Polyaddition Reaction of Diphenylsilane to Diallyl Carboxylate

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The monofunctional addition reaction of phenylsilane or methyl diethoxysilane to allyl acetate was first studied by Speier and coworkers[1,2], and 3-(phenylsilyl) propyl acetate and 3-(diethoxy methylsilyl)propyl acetate were prepared by this method under the influence of *tert*-butyl hydroperoxide. The addition reaction of trichlorosilane and methyl dichlorosilane to allyl acetate was also studied under the influence of platinum catalyst[3].

As an example of the bifunctional addition reaction, we have reported in the previous short communication, the polyaddition reaction of diphenylsilane to diallyl phthalate[4].

In the present work we have tried to extend the reaction in order to obtain larger molecules which might have more interesting properties. Some experiments using diallyl phthalate and diphenylsilane at various reaction conditions (reaction temperature, catalyst concentration and monomer concentration) are summarized in Tables II—VI.

The new method of polymer synthesis was further extented to the polyaddition reaction of diphenylsilane and the following diallyl carboxylate : diallyl oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate and terephthalate.

Experimental

Materials.—*Diphenylsilane.* — Diphenylsilane was prepared from diphenyldichlorosilane and lithium aluminum hydride by ordinary method[5]. Three hundred and four grams (1.2 mol.) of diphenyldichlorosilane was added to 25 g. (0.68 mol.) of lithium aluminum hydride in 300 ml. of anhydrous ether. The solution was refluxed for several hours and hydrolyzed with 260 ml. of dilute hydrochloric acid. The ethereal layer was distilled to give 215 g. of diphenylsilane b. p. 109°C/7 mmHg, n_D^{20} 1.5799, d_4^{20} 0.9970.

Diallyl Phthalate. — The commercial product was distilled under reduced pressure before use. The portion boiling at 155°C/6 mmHg, n_D^{20} 1.5205, d_4^{20} 1.1205, was used in the polyaddition reaction.

Other Diallyl Carboxylates. — Diallyl carboxylates were prepared by the method described previously[6]. Their physical properties were listed in Table I.

TABLE I. PHYSICAL PROPERTIES OF DIALLYL CARBOXYLATES

Diallyl carboxylates	B. p. °C/mmHg	n_D^{20}	d_4^{20}
Oxalate	104～106/15	1.4470	1.0890
Malonate	115/4	1.4480	1.0643
Succinate	112～113/8	1.4514	1.0559
Adipate	136～138/8	1.4539	1.0226
Sebacate	181～183/9	1.4564	0.9788
Phthalate	155/6	1.5205	1.1205
Isophthalate	163/8	1.5250	1.1213
Terephthalate	166～167/8	—	—

Catalyst. — Prepared by dissolving 0.518 g. of commercial $H_2PtCl_6 \cdot 6H_2O$ (10^{-3} mol.) in 100 ml. *tert*-butyl alcohol.

Polyaddition Reaction.—To the equimolar mixture of diphenylsilane, and to diallyl carboxylate in a glass tube was added a constant amount of chloroplatinic acid solution. The tube was then sealed in a nitrogen atmosphere, and heated for several hours in a dry oven of constant temperature. The reaction product was dissolved in 100 ml. of acetone, and filtered. To the filtrate 30 ml. of water was added and reprecipitated. The precipitates were separated by decantation and dried in a vaccum desiccator at 50°C for 7 days until it reached constant weight.

Determination of Molecular Weight.—The molecular weight was calculated from the freezing point depression in benzene.

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[1] J. L. Speier et al., *J. Am. Chem. Soc.*, **78**, 2278 (1956).
[2] J. L. Speier et al., ibid., **79**, 974 (1957).
[3] L. G. Goodman et al., ibid., **79**, 3073 (1957).
[4] K. Kojima., This Bulletin, **31**, 666 (1958).
[5] R. A. Benkeser et al., *J. Am. Chem. Soc.*, **74**, 648 (1952).
[6] K. Kojima et al., *Reports of the Research Institute of Dental Materials Japan*, **8**, 136 (1957).

Determination of Inherent Viscosity.—One fifth of a gram of solvent free polymer was dissolved in 50 ml. of benzene and the viscosity was determined by an Ostwald type viscosimeter at 25°C.

Results and Discussion

The preliminary experiment for determing conditions which favor formation of polyaddition products were carried out using diphenylsilane and diallyl phthalate.

Temperature Dependence.—Polymerization of diphenylsilane with diallyl phthalate was carried out at various temperatures. The results are given in Tables II, III and IV.

The largest polymer was prepared at 120°C, 48 hr. and 0.1 ml. catalyst. The degree of polymerization increased as the conversion became higher. Higher reaction temperature also seemed to increase the degree of polymerization. It became clear that the addition reaction was of second order at the initial stage (Figs. 1 and 2), and the k values were $k_{80}=2.5$, $k_{100}=5.2$ and $k_{120}=13.2\times10^{-8}$ g./sec. mol. When the logarithm of the initial rates of polymerization was plotted against reciprocals of temperatures ($1/T$), a good straight line was obtained (Fig. 3). The over-all activation energy calculated from the slope in

TABLE II. POLYADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE AT 80°C

Reaction time, hr.	Conversion %	Mot. wt.	[η]
3	3.5	421	0.5
6	5.1	482	0.5
12	9.8	718	0.6
24	17.9	789	0.6
48	24.8	877	0.6

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-8} mol./ml. were used.

TABLE III. POLYADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE AT 100°C

Reaction time, hr.	Conversion %	Mol. wt.	[η]
3	5.2	498	0.5
6	9.7	663	0.6
12	18.8	880	0.6
24	31.9	1288	0.7
48	46.4	1394	0.7

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-8} mol./ml. were used.

TABLE IV. POLYADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE AT 120°C

Reaction time, hr.	Conversion %	Mol. wt.	[η]
3	10.9	510	0.6
6	22.9	783	0.6
12	34.7	1079	0.6
24	55.9	1583	0.7
48	70.6	1688	0.7

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-8} mol./ml. were used.

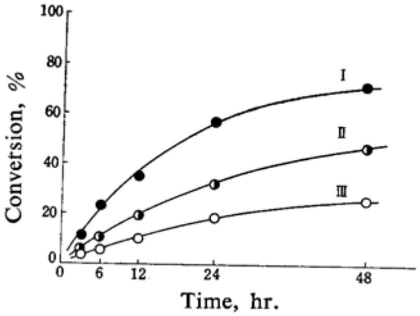

Fig. 1. Correlation of conversion percent with time.
I for reaction temperature 120°C (●), II for 100°C (◑), III for 80°C (○).

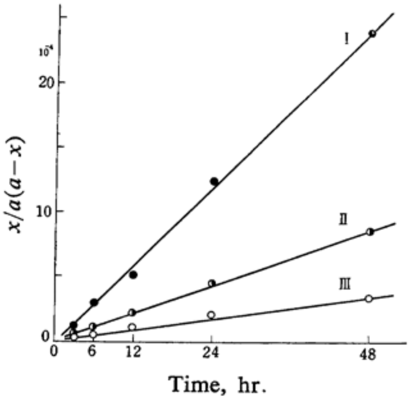

Fig. 2. Correlation of $x/a(a-x)$ with time.
I for reaction temperature 120°C (●), II for 100°C (◑), III for 80°C (○).

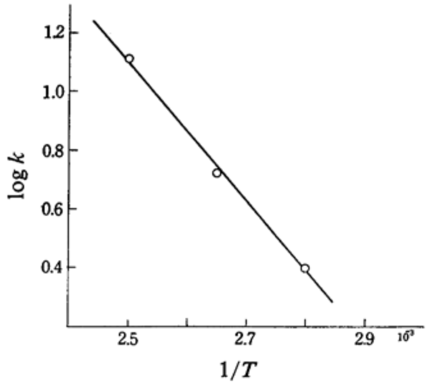

Fig. 3. Correlation of $\log k$ with $1/T$.

Fig. 3 was found to be 12 kcal./mol. for this reaction.

Effect of the Catalyst Concentration. — The data for the effect of the catalyst concentration is given in Table V, and the dependence of the initial rate of polymerization upon the concentration of catalyst are shown in Fig. 4.

TABLE V. EFFECTS OF CATALYST CONCENTRATION IN ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Catalyst conc. mol./ml.	Conversion %	Mol. wt.	[η]
5×10^{-8}	21.2	758	0.6
10	29.7	836	0.6
15	44.9	746	0.6
20	65.5	660	0.6
25	68.6	773	0.6

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. were used and were heated at 110°C., 6 hr.

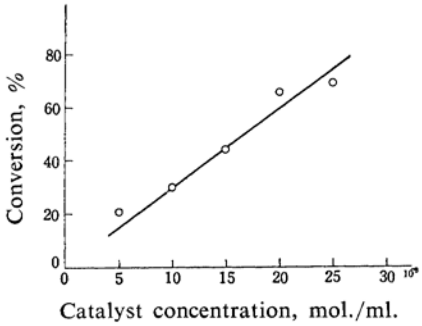

Fig. 4. Effect of catalyst concentration.

It is evident that the initial rate of polymerization is proportional to the concentration of chloroplatinic acid solution. The molecular weight of the polymer, however, is almost independent of the concentration of the catalyst.

Effect of Initial Monomer Concentration. — The relationship between initial rate of polymerization and the concentration of diphenylsilane-diallyl phthalate mixture in toluene was studied at 110°C. The data for the rate of diminution of monomer concentration are given in Table VI and Fig. 5.

TABLE VI. EFFECTS OF INITIAL MONOMER CONCENTRATION IN ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Monomer conc. g./ml.	Conversion %	Mol. wt.	[η]
50×10^{-2}	66.3	870	0.6
33	36.7	627	0.6
25	33.5	597	0.5
20	24.6	545	0.5
10	15.5	463	0.5

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 20×10^{-8} mol./ml. were used and were heated at 110°C, 24 hr.

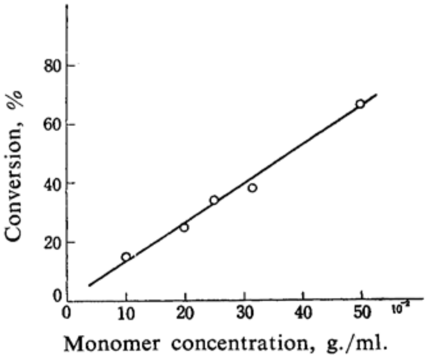

Fig. 5. Effect of initial monomer concentration.

It is clear that the initial rate is proportional to the concentration of diphenylsilane—diallyl phthalate mixture.

The above result indicates that the over-all rate of polyaddition reaction, k_p of diphenylsilane with diallyl phthalate is proportional to the initial monomer concentration (M) and to the catalyst concentration (C).

$$k_p \propto (M)(C)$$

The molecular weight of the polymer is proportional to the initial monomer concentration, but independent of the catalyst concentration.

Polyaddition Reaction of Diphenylsilane to Diallyl Carboxylates. — Similar experiments of diphenylsilane to diallyl oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate, and terephthalate were carried out. The results obtained are shown in Table VII.

TABLE VII. ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL CARBOXYLATES

Diallyl carboxylate	Conversion %	Mol. wt.	[η]	Si Calc. %	Si Found %
Oxalate	27.5	650	0.6	7.93	8.64
Malonate	59.5	990	0.6	7.62	7.36
Succinate	64.9	1080	0.6	7.34	7.38
Adipate	55.8	1120	0.6	6.84	7.58
Sebacate	76.3	1170	0.6	6.02	5.45
Phthalate	73.6	1860	0.7	6.52	6.24
Isophthalate	66.5	—	—	6.52	6.49
Terephthalate	53.0	—	—	6.52	6.35

Diallyl carboxylate 0.02 mol. and diphenylsilane 0.02 mol. were used and were heated at 110°C, 50 hr.

Addition products were viscous oily liquids, but the adducts of diphenylsilane to diallyl phthalate and isophthalate and terephthalate were light yellow, glassy solid, and were useful as adhesives. Their softening temperatures were ca. 108°, 120°and >200°C.

Summary

The polyaddition reaction of diphenylsilane to diallyl phthalate was studied. The reaction was found to be of the second order at the initial stage. The over-all rate is proportional to the initial monomer and catalyst concentration. The over-all activation energy calculated for this reaction was found to be 12 kcal./mol. at 80~120°C.

By a similar method following polyesters have been prepared from diphenylsilane and diallyl carboxylates: Polydiphenylsilylene 3, 3′-bis(trimethylene)oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate and terephthalate. Their molecular weight and inherent viscosity were determined and properties have been described.

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