

Structure of the Products of the Cyclooligomerization of Sulfur Dioxide with Diethyl Diallylmalonate

Jui-Yi Tsai and Philip B. Shevlin*

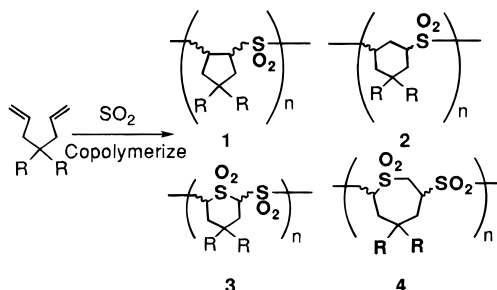
Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312

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The AIBN-initiated cooligomerization of sulfur dioxide with diethyl diallylmalonate in the presence of bromotrichloromethane or thiophenol was investigated. ES/MS and NMR studies show that 1:1 cooligomers of cis-linked 5-membered rings are formed. Electrospray mass spectrometry demonstrates that, in the case of CCl_3Br , the end group is $-\text{CH}_2\text{Br}$, and ^{13}C NMR demonstrates that the other end group is $-\text{Cl}_2\text{CCl}_3$. The thiophenol reaction leads to end groups of either $-\text{CH}_3$ or $-\text{CH}_2\text{-SO}_2\text{H}$ with PhSCH_2 at the other end. The molecular weight of oligomers was inversely proportional to the concentration of the chain-transfer agent. The polymerization chain transfer constants for bromotrichloromethane and thiophenol are 4.63×10^{-4} and 8.10×10^{-4} , respectively, at 81°C .

Introduction

Although the cyclooligomerization of sulfur dioxide with 1,6-heptadienes is a typical example of an alternating copolymerization,^{1,2} the structure of the polymer and the mechanism of polymerization has not been fully established.^{3–5} Possible structures for these polymers include five- and six-membered-ring 1:1 copolymers **1** and **2** and six- and seven-membered-ring 1:2 copolymers **3** and **4**. Although analogy with free radical cyclizations



of 5-hexenyl radicals favors structure **1** with cis linkages between the rings,⁶ this has not been established. In order to determine the structure of the copolymers in these reactions, we have used the chain-transfer agents BrCCl_3 and thiophenol to generate low molecular weight cooligomers of diethyl diallylmalonate, **5**, and SO_2 ,^{7–9} which we have characterized using electrospray mass spectrometry (ES/MS) and NMR. The NMR spectrum

Table 1. Effect of the Concentration of Chain-Transfer Reagent on $M_{n,avg}$ in the Cyclooligomerization of **5** and SO_2

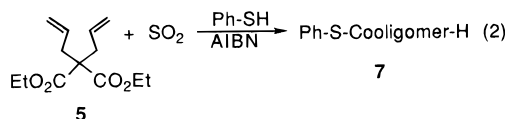
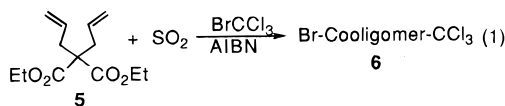
$\text{CCl}_3\text{Br}/5$	$\text{PhSH}/5$	$M_{n,avg}$
0.33		4500 ^a
0.5		3500 ^a
0.8		2300 ^a
1.0		1800 ^a
	0.25	1316 ^b
	0.5	1062 ^b
	0.85	850 ^b
	1.0	737 ^b

^a $M_{n,avg}$ was determined by GPC. ^b $M_{n,avg}$ was determined by comparing the integrated area of the ethyl groups on the chain to that of the benzene ring on the end group in the ^1H NMR.

of the copolymer formed in the absence of chain-transfer agents has also been examined.

Result and Discussion

Oligomerizations were carried out on equimolar mixtures of diethyl diallylmalonate, **5**, and SO_2 in acetonitrile to which was added 2% AIBN and varying amounts of either BrCCl_3 or thiophenol. The solutions were degassed and heated at 81°C to effect the oligomerizations in eqs 1 and 2. When BrCCl_3 was used as the chain-transfer



reagent, the number average molecular weight ($M_{n,avg}$) of the oligomers was measured by gel permeation chromatography (GPC). In the case of chain transfer by thiophenol, $M_{n,avg}$ was measured by integrating the signals for the phenyl group in the ^1H NMR spectrum and comparing their areas with those of the ethyl protons in the ethoxy groups. Values of $M_{n,avg}$ as a function of chain-transfer reagent concentration are shown in Table 1.

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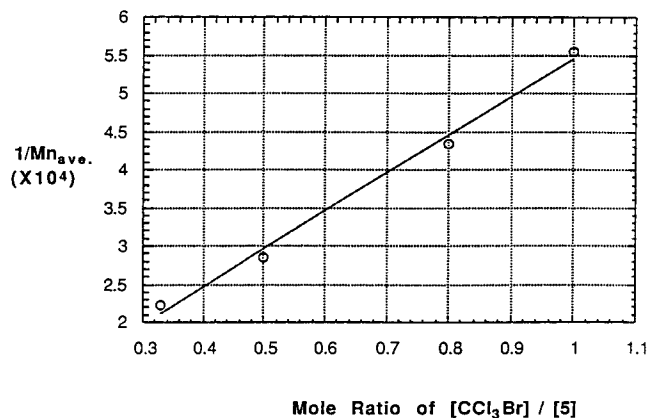


Figure 1. $1/M_{n_{\text{ave}}}$ as a function of the $\text{CCl}_3\text{Br}:\mathbf{5}$ ratio at 81°C ($C = 4.6 \times 10^{-4}$).

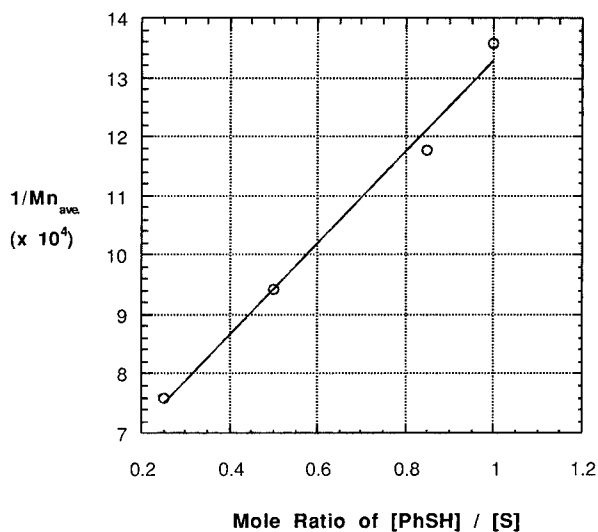


Figure 2. $1/M_{n_{\text{ave}}}$ as a function of the $\text{PhSH}:\mathbf{5}$ ratio at 81°C ($C = 8.1 \times 10^{-4}$).

In both oligomerizations, it was found that $M_{n_{\text{ave}}}$ was inversely proportional to the concentration of chain-transfer reagent. Thus, plots of $1/M_{n_{\text{ave}}}$ as a function of the concentration of chain-transfer agent are linear and follow the relation in eq 3 in which $M_{n_{\text{ave}}}$ is the number

$$1/M_{n_{\text{ave}}} = 1/M_{n_{\text{ave}}^0} + CR \quad (3)$$

average molecular weight in the absence of chain-transfer reagent, R is the ratio of chain-transfer agent to monomer, and C is the polymerization chain-transfer constant.^{10–13} Figures 1 and 2 show plots of $1/M_{n_{\text{ave}}}$ vs R that lead to polymerization chain-transfer constants of 4.6×10^{-4} and 8.1×10^{-4} for BrCCl_3 and PhSH , respectively. These studies demonstrate that we can control the molecular weight of the oligomers and are in a position to characterize these oligomers spectroscopically.

Investigation of Oligomer Composition by Electroscopy Mass Spectrometry.¹⁴ In order to determine

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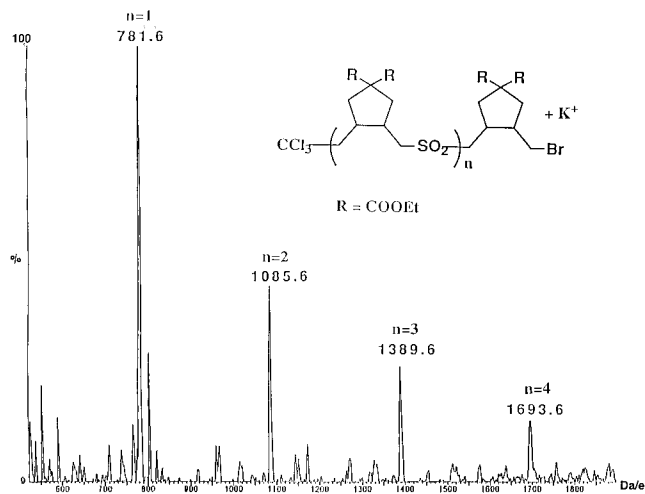
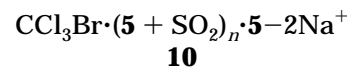
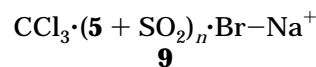
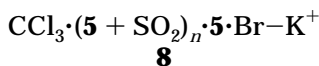


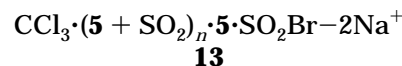
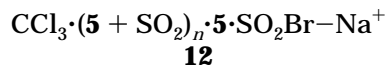
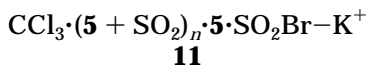
Figure 3. ESI spectra of structure **8**. The observed ions are summarized in Table 2.

the stoichiometry of the oligomers, we have carried out ES/MS studies to measure the molecular weight of the repeating unit. If there is a 1:1 ratio of **5** to SO_2 , as in **1** and **2**, the molecular weight of the repeating unit will be 304. However, structures **3** and **4**, which have a 1:2 ratio of **5** to SO_2 , will have repeating units with $\text{MW} = 368$.

It was found that addition of potassium ions to a 1:1 acetonitrile/water solution of oligomer **6** gave a sample that exhibited the ES mass spectrum in Figure 3 with peaks for $m/z = 477.6 + (304.4)_n$ ($n = 1-4$) corresponding to an oligomer of composition **8**. When sodium ions were added to the oligomeric mixture, two new series of peaks with $m/z = 461.6 + (304.4)_n$ and $m/z = 243.25 + (152.2)_n$ for oligomers of composition **9** and **10** were observed.



These data indicate a 1:1 ratio of **5** to SO_2 in oligomer **6**. The oligomer composition remained unchanged when the oligomerization was carried out in an excess of SO_2 . Since peaks corresponding to oligomer compositions **11**–**13** were not found, these data indicate the terminating



group on the oligomer is $-\text{Br}$ rather than $-\text{SO}_2\text{Br}$. This result most probably reflects the fact that the sulfinyl radical is unable to abstract bromine from bromotrichloromethane for thermodynamic reasons. Treatment of oligomer **6** with thiourea, in an experiment designed to displace a terminal primary bromide (eq 4), gave a

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Table 2. ES/MS Spectra for Various Telomer Compositions

oligomer composition	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
8	477.6 + (304) $_n$	781.6	1085.6	1389.6	1693.6			
14	435.5 + (304) $_n$	739.5	1043.5	1347.5	1651.5			
16	628.5 + (304) $_n$	932.5	1236.5	1540.5				
9	461.5 + (304) $_n$	765.5	1069.5	1373.5	1677.5	1981.5		
10	242.3 + (152) $_n$			1154.3	1306.3	1458.3	1610.3	1762.3
17	389.1 + (304) $_n$	693.1	997.1	1303.1				
18	453.1 + (304) $_n$	757.1	1061.1					

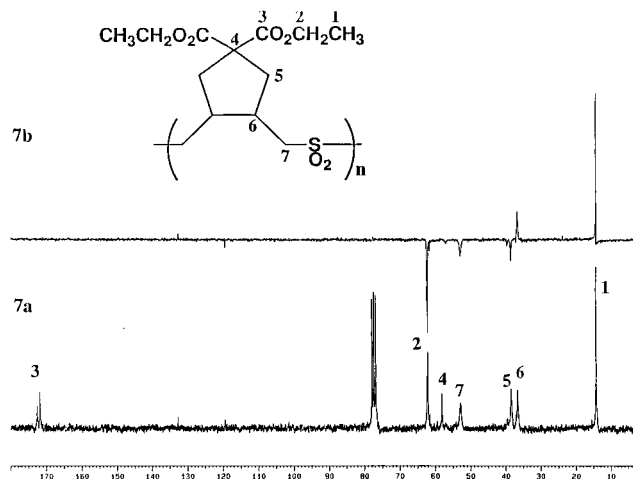


Figure 7. (a) ^{13}C NMR spectra of the copolymer of **5** and SO_2 . (b) DEPT NMR spectra of the copolymer of **5** and SO_2 .

NMR spectrum of this latter copolymer (Figure 7a) is quite simple and immediately allows us to assign the higher symmetry structure **1** to the polymer backbone. The spectrum shows two carboxy groups and four additional carbons that can be assigned to the polymer backbone. A DEPT experiment (Figure 7b) reveals that two of these carbons are CH_2 carbons, one is a CH carbon, and the final signal is due to a quaternary carbon. Figure 8 shows ^{13}C NMR assignments for this and related compounds. It is clear that the spectrum of the copolymer is inconsistent with the less symmetric structure **2**, which would have three types of methylene carbons and two methyne carbons in its backbone. Moreover, a comparison of the position of the ^{13}C signal for the carbon α to the SO_2 in model compound **19** ($\delta = 55.7$ ppm, Figure 8) indicates that the peak close to this chemical shift ($\delta = 52.8$ ppm) is a methylene group adjacent to the sulfone in the polymer. The fact that the ^{13}C NMR of the copolymer shows two carboxy groups demonstrates that the two methylene groups attached to the cyclopentane ring in the polymer are cis to one another.¹⁶

Having established the structure of the backbone in copolymer **1**, we now turn our attention to an examination of the NMR spectra of cooligomers **6** and **7** in order to obtain information regarding the initiation and termination steps. In this connection, it is useful to compare the NMR spectrum of model compound **20** with that of cooligomer **6**. In cooligomer **6**, the fact that a peak corresponding to CCl_3CH_2 is observed at $\delta = 98.97$ ppm indicates that the initiating step is addition of CCl_3 to **5** (eq 6) rather than initial reaction between CCl_3 and SO_2 followed by addition to **5** (eq 7). Moreover, the observation of the CH_2Br peak at $\delta = 32.50$ ppm confirms our earlier conclusion, on the basis of mass spectral data, that

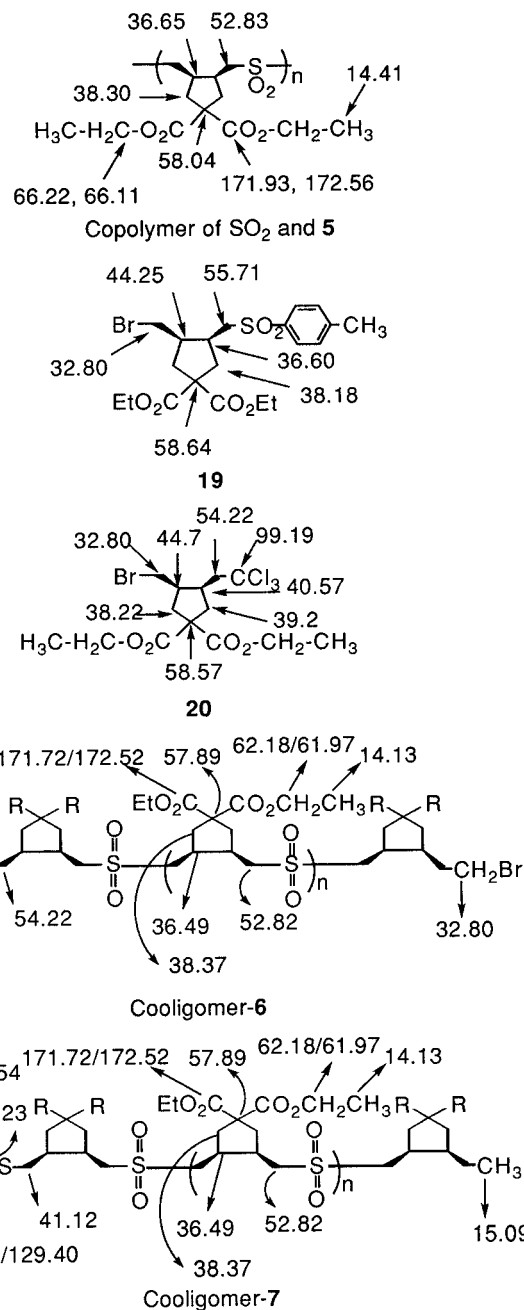
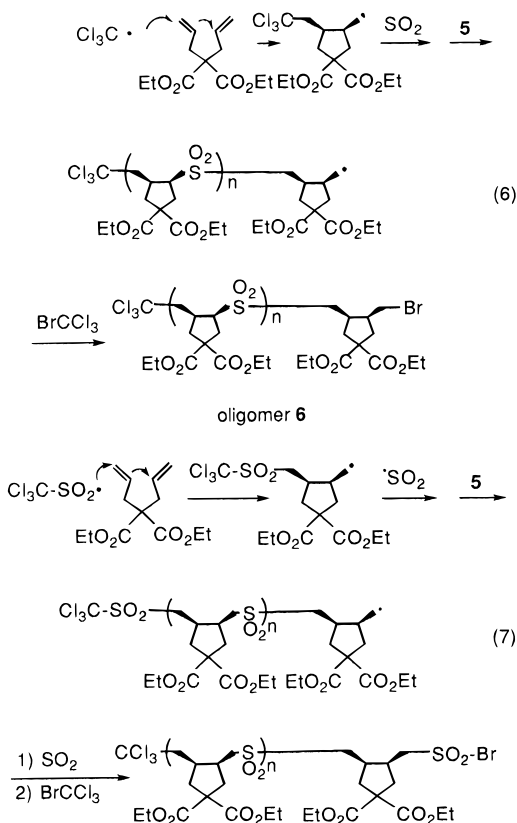


Figure 8. ^{13}C NMR assignments for cooligomers and related compounds.

termination results from abstraction of a bromine by a CH_2 in the growing polymer (eq 6) rather than bromine abstraction by a sulfinyl radical (eq 7).

An examination of ^1H and ^{13}C spectra of oligomer **7**, generated using PhSH as the chain-transfer agent, leads to similar conclusions allowing us to assign the structure in Figure 6 to this oligomer. As indicated earlier, there are two forms of this oligomer that differ in their

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terminating groups. When oligomerization is terminated by hydrogen abstraction by a CH₂, the methyl group produced appears at $\delta = 15.09$ in the ¹³C spectrum and as a doublet at 0.91 in the ¹H NMR spectrum.

Summary and Conclusions. These investigations demonstrate that the molecular weight of telomers generated in the cyclopolymerization of 1,6-heptadienes with SO₂ can be controlled by the addition of chain-transfer agents. The low molecular weight oligomers thus produced can be conveniently characterized by ES/MS methods. These mass spectral measurements along with NMR studies lead to the conclusion that the key step in the polymerization sequence is a free-radical cyclization that proceeds analogously to that observed in the well-studied cyclization of 5-hexenyl radicals.¹⁷ We are continuing these studies in the hope of generating new cooligomers analogous to **1** with interesting groups in the 4-position of the cyclopentane ring.

Experimental Section

General Information. All ¹H and ¹³C NMR were recorded on Bruker AM 250 or Bruker AM 400 spectrometers. Positive-

ion ES/MS were obtained on a Fisons Trio 2000 Quadrupole spectrometer with a mass-to-charge (*m/z*) range up to 3000. The electrospray source was heated to 50 °C. Sample solutions were introduced into a mass spectrometer source with a syringe pump at a flow rate of 0.4 mL h⁻¹. The data system was operated as multichannel analyzer, and several scans were summed to obtain the final spectrum. Samples for ES/MS were prepared by dissolving 1 mg of oligomer in 10 mL of a 1:1 acetonitrile–water solution. Solutions containing sodium or potassium salts were prepared by adding 0.5 mg of the corresponding hexafluorophosphate to 0.5 mL of solution and sonicating briefly. The solution was removed from the excess salt with a pipet and directly analyzed. GPC was conducted using THF as the eluting solvent with a Waters 510 single-pump system, Waters HR 0.5 (7.8 × 300 mm, 5μ), Waters HR1 (7.8 × 300 mm, 5μ) and Waters ultrastaygel 10⁴ A in series, and a Waters R401 differential refractometer. The apparatus was calibrated using polystyrene standards to produce a calibration curve of molecular weight as a function of polymer retention time. Sulfur dioxide was purified by passing through a P₂O₅ column, condensing, and redistilling.

General Procedure of Telomerizations. Diallyl diethylmalonate, **5**, chain-transfer reagent (CCl₃Br or thiophenol), and AIBN (2% relative to monomer) were placed in a glass tube. Acetonitrile was added as solvent to maintain the monomer concentration at 0.1 M. The tube was attached to the vacuum line and the desired amount of sulfur dioxide distilled in. Sulfur dioxide was varied from 1 to 4 equiv relative to **5**. The tube was degassed and sealed off under vacuum. The reaction vessel was heated at 81 °C (boiling acetonitrile) for 5 h. At the conclusion of the reaction, volatiles were removed at reduced pressure and the residue passed through a silica gel column to remove the remaining monomer and cyclized monomeric product (petroleum ether:ethyl acetate = 8:2). The oligomer was then eluted from the column with methanol. ESP-MS demonstrated that the oligomer composition was unaffected by changes in SO₂ concentration.

Replacement of Primary Bromide in Oligomers with Thiourea.¹⁸ Oligomer and excess thiourea were placed in a 50 mL flask and refluxed in absolute ethanol for 10 h. The mixture was cooled, an equal volume of water was added, and the solution was heated until it became homogeneous. Addition of concentrated hydrochloric acid precipitated the thiourea salt.

Incorporation of Dimethyldiallylammonium Chloride into the Copolymer of **5 and SO₂.** Diallyl diethylmalonate (**5**, 0.1 g, 0.416 mmol), dimethyldiallylammonium chloride (**15**, 6.7 mg, 0.0416 mmol), CCl₃Br (41.34 mg, 0.21 mmol), AIBN (2% relative to monomer), and methanol (1 mL) were placed in a glass tube. The tube was attached to a vacuum line and SO₂ (0.0266g, 0.416 mmol) distilled in. The tube was degassed and sealed off. The reaction vessel was heated at 81 °C (boiling acetonitrile) for 5 h. At the conclusion of the reaction, volatiles were removed at reduced pressure and the residue passed through a silica gel column to remove the remaining monomer and cyclized monomeric product (petroleum ether:ethyl acetate = 8:2). The oligomer was then eluted from the column with methanol.

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