

## Copolymerizations of Vinyl Silanes

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### INTRODUCTION

High polymers containing silicon have attained a secure industrial foothold in applications for which their novel properties make them particularly suitable. However, not much work has been reported on the polymerization of unsaturated silicon compounds through the vinyl group. A recent article by Wagner *et al.*<sup>1</sup> mentions copolymerization with such common monomers as methyl methacrylate, styrene, and vinyl acetate, but determinations of the reaction rates have not been reported. The work reported here is the result of a preliminary study of the copolymerization behavior of twelve vinyl silanes. Copolymerizations with monochlorostyrene vinyl chloride, and acrylonitrile were studied because experience has shown these monomers to be useful and convenient in defining the copolymerization characteristics of a new monomer.

### EXPERIMENTAL

The twelve vinyl silanes studied were obtained from the Research Laboratory of the Linde Air Products Company. These alkoxyasilanes, with the exception of 6-triethoxysilylbicyclo[2.2.1]heptene-2, were prepared by addition of the desired alcohol to the corresponding chlorosilane. The chlorosilanes used were of good purity. Residual hydrolyzable chlorine was removed from the silicon esters by distillation from a small amount of sodium alkoxide or sodium bicarbonate. The final products gave a negative test for chloride with alcoholic silver nitrate. In the case of allyltriethoxysilane, quinoline was used as a hydrogen chloride acceptor during the addition of the alcohol to the chlorosilane to prevent side reactions. 6-Triethoxysilylbicyclo[2.2.1]heptene-2 was prepared by a Diels-Alder reaction between cyclopentadiene and vinyltriethoxysilane.<sup>1</sup> The monochlorostyrene was prepared in this laboratory and consisted of a mixture of approximately equal amounts of the ortho and para isomers. Both the vinyl chloride and the acrylonitrile were commercial grades of the uninhibited monomer and these were used without further purification. An approximately 25% solution by weight of diacetyl peroxide in dimethyl phthalate (Buffalo Electro-Chemical Company) was used as the catalyst in all polymerizations. A commercial grade of anhydrous acetone (less than 0.05% water) was used as the solvent.

All copolymerizations were carried out in sealed Pyrex tubes containing 10 grams of the combined monomers, 10 grams of acetone, and 0.1 gram of contained diacetyl peroxide. The tubes were thoroughly flushed with nitrogen before sealing. They were maintained at  $50 \pm 0.5^\circ\text{C}$ . in a water bath while being rocked at about 20 cycles per minute. The resin was isolated by precipitation in isopropanol, dried at  $50^\circ\text{C}$ ., and analyzed. Nitrogen analyses were multiplied by a factor of 1.05, which has been found necessary to obtain the theoretical amount in the Kjeldahl analysis of polyacrylonitrile.

Although resins were obtained from the copolymerizations with monochlorostyrene all analyzed so high in monochlorostyrene content (by

TABLE I  
COPOLYMERIZATION WITH VINYL CHLORIDE

Silane	Time, hrs.	Con- version, %	$M_1$	$m_1$
Vinyltrimethoxy.....	10	14	0.847	0.857
	32	7	0.504	0.637
Vinyltriethoxy.....	—	21	0.965	0.964
	5	12	0.924	0.923
	22	35	0.924	0.942
	22	13	0.924	0.908
	9	24	0.876	0.853
	20	23	0.670	0.728
	25	13	0.566	0.698
Vinyltriisopropoxy.....	7	24	0.897	0.892
	11	5	0.612	0.682
Vinylmethyldiethoxy.....	10	12	0.856	0.881
	30	2	0.523	0.770
Vinylethyldiethoxy.....	4	11	0.918	0.927
	14	15	0.807	0.826
	16	6	0.650	0.797
Vinylphenyldiethoxy.....	10	14	0.892	0.891
	32	7	0.604	0.613
Allyltriethoxy.....	4	6	0.929	0.961
	5	4	0.830	0.917
	12	1	0.685	0.893
Propenyltriethoxy.....	2	3	0.929	0.989
	5	8	0.831	0.728
	16	11	0.686	0.956
2-Butenyltriethoxy.....	10	11	0.891	0.799
	32	>1	0.599	—
$\Delta^3$ -Cyclohexenyltriethoxy.....	30	14	0.901	0.822
	32	>1	0.629	—
6-Triethoxysilylbicyclo- [2.2.1]heptene-2.....	7	13	0.942	0.976
	14	14	0.860	0.902
	16	6	0.732	0.839
$\alpha$ -Chlorovinyltriethoxy.....	6	6	0.970	0.883
	33	19	0.935	0.805

chlorine analysis), it is doubtful any significant copolymerization took place. The data for the copolymerizations with vinyl chloride are given in Table I and for the copolymerizations with acrylonitrile in Table II.  $M_1$  and  $m_1$  are the mole fractions of vinyl chloride, or acrylonitrile in the monomer and copolymer, respectively.

TABLE II  
COPOLYMERIZATION WITH ACRYLONITRILE

Silane	Time, hrs.	Con- version, %	$M_1$	$m_1$
Vinyltrimethoxy.....	0.75	3	0.867	0.982
	7	4	0.545	0.891
Vinyltriethoxy.....	1.7	14	0.935	1.000
	8	18	0.705	0.957
	16	11	0.606	0.929
	25	6	0.473	0.833
Vinyltriisopropoxy.....	0.75	7	0.911	0.986
	3.5	7	0.652	0.931
Vinylmethyldiethoxy.....	0.75	5	0.876	0.978
	7	5	0.564	0.897
Vinylethyldiethoxy.....	1.75	18	0.885	0.990
	3.75	3	0.585	0.928
Vinylphenyldiethoxy.....	0.75	4	0.907	0.994
	7	7	0.642	0.924
Allyltriethoxy.....	2.5	7	0.852	0.902
	14	1	0.490	0.738
Propenyltriethoxy.....	1.0	5	0.900	0.996
	2.3	0	0.624	—
2-Butenyltriethoxy.....	1.25	7	0.906	0.994
	7	5	0.638	0.945
$\Delta^3$ -Cyclohexenyltriethoxy.....	1.25	3	0.915	0.994
	7	3	0.664	0.963
6-Triethoxysilylbicyclo- [2.2.1]heptene-2.....	6.5	7	0.918	0.897
	13	0	0.674	—
$\alpha$ -Chlorovinyltriethoxy.....	11	11	0.864	0.861
	30	1	0.515	0.587
	16	44	0.515	0.959

## DISCUSSION

In all of these systems the polymerization rates decreased rapidly as the concentration of the alkoxysilane increased, thus making it difficult to secure data over the entire range of monomer compositions. Consequently there is uncertainty about the copolymerizations in the range of high alkoxysilane concentrations. It appears, however, that the data can best be fitted by assuming that the reactivity ratio  $r_2$  (where the alkoxysilane is  $M_2$ ) is equal to zero. This indicates a very low rate constant for self-propagation, a conclusion supported by our observations that these monomers show no tendency to polymerize by themselves under the conditions

of these experiments. Making this assumption the reactivity ratio,  $r_1$ , was calculated by fitting the best theoretical curves to the data. The values for these reactivity ratios, when  $M_1$  is either vinyl chloride or acrylonitrile, are given in Table III.

TABLE III  
REACTIVITY RATIOS

Silane	With vinyl chloride	With acrylo- nitrile
Vinyltrimethoxy.....	0.8	6.0
Vinyltriethoxy.....	0.9	4.5
Vinyltriisopropoxy.....	0.8	6.5
Vinylmethyldiethoxy.....	1.2	6.0
Vinylethyldiethoxy.....	1.0	9.0
Vinylphenyldiethoxy.....	0.7	8.3
Allyltriethoxy.....	2.0	1.7
Propenyltriethoxy.....	8.0	20.0
2-Butenyltriethoxy.....	0.4	10.0
$\Delta^3$ -Cyclohexenyltriethoxy.....	0.4	12.0
6-Triethoxysilylbicyclo[2.2.1]heptene-2.....	1.6	0.7
$\alpha$ -Chlorovinyltriethoxy.....	0.2	0.7

Inspection of these results shows that the three vinyltrialkoxysilanes have quite similar reactivities that are not much different from the vinylalkyldiethoxysilanes. Replacing the vinyl group with other types of substituents made much greater differences in the reactivity ratios. The high values for the reactivity ratios with propenyltriethoxysilane seem out of line and may be in error. On the other hand the much lower reactivity ratios obtained with  $\alpha$ -chlorovinyltriethoxysilane are not unexpected in view of the effect of such chlorine substitution on the reactivity of other vinyl monomers.

Although the reactivity ratios were on the whole quite similar, there were much greater differences in the over-all rates of polymerization. In this respect the vinyltrialkoxysilanes yielded much better rates than the other silanes. Attempts were made to determine the reduced viscosities of these copolymers. Most of the copolymers with vinyl chloride were insoluble in all common solvents after being dried, although these resins were soluble before precipitation and drying. Most of the copolymers with acrylonitrile were soluble in dimethylformamide. The reduced viscosities of these copolymers showed that increasing the concentration of silane in the initial monomer resulted in a lowering of the polymer reduced viscosity. This effect was less for the vinyltrialkoxysilanes than for the other silanes.

It is possible to prepare reasonably high molecular copolymers of these silanes either with vinyl chloride or with acrylonitrile and advantage might be taken of the tendency to crosslink to prepare resins that could be insolubilized. Probably  $\alpha$ -chlorovinyltriethoxysilane, or one of the vinyltrialkoxysilanes, offers the best opportunity for practical use.

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### Reference

1. G. H. Wagner, *et al.*, *Ind. Eng. Chem.*, **45**, 367 (1953).

### Synopsis

A brief experimental investigation was made of the copolymerization of twelve alkoxy-silanes with monochlorostyrene, vinyl chloride, and acrylonitrile. These new monomers include vinyltrimethoxy-, vinyltriethoxy-, vinyltriisopropoxy-, vinylmethyldiethoxy-, vinylthyldiethoxy-, and vinylphenyldiethoxy-silanes as well as allyl-, propenyl-, 2-butenyl-,  $\Delta^3$ -cyclohexenyl-, 6-triethoxysilylbicyclo[2.2.1]heptene-2, and  $\alpha$ -chlorovinyltriethoxysilanes. No copolymerization took place with monochlorostyrene. In the copolymerizations with vinyl chloride, and with acrylonitrile, the reactivity ratio  $r_2$  was assumed to be zero and the value of  $r_1$  determined.

### Résumé

Une brève étude expérimentale a été faite au sujet de la copolymérisation de douze alcoyloxysilanes avec le monochlorostyrène, le chlorure de vinyle, et l'acrylonitrile. Parmi ces nouveaux monomères on trouve: la vinyltriméthoxy-, la vinyltriéthoxy-, la vinyltriisopropoxy-, la vinylméthyldiéthoxy-, la vinyléthyldiéthoxy-, et la vinylphényldiéthoxy-silanes; de même on a utilisé l'allyl-, la propényl-, la 2-butényl-,  $\Delta^3$ -cyclohexényl-, 6-triéthoxysilylbicyclo[2.2.1]-heptène-2 et l' $\alpha$ -chlorovinyltriéthoxysilane. Aucune copolymérisation n'a eu lieu avec le monochlorostyrène. Dans les copolymérisations avec le chlorure de vinyle, et avec l'acrylonitrile, on a posé le rapport de réactivité  $r_2$  égal à zéro, et la valeur de  $r_1$  a été déterminée.

### Zusammenfassung

Es wurde eine kurze experimentelle Untersuchung der Copolymerisation von zwölf Alkoxysilanen mit Monochlorostyrol, Vinylchlorid und Acrylonitril ausgeführt. Diese neuen Monomere umschliessen: Vinyltrimethoxy-, Vinyltriäthoxy-, Vinyltriisopropoxy-, Vinylmethyldiäthoxy-, Vinyläthyldiäthoxy- und Vinylphenyldiäthoxy-Silane wie auch Allyl-, Propenyl-, 2-Butenyl-,  $\Delta^3$ -Cyclohexenyl-, 6-Triäthoxysilyl-bicyclo[2,2,1]heptene-2 und  $\alpha$ -Chlorovinyltriäthoxysilane. Mit Monochlorostyrol trat keine Copolymerisation auf. Bei den Copolymerisationen mit Vinylchlorid und mit Acrylonitril wurde der Reaktivitätskoeffizient  $r_2$  als Null vorausgesetzt, und der Wert von  $r_1$  bestimmt.

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