Polymer Bulletin 5, 331-333 (1981)

Polymer Bulletin

Redox 1:1 Alternating Copolymerization of Cyclic Acyl Phosphonite with 4,4'-Diphenoquinones

Shiro Kobayashi, Masahisa Okawa, Masahiro Niwano and Takeo Saegusa

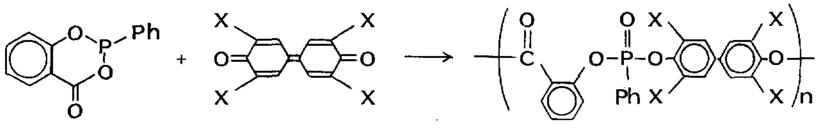
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University,
Kyoto, 606, Japan

Summary

A cyclic phosphonite(1) was copolymerized with 4,4'-diphenoquinones (2a-2c) to give 1:1 alternating copolymers (3a-3c) consisting of a carboxylic acid ester and a triaryl phosphonate ester. Copolymerization took place without added initiator. During the reaction 1 was oxidized whereas 2 was reduced ("redox copolymerization"). A mechanism involving a genetic zwitterion intermediate (4) is proposed for the copolymerization.

Introduction

We have recently reported 1:1 alternating copolymerizations of cyclic acyl phosphonite or phosphite with p-benzoquinones to produce copolymers consisting of carboxyl ester group and phosphonate or phosphate in the main chain (SAEGUSA et al, 1979). The present paper describes an extension of this study, namely, the alternating copolymerization of a cyclic acyl phosphonite, 2-phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (1) with 4,4'-diphenoquinones (2). The combination of 1 and 2 produced alternating copolymers of phosphonate-ester type (3) in which 1 was oxidized whereas 2 was reduced ("redox copolymerization").



1

2a; X=H
b; X=CH3
c; X=Cl

3a; X=H
b; X=CH3
c; X=Cl

Results and Discussion

An equimolar reaction of 1 and 2a in PhCN at 110°C for 80 hr gave white powdery polymeric materials in 57% yield after precipitation and drying in vacuo. Copolymerization results of 1 with 2b and 2c are given in TABLE 1. All polymers are powdery materials soluble in polar organic solvents such as $CHCl_3$, DMF, and DMSO but insoluble in diethyl ether and water. Polymer 3b is pale yellow and 3c is white. The molecular weights of the polymers were higher in the reaction at 110°C than those at 150°C.

0170-0839/81/0005/0331/$01.00

TABLE 1
Redox Alternating Copolymerization of 1 with 2 [a]

No	2	Solvent PhCN(ml)	Reaction		Polymer		
			Temp(°C)	Time(hr)	Yield(%)	Structure	Mol.Wt.[b]
1	2a	3.0	110	80	57	3a	3820
2	2a	1.5	150	50	30	3a	2770
3	2b	3.0	110	70	71	3b	4430
4	2b	1.5	150	60	57	3b	2300
5	2c	3.0	110	80	75	3c	8590
6	2c	1.5	150	70	40	3c	1530

a) 1=2=3.0 mmol in PhCN solvent.
b) Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.

The copolymer structure was determined by IR, ^{31}P NMR spectroscopy, and elemental analysis. The IR spectrum of polymer sample No 1 shows characteristic stretching bands at 1740 cm^{-1} (νc=o) and 1260 cm^{-1} (νp=o). The ^{31}P NMR of the copolymer showed a signal at +12.2 ppm indicating the triphenyl phosphonate ester structure 3a (TABLE 2). The results of elemental analysis (TABLE 3) were in good agreement with the calculated values of the 1:1 composition of 1 and 2a.

TABLE 2
Spectroscopic Data for Copolymers

Sample No	$\delta(^{31}P)$[a] ppm	IR(KBr) cm^{-1}	
		νc=o	νp=o
1	+12.2	1740	1260
3[b]	+11.8	1745	1250
5	+12.4	1760	1290

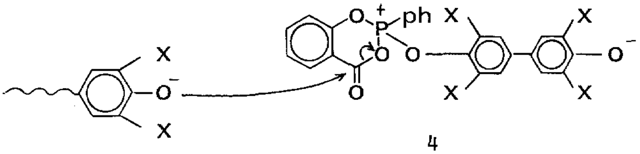
a) Chemical shift is positive to the downfield relative to external H_3PO_4. b) ^1H NMR data ($CDCl_3$ with TMS); δ6.8-8.2 (aromatic protons, 13H) and δ2.2 (methyl protons, 12H).

TABLE 3
Elemental Analyses of Copolymers

Sample No	Formula [a]		C	H	P	Cl
1	$(C_{25}H_{17}O_5P)_n$	Calcd	70.10	4.00	7.23	
		Found	69.28	4.30	7.28	
3	$(C_{29}H_{25}O_5P)_n$	Calcd	71.89	5.20	6.39	
		Found	71.39	5.26	6.19	
5	$(C_{25}H_{13}O_5PCl_4)_n$	Calcd	53.04	2.31	5.47	25.05
		Found	53.13	2.15	4.96	24.68

a) The 1:1 composition of 1 and 2.

The above copolymerization is considered to proceed via the following way. First, the interaction of 1 with 2 gives a genetic zwitterion 4 in which 1 behaves as a nucleophilic monomer (M_N) whereas 2 acts as an electrophilic one (M_E). Then, the phenolate type anion of 4 attacks the carbonyl carbon of the another 4 via the Arbuzov type reaction to give rise to a unit 3 having carboxylate and phosphonate groups.



4

Thus, successive reactions between two molecules of 4 and/or between 4 and a macrozwitterion lead to the production of 1:1 alternating copolymer 3. During the copolymerization 1 was oxidized whereas 2 was reduced ("redox copolymerization") accompanied by the disappearance of the deep color of monomer 2 in the resulting polymer 3.

Experimental

Materials. 1 was prepared as reported previously (SAEGUSA et al, 1979). 2a and 2c were obtained by oxidation of 4,4'-dihydroxydiphenyl and 3,3',5,5'-tetrachloro-4,4'-dihydroxydiphenyl (MAGATTI, 1880) with lead tetraacetate in 46% and 70% yield, respectively (KÖNIG et al, 1960): 2a, brown crystals, mp 165°C (dec.), IR (KBr) 1635 cm^{-1} (νc=o), and 2c; red-orange crystals, not melted, ^1H NMR (DMSO-d_6) δ 8.71, IR (KBr) 1640 cm^{-1} (νc=o). The coupling reaction of 2,6-dimethylphenol was performed by isoamyl nitrite to give red-brown crystals 2b; mp 208-210°C, ^1H NMR ($CDCl_3$) δ 2.15 (12H) and δ 7.71 (4H), IR (KBr) 1636 cm^{-1} (νc=o) (JERUSSI, 1970).

Copolymerization. A typical example of No 1 was carried out as follows. A mixture of 1 (732 mg, 3.0 mmol) and 2a (553 mg, 3.0 mmol) was dissolved in 3.0 ml of PhCN in a test tube under nitrogen. The tube was sealed and kept at 110°C for 80 hr. Then, tube was opened and the reaction mixture was poured into a large amount of diethyl ether to precipitate polymeric materials. The copolymer was separated and dried in vacuo to give 732 mg (57% yield) of 3a.

References

JERUSSI, R. A. : J. Org. Chem. 35, 2105 (1970).

KÖNIG, K. H., SCHULZE, W., and MÖLLER, G. : Chem. Ber. 93, 554 (1960).

MAGATTI, G. : Chem. Ber. 13, 224 (1880).

SAEGUSA, T., KOBAYASHI, T., CHOW, T.-Y., and KOBAYASHI, S. : Macromolecules 12, 533 (1979).

Received and accepted August 7, 1981