of 7 and 8. The polymerization was carried out in a sealed tube in every case. Amounts of catalyst and solvent are listed in Tables II and IV which also contain the polymerization conditions.

To solid monomer (1.0–1.5 mmol) in a tube with a stirrer tip were introduced BF_3OEt_2 by syringe or benzylsulfonium salt 11 (solid) and subsequently dry solvent. The tube was degassed by repeated cooling and pumping and sealed. The heterogeneous mixture was stirred at a set temperature. The polymerization was terminated by adding small amount of triethylamine after cooling and opening the tube. The resulting mixture, generally homogeneous, was diluted by methylene dichloride (2–4 mL) and precipitated into *n*-hexane (200 mL) or methanol (100–150 mL). After allowing the mixture to stand overnight, the solvent was

Table III
Spectral and Analytical Data of Polymers of 9 and 12

polymer	IR,[a] cm^{-1}	^{1}H NMR, δ[b]	^{13}C NMR, δ[c]		elem anal. found	elem anal. calcd
9,[d] colorless viscous oil	2930, 2860, 1745, 1450, 1406, 1255, (1280–1230),[e] 997, 941, 790, 756	4.10 (d, 4 H, CH_2OCO_2), 2.11 (br s, 2 H, CH), 1.50 (br s, 8 H, CH_2)	155.3 (s), 68.2 (t), 36.5 (d), 26.1 (t), 23.1 (t)	H C	7.67 59.31	8.29 63.51
12,[f] colorless (white solid soften at >50 °C)	3072, 3030, 2862, 1743, 1456, 1392, 1265, 1238, 1074, 914, 904, 765, 721	7.29 (br s, 8 H, Ar), 5.20 (s, 4 H, CH_2OCO_2), 4.55 (br s, 4 H, CH_2O)	154.7 (s), 136.3 (s), 133.7 (s), 130.3 (–), 130.0 (–), 129.2 (d), 128.9 (d), 128.6 (d), 128.1 (d), 70.0 (t), 67.0 (t)	H C	5.45 70.29	5.67 71.80

[a] Neat for **9** and KBr for **12**. [b] In $CDCl_3$. [c] In $CDCl_3$: s, singlet; d, doublet; t, triplet. [d] Polymer obtained from Table II, run 8 ($\bar{M}_n$ 8700). [e] Broad peak ranging from 1280 to 1230 cm^{-1}. [f] Polymer obtained from Table IV, run 2 ($\bar{M}_n$ 2700).

Table IV
Cationic Polymerization of 8

run	[C][a]	solv[b]	cat (mol %)[c]	temp, °C	time	polym yield, %[d] insol	polym yield, %[d] sol[e]	$\bar{M}_n$ (M*)[f]	$\bar{M}_s/\bar{M}_n$
1	3.9	NB	L (3)	150	10 min	95[i]			
2	2.5	NB	L (3)	150	20 min	99[i]		2700 (4900)	2.46
3[g]	5.1	NB	T (3)	150	2 min	57[k]	37[k]	1300 (1100)[j]	4.74[j]
4	4.0	NB	T (3)	120	3 min	73	26	4200 (18100)	7.49
5	4.0	NB	T (5)	80	15 min	87	13	4000 (14000)	4.79
6	4.4	DCE	B (5)	RT[h]	26 h	86	14	4500 (7000)	2.59
7	4.0	DCE	T (3)	RT	24 h	84	16	2900 (6300)	3.02
8[g]	3.4	NB	B (3)	RT	24 h		71[k]	2700 (5200)[j]	8.12[j]
9	2.0	NB	B (3)	RT	7.5 h	85	15	9200 (14100)	18.55
10	3.4	CB	B (3)	RT	24 h	90	10	2900 (5100)	2.57

[a–c,e,f,h,i] Same as those of Table II. [d] Absolute yield of insoluble and soluble parts in methanol. [g] Gel polymer was obtained. [j] GPC data of the soluble polymer permeated through a membrane filter. [k] Yields of insoluble and soluble parts in chloroform.

decanted, leaving the insoluble part. The soluble part was isolated by evaporation of the solvent.

Spectral and analytical data of the insoluble parts (polymers **9** and **12**) are shown in Table III.

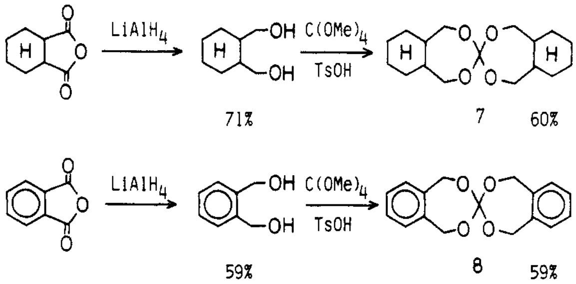
Isolation and Characterization of 2-Oxabicyclo[3.4.0]nonane 10 in the Polymerization of 7. The soluble part as *n*-hexane solution obtained in the polymerization of **7** (Table II, run 7) was concentrated under reduced pressure to afford low molecular weight materials. The residual mixture was directly analyzed by GC and GC–MS. In the GC (Shimadzu GC-4CPF, FID detector, column SE-30, 1 m, flow rate of N_2 30 mL/min, column temp 80 °C) two peaks were confirmed, one of which (t_r 1.31 min) was chlorobenzene by comparison with that of authentic sample. The other peak (t_r 5.68 min) had the following mass spectrum: m/z 126 (M^+, 32%), 108($[M - 18]^+$ 14%, 95($[M - 31]^+$, 46%, 81 ($[M - 45]^+$ 100%, 68$[M - 58]^+$, 39%, 67($[M\text{-}59]^+$, 67%), corresponding to **10**. ^{1}H NMR spectrum of the distillation product of the mixture (bp 100 - 120°C/5 mmHg); ($CDCl_3$, δ) 7.24(s, 5H, chlorobenzene), 3..7–3.44 (m, 4H, $-CH_2-O-$), 2.14 (brs, 2 H, -CH), 1.46 (brs, 8 H, $-CH_2-$).

Reaction of Polymer 12 with BF_3OEt_2. The powdered polymer **12** obtained from **8** (160 mg, $\bar{M}_n$ 2700; $\bar{M}_w/\bar{M}_n$ 3.88) was mixed with BF_3OEt_2 (3.5 μL, 5 mol %) in dry chlorobenzene (100 μL) in a sealed tube, according to the procedure described for the polymerization of **7** and **8**. The viscous mixture was stirred at room temperature for 24 h. After quenching with triethylamine [one drop in methylene dichloride (2 mL)], the mixture was precipitated into methanol (70 mL). The insoluble part was separated by decantation and showed no loss of weight (recovery; 155 mg, 97%) and no change in molecular weight by GPC (M_n 2600, $\bar{M}_w/\bar{M}_n$ 3.24) and ^{1}H NMR and IR spectra.

Results and Discussion

Syntheses of Monomers 7 and 8. New SOC monomers **7** and **8** were prepared by $LiAlH_4$ reduction of the corresponding 1,2-dicarboxylic anhydrides followed by acid-catalyzed condensation with 0.5 mol of tetramethyl orthocarbonate, according to the previously reported method (Scheme II).[13] However, in the derivation from diol to **7**, usual condensation conditions (heat at 120 °C) could not be applied because of the instability of product **7** under such conditions. For this reason, not only the reaction at room temperature but also subsequent speedy workup were required (see Experimental Section). This is consistent with observed high sensitivity of **3** toward cationic conditions.

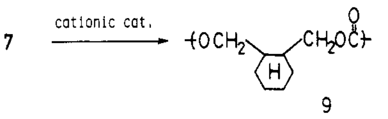
Scheme II

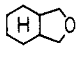


Characterization of **7** and **8** was easily accomplished by the physical and spectral data as well as microanalyses data, which are listed in Table I. A characteristic feature is confirmed in ^{13}C NMR spectra in which central quaternary carbon shieldings appeared at 123.2 (**7**) and 124.0 (**8**) ppm. These values are as estimated from our previous study.[15] Other data also support these structures.

Cationic Polymerization of 7. Polymerization of **7** was carried out under some different conditions which are summarized in Table II. SOC **7** was polymerized at first in the presence of BF_3OEt_2 in ethylene dichloride at room temperature (run 8); similar conditions are reported by Sakai et al.[6] (Scheme III). The initial heterogeneous mixture turned homogeneous within a few hours as the polymerization proceeded. The polymer obtained as viscous oil after 24 h was identified as polycarbonate **9** from various spectral data (Table III). Namely, typical spectral features are strong absorptions at 1745 and 1225 cm^{-1} in IR, low-field-shifted carbonyl carbon signal at 155.3 ppm

Scheme III





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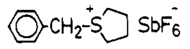

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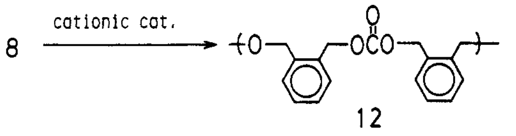
Scheme IV



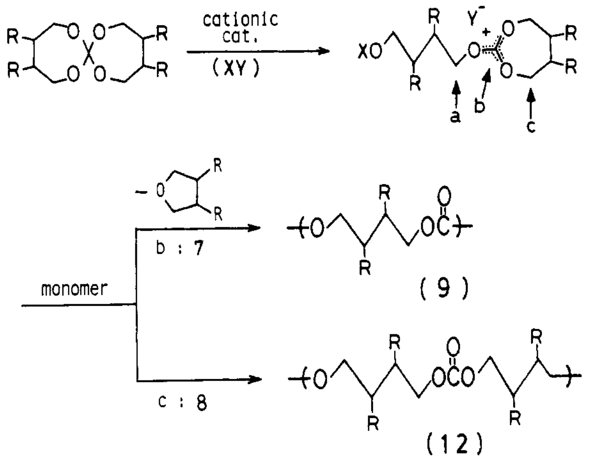
in ^{13}C NMR, and simple spectral patterns in both ^1H and ^{13}C NMR due to high symmetry of the repetition unit. Molecular weight ($\bar{M}_n$) of the insoluble part in methanol (run 8) was 8700 by GPC based on polystyrene while the soluble part consisted of a mixture of several oligomers having $\bar{M}_n$ 1000–2500 estimated by GPC. Since ^1H NMR and IR spectra of both the soluble and insoluble parts are very similar, the products undoubtedly have the same polycarbonate structures, although the degree of the polymerization (DP) is different. Furthermore, the eliminated moiety, 2-oxabicyclo[3.4.0]nonane (**10**) was obtained from the soluble part and was identified by GC–MS [*m/z* 126 (M^+, 32%)] and ^1H NMR spectrum. These results are entirely in accordance with Sakai's report for **3**.[6] In the polymerizations under several different conditions (Table II) almost the same results were obtained.

In order to investigated the behavior of **7** in detail, **7** was examined in the polymerization initiated by a thermally latent catalyst, benzylsulfonium salt **11**[12] (runs 1 and 2), which is known to initiate the polymerization at temperature over 80 °C.[8] The polymerization resulted in similar characteristics as obtained above. Thus, the cationic polymerization of **7** always gives only polycarbonate **9** under all the conditions tested.

Cationic Polymerization of 8. As shown in Table IV, the cationic polymerization of **8** was carried out with the same catalysts and solvents as in the case of **7**. The monomer **8**, as described above, had a high melting point (261–263 °C) and was hardly soluble even in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and nitrobenzene. Although hot nitrobenzene was a rather good solvent, the polymerization system still remained heterogeneous at first. However, the mixture soon became homogeneous, within 5 min at 150 °C under the polymerization conditions using **11** (runs 1 and 2). The polymerization finished within 20 min at 150 °C. The polymer **12** was obtained as a white solid in high yield by precipitation into *n*-hexane (runs 1 and 2) (Scheme IV).

By the use of $Ph_3C^+BF_4^-$ as catalyst (runs 4 and 5), similar polymer was obtained in the polymerizations at 120 and 80 °C in nitrobenzene. In these cases, some amount of soluble polymer in methanol was formed, which had $\bar{M}_n$ (1000–2000) lower than that of the insoluble polymer ($\bar{M}_n$ 4000–4200). On the other hand, it was found that even at room temperature the polymerization of **8** proceeded slowly by the catalysis of BF_3OEt_2 or $Ph_3C^+BF_4^-$ in any one of the three solvents used. It took several hours, however, to make the initial heterogeneous mixture of **8** homogeneous. The polymer thus obtained at room temperature was also a white solid having a softening point over 50 °C.

Scheme V



Both prolonged reaction period in the room temperature polymerization with BF_3OEt_2 (runs 8 and 9) and high temperature in the polymerization with $Ph_3C^+BF_4^-$ (runs 3–5) resulted in the formation of gel polymer. This seems to be related to somewhat complicated GPC patterns and large $\bar{M}_w/\bar{M}_n$ values.

Surprisingly, polymer **12** showed different spectral characteristics from those of **9**, as shown in Table III. That is, unlike **9**, two broad singlet peaks of methylenes appeared at 5.20 and 4.55 ppm, respectively, in ^1H NMR, and further ^{13}C NMR showed two carbon signals (70.0 and 67.0 ppm) corresponding to carbons adjacent to carbonate and ether oxygens, respectively. These data obviously indicated the polymer was a poly(ether–carbonate) alternative copolymer. IR spectrum supported the structure **12** by C–O ether stretchings at 1060 and 1075 cm^{-1} which were absent in that of **9**. The other data also suggested a carbonate structure by 1745 and 1250 cm^{-1} in IR and 254.7 ppm in ^{13}C NMR. Furthermore, we could not detect any byproduct eliminated such as 2,5-dihydro[*b*]benzofuran from the soluble part. In addition, the polymer **12** is also stable and no such type of elimination product was observed in the reaction with BF_3OEt_2 even for 24 h at room temperature.

Consequently, the polymerization of **8** gives poly(ether–carbonate **12** independent of solvent, temperature, and catalyst.

Comments on Polymerization Mechanism. As mentioned above, two clearly differentiated polymerizations were demonstrated. This seems to suggest that the polymerization course is determined by the electrophilicity of reaction site of the propagating cationic species. Namely, as illustrated in Scheme V, among possible three sites attacked by the monomer (see also Scheme I), attack along path *b* produces the polymer **9** where R,R = $-(CH_2)_4^-$, while attack takes place along path *c* to afford the polymer **12** where R,R = benzo. Considering the attack along path *c*, clearly the propagating species of benzo derivatives **8** is more reactive, i.e., more electrophilic, than that of **7**. The behavior of **2** and **8** is very similar.

From another viewpoint, it seems that the attack along path *b* predominates over that along path *c* in certain seven-membered SOCs (**3** and **7**). The same behavior is observed in **2**, its derivatives, and **8**, in which path *c* is strongly favored. Although the exact reason is unclear, it is also conceivable that stability of the leaving moiety plays an important role in determining the reaction course, as suggested generally in the nucleophilic substitution. Formation of a four-membered oxetane derivative is much less favorable and actually does not occur at all in the case of **2** and its derivatives. As for **8**, dihydrobenzofuran structure is considered to be less stable than furan or its derivatives like 10, due to its antiaromatic 4π system.

Conclusions. In this work we have prepared two new seven-membered SOCs and studied their cationic ring-opening polymerization in comparison with those of other SOCs. We have concluded that (i) SOCs bearing spiro[6.6]tridecane skeletons afford polycarbonate or poly(ether-carbonate) on cationic ring-opening polymerization, depending on the structure of SOC, but independent of solvent, temperature and catalyst; (ii) the attack of monomer on the ring methylene carbon adjacent to oxygen actually occurs; and (iii) the polymerization course may be determined by electrophilicity of the attacked site of the propagating species or leaving ability of the eliminated moiety. The examples described in this study are expected to contribute to designing more reactive SOCs.

Registry No. 7, 103545-44-4; 7 (homopolymer), 112795-42-3; 8, 103541-92-0; 5 (homopolymer), 112795-43-4; 10, 4743-54-8; $C(OMe)_4$, 1850-14-2; 2-$HOCH_2C_6H_4CH_2OH$, 612-14-6; hexahydrophthalic anhydride, 85-42-7; 1,2-bis(hydroxymethyl)cyclohexane, 3971-29-7; phthalic anhydride, 85-44-9.

References and Notes

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A Reexamination of the Synthesis of Liquid Crystalline Side-Chain Polyacrylates via Liquid-Liquid Phase-Transfer Catalysis

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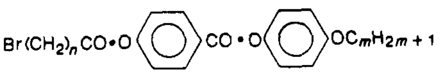
ABSTRACT: We have reexamined the synthesis of liquid crystalline side-chain polyacrylates under liquid-liquid phase-transfer conditions as first reported by Keller. Instead of the polymeric liquid crystals, the hydrolysis of the mesogen and a subsequent nucleophilic substitution reaction were found to predominate over the anticipated reaction between the carboxylate group and the mesogen. The present results are consistent with the high pH conditions prevailing in the poly(sodium acrylate) solution as determined previously. The control of the pH value in the reaction medium is perceived to be crucial in determining the reaction pathway.

I. Introduction

Chemical modification of functional polymers via phase-transfer catalysis has been an active area of research for the past several years because of the utility of the polymer products in the study of polymer-supported organic reactions.[1-3] More recently, Keller[4-7] has reported the first syntheses of mesomorphic polyacrylates and polymethacrylates in a liquid-liquid configuration by using tetrabutylammonium bromide as a phase-transfer catalyst. The idea originated from extensive research in the past on phase-transfer catalysis involving simple electrolytes.[8-10] Compared to direct polymerization of functional monomers, the chemical modification approach is attractive for its apparent simplicity.[11] However, Fréchet[12] also pointed out that the failure to perceive organic reactions involving polymeric substrates and that the lack of thorough characterization of polymer products have given rise to questionable results in the literature.

In the present work we reexamined the chemical modification of poly(sodium acrylate) with liquid crystal mesogens of the general structure



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under liquid-liquid phase-transfer conditions. Our results suggest that the observations of mesomorphism alone (with polarized optical microscopy and differential scanning calorimetry) are not sufficient for the structural assignment of polymer liquid crystals derived from polymeric substrates. In fact, nuclear magnetic resonance (NMR) spectroscopy turned out to be very useful in the structural elucidation of the products.

II. Results and Discussion

Liquid crystal mesogens shown as I were prepared following the procedures reported by van Meter and Klanderman[13] and by Hassner and Alexanian[14] using p-hydroxybenzoic acid, p-alkoxyphenol, and ω-bromo-

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