Notes

Alternating Copolymerization of 2-Phenyl-1,3,2-dithiaphospholane with Acrylic and Methacrylic Acids

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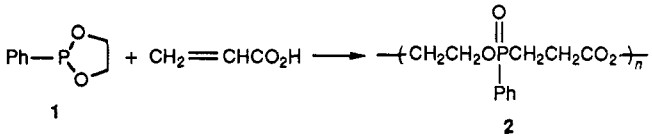
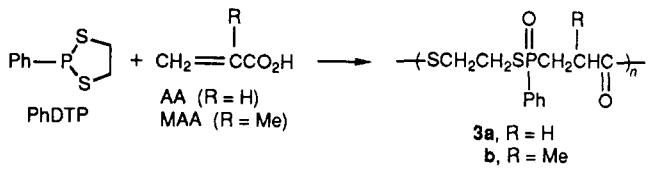
In the course of our studies on alternating copolymerizations via zwitterion intermediates from a nucleophilic monomer (M_N) and an electrophilic one (M_E), phosphorus(III) compounds have served as good M_N monomers.[1] Cyclic phosphonites of 2-phenyl-1,3,2-dioxaphospholane (**1**)[2] and 2-phenyl-1,3,6,2-trioxaphosphocane[3] have been



1 **2**

combined as M_N with acrylic acid (AA) or methacrylic acid (MAA) as M_E to give alternating copolymers. For example, **1** and AA produced a 1:1 alternating copolymer of a phosphinate–ester structure, **2**.[2] The present paper describes a new alternating copolymerization using 2-phenyl-1,3,2-dithiaphospholane (PhDTP), an *S*-analogue of monomer **1**, as M_N. PhDTP has been copolymerized with M_E monomers of AA and MAA without added initiator to produce 1:1 alternating copolymers of a phosphinothiolate–thioester structure, **3a** and **3b**. These copolymers were produced via a reaction mode different from that of **1** and AA.



PhDTP AA (R = H) MAA (R = Me)

3a, R = H
b, R = Me

Results and Discussion

The copolymerization of PhDTP[4] with AA or MAA was carried out in benzonitrile or in chloroform. A typical run was as follows. An equimolar mixture of PhDTP and AA (3.0 mmol each) in 1.5 mL of benzonitrile was kept under nitrogen for 60 h at 80 °C. A usual work-up procedure gave a white powdery polymeric material (78% yield) melting at 42–50 °C. The copolymer was hygroscopic and soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, acetone, PhCN, CH_3CN, CH_3OH, DMF, and DMSO but insoluble in solvents like benzene, diethyl ether, *n*-hexane, and water. Its molecular weight was 1560 by vapor pressure osmometry.

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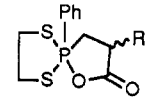
The copolymer structure was determined as phosphinothiolate–thioester structure **3a** by IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopy as well as elemental analysis. The IR spectrum of the copolymer showed strong bands at 1690 cm^{-1} due to ν(C(=O)S) and 1210 cm^{-1} due to ν(P=O). The ^1H NMR spectrum ($CDCl_3$) showed a broad multiplet signal at δ 1.7–3.5 (8 H) and a broad signal at δ 7.2–8.2 (5 H). In the ^{31}P NMR spectrum ($CHCl_3$) a singlet peak at δ +40.8 was observed. The ^{13}C NMR spectrum ($CDCl_3$) of the copolymer showed a characteristic signal at δ +196.8 (d, J = 14 Hz; with Me_4Si standard) ascribable to the carbonyl group of C(=O)S–.[5] Anal. Calcd for the 1:1 composition, $[C_{11}H_{13}O_2PS_2\cdot(H_2O)_{0.4}]_n$: C, 47.27; H, 4.98; P, 11.08. Found: C, 47.42; H, 4.98; P, 10.82. All these data support the copolymer structure **3a**, i.e., a 1:1 alternating arrangement of PhDTP and AA. Copolymerization results are given in Table I.

Analogously, the copolymerization of PhDTP with MAA was carried out, for example, in chloroform at 60 °C for 70 h. A white powdery material was obtained in 71% yield, which melted at 49–55 °C (molecular weight 1310). The structure of the copolymer was determined as a 1:1 alternating one of PhDTP and MA having a phosphinate–thioester repeating unit (**3b**) on the basis of the following data. ^1H NMR ($CDCl_3$): δ 1.1–1.3 (d, 3 H), 1.8–3.4 (br, 7 H), 7.1–8.2 (5 H). ^{31}P NMR ($CDCl_3$): +40.8 (s). ^{13}C NMR ($CDCl_3$): δ +201.2 (d, C=O, J = 12 Hz). IR (KBr): 1690 (ν(C=O)) and 1210 cm^{-1} (ν(P=O)). Anal. Calcd for the 1:1 composition, $[C_{12}H_{15}O_2PS_2\cdot(H_2O)_{0.3}]_n$: C, 49.40; H, 5.39; P, 10.61. Found: C, 49.77; H, 5.37; P, 9.98.

The molecular weight of all copolymers **3a** and **3b** produced at temperatures examined is not so high, which is similar to the copolymerization of **1** with AA to produce **2**.[2] The present copolymerization at a higher reaction temperature for a longer reaction time may produce copolymers **3** of higher molecular weight.

In order to shed more light on the copolymerization mechanism the reaction of PhDTP with AA was carried out at lower temperatures. An equimolar mixture of PhDTP and AA in diethyl ether at 5–15 °C gave white needlelike crystals (mp 98–99 °C), whose structure was determined as spiro(acyloxy)phosphorane **4a**, a new pentacovalent phosphorus species. The isolated phosphorane **4a** was heated and produced polymer **3a** quantitatively (Table I, entry 5). Analogously, the reaction of PhDTP with MAA at 5–10 °C in diethyl ether produced spiro(acyloxy)phosphorane **4b** (mp 103–104 °C). Heating of **4b** in $CHCl_3$ quantitatively gave polymer **3b** (Table I, entry 10).



4a, R = H
b, R = Me

These data are taken to support the supposition that spiro(acyloxy)phosphorane (**4**), a 1:1 reaction product of PhDTP with AA or MAA, is an intermediate in polymer

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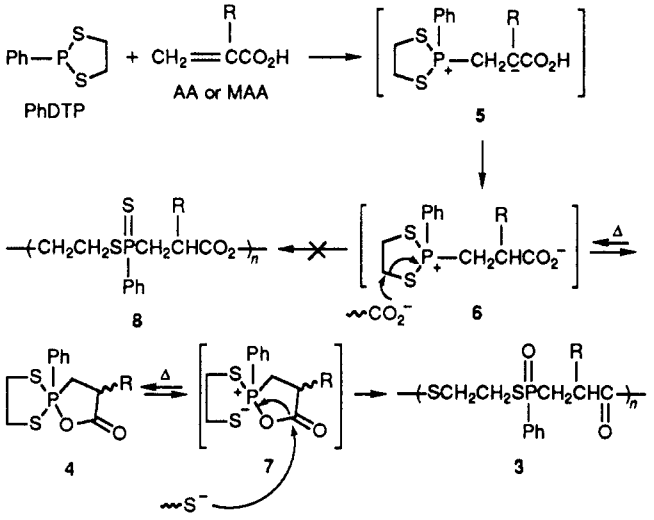
Table I
Alternating Copolymerization of 2-Phenyl-1,3,2-dithiaphospholane (PhDTP) with Acrylic (AA) and Methacrylic Acids (MAA)[a]

entry	M_E	solvent (mL)	temp, °C	time, h	copolymer yield, %	copolymer structure	copolymer mol wt[b]
1	AA	PhCN (1.5)	120	50	91	**3a**	1160
2	AA	PhCN (1.5)	80	60	78	**3a**	1560
3	AA	$CHCl_3$ (0.5)	80	60	84	**3a**	1520
4	AA	$CHCl_3$ (0.5)	60	85	88	**3a**	1250
5		*c*	100	60	quant	**3a**	1180
6	MAA	PhCN (0.5)	80	60	68	**3b**	1250
7	MAA	PhCN (0.5)	60	70	67	**3b**	1230
8	MAA	$CHCl_3$ (0.5)	60	70	71	**3b**	1310
9	MAA	$CHCl_3$ (0.5)	45	95	64	**3b**	1400
10		*d*	80	60	quant	**3b**	1370

[a] PhDTP = AA or MAA = 3.0 mmol except for entry 5 and 10. [b] Determined by vapor pressure osmometry in $CHCl_3$ at 35 °C. [c] Isolated phosphorane **4a** was heated without solvent. [d] Isolated phosphorane **4b** (3 mmol) in 0.5 mL of $CHCl_3$ was heated.

Scheme I



formation. A possible mechanism for the copolymerization is given in Scheme I. The first step is the Michael-type addition of PhDTP as M_N to AA (or MAA) as M_E to produce a phosphonium–carbanion intermediate, **5**, followed by a proton transfer giving rise to a phosphonium–carboxylate zwitterion, **6**. At lower temperatures **6** cyclizes to form spiro(acyloxy)phosphorane (**4**), which was even isolated as a crystalline solid. Under polymerization conditions of higher temperatures, **4** is equilibrated with a phosphonium–thiolate zwitterion, **7**, rather than with a zwitterion, **6**. Therefore, **7** is a genetic zwitterion responsible for both initiation and propagation. Subsequent reactions of **7** lead to the formation of polymer **3** of phosphinothiolate–thioester structure, i.e., a 1:1 alternating copolymer of PhDTP and AA (or MAA). It should be emphasized that copolymer **8** of thiophosphinothiolate–ester structure was not produced. The formation of **8** is expected from **6**, which is a similar type of zwitterion involved in the copolymerization of **1**, an *O*-analogue of PhDTP, with AA to produce **2**. This results indicates that the S–P bond in **4** is readily cleaved to give a highly reactive zwitterion, **7**, which is directly involved in producing polymer **3**.

Experimental Section

PhDTP was prepared according to procedures reported.[4] The reaction of dichlorophenylphosphine with ethane-1,2-dithiol in the presence of triethylamine gave PhDTP (86% yield). Bp: 105 °C (0.2 mmHg). ^{31}P NMR ($CHCl_3$ with 85% H_3PO_4 external standard): δ +45.3 (s).

A typical procedure of copolymerization (entry 2) was as follows. A mixture of PhDTP and AA (3.0 mmol each) in 1.5 mL of PhCN was placed in a tube under nitrogen. The tube was shaken, sealed, and kept at 80 °C for 60 h. The reaction mixture was poured into a large amount of diethyl ether to precipitate polymeric materials. The reprecipitation procedure was repeated twice using $CHCl_3$ as a good solvent and diethyl ether as a poor solvent. After drying in vacuo 0.64 g of a white powder was obtained (78% yield).

Preparation of spiro(acyloxy)phosphorane (**4**) was carried out as follows. An equimolar mixture of PhDTP and AA (3 mmol) in 3 mL of diethyl ether was kept at 5–15 °C for 20 days under nitrogen. Then, white crystals precipitated, which were separated and recrystallized from diethyl ether–chloroform to give 0.45 g (55% yield) of **4a**. Mp: 98–99 °C. ^1H NMR ($CDCl_3$ with TMS): δ 2.10–3.51 (br m, 8 H, PCH_2CH_2 and SCH_2CH_2S), 7.05–8.10 (5 H, C_6H_5). ^{31}P NMR ($CHCl_3$ with 85% H_3PO_4 external standard): δ −3.3 (s). IR (KBr): 1720 cm^{-1} (ν(C=O)). Anal. Calcd for $C_{11}H_{13}O_2PS_2 \cdot (H_2O)_{0.5}$: C, 46.95; H, 5.01; P, 11.01. Found: C, 46.76; H, 5.07; P, 10.99.

A similar procedure using PhDTP and MAA gave spirophosphorane **4b** in 41% yield as white crystals. Mp: 103–104 °C. ^1NMR ($CDCl_3$): δ 1.23 (d, 3 H, CH_3), 1.83–3.60 (br m, 7 H, PCH_2CH and SCH_2CH_2S), 6.92–8.05 (5 H, C_6H_5). ^{31}P NMR ($CHCl_3$): δ −10.3 (s). IR (KBr): 1710 cm^{-1}. Anal. Calcd for $C_{12}H_{15}O_2PS_2 \cdot (H_2O)_{0.1}$: C, 50.02; H, 5.32; P, 10.75. Found: C, 49.90; H, 5.41; P, 10.75.

References and Notes

(1) For comprehensive reviews, see: (a) Kobayashi, S.; Saegusa, T. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: Essex, England, 1984; Chapter 11. (b) Kobayashi, S.; Saegusa, T. In *Alternating Copolymers*; Cowie, J. M. G., Ed.; Plenum Publishing Co.: New York, London, 1985; Chapter 5.
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