Macromolecules 1988, *21*, 2314–2318

A New Class of Polymerizable Sulfur Heterocycles. Cationic Ring-Opening Polymerization of Spiro Tetrathioorthocarbonate

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Received May 19, 1987

ABSTRACT: Polymerization of spiro tetrathioorthocarbonates (STOCs) having five- to seven-membered rings was carried out under cationic conditions. Five-membered STOC **1** afforded quantitatively poly(ethylene sulfide) (PES, **4**) with complete extrusion of ethylene trithiocarbonate (ETC), although six-membered STOC **2** hardly reacted. Seven-membered STOC **3** underwent cationic ring-opening polymerization at more than 100 °C and at room temperature, to give insoluble polymers as yellow and white resins (**5** and **9**), respectively. The polymer structure was studied in detail by IR, NMR, and elemental analysis. The polymer of **3** was made up of three different segments, thioether–trithiocarbonate **6**, trithiocarbonate **7**, and singly ring-opened tetrathioorthocarbonate **8**. In the polymer **9** at room temperature, the main segment was **8**, while the polymer **5** at high temperature had two major segments, **7** and **8**. From the results, a possible polymerization mechanism was assumed, which involved a propagating tris(alkylthio)carbenium ion (**12**).

Introduction

Cationic ring-opening polymerization of spiro orthocarbonates (SOCs) has extensively been studied over a decade by Sakai et al.[1] and Bailey and Endo et al.[2,3] Sakai first studied and reported the modes of cationic polymerization of SOCs strongly depending upon the ring size.[1] Thereafter interest has been focused on the characteristics of SOCs as monomers that undertake expansion in volume on polymerization and the application of their polymerization.[2-4] No report has appeared so far on the polymerization of such spiro monomers having heteroatoms other than oxygen. Introduction of a sulfur atom into SOC instead of an oxygen atom is interesting in the light of special effect of the sulfur atom on the structure and property of the polymer and the polymerization mode. Among a limited number of sulfur heterocycles undergoing ring-opening polymerization,[5] the only example of a spirocyclic system was reported by Goethals and DuPrez, with 2-oxa-6-thiaspiro[3.3]heptane.[6] In this case, one of the two rings (thietane ring) was preferentially cloven to yield a polysulfide having an oxetane ring in the cationic polymerization. Recently, we have extended the cationic polymerization of SOCs to their sulfur analogues, spiro tetrathioorthocarbonates (STOCs). In this article we present the first report on the cationic polymerization of STOCs bearing five- to seven-membered rings.

Experimental Section

FT-IR spectra were obtained with a JASCO FT/IR-3. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL PMX-60 and JEOL FX-100 (FT mode) spectrometers, respectively, using tetramethylsilane (TMS) as internal standard. Determination of molecular weight ($\bar{M}_n$) by gel permeation chromatography was carried out with a Toyo Soda HPLC CCP & 8000 system equipped with three polystyrene gel columns (TSK gel G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent. Measurement of inherent viscosity [η] was performed at 50 °C in *p*-chlorophenol by using the Ubbelohde's apparatus. For measurement of NMR and viscosity, polymer samples were dissolved into *p*-chlorophenol by heating at 120–150 °C for 10–15 min.

Solvents used in the polymerization were distilled and stored over drying agents according to common methods. Catalysts BF_3OEt_2 (B), CF_3SO_3H (F), and $Ph_3C^+SbCl_6^-$ (T) were used as received (extra pure grade reagents). Benzylsulfonium salt $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2}SbF_6^-$ (L) was prepared according to our method.[7]

Synthesis of Monomers 1–3.[8] A mixture of an alkanedithiol (20 mmol), tetramethyl tetrathioorthocarbonate[9] (10 mmol, 2.0 g), and *p*-toluenesulfonic acid (100 mg) in dry benzene (50 mL) was refluxed for 10–20 h (2–5 h in the case of **3**). After cooling, addition of triethylamine (0.5 mL) was followed by evaporation of the solvent. The residue was triturated with ethanol and the white solid was collected by filtration.

1: yield 75–81%; mp 137–139 °C (lit.[8] 141 °C); ^1H NMR δ ($CDCl_3$) 3.48 (s); ^{13}C NMR δ ($CDCl_3$) 85.4 (s), 42.1 (t). **2**: yield 92%; mp 116 °C (lit.[8] 116 °C); ^1H NMR δ ($CDCl_3$) 3.25–2.95 (m, 8 H), 2.30–1.88 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 57.8 (s), 28.8 (t), 24.6 (t). **3**: recrystallized from benzene–ethanol, yield 44%; mp 161–163 °C (lit.[8] 165 °C); ^1H NMR δ ($CDCl_3$) 2.92 (m, 4 H), 2.03 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 78.4 (s), 31.8 (t), 31.0 (t).

Cationic Polymerization: A General Procedure. A monomer STOC (1.0–2.0 mmol), a catalyst (3–10 mol %), and, when necessary, a dry solvent (100–300 wt%) were mixed in a Pyrex tube in which a small magnetic stirrer tip was placed. The tube was degassed by repeated cooling and pumping and sealed. Then the mixture was stirred at a set temperature (see tables). After a certain period, CH_2Cl_2 (ca. 2 mL) and triethylamine (0.1 mL) were added and the mixture was filtered. The solid material was washed with CH_2Cl_2. The filtrates were combined as the solubles while the insoluble solid polymer was collected.

Characterization of PES 4: white powder, mp > 200 °C (dec); IR (KBr) 2928, 1427, 1184, 1145, 721, 671 cm^{-1}; ^1H NMR δ (*p*-chlorophenol, external TMS) 2.60. Anal. Found (calcd): H, 7.19 (6.70); C, 39.00 (39.96).

Oxidation of 4 with H_2O_2 in AcOH at 90 °C. To a heterogeneous solution of **4** (70 mg) in acetic acid (1.0 mL) was added 30% H_2O_2 (0.4 mL), and the mixture was heated to 90 °C for 5 min. The insoluble material was filtered and washed with CH_2Cl_2. IR (KBr) 2989, 2930, 1427, 1305 (SO_2), 1132 (SO_2), 1033 (SO), 777 cm^{-1}.

Characterization of Polymers (5 and 9) of STOC 3. The insoluble part in CH_2Cl_2 was subjected to measurement of IR spectrum and to elemental analysis. Further, the polymer was dissolved into *p*-chlorophenol at 80–120 °C, to which (yellow viscous solution) was added $CDCl_3$/TMS in order to record ^1H NMR spectrum.

5 (e.g., B/PhH/120 °C): mp > 240 °C; IR (KBr) 2901, 2850, 1431, 1400, 1275, 1062 (C=S), 1020, 811 cm^{-1}. Anal. Found (calcd for segment **6**): H, 6.04 (6.39); C, 40.52 (42.81); S, 51.35 (50.80). ^1H NMR, see Figure 1A; ^{13}C NMR δ [*p*-ClC_6H_4OH–$CDCl_3$ (1:1)] 225.0 (s), 76.1 (s), 36.4 (t), 32.0 (t), 31.0 (t), 27.3 (t) (Figure 2A). **9** (e.g., B/CH_2Cl_2/room temperature): mp > 240 °C; IR (KBr) 2931, 2860, 1437, 1281 cm^{-1}. Anal. Found (calcd for segment structure **8**): H, 6.44 (6.39); C, 43.00 (42.81); S, 49.00 (50.80). ^1H NMR, see Figure 1C; ^{13}C NMR δ [*p*-ClC_6H_4OH–$CDCl_3$ (1:1)] 225.9 (s), 224.5 (s), 76.0 (s), 38.8, 36.4 (t), 32.6, 32.0 (t), 30.9 (t), 24.1 (Figure 2B).

Determination of Segment Ratio (Table IV). The segment ratios (x, y, and z for **6**, **7**, and **8**) were estimated from elemental analysis and ^1H NMR integration data. The ratio $(x + z)/y$ was given as a mean value of those calculated for both H and C from observed analytical data and the calculated values for two segments **6** (or **8**) and **7**. On the other hand, ^1H NMR integration ratio of the peaks at 2.86 and 3.25 ppm offered ratio of $(x + 2y)/(x + 2z)$. The segment ratio was determined by the above two equations as well as the relation $x + y + z = 100$.

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Table I
Cationic Polymerization of Five-Membered STOC 1

run	cat. (mol %)[a]	solv	temp/ °C	time/ min	conv/ %	yield/% ETC[b]	yield/% PES[c]
1[d]	B (5)	none	140	5	100	92	100[e]
2	B (12)	PhH	110	90	100	91	
3	L (3)	PhCl	145	10	92	88	90
4	L (3)	PhCl	120	20	77	73	

[a] B, BF_3OEt_2; L, $PhCh_2\overline{S^+CH_2CH_2CH_2C}H_2SbF_6^-$. [b] Ethylene trithiocarbonate. [c] Poly(ethylene sulfide). [d] After STOC 1 melted, catalyst B was added in an open system. [e] [η] 1.4 dL/g at 2.0 g/dL in *p*-chlorophenol at 50 °C.

In the soluble part in CH_2Cl_2, the recovered STOC **3** and the produced THT (in the polymerization at high temperature) were detected and their yields were determined by GC analyses using authentic samples. The soluble part contained a small amount of CH_2Cl_2-soluble polymer, which, however, gradually became insoluble in CH_2Cl_2 after several days.

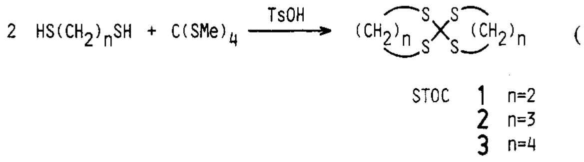
Reaction of Polymer 10 under Cationic Conditions. Polymer **10** was prepared by above procedure (F/PhCl/room temperature; segment ratio $x = 24$, $y = 8$, and $z = 68$). A heterogeneous solution of the white polymer **10** (1135 mg, 0.54 mmol) in chlorobenzene (0.5 mL) was heated in a sealed tube at 120 °C for 2 h. No THT elimination was detected in the organic solvent (GC).

To that sample, thermal latent catalyst (L, 5 mg) was added and the sealed polymerization tube was heated at 120 °C for 1 h. After similar workup, yield of yellow polymer **11** was 52 mg (39%). From the filtrate as soluble part in CH_2Cl_2 was obtained a mixture of products (80 mg), which contained 21 mg (36%) of THT (by GC). The segment ratio of **11** was $x = 34$, $y = 32$, and $z = 34$.

10: IR (KBr) 2912, 2849, 1433, 1276 cm^{-1}. Anal. Found (calcd for segment structure **6**): H, 6.28 (6.39); C, 42.32 (42.81); S, 49.65 (50.80); ^1H NMR, see Figure 1D. **11**: IR (KBr) 1049 (C=S) cm^{-1}. Anal. Found: H, 5.88; C, 40.68; S, 54.11. ^1H NMR, see Figure 1E.

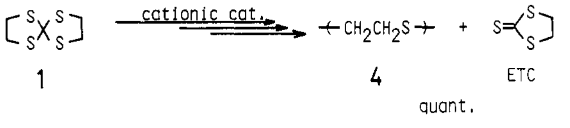
Results and Discussion

Synthesis of Spirocyclic Monomers. Three types of STOCs (**1**–**3**) having different ring size were prepared by condensation of corresponding dithiols with tetramethyl tetrathioorthocarbonate[9] according to eq 1.[8] All STOC monomers were sufficiently thermally stable, at least up to 150 °C.



(1)

Cationic Polymerization of STOCs. (1) Five- and Six-Membered STOCs. Five-membered STOC **1** was polymerized at a temperature above 110 °C in the presence of a cationic catalyst such as BF_3OEt_2 (B) and thermal latent catalyst $PhCH_2\overline{S^+CH_2CH_2CH_2C}H_2SbF_6^-$ (L).[7] Red heterogeneous products were identified as a mixture of poly(ethylene sulfide) (PES, **4**) and ethylene trithiocarbonate (ETC) (eq 2). Table I reveals quantitative yields of PES and ETC independent of the catalyst in both bulk and solution polymerizations. ETC was confirmed by comparison with authentic sample in ^1H NMR (δ 4.05 ppm, singlet, STOC **1**; δ 3.48 ppm), GC, and IR ($\nu_{C=S}$ 1080 cm^{-1}). PES **4**, a white powder (mp > 200 °C, [η] 1.4 dL/g (run 1) in *p*-chlorophenol at 50 °C) which was insoluble in $CHCl_3$, THF, DMF, DMSO, etc., was identified by ^1H NMR in *p*-chlorophenol[10] and exhibited a broad singlet at 2.60 ppm. Furthermore, the obtained polymer PES was oxidized with hydrogen peroxide in acetic acid to yield polymer that showed ν_{SO} (1033 cm^{-1}) and ν_{SO_2} (1132 and 1305 cm^{-1}) in IR. This result strongly supported the structure **4**.



(2)

Six-membered STOC **2** very sluggishly produced a complex mixture of products as dark green oil. None of them could be identified clearly except for the monomer **2** recovered (e.g., catalyst L/120 °C/16 h/chlorobenzene, conversion ca. 50%).

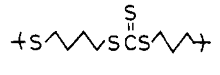
Table II
Cationic Polymerization of Seven-Membered STOC 3 in Chlorobenzene

run	cat. (mol %)[a]	temp/ °C	time/ min	conv/ %	yield/% insol[b]	yield/% sol[c]	yield/% THT[d]
1	B (10)	150	20	90	68		
2	B (4)	100	360	71	14	60	20
3	L (3)	120	20	76	65[e]	24	
4	L (3)	100	180		16	81	
5	L (3)	100	660		32	56	50
6	L (3)	80	180	0	0	99	0
7	T (3)	100	300		25	44	34

[a] B, BF_3OEt_2; L, $PhCH_2\overline{S^+CH_2CH_2CH_2C}H_2SbF_6^-$; T, $Ph_3C^+SbCl_6^-$. [b] Insoluble part in CH_2Cl_2. [c] Soluble part in CH_2Cl_2, which contained STOC **3** recovered. [d] Tetrahydrothiophene (yield in mol % versus monomer used). [e] [η] 3.2 dL/g at 4.0 g/dL in *p*-chlorophenol at 50 °C.

(2) Seven-Membered STOC. In contrast to **2**, cationic polymerization of seven-membered STOC **3** in chlorobenzene proceeded well at more than 100 °C, with the catalyst L, B, or T ($Ph_3C^+SbCl_6^-$), to precipitate yellow resin polymer (mp > 240 °C). In the case of the catalyst L, the polymerization did not proceed at 80 °C (180 min), in consistent with reported low activity at less than 80 °C.[7] No serious difference was observed in the activity among the catalysts used. The polymer **5** collected ([η] 3.2 dL/g (run 1) in *p*-chlorophenol at 50 °C) was insoluble in $CHCl_3$, THF, DMF, DMSO, etc. but, like **4**,[10] was soluble only in hot *p*-chlorophenol. The fractions soluble in CH_2Cl_2 consisted of a mixture of monomer **3** and low molecular weight oligomers which were analyzed by GPC. As shown in Table II, the yield of polymer insoluble in CH_2Cl_2 increased as the temperature was raised and the polymerization time was prolonged.

In the ^1H NMR of the polymer **5** in *p*-chlorophenol–$CDCl_3$, the signal at 2.86 ppm is assigned to methylene protons adjacent to the thioether sulfur and that at 3.25 ppm is assigned to the methylene protons adjacent to trithiocarbonate sulfur (Figure 1A). The ratio of the two peaks suggested that the polymer structure could not be explained only by a polythioether–trithiocarbonate structure **6** (Figure 1B), which is expected for a polymer of the six-membered SOC. Meanwhile, from the soluble part in CH_2Cl_2, from 20 to 50% of tetrahydrothiophene (THT) was observed besides recovered **3** in each case. This seemed to imply the involvement of the polytrithiocarbonate structure **7**, as in the case of seven-membered SOC which eliminates tetrahydrofuran on polymerization.[1] Similarly, the structure **7** was not the only one constructing this polymer. Accordingly, the polymer **5** was suggested to have segments of both **6** and **7**. Indeed, elemental


6


7

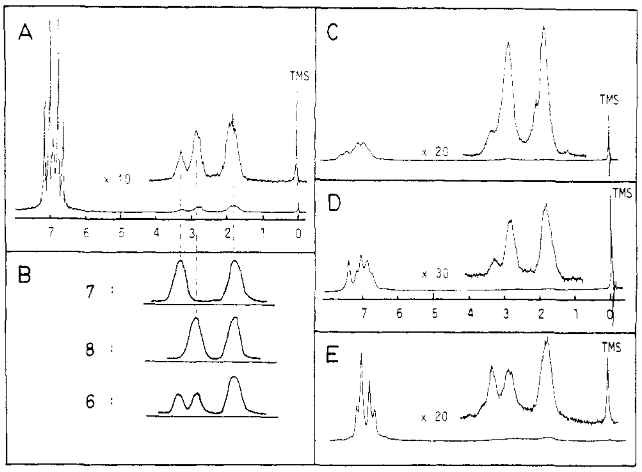
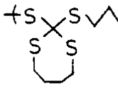


Figure 1. ^{1}H NMR spectra (60 MHz, p-ClC$_6$H$_4$OH-CDCl$_3$ 50/50 v/v%). (A) Polymer **5** obtained from **3** under conditions of B, 3 mol %/120 °C/PhH/1.5 h. (B) Expected spectra for the segments **6**, **7**, and **8**. (C) Polymer **9** obtained from **3** under conditions of B, 3 mol %/room temperature/CH$_2$Cl$_2$/4 days. (D) Polymer **10** obtained from **3** under conditions of F, 12 mol %/room temperature/PhCl/21 h. (E) Polymer **11** obtained from polymer **10** (spectrum D) under conditions of L, 2 mol %/120 °C/PhCl/1 h.

analysis of **5** showed the values (H, 6.04; C, 40.52; S, 51.35) located between the values calculated for **6** (H, 6.39; C, 42.81; S, 50.80) and **7** (H, 4.91; C, 36.55; S, 58.54). However, the NMR spectrum of **5** (Figure 1A) could not be obtained even by combining two NMR spectra, expected for the structures **6** and **7**, in any ratio (Figure 1B). In addition to these results, the larger peak area of the 2.86 ppm signal than that of the 3.25 ppm peak undoubtedly indicated that the number of methylene groups adjacent to the thioether is greater than that adjacent to trithiocarbonate. Thus, the above results obtained led us to devise a new segment **8**, a singly ring-opened structure (NMR predicted, see Figure 1B). This comes from the cationic polymerization of a bicyclo orthoester, which affords singly and doubly ring-opened structures as repetition units, depending upon the polymerization temperature.[11,12] Then, it made possible to explain various data given for the polymer **5** by combining these three segments (**6**–**8**) in a certain ratio.



8

$$-\!(6)_x(7)_y(8)_z\!-$$

On the other hand, the polymerization of **3** at room temperature was found to occur with catalyst such as B, T, and F (CF$_3$SO$_3$H) (Table III). However, the obtained polymer **9**, insoluble in CH$_2$Cl$_2$, was a white or faintly yellow powder (mp > 240 °C, [η] 4.2 dL/g (run 1) in p-chlorophenol at 50 °C). From GPC analyses, the soluble part was a mixture of monomer **3** and low molecular weight oligomers ($\bar{M}_n$ < 880 based on polystyrene standard) in all cases. This polymer also had quite low solubility but showed no or traceable $\nu_{C=S}$ in the IR, in accordance with the absence of yellow color found in **5**. Further, no or less than 5% THT was observed from the soluble part in CH$_2$Cl$_2$. In the NMR of **9**, the signal at 3.25 ppm, corresponding to methylene adjacent to trithiocarbonate sulfur, largely decreased (Figure 1C) in comparison with that of **5** (Figure 1A). Analytical data of **9** also supported the above observations. Namely, the found values were entirely equal to those calculated for segment **6** or **8**. Furthermore, the highly enhanced ratio of [(**6** + **8**)/**7**, i.e., (x + z)/y], calculated from the elemental analysis, was well consitent with the ^{1}H NMR spectrum, when the predicted spectra for segments **6**–**8** (Figure 1B) are acceptable.

Table III

Cationic Polymerization of STOC 3 at Room Temperature

run	cat. (mol %)[a]	solv (vol %)[b]	time/h	conv/%	yield/% insol[c]	sol[d]	THT[e]
1	F (12)	PhCl (300)	21	100	69[f]	32	0
2	F (8)	CH$_2$Cl$_2$ (300)	2.5		26	75	0
3	B (3)	CH$_2$Cl$_2$ (300)	92	100	44	48	5
4	T (3)	CH$_2$Cl$_2$ (300)	28	95	42		0

[a] F, CF$_3$SO$_3$H; B, BF$_3$OEt$_2$; T, Ph$_3$C$^+$SbCl$_6^-$. [b] Solvent volume in wt %. [c] Insoluble part in CH$_2$Cl$_2$. [d] Soluble part in CH$_2$Cl$_2$. [e] Tetrahydrothiophene (yield in mol % versus monomer used). [f] [η] 4.2 dL/g at 6.0 g/dL in p-chlorophenol at 50 °C.

Table IV

Segment Ratios of Polymers Derived by Cationic Polymerization of Seven-Membered STOC 3

run	cat.[a]/temp[b]/time[c]	(x + z)/y[d]	A/B[e]	seg ratio/%[f] x	y	z
1	L (3)/100/90	79/21	32/68	22	21	57
2	L (3)/100/180	63/37	40/60	6	37	57
3	L (3)/100/360	53/47	50/50	6	47	47
4	L (3)/100/660	45/55	56/44	2	55	43
5	B (4)/100/360	70/30	42/58	24	30	46
6	T (3)/100/300	45/55	64/36	18	55	27
7	F (12)/RT/21 h	92/8	20/80	24	8	68
8	B (3)/RT/92 h	100/0	12/88	24	0	76

[a] See Tables I–III. [b] In °C. [c] In min. [d] Calculated from elemental analysis data. [e] A, x + 2y; B, x + 2z. The (A/B) was ^{1}H NMR integration ratio of two peaks at 2.86 (A) and 3.25 (B). [f] x, segment **6**; y, segment **7**; z, segment **8**. The ratio was determined by calculation with (x + z)/y and A/B.

On the basis of the above results, the segment ratios [x (**6**), y (**7**), and z (**8**)] of some selected polymers were estimated from both ^{1}H NMR integrations and elemental analyses (Table IV). Although some extent of experimental error should be taken into account, the inspection of data in Table IV revealed good agreement with the results described so far: for instance, (i) an extremely low content of segment **7** in the polymer obtained at room temperature (runs 7 and 8), (ii) gradual increase of segment **7** with increase of polymerization time, and so on. Consequently, the polymers obtained at higher temperature consist of two major segments **7** (y = 21–55%) and **8** (z = 27–57%), while polymer **9** mainly involves segment **8** (z = 68–76%).

The above results on polymer composition were supported by ^{13}C NMR [at 80 °C in p-chlorophenol–CDCl$_3$ (1:1)] of the two kinds of polymers (**5** and **9**) (Figure 2). In the ^{13}C NMR of **5** (Figure 2A), a clear characteristic signal at 225.0 ppm corresponding to the trithiocarbonate carbon appeared, while the strength of this signal considerably decreased (ca. one to ten) in the case of **9** (225.9 and 224.5 ppm) (Figure 2B). Furthermore, both peaks at 36.4 and 27.3 ppm based on methylene carbons of the structures **7** and **6** (partly) were much higher in **5** than in **9**. In accordance with this, both signals appearing at 32.0 and 30.9 ppm, corresponding to the structures **8** and **6** (partly), were major peaks in the spectrum of **9**. In both polymers, a very small signal at 76 ppm (a peak overlapped with CDCl$_3$) was confirmed and might be assigned to the orthocarbonate quaternary carbon. Therefore, the ^{13}C NMR data can well reflect the proposed segment structures and ratios.

In order to support the segment structures estimated, the white polymer **10** prepared at room temperature

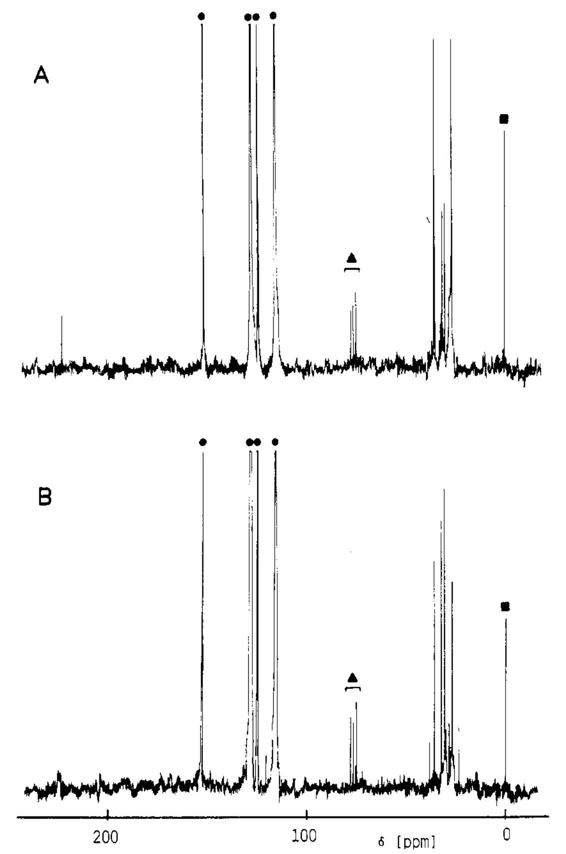
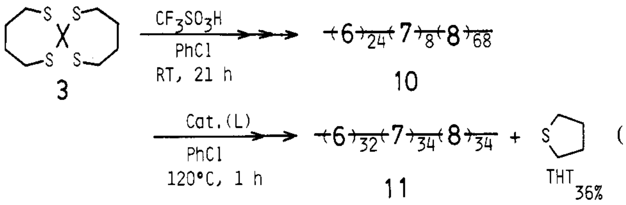


Figure 2. ^{13}C NMR spectra at 80 °C in *p*-chlorophenol–$CDCl_3$ (50/50 v/v%) [(■) TMS, (▲) $CDCl_3$, and (●) *p*-chlorophenol]. (A) Polymer (yellow, **5**) obtained in the polymerization of **3** with catalyst B in benzene at 120 °C. (B) Polymer (white, **9**) obtained in the polymerization of **3** with catalyst B in CH_2Cl_2 at room temperature.

(catalyst F/CH_2Cl_2/21 h: x = 24, y = 8, and z = 68) was treated with catalyst L at 120 °C for 1 h in PhCl (eq 3).

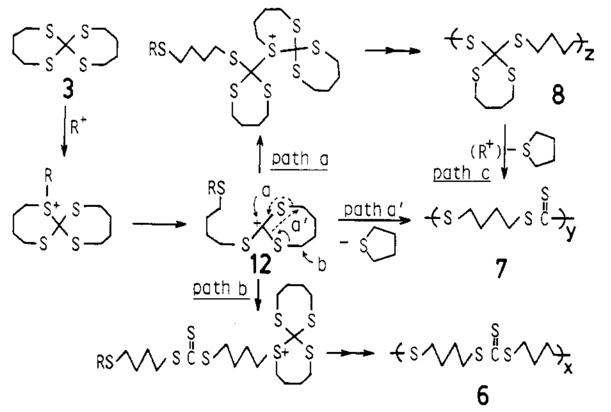


(3)

From the soluble part in CH_2Cl_2, THT was found in 36% yield. In the absence of the catalyst no THT and no change of the polymer color were observed under the same conditions, whereas yellow colored resin **11** obtained as the insoluble part had a segment ratio of x = 34, y = 32, and z = 34. This change of the ratio corresponds to the enhancement of the signal area at 3.25 ppm in ^{1}H NMR as expected (Figure 1D,E). Thus, segment **8** was proved to eliminate THT under the polymerization conditions at high temperature. This elimination would give rise to an increase of the segment **7**.

The reason the polymers obtained from **3** are insoluble in common solvents is unknown at the present time, but it may be attributed to some cross-linking, because segment **8** is cross-linkable by ring-opening to cause C–S bond formation between the polymer chains. The fact that the polymers become soluble into *p*-chlorophenol on heating would be explained by assuming the cleavage of the cross-linked C–S bond by a solvent such as an acid, since the C–S bond of tetrathioorthocarbonate is known to be quite susceptible toward acid. In fact, longer heating of the polymers in *p*-chlorophenol at 150–180 °C led to a clear decrease of viscosity along with a color change from yellow to dark brown and evolution of THT, which certainly correspond to the proposed decomposition.

Scheme I



The plausible mechanism of the polymerization of **3** is illustrated in Scheme I. The polymerization proceeds via stable single-ring-opened tris(alkylthio)carbenium ion **12**, a key propagating species. This species is capable of being attacked by the second monomer to give each segment via path a, a′, or b. Path a would be kinetically predominant. Path a′ is one of the possible pathways but would be minor one. Although conversion of **8** to **6** under the polymerization condition cannot be ruled out, path **b** is likely to occur, as found in the case of six-membered SOCs.[2,3] At high temperature, path c becomes important. Elimination of THT from segment **8** through path c is unequivocal and might cause the cleavage of the polymer main chain as well as transformation to segment **7**.

Summary

Thus, spiro tetrathioorthocarbonates (STOCs) were proved to be new sulfur-contaning cyclic monomers, undergoing cationic ring-opening polymerization, even at room temperature. The polymerizability of STOCs was studied from the viewpoint of ring size. Meanwhile, five-, or six-, and seven-membered SOCs form polyether, poly(ether–carbonate), and polycarbonate, respectively, on cationic polymerization.[1] Recently, we have shown the first example of a seven-membered SOC that gives a poly(ether-carbonate).[13] In comparison with the behavior of such SOCs, five-membered STOC **1** resembled SOC, while six-membered STOC had much less polymerizability than SOC. The polymerization of **3** was rather complicated and was described in this paper. As a result, the polymer of **3** was constructed of three different segments (**6**–**8**). Unlike SOCs, both a singly ring-opened segment (**8**) and a fully ring-opened isomerization segment (**6**) were suggested. Segment **8** became the main segment when the polymerization was employed at room temperature. Segment **7** was had an analogous structure to that of the polymer of the seven-membered SOC. Further study on several problems such as volume change on polymerization, copolymerization, etc. is in active progess.

Registry No. 1 (homopolymer), 114532-93-3; 1 (SRU), 24936-67-2; 3 (homopolymer), 114532-94-4.

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Chemistry of Surface-Hydroxylated Poly(chlorotrifluoroethylene)[1]

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ABSTRACT: Hydroxyl groups have been introduced to the surface of poly(chlorotrifluoroethylene) (PCTFE) by reaction of PCTFE film samples with the protected alcohol-containing lithium reagent, acetaldehyde lithiopropyl ethyl acetal (LiPrO*P*), and subsequent deprotection. The density of hydroxyl groups (the depth of the modification reaction) in the modified film surface (PCTFE-OH) can be controlled with reaction temperature. The concentration of hydroxyl groups has been determined to be four OH groups per five PCTFE repeat units. PCTFE-OH has been converted to a range of modified surfaces using standard hydroxyl group transformations: Reaction with *p*-toluenesulfonyl chloride yields the *p*-toluenesulfonate (PCTFE-OTs). PCTFE-OTs reacts with chloride, bromide, and cyanide to yield PCTFE-Cl, PCTFE-Br, and PCTFE-CN, respectively. PCTFE-OH reacts with acetyl chloride, trichloroacetyl chloride, pentafluorobenzoyl chloride, and adipoyl chloride to give the corresponding surface-confined esters. Adipoyl chloride reacts to give primarily the diester. Trichloroacetyl isocyanate, α,α,α-trifluoro-*p*-tolyl isocyanate, and hexamethylene diisocyanate react with PCTFE-OH to yield the urethanes and diurethane. Trimethylchlorosilane reacts with PCTFE-OH to yield the trimethyl(surface alkoxy)silane; dimethyldichlorosilane yields the dimethyl(surface dialkoxy)silane. PCTFE-OH reacts with methyltrichlorosilane to yield what analyzes to be methylchloro(surface dialkoxy)silane and with tetrachlorosilane to yield what analyzes to be chloro(surface trialkoxy)silane. Reactions of PCTFE-OH with (2-cyanoethyl)trichlorosilane, (3-cyanopropyl)dimethylchlorosilane, and (3-(methacryloxy)propyl)dimethylchlorosilane yield (2-cyanoethyl)(surface trialkoxy)silane, (3-cyanopropyl)dimethyl(surface alkoxy)silane, and (3-(methylacryloxy)propyl)dimethyl(surface alkoxy)silane, respectively. Thionyl chloride reacts with PCTFE-OH to give the sulfite. Reaction of PCTFE-OH with phosphorous tribromide does not yield a single functional group containing product: It yields surface-confined phosphite, surface phosphinous acid, and PCTFE-Br. Oxidation of PCTFE-OH with dicyclohexyl carbodiimide, Me$_2$SO, and anhydrous phosphoric acid yields the aldehyde (PCTFE-CHO) and with pyridinium dichromate in DMF yields the carboxylic acid (PCTFE-COOH). The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance infrared spectroscopy (ATR IR), and contact angle analysis. Monitoring the reaction of PCTFE-OH with pentafluorobenzoyl chloride by each of these techniques suggests that the reactions proceed at a uniform rate throughout the hydroxylated layer. The reactions were carried out on PCTFE-OH samples that contained ~1500 Å thick modified surfaces to facilitate ATR IR analysis. That the same chemistry is feasible by using PCTFE-OH containing ~50 Å thick modified surfaces was demonstrated by carrying out three reactions on this substrate: the preparation of the ester using trichloroacetyl chloride, the preparation of PCTFE-OTs, and the displacement of the tosylate with bromide.

Introduction

Chemistry at polymer surfaces and interfaces is central to many polymer materials applications.[2,3] We have begun a research program directed at preparing specific polymer surfaces and interfaces with well-defined chemical compositions. With these model substrates we hope to be able to draw surface structure-property and structure-reactivity relations and learn how to predict particular properties with knowledge of the chemical structure as well as impart desired properties by introducing specific functional groups in specific locations, densities, and patterns. We have chosen to study chemically resistant (unreactive) polymers containing versatile organic functional groups at their surfaces to meet the above objectives. The advantages of these materials as substrates have been discussed in detail.[4] Briefly, polymer film samples with inert bulk and reactive surfaces can be modified by using a range of conditions which limit changes to surface chemical ones and do not alter the structure or properties of the bulk. The first phase of this research has involved developing surface-selective modification reactions for poly(chlorotrifluoroethylene) (PCTFE),[4] poly(tetrafluoroethylene) (PTFE),[5] poly(vinylidene fluoride) (PVF$_2$),[6] and polypropylene (PP).[7,8] The second phase involves incorporation of specific versatile functional groups, either in the modification reactions or by further reactions of modified surfaces. We have reported the introduction of carboxylic acid, aldehyde, and alcohol functional groups onto the surface of

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