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Copolymers

Ring-Opening Spontaneous Alternating Copolymerization of a Dithiadiphosphetane Disulfide with Cyclic Ethers

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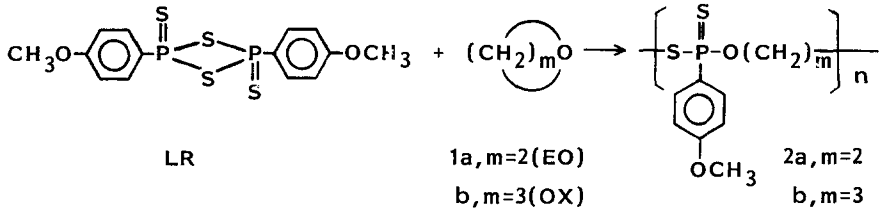
SUMMARY

Alternating copolymerizations of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide(Lawesson's reagent, LR) with some cyclic ethers(1) are described. The cyclic ethers used were ethylene oxide(EO) and oxetane(OX). The copolymerization took place without catalyst at room temperature. The copolymers obtained were of phosphonodithioate structure (2) having 1/2:1 composition of LR and 1. The present copolymerization is the first example of the 1/2:1 composition in an alternating arrangement. The copolymerization mechanism has been discussed.

INTRODUCTION

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent, LR) has in recent years attracted much attention as a thiation reagent and in synthesis of *P*-heterocycles(1). In a series of our studies on spontaneous copolymerizations(2) we have found that LR is a reactive comonomer to-produce alternating copolymers. The present paper describes the copolymerization of LR with cyclic ethers(1) to give copolymers of phosphonodithioate structure(2), an alternating arrangement of 1/2×LR and 1.



LR

1a, m=2(EO)
b, m=3(OX)

2a, m=2
b, m=3

RESULTS AND DISCUSSION

Ring-Opening Alternating Copolymerization

A mixture of LR and a cyclic ether was allowed to react each other in benzene at room temperature under nitrogen. LR is a pale yellow crystal which is not soluble in benzene. As the reaction proceeded the reaction mixture became homogeneous and increasingly viscous. After ordinary work-up procedures white powdery polymeric materials were obtained. Copolymerization results are given in Table 1.

The structure of copolymer was determined by ^{31}P, ^{1}H, and ^{13}C NMR as well as IR spectroscopy and by elemental analysis. The ^{31}P NMR spectrum of the copolymer obtained from LR and ethylene oxide(EO)(sample No 1 in Table 1)

Table 1
Ring-Opening Alternating Copolymerization of LR with Cyclic Ethers(**1**)[a]

No	**1**[b]	LR:**1** molar ratio	Time (hr)	Copolymer Yield(%)[c]	Mol.wt.[d]	Mp(°C)
1	EO	1:2	1.5	40	8190	
2	EO	1:2	15	79	11750	
3	EO	1:2	336	99	19400	57~59
4	EO	1:4	15	69	9160	
5	EO	1:10	168	60	6200	45~47
6	EO	1.3:1	168	95	4750	
7	OX	1:2	5.5	48	6660	
8	OX	1:2	48	81	7700	51~54
9	OX	1:10	12	88	7540	
10	OX	2.5:1	12	99	4650	

a) [LR] + [cyclic ether, **1**] = 6.0 mmol in 2 ml of benzene under nitrogen at room temperature.
b) EO; ethylene oxide, OX; oxetane.
c) White powdery materials.
d) Determined by vapor pressure osmometry in $CHCl_3$ at 40°C.

showed a single peak at 96.1 ppm, indicating the only one sort of phosphorus unit of *O*-alkyl *S*-alkyl arylphosphonodithioate structure(**2a**). In the ^1H NMR spectrum($CDCl_3$)(Figure 1) four kinds of signal are observed; a broad signal at δ2.5-3.2(2H, SCH_2), a sharp singlet at δ3.6(3H, OCH_3), a broad signal at δ3.6-4.2(2H, OCH_2), and an A_2B_2 type quartet due to aromatic protons at δ6.8(2H, J_{HCCP}=3.2 Hz) and δ7.7(2H, J_{HCCCP}=15 Hz). The ^{13}C NMR spectrum($CDCl_3$ with Me_4Si)(Figure 2) shows a doublet at 33.5 ppm(J_{CSP}=9.6 Hz, SCH_2), a singlet at 55.6 ppm(OCH_3), a doublet at 64.1 ppm (J_{COP}=3.8 Hz, OCH_2), a doublet at 114.3 ppm(J_{CCP}=15.7 Hz, β-carbon), a doublet at 126.2 ppm(J_{CP}=129 Hz, α-carbon), a doublet at 132.9 ppm (J_{CCCP}=13 Hz, γ-carbon), and a doublet at 163.2 ppm(J_{CCCCP}=3.5 Hz, δ-carbon). In the IR spectrum a band at 750 cm^{-1} due to $\nu_{P=S}$ was observed and no $\nu_{P=O}$ band was detected around 1200 cm^{-1}. All these spectral data strongly support the structure of **2a**, a 1/2:1 alternating copolymer of LR and EO. The 1/2:1 composition of the copolymer was also supported by elemental analysis(Table 2).

Table 2
Elemental Analysis of Copolymers(**2**)

Sample No	Found C	H	P
2[a]	43.71	4.48	12.70
3[a]	43.84	4.48	12.81
4[a]	43.13	4.38	11.45
5[a]	43.38	4.44	12.67
6[a]	43.00	4.30	12.80
8[b]	45.92	5.06	11.99
9[b]	45.29	5.02	11.86
10[b]	45.66	4.84	12.68

a) Calcd for $(C_9H_{11}O_2PS_2)_n$:C, 43.89; H, 4.50; P, 12.58.
b) Calcd for $(C_{10}H_{13}O_2PS_2)_n$:C, 46.14; H, 5.03; P, 11.90.

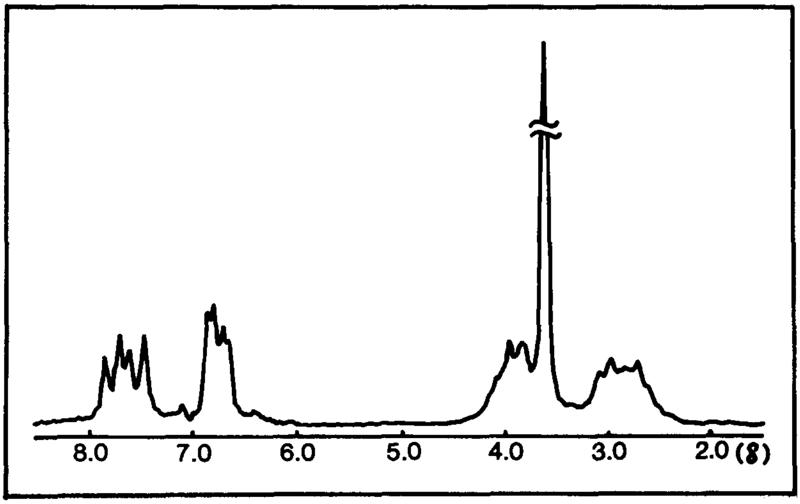


Figure 1. ^1H NMR spectrum of polymer 2a.

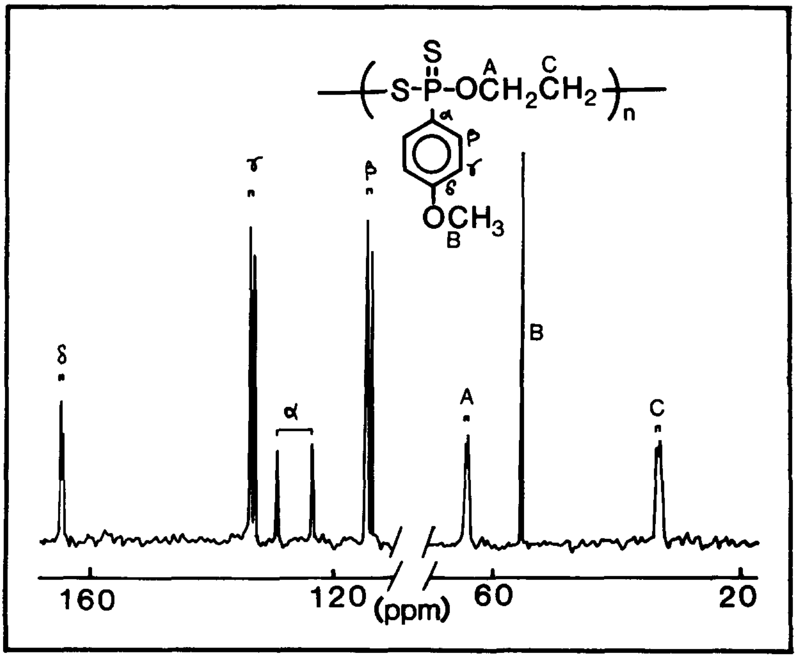
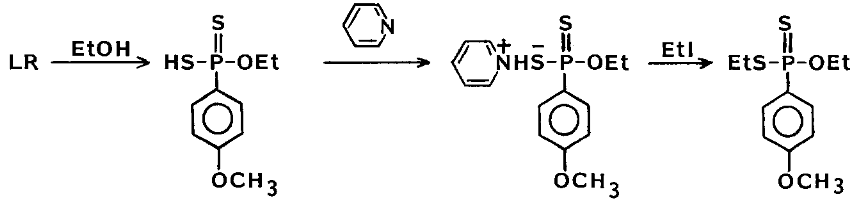


Figure 2. $^{13}C\{^1H\}$ NMR spectrum (22.6 MHz, $CDCl_3$ with TMS) of polymer 2a.

To confirm further the unit structure 2, a model compound (5) was prepared according to the following procedure:



3 4 5

The ^{31}P NMR spectrum of *O*-ethyl *S*-ethyl 4-methoxyphenylphosphonodithioate 5 ($CDCl_3$) showed a singlet at 95.6 ppm and the IR spectrum 5 exhibited a band at 750 cm^{-1} assignable to $\nu_{P=S}$. These data are very close to or identical with those of the copolymer (sample No 1).

The copolymer structure(**2b**) obtained by LR and oxetane(OX)(sample No 6) was determined based on the following data. ^{31}P NMR($CDCl_3$); 96.6 ppm (singlet). ^{1}H NMR($CDCl_3$); a triplet like broad signal at δ1.5-2.0(2H, $\cdot CCH_2C$), a multiplet at δ2.4-3.0(2H, SCH_2), a sharp singlet at δ3.6(3H, OCH_3), a broad signal at δ3.6-4.2(2H, OCH_2), and an A_2B_2 type quartet due to aromatic protons at δ6.8(2H, J_{HCCP}=3.2 Hz) and δ7.7(2H, J_{HCCCP}=15 Hz). ^{13}C NMR($CDCl_3$); 30.0 ppm(d, J_{CSP}=3.5H, SCH_2), 30.7 ppm(m, CCH_2C), 55.5 ppm (s, OCH_3), 63.7 ppm(d, J_{COP}=6.1 Hz, OCH_2), 114.1 ppm(d, J_{CCP}=16.5 Hz, β-carbon), 126.6 ppm(d, J_{CP}=128.1 Hz, α-carbon), 132.7 ppm(d, J_{CCCP}=14 Hz, γ-carbon), and 162.9 ppm(d, J_{CCCCP}=3.5 Hz, δ-carbon). IR(liquid film) 730 cm^{-1} ($\nu_{P=S}$). All these spectral data coupled with elemental analysis data(Table 2) led to the copolymer structure of **2b**, a 1/2:1 alternating copolymer of LR and oxetane.

It should be noted that the copolymerization took place without added initiator at room temperature to give 1/2:1 alternating copolymers of high molecular weight. Furthermore, the 1/2:1 composition of the copolymers was always attained regardless of the feed molar ratio, e.g., 1:10-1.3:1 for LR/EO systems and 1:10 to 2.5:1 for LR/OX systems(Table 1). Thus, the monomer reactivity ratios are $r_{LR}=r_{EO}=0.0$(the composition curve in Figure 3) and $r_{LR}=r_{OX}=0.0$, respectively.

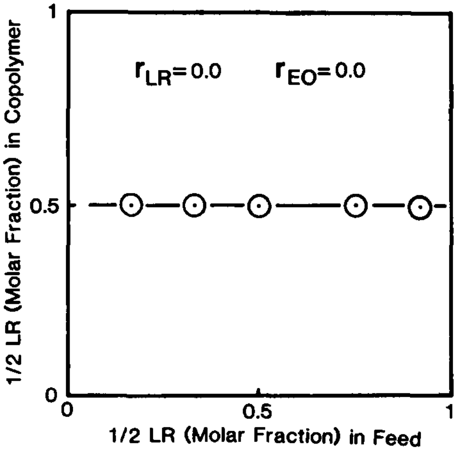
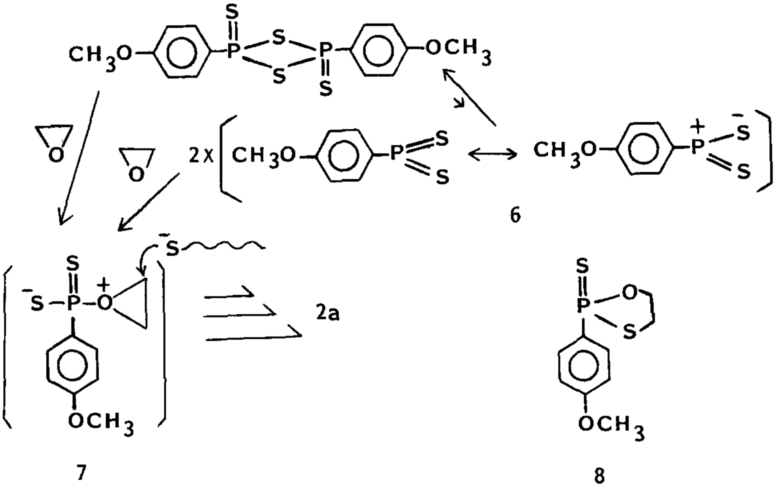


Figure 3. Copolymer composition curve of the LR-EO copolymerization.

Copolymerization Mechanism

The present copolymerization is probably explained by a mechanism involving zwitterion intermediates. The following scheme is given by taking the LR-ethylene oxide system as an example. Zwitterion 7 is a key-intermediate. 7 is produced by a direct nucleophilic attack of ethylene oxide onto the phosphorus atom of LR and/or by a nucleophilic attack of ethylene oxide onto the phosphorus of phenylthionophosphine sulfide(6) which is present in equilibrium with LR. Subsequent reactions of 7 will reasonably explain the production of copolymer **2a**. At present, we can not exclude the possibility that 7 gives a cyclic product 8 and the ring-opening polymerization of 8 leads to the production of copolymer **2a**. Anyhow, LR acted as an electrophilic monomer whereas ethylene oxide behaved as a nucleophilic one.



The copolymerization of LR with ethylene oxide was monitored by ^{31}P NMR spectroscopy. However, none of these intermediates assignable to 6, 7, and 8 was detected. Therefore, the copolymerization involves reactive, short-lived species at a very low concentration as active intermediates.

EXPERIMENTAL

Materials

All solvents were purified by distillation under nitrogen. Ethylene oxide obtained from Meisei kagaku Co.(Kyoto) and a commercial reagent of oxetane (Tokyo kasei Co.) were purified before use.

Synthesis of 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide(Lawesson's reagent, LR).

LR was synthesized as reported(3). A mixture of 54 g (0.5 mole) of anisole and 22.2 g (0.05 mole) of P_4S_{10} was stirred and heated to reflux under nitrogen. When the temperature reached 120°C hydrogen sulfide began to evolve. The temperature was gradually raised to 150°C and kept for 1.5 hr; during this period P_4S_{10} completely disappeared and a clear light orange solution was formed. Shortly afterwards precipitation of a light yellow solid was observed. After 3 hr total refluxing time, the evolution of hydrogen sulfide finished. On cooling, the bulk of the yellow thionophosphine sulfide crystallized. The product was washed twice with benzene (25 ml × 2) and dried *in vacuo*. The yield was 43 g (100%).

Synthesis of a Model Compound **5**

O-Ethyl *S*-ethyl 4-methoxyphenylphosphonodithioate **5** was prepared as follows. The reaction of LR (0.30 g, 0.74 mmol) and EtOH (0.09 ml, 1.48 mmol) in 3 ml benzene at 60°C for 3 hr under N_2 gave **3** *in situ* ($\delta(^{31}P)$: +85.3). Then, **4** ($\delta^{31}(P)$: +104.4) was prepared *in situ* with the addition of pyridine (0.124 ml, 1.54 mmol). The reaction mixture was then cooled down to 0°C and 0.123 ml of ethyl iodide in 3 ml benzene was dropped. **5** was synthesized quantitatively *in situ* as monitored by ^{31}PNMR after stirring for 1 hr at room temperature. In order to avoid *O*-*S* scrambling which may occur at higher temperature, **5** was purified by passing through a short silica gel column instead of distillation. Evaporation of benzene gave 0.29 g(70%) of **5** as a yellow liquid. ^{31}P NMR($CDCl_3$); +95.6 ppm. ^{1}H NMR ($CDCl_3$); δ1.3 (m, 6H, CCH_3), δ2.8 (m, 4H, OCH_2, SCH_2), δ3.8 (s, 3H, OCH_3), δ4.1 (m, 2H, OCH_2), δ6.8 (q, 2H, J_{HCCP}=3.2 Hz), δ7.8 (q, 2H, J_{HCCCP}=15 Hz). ^{13}C NMR($CDCl_3$); 15.4 ppm (d, J_{CCSP}=5.2 Hz, $SCCH_3$), 15.8 ppm (d, J_{CCOP} =7.8 Hz, $OCCH_3$), 27.7 ppm (d, J_{CSP}=3.4 Hz, SCH_2), 55.2 ppm (s, OCH_3), 61.4 ppm (d, J_{COP}=6.1 Hz, OCH_2), 113.7 ppm (d, J_{CCP}=15.7 Hz, β-carbon), 128.0 ppm (d,J_{CP}=127.3 Hz, α-carbon), 132.4 ppm (d, J_{CCCP}=13.1 Hz, γ-carbon), and 162.5 ppm (d, J_{CCCCP}=3.5 Hz, δ-carbon). IR(liquid film);750 cm^{-1} ($\nu_{P=S}$). MS;m/e=276. *Anal.* Calcd for $C_{11}H_{17}O_2PS_2$: C, 47.81%; H, 6.20%; P, 11.21%. Found: C, 47.88%; H, 6.17%; P, 11.34%.

Copolymerization

A typical copolymerization experiment was carried out as follows. Ethylene oxide (0.15 ml, 3.00 mmol) was added dropwise into a suspension of LR (0.59 g, 1.50 mmol) in 0.75 ml of benzene with stirring at 0°C under nitrogen. The tube was kept at room temperature overnight. Then, the polymeric materials was obtained by precipitation of the reaction mixture into a large amount of diether ether, which was separated and dried *in vacuo* to give 0.57 g of copolymer **2a** (79% yield).

Measurements.

^{1}H NMR spectra were recorded on a HITACHI R-20B (60 MHz) spectrometer. A HITACHI R-900 spectrometer was used to record ^{31}P (36.43 MHz) and ^{13}C NMR (22.63 MHz) spectra. IR spectra were recorded with a HITACHI 260-50 IR spectrophotometer. Molecular weight data were obtained using a CORONA 117 vapor pressure osmometer.

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