Polymer 40 (1999) 6539–6543

polymer

The double ring-opening polymerization of sulfur containing spiro orthocarbonates

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Received 10 September 1998; received in revised form 1 December 1998; accepted 1 December 1998

Abstract

The polymerization of new sulfur containing spiro orthocarbonates with the ability to undergo double ring-opening is reported. Various initiators were used in the cationic polymerization study, and the polymer structure determined. The polymerization is proposed to occur via a controlled tandem double ring-opening mechanism. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Spiro orthocarbonates; Double ring-opening; Poly(thioether-monothiocarbonates)

1. Introduction

Half a century [1] has elapsed since the ring-opening of cyclic monomers was reported to minimize volume shrinkage on polymerization. There are many potential applications for such materials including dental composites, film coatings, adhesives and precision castings.

Various cyclic monomers including vinyl cyclopropanes and spiro orthoesters (SOEs) have reportedly [2,3] shown essentially zero, or even positive changes in volume when polymerized. Spiro orthocarbonates (SOCs, **1**) have received the most attention, and it has been claimed [3,4] that some SOC monomers show significant volume expansion upon cationic polymerization. The highly strained nature of the SOC systems results in many of the monomers being unstable; some even decompose when exposed to atmospheric moisture [5]. In an effort to balance the stability and polymerizability, heteroatoms other than oxygen were used in the SOC systems. Endo and coworkers reported [6] the cationic polymerization of different spiro tetrathioorthocarbonates (STOCs, **2**), however they found that the STOCs which polymerized were generally prone to fragmentation, and suffered from solubility problems. The polymerization of a N,S-ring SOC has been published [7], but the work was limited by an inability to produce workable quantities of monomer and polymer (Fig. 1).

The approach used in these laboratories employs the sulfur containing SOCs **3** and **4**; it is envisaged that the partial substitution of sulfur with oxygen would provide more stable monomers and impart superior properties in the polymer, whilst maintaining a moderate level of solubility. Also, the incorporation of an *exo*-methylidene group offers the opportunity of additional cationic pathways, possible crosslinking sites, as well as the possibility of using free radical polymerization conditions. In this article we report the first cationic polymerization of the sulfur containing spiro orthocarbonates **3** and **4** (Fig. 2).

2. Materials and methods

2.1. Apparatus

^1H and ^{13}C NMR spectra of monomers and polymers were recorded on a Varian Unity Plus 400 Spectrometer. IR spectra were obtained with a BioRad FTS-60A Fourier-transform IR spectrometer. Molecular weight and its distribution were determined by gel permeation chromatography (GPC) on a Waters 510 system equipped with three polystyrene gel columns (500, 10^3 and 10^3). The eluent was tetrahydrofuran, (flow rate 1.0 mL/min) and a refractive index detector was used by comparison with polystyrene standard samples. The software package used in the analysis was Baseline.

2.2. Chemicals

Initiators boron trifluoride etherate BF_3OEt_2 (Aldrich), tin(IV)chloride $SnCl_4$ (Aldrich), triphenylcarbenium

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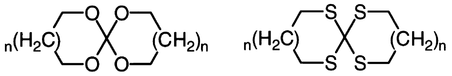
PII: S0032-3861(98)00838-6



1 **2**

Fig. 1. Various SOCs 1 and STOCs 2.

tetrafluoroborate $Ph_3C^+BF_4^-$ (Aldrich), and trifluoromethanesulfonic anhydride $(CF_3SO_2)_2O$ (Aldrich) were used as received. Chlorobenzene and dichloroethane (DCE) were distilled from calcium hydride and stored over molecular sieves (4 Å).

2.3. Synthesis of monomers 3 and 4

The sulfur containing SOCs **3** and **4** were synthesized via a two step procedure from 1,1-dichloro-1,1-diphenoxymethane **5** (Scheme 1) [8]. The precursor 2-methylidenepropane-1,3-dithiol was isolated following a literature procedure modified in our laboratories [9]. The relative hydrolytic stability of monomers **3** and **4** was greater than their oxygen SOC analogues, and this is consistent with the X-ray data from our crystallographic study [10].

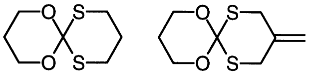
2.4. Polymerization of 3 typical procedure

The monomer **3** (0.200 g, 1.04 mmol) was introduced into a two neck flask connected to a Schlenk line, to which dichloroethane was added (0.880 mL, 1.0 M). The flask underwent three freeze-pump-thaw cycles, and was filled with an atmosphere of argon. The flask was then heated to 40°C, at which time the initiator $Ph_3C^+BF_4^-$ (10.3 mg, 3 mol%) in dichloromethane (0.162 mL) was injected as a standard solution. The mixture was stirred (20 h) and then quenched with triethylamine (0.3 mL) in dichloroethane (1.0 mL). All of the material was added dropwise to stirred *n*-hexane (50 mL) and allowed to stand overnight, during which time a cloudy material oiled out. The *n*-hexane was removed by decantation, the residue was taken up in dichloromethane and dried in vacuo yielding an opaque, tacky resin (0.006 g, 33%).

IR (NaCl, cm^{-1}) 2927, 1704, 1462, 1438,1422, 1258, 1187, 1148, 1084; ^{1}H NMR ($CDCl_3$, δ) 7.41–7.39 (m), 7.29–7.19 (m), 4.31 (t, 2H), 2.96 (t, 2H), 2.63–2.57 (m, 4H), 1.98–1.90 (m, 4H). ^{13}C NMR ($CDCl_3$), δ 170.8, 144.6, 129.5, 127.8, 126.6, 65.8, 30.5, 29.7, 29.3, 28.5, 28.1. GPC M_n 2500, M_w/M_n 3.15.

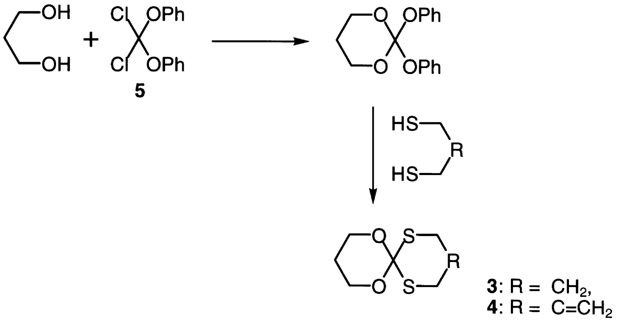
The *n*-hexane layer was concentrated under reduced pressure resulting in the isolation of recovered monomer (0.129 g, 65%).

Any dichloromethane insoluble polymer component was weighed and analyzed using ^{13}C and ^{1}H NMR spectroscopy in d_5 pyridine at elevated temperatures (Figs. 3, 4).



3 **4**

Fig. 2. Sulfur containing SOCs.



Scheme 1.

3. Results and discussion

Table 1 summarizes the polymerization results of monomer 3 with a range of initiators. Previous work [11] indicates that double ring-opening is an important pathway in the cationic polymerization of similar SOCs and preliminary results indicated that such processes were occurring in the spiro dithio dioxo orthocarbonate STOOC **3**. There are three potential pathways for the double ring-opening polymerization of the STOOC **3**. The first is exclusive reaction via either of the oxygen heteroatoms to yield the poly(ether-dithiocarbonate) **6**, (Scheme 2, path a). The second is a similar reaction pathway at one of the sulfur heteroatoms to yield the poly(thioether-monothiocarbonate) structure **7**, (Scheme 2, path b). And the third is a combination of oxygen and sulfur heteroatom reactions which would produce a mixed poly(ether-carbonate) structure.

The uncomplicated nature of the ^{1}H NMR and ^{13}C NMR spectra of the isolated polymers from **3** suggests that a single mechanistic pathway is occurring, thus it is unlikely to be a mixed poly(ether-carbonate) structure. The spectral data of the polymers produced from **3** is consistent with a double ring-opening mechanism, yielding the poly(thioether-monothiocarbonate) structure **7**, as shown as path ‘b’ (Scheme 2). The absence of a thiocarbonyl peak in the IR and ^{13}C NMR spectra indicates that without the occurrence of rearrangement reactions, path ‘a’ of Scheme 2 is not occurring. This is also evidence to support the theory that a mixture of pathways ‘a’ and ‘b’ is not taking place.

The structure of the polymer was determined using 2D HETCOR spectral data. The triplet at δ 4.31 ppm (Fig. 1) in the ^{1}H NMR can be assigned to a methylene adjacent to an oxygen atom, and the corresponding carbon resonance at δ 65.8 ppm (Fig. 2) in the ^{13}C NMR suggests it is part of a carbonate structure. The position of the resonance at δ 2.96 ppm (Fig. 1) suggests it may a methylene group adjacent to a thionocarbonate structure. The apparent quartet at δ 2.59 ppm (Fig. 1) in the ^{1}H NMR was shown to be two overlapping triplets, and their ^{13}C chemical shifts of

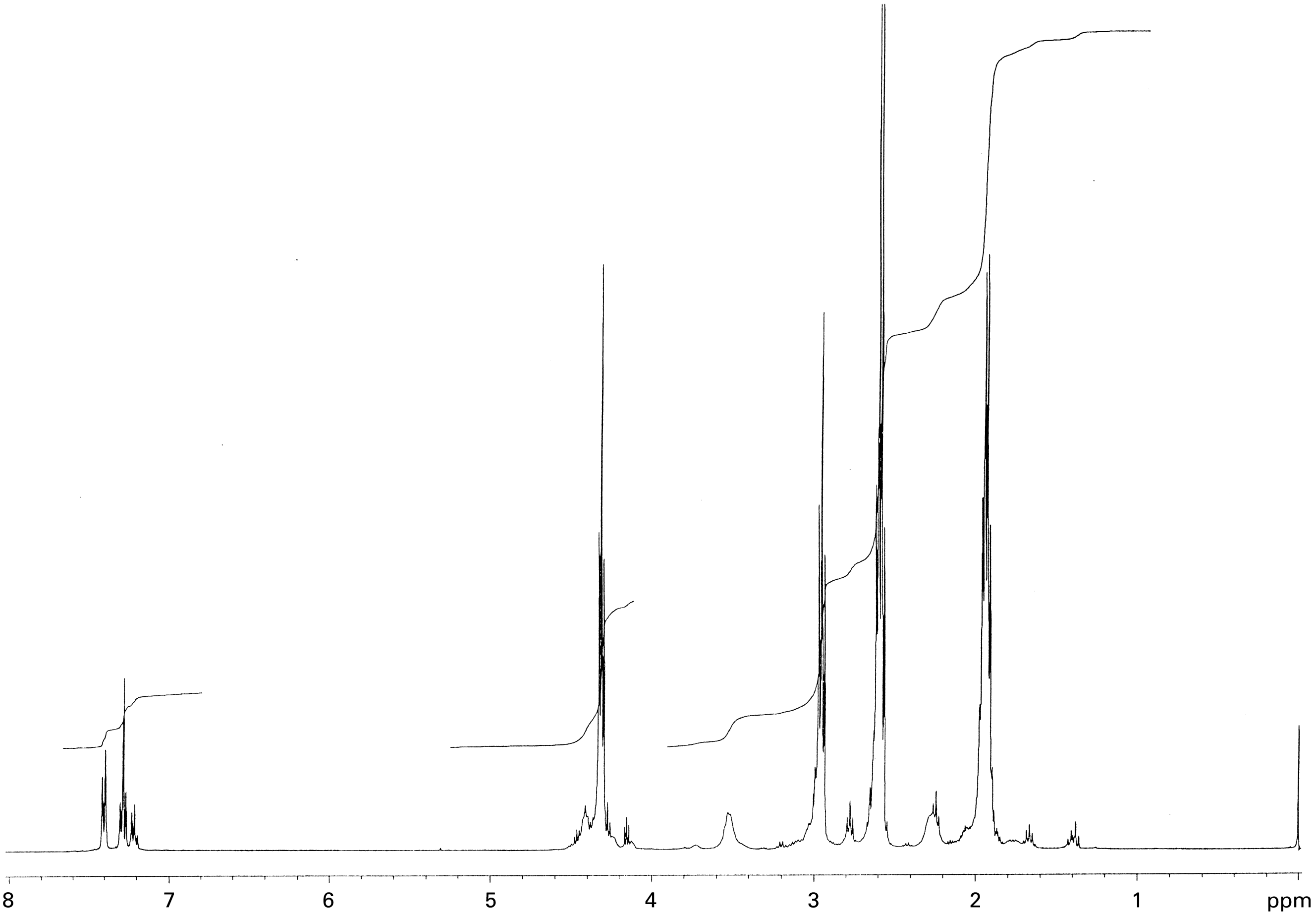


Fig. 3. ^{1}H NMR spectra of the cationic polymerization of STOOC 3.

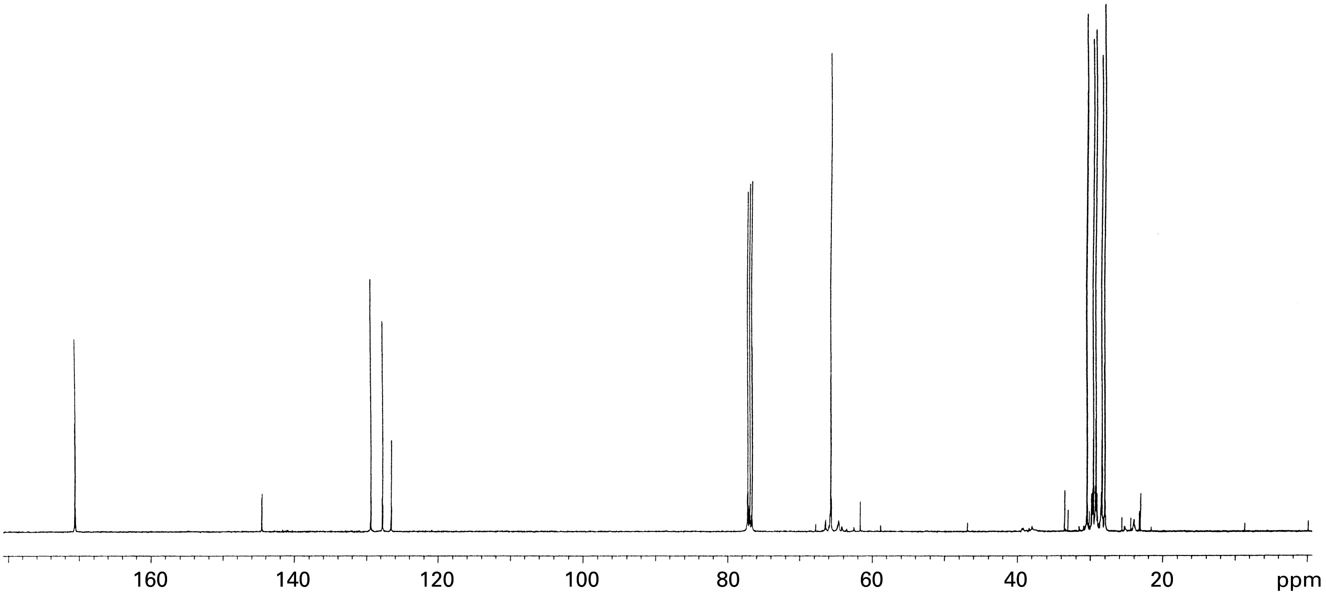


Fig. 4. ^{13}C NMR spectra of the cationic polymerization of STOOC 3.

Table 1
Cationic Polymerization of STOOC 3

Initiator[a]	Solvent	Temp (°C)	CH_2Cl_2 sol (%)	CH_2Cl_2 insol (%)	M_n (M_w/M_n)
BF_3OEt_2	$Cl(CH_2)_2Cl$	40	33		900 (5.0)
BF_3OEt_2	PhCl	100	19		[b]
$Ph_3C^+BF_4^-$	$Cl(CH_2)_2Cl$	40	35		2,500 (3.2)
$SnCl_4$	$Cl(CH_2)_2Cl$	40	3		n.d.
$SnCl_4$-H_2O	$Cl(CH_2)_2Cl$	40	15		[b]
$(CF_3SO_2)_2O$	$Cl(CH_2)_2Cl$	40	34	19	700 (7.8)

[a] 3mol %, dichloroethane 1.0 m, 20 h.
[b] Would not dissolve in the GPC solvent.

approximately δ 30 ppm indicate they are similar thioether resonances. The integration was as required for these assignments. The IR speak at 1704 cm^{-1} and ^{13}C resonance at δ 170.8 ppm are consistent with the presence of a carbonyl carbon.

The well defined nature of the ^1H and ^{13}C NMR spectra suggested that the molecular weight of the dichloromethane soluble polymers under analysis was low; this was confirmed using GPC. Generally, the M_n of these polymers ranged from 700 to 2,500 depending on the polymerization conditions.

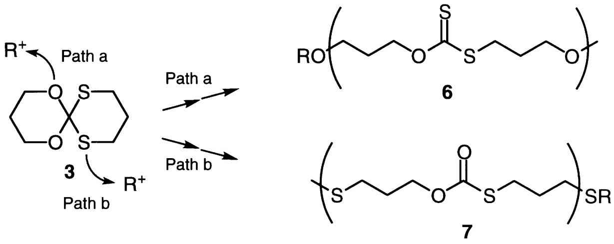
For the polymer from $Ph_3C^+BF_4^-$, the well defined nature of the phenyl groups of the triphenylcarbenium initiator fragment meant that correlation between the GPC and NMR results was possible. From GPC, the estimated degree of polymerization was approximately 12 monomer units. Integration of the initiator to polymer ratio by ^1H NMR indicated approximately one initiator fragment per 20 monomer units. Integration of the triethyl amine end groups suggested that approximately one end group per 16 monomer units was present. Given that GPC uses polystyrene standards, these results are in general agreement, that is a DP of 12–20 units.

The polymers produced that were insoluble in dichloroethane were studied with ^1H and ^{13}C NMR techniques using d_5-pyridine at 90°C and their structure was found to be similar to the more soluble polymer components. However, as they were not soluble in many common solvents their molecular weight could not be estimated by GPC.

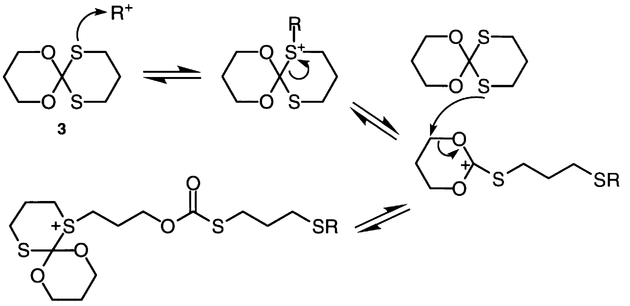
The most probable mechanism of the formation of **7** is illustrated in Scheme 2, in which the electron deficient initiator moiety attacks sulfur in preference to either of the oxygen atoms. There are literature examples [12,13] of sulfur reacting preferentially to oxygen consistent with it being more nucleophilic; however it also appears that the sulfonium salt is more stable than the corresponding oxonium salt, and is thus favoured by the equilibria. A recent X-ray study [10] of **3** revealed that the axial spiro C–S bond is considerably lengthened because of the presence of an anomeric effect, which may provide the site for the first ring-opening. Also, as the spiro C–O bonds of the adjacent 1,3-dioxane ring contain a considerable amount of sp^2 character, this would assist in the delocalization of positive charge between them. This stabilization could facilitate the addition of another monomer unit, allowing the second tandem ring-opening to occur. The formation of the more stable carbonyl group, a result normally attributed to more effective π-bonding [14], would be favoured over the formation of a thiocarbonyl group. Importantly, in all polymers analyzed, no evidence of monomer fragmentation upon polymerization was found (Scheme 3).

3.1. Relative reactivity of cationic catalysts

All four initiators trialed produced polymer in various yields. Tin(IV) chloride provided only a 3% polymer yield, however this was in the absence of a co-initiator. Previous work [15] has shown that the polymerization of styrene with metal halides requires the presence of a co-initiator, commonly water is used. When Tin(IV) chloride was combined with one equivalent of water prior to addition, the polymer yield was increased to 15% (Table 1).



Scheme 2.



Scheme 3.

Table 2
Cationic polymerization of MSTOOC 4

Initiator	Solvent	Temp (°C)	CH_2Cl_2 sol (%)	CH_2Cl_2 insol (%)	M_n (M_w/M_n)
BF_3OEt_2	$Cl(CH_2)_2Cl$	40	58		900 (5.2)
BF_3OEt_2	—	100	28	55	2,000 (5.9)

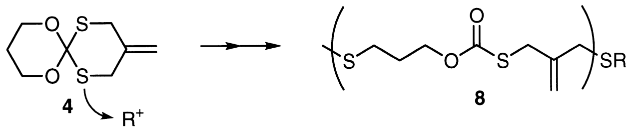
In the presence of the Lewis acid, BF_3OEt_2 at 40°C, a modest yield of oligomer was isolated. The yield, in conjunction with the low molecular weight and polydisperse nature of the material, can be rationalized by assuming there is a reasonable degree of chain termination in this polymerization. Consistent with this suggestion is NMR data that shows there are fewer triethyl amine end groups in the polymers than would be predicted from the GPC results. The difficulty in studying these initiators such as BF_3OEt_2 is that they generally lead to poorly defined polymers in these systems. Although the cationic initiator BF_3OEt_2 has been used for many years, in many cases the efficiency of the initiator and the structure of the counterions are not known with any certainty.

When compared under the same conditions, the cationic initiators $Ph_3C^+BF_4^-$ was found to produce a similar quantity of insoluble material to the BF_3OEt_2 polymerization. The polymer produced from $Ph_3C^+BF_4^-$ yielded a GPC result that was consistent with the quantity of initiator fragments determined by integration of the NMR. This result suggests chain termination is less significant in this system.

Triflic anhydride $(CF3SO_2)_2O$ was the only initiator to yield a highly insoluble polymer component under solution conditions. The high level of monomer conversion and production of an insoluble polymer are indicators that the initiator and counterion are very effective at initiating and propagating the reaction.

3.2. Polymerization of **4**

Table 2 summarizes the results obtained from the cationic polymerization of **4**. Using similar conditions for the polymerization of monomers **3** and **4** (BF_3OEt_2, 40°C, 20 h), the yield of material isolated for the *exo*-methylidene monomer **4** was almost double that of **3**. Interestingly, the estimated molecular weight and broad polydispersity were the same as the results obtained for **3**. In the absence of a polymerization solvent an insoluble material was produced, the isolated yield of which was 55%. Analysis of the ^1H and ^{13}C spectra indicates that the mechanism of polymerization is similar to **3**, producing the poly(thioether-monothiocarbonate) **8** shown in Scheme 4. Integration of the ^1H polymer spectra suggests that the monomer's *exo*-methylidene groups do no react with any of the cationic initiators. The low molecular weight material **8** isolated may be viewed as a macromer, as it contains pendant double bonds in the backbone. These double bonds are available for cross-linking via a free radical polymer mechanism, a situation adopted in previous methylidene–SOC systems [16,17] (Fig. 4).



Scheme 4.

4. Conclusion

The polymerization of different sulfur containing SOCs (3 and 4) was achieved using various cationic initiators. The results for both monomers indicated that the polymers produced are the result of a specific tandem double ring-opening mechanism, yielding the poly(thioether-monothiocarbonates) shown. There was no evidence of the *exo*-methylidene group reacting with the cationic initiators. In addition, the stability of the sulfur containing SOCs was found to be greater than the analogous SOC monomers. The absence of fragmentation upon polymerization, in association with the double ring-opening mechanism makes such molecules new candidates as expanding monomers.

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