Polymer Bulletin 3, 219-224 (1980)

Polymer Bulletin

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Preparation of Homo- and Co-Dimers of Styrene Derivatives Using Phosphate

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Summary

Dimers were preferably obtained in the oligomerization of styrene derivatives by diphenyl hydrogen phosphate. The reaction was assumed to proceed through the formation of esters from the monomers and diphenyl hydrogen phosphate as intermediate. This assumption was confirmed by the fact that treatment of the esters with alternative styrene derivatives gave linear codimers.

Introduction

The dimerization of styrene by use of acidic catalysts such as sulfuric acid (ROSEN, 1953; CALDER et al., 1969) has been studied which generally gave a mixture of the linear unsaturated dimer and cyclic dimer. The selective dimerization of styrene to linear unsaturated dimer (1,3-diphenyl-1-butene) by super acid was recently reported by Higashimura (SAWAMOTO et al., 1975; HIGASHIMURA, 1977; NISHII, 1977).

In this paper, we report the mechanism of the dimerization and preparation of codimers of styrene derivatives by using phosphates.

Experimental

Diphenyl hydrogen phosphate (II). Diphenyl phosphorochloridate was hydrolyzed to give II according to the method of Müller (BRIGL, 1939).

1-p-Chlorophenylethyl diphenyl phosphate (III, X=Cl). To a mixture of 1-p-chlorophenylethyl alcohol and pyridine was added diphenyl phosphorochloridate dropwise at 0°C and the mixture was stirred for a further few hours before the addition of water and extraction with ether. The extracts were washed with dilute sulfuric acids, dilute solution of sodium hydrogen carbonate and water and dried. The solution was filtered and evaporated in vacuo to give 1-p-chlorophenylethyl diphenyl phosphate (III, X=Cl).

0170-0839/80/0003/0219/$01.20

Anal. ^{1}H NHR ($CDCl_3$) δ 1.50 (d, CH_3, 3H), δ 4.65 (m, CH, 1H), δ 7.15-7.30 ($-C_6H_4Cl$ and 2 $-C_6H_5$, 14H)

1-Phenylethyl diphenyl phosphate (III, X=H). This phosphate was prepared by similar method described above. Anal. ^{1}H NHR ($CDCl_3$) δ 1.6 (d, CH_3, 3H), δ 4.65 (m, CH, 1H), δ 7.1-7.3 (3 $-C_6H_5$, 15H)

Preparation procedure of homo and co-dimers. A mixture of phosphate and styrene derivatives in a test tube was kept at a desired temperature. The product was analysed by gel-permeation and gas chromatography.

Results and Discussion

Oligomerization of styrene derivatives by diphenyl hydrogen phosphate (II). The reaction of styrene derivatives with a small amount of diphenyl hydrogen phosphate (II) was carried out at 120°C for twenty four hours without solvent. The results are summarized in Table 1.

TABLE 1

Composition of oligomers formed by II at 120° C$^{a)}$

Monomer	Product Composition (%)$^{b)}$		
	Dimer	Monomer	≥Trimer
α-MeSt	91	5	4
St	62	30	8
p-Cl-St	58	38	6
p-MeO-St	23	2	75

a) [Monomer]/[II] = 10

b) Based on the amount of the monomer added

α-Methylstyrene (α-MeSt) gave a mixture of two unsaturated dimers in high yields. Styrene (St) and p-chlorostyrene (p-Cl-St) provided also linear and unsaturated dimers in good yields, while p-methoxystyrene (p-MeO-St) gave higher oligomers because of its high cationic reactivity. Figure 1 shows the time-conversion curves for the yield of styrene dimer with mole ratios of $[St]/[(PhO)_2P(O)OH]$ of 2 and 10 at 50 and 120°C. Higher concentration of diphenyl hydrogen phosphate (II) favored the dimerization and maximum yield of dimers as high as 75% was obtained. At 120°C the reaction underwent more rapidly and the yield decreased after a maximum yield was attained. It may be possible that the dimer produced was protonated again and propagated to give higher oligomers.

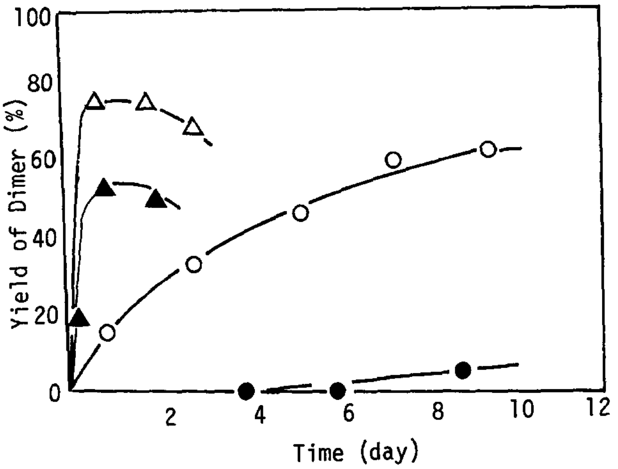
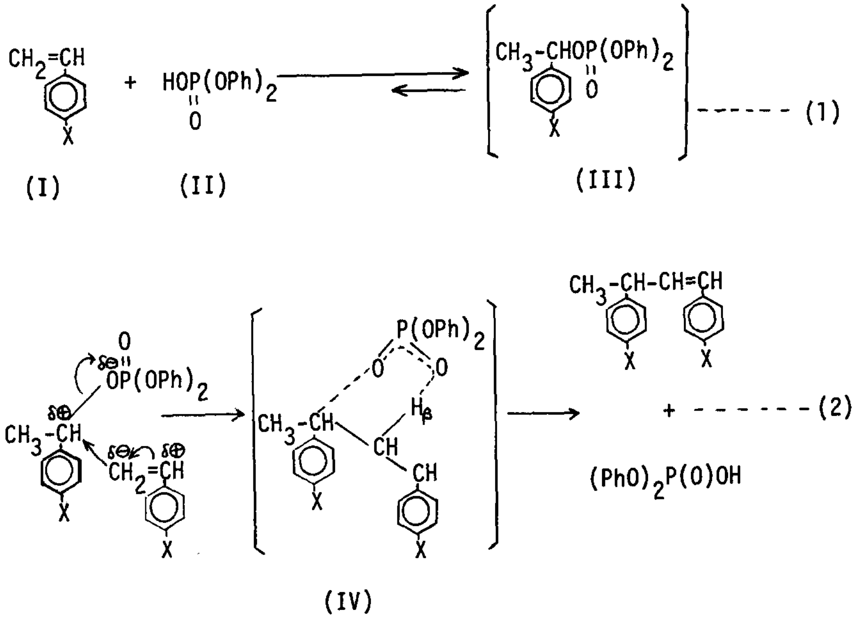


Fig. 1: Effect of temperature and molar ratio on the yield of styrene dimer

▲ : [St]/[II] = 10, 120°C ; △ : [St]/[II] = 2, 120°C

● : [St]/[II] = 10, 50°C ; ○ : [St]/[II] = 2, 50°C



Scheme 1

The overall dimerization has been postulated to involve the following individual steps (Scheme 1). First, styrene derivatives (I) react with diphenyl hydrogen phosphate to form a phosphate (III) as intermediate (eq. 1). This differs from the dimerization of styrene derivatives by super acid where production of stable ion-pair of propagation species and counter anion was assumed (HIGASHIMURA, 1977; NISHII, 1977). The second step in the reaction would be presented by an attack of another monomer followed by elimination of diphenyl hydrogen phosphate (II) to form dimers (eq. 2). Diphenyl phosphate anion as a leaving group takes a position in IV to have a substantial interaction with β-hydrogen. Proton elimination from the growing species is naturally facilitated at high temperature. These factors will lead to the predominant dimerization of styrene. Since the addition of diphenyl hydrogen phosphate (II) to the dimer produced might be difficult by steric hindrance, only a small amount of oligomers ($\geq$ trimer) was produced.

In order to examine the above assumption, 1-phenylethyl diphenyl phosphate (III, X=H) was separately prepared from 1-phenylethyl alcohol and diphenylphosphorochloridate as a model compound of the addition

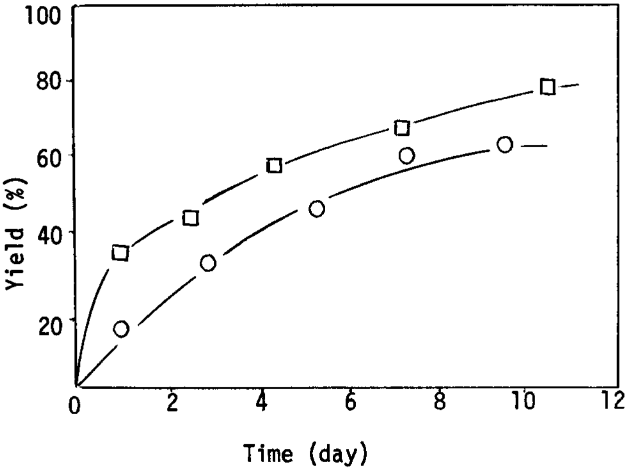
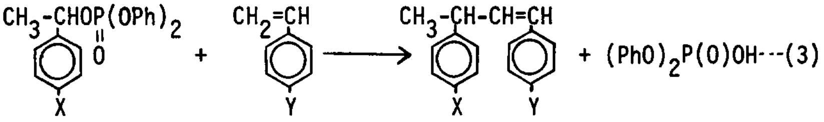


Fig. 2: Styrene dimer formation curves by the reaction of styrene with II and with III at 50°C

○ : [St]/[II] = 2 ; □ : [St]/[III] = 1

intermediate with styrene monomer. In fact the reaction of the phosphate (III, X=H) and styrene resulted in the formation of the same type linear unsaturated dimer with reasonable yield. The total concentration of the styrene unit was regulated to be identical in both reactions (eq. 1-2 and 3, X=Y=H), where the ratios of $[St]/[(PhO)_2P(O)OH]=2$ and $[St]/[CH_3CH(Ph)OP(O)(OPh)_2]=1$ were used respectively. It was also found that the yield of dimer from the reaction of styrene and 1-phenylethyl diphenyl phosphate (III, X=H) was kept higher than that of styrene dimerization with diphenyl hydrogen phosphate (II) during course of the reaction (Fig. 2). These results may be taken to support the assumed reaction mechanism.

Preparation of codimers. The reaction mechanism of dimerization mentioned above seems to enable us to obtain a codimer by the reaction of an ester (III), as the addition product of one monomer to diphenyl hydrogen phosphate (II), with another monomer as shown in eq. 3. 1-p-Chlorophenylethyl diphenyl phosphate (III, X=Cl) was treated with styrene (I, X=H) at 50°C to afford codimer (V, X=Cl, Y=H) in 33% yield. Results are shown in Table 2. The codimer (V, X=H, Y=Cl) with reverse order of monomer addition was made with 43% yield by the reaction of 1-phenylethyl diphenyl phosphate (III, X=H) with p-chlorostyrene (I, Y=Cl)



(III) (I) (V) (II)

TABLE 2

Composition of dimers formed by the reaction of III with I[a)]

III	I	Time, day	Yield[b)], %		
			Codimer(V)	St dimer	p-Cl-St dimer
X=Cl	Y= H	6	33	3	2
X= H	Y=Cl	5	43	9	5

a) [I]/[III] = 4, at 50°C

b) Determined by GC

under the identical conditions. In both cases, the yields of each homo-dimer of styrene and p-chlorostyrene were quite low. Only small amounts of higher oligomers were detected by GPC. The codimer formation reaction competes with spontaneous decomposition of the ester (III) itself to styrene derivative monomer and diphenyl hydrogen phosphate (II).

Further study of this codimerization reaction is in progress and results will be published later.

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Received and accepted August 26, 1980