# RADICAL COPOLYMERIZATION OF
# VINYLTRIMETHYL(PHENYL)SILANES WITH ACRYLONITRILE*

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One method of modifying the properties of polymers is by copolymerizing different monomers. The introduction of units of some other type into a macromolecular chain sometimes has a marked effect on polymer properties, such as the glass transition temperature, heat resistance, solubility, etc.

Moreover data is obtainable regarding the reactivity of the comonomers in studies of copolymerization reactions.

Much information has been published in regard to vinyl derivatives of silicon, but only a few authors [1–3] have reported on the reactivity of alkenylsilanes.

In an earlier investigation we reported on the radical copolymerization of vinyltrimethyl(phenyl)silanes with styrene and methyl methacrylate [4]. It is now our aim to determine the relative activity of vinyltrimethyl(phenyl)silanes in copolymerization reactions with acrylonitrile in view of the highly reactive nature of the acrylonitrile radical.

## EXPERIMENTAL

Vinyltrimethylsilane (VTMS) and vinylphenyldimethylsilane (VPDMS) were obtained by organomagnesium synthesis from the appropriate vinylchlorosilanes [5]. After drying over calcium chloride and metallic sodium the monomers were distilled in a rectifying column. VTMS: b.p. $54.6°/744$ mm, $n_D^{20}$ $1.3910$; VPDMS: b.p. $82°/20$ mm, $n_D^{20}$ $1.5048$.

Acrylonitrile was purified by the Bamford-Jenkins method [6] and kept over calcium hydride. Immediately prior to the polymerization the acrylonitrile was distilled under reduced pressure. N,N-Dimethylformamide (DMFA) underwent azeotropic distillation with benzene, and was kept over calcium hydride.

The copolymerization of vinyltrimethyl(phenyl)silanes with acrylonitrile was performed in sealed ampoules evacuated to $10^{-3}$ mm, in bulk or in dimethylformamide (DMFA) solution at $70°$. Benzoyl peroxide was used as initiator. The initiator concentration was $0.01$ mole/l., and the total concentration of monomers amounted to 4–5 mole/l.

The monomers and the solvent used in the copolymerization were dry and of chromatographic purity. The product copolymers were precipitated with methanol or water, and dried to constant weight.

Copolymers of vinyltrimethyl(phenyl)silanes and acrylonitrile are faintly coloured powders, readily soluble in DMFA. The composition of the copolymers was determined from their silicon content.

The products obtained are true copolymers as vinylsilanes do not polymerize under the conditions of our experiments, and the formation of a mechanical mixture of homopolymers would also be impossible.

## DISCUSSION OF RESULTS

Table 1 contains some results of experiments in the copolymerization of vinyltrimethyl(phenyl)silanes with acrylonitrile.

The tabulated data show that acrylonitrile-enriched copolymers are obtained whatever the initial ratio of monomers. The experimental results show that the multiple bond of the vinylsilanes is not very active during the radical copolymerization with acrylonitrile. As the silane content of the initial mixture increases the copolymer yield is reduced (Fig. 1) and the intrinsic viscosity drops (Table 1). For instance, even when 10 mole % of VPDMS are added to acrylonitrile, the

TABLE 1. COPOLYMERIZATION OF VINYLTRIMETHYL(PHENYL)SILANES WITH ACRYLONITRILE

| Content of vinylsilanes in initial monomer mixture | | Polymeri- zation time, hr | Copolymer yield, % | Content of Si in copo- lymer, % | Mole frac- tion of vinyl- silane in co- polymer | $[\eta]$, dl/g |
|---|---|---|---|---|---|---|
| mole frac- tion | % by wt. | | | | | |
| *Copolymerization of VTMS with acrylonitrile* | | | | | | |
| 0·150 | 25·0 | 20·0 | 70·15 | 1·55 | 0·030 | 5·49 |
| 0·261 | 40·0 | 20·0 | 56·0 | 2·38 | 0·047 | 4·75 |
| 0·347 | 50·0 | 20·0 | 47·2 | 2·80 | 0·056 | 3·61 |
| 0·440 | 60·0 | 20·0 | 27·2 | 3·09 | 0·061 | 2·71 |
| 0·615 | 75·0 | 20·0 | 18·4 | 3·75 | 0·074 | 1·95 |
| 0·826 | 90·0 | 20·0 | 6·7 | 4·47 | 0·092 | 1·10 |
| *Copolymerization of VPDMS with acrylonitrile* | | | | | | |
| 0·091 | 25·0 | 20·0 | 73·5 | 1·85 | 0·039 | 5·10 |
| 0·170 | 40·0 | 20·0 | 65·0 | 2·72 | 0·054 | 3·91 |
| 0·243 | 50·0 | 20·0 | 50·1 | 3·10 | 0·065 | 3·42 |
| 0·329 | 60·0 | 20·0 | 39·5 | 4·80 | 0·109 | 2·78 |
| 0·496 | 75·0 | 20·0 | 19·5 | 5·41 | 0·121 | 1·91 |
| 0·745 | 90·0 | 20·0 | 7·6 | 7·15 | 0·184 | 1·14 |

*Note*: $c_i = 0·01$ mole/l.; $c_m = 10$ mole/l. 70°. Experiments carried out in bulk.

reduction in the polymerization rate for the latter is more than halved. (Fig. 2). This is probably because the polymeric radical with the vinylsilane unit at the chain end is considerably less active than the polyacrylonitrile radical, which
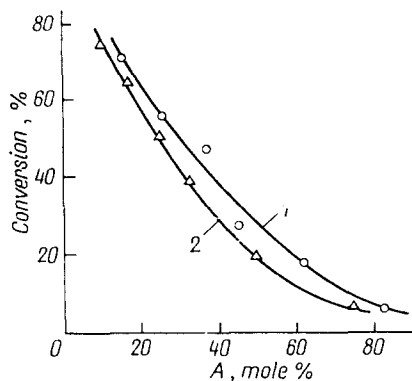
FIG. 1.                                FIG. 2.

FIG. 1. Copolymer yield vs. vinylsilane content in monomer mixture $(A)$: 1—
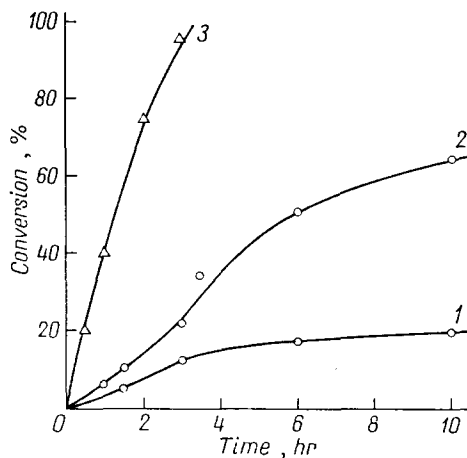VTMS+acrylonitrile, 2—VPDMS+acrylonitrile.

FIG. 2. Kinetics of copolymerization of VPDMS with acrylonitrile VPDMS
content in initial monomer mixture (mole%): 1—25, 2—10, 3—0.

TABLE 2. COPOLYMERIZATION OF VINYLTRIMETHYL(PHENYL)SILANES WITH ACRYLONITRILE
(LOW CONVERSIONS)

| Mole fraction of vinylsilane in monomer mixture | Copolymer yield, % | Si content, % | Mole fraction of vinylsilane in copolymer | Mole fraction of vinylsilane in monomer mixture | Copolymer yield, % | Si content, % | Mole fraction of vinylsilane in copolymer |
|---|---|---|---|---|---|---|---|
| VTMS+acrylonitrile* | | | | VTMS+acrylonitrile[†] | | | |
| 0·400 | 2·20 | 6·90 | 0·136 | 0·400 | 3·00 | 2·65 | 0·053 |
| 0·500 | 3·30 | 7·80 | 0·176 | 0·500 | 2·50 | 3·21 | 0·065 |
| 0·600 | 3·10 | 10·10 | 0·240 | 0·600 | 3·40 | 3·57 | 0·072 |
| 0·750 | 2·50 | 14·20 | 0·358 | 0·750 | 6·60 | 4·10 | 0·086 |
| VPDMS+acrylonitrile* | | | | VPDMS+acrylonitrile[†] | | | |
| 0·400 | 5·5 | 5·80 | 0·139 | 0·400 | 2·30 | 3·82 | 0·085 |
| 0·500 | 5·8 | 7·20 | 0·200 | 0·500 | 4·15 | 4·23 | 0·094 |
| 0·600 | 3·5 | 9·18 | 0·284 | 0·600 | 4·90 | 5·41 | 0·111 |
| 0·750 | 2·1 | 11·30 | 0·380 | 0·750 | 4·70 | 7·40 | 0·195 |

Note: $c_i = 0.01$ mole/l., $c_n = 5$ mole/l., 70°.
* Solvent—DMFA
[†] Experiments carried out in bulk.

means that the addition of either of the monomers will be considerably less rapid
than in the case of a radical terminating in an acrylonitrile unit. Steric factors
are probably of considerable importance here: the presence of a bulky $R_3Si$ group

at the end of the polymeric radical may well impede the addition of the next monomer molecule.

The copolymerization constants were obtained with a view to determining the reactivity of the silicon-olefins under review during the copolymerization with acrylonitrile. The results of some of these experiments are given in Table 2.

The tabulated data show that the copolymer compositions depend on the copolymerization conditions. The content of Si in the copolymers obtained in bulk is much lower compared with those obtained in solution. The homogeneity
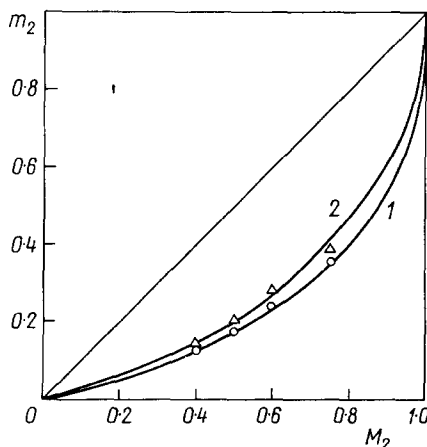
Fig. 3. Copolymer composition vs. composition of monomer mixture at low conversions: *1*—VTMS+acrylonitrile, *2*—VPDMS+acrylonitrile, $M_2$—vinylsilane content in initial monomer mixture, $m_2$—vinylsilane content in copolymer.

of the medium is probably a factor of great importance here. In contrast to the solution polymerization the bulk polymerization of acrylonitrile involves loss of the homogeneity of the system in the process owing to the separation of polymer in the form of solid phase particles. The polymer separating out contains "trapped" macroradicals, and the capacity of the latter for further growth will in this case depend on the extent to which the polymer swells and on the rate of monomer diffusion to active centres.

In the case of copolymerization there are two types of monomer molecule participating in the act of propagation, the acrylonitrile and vinylsilane molecules with their dissimilar diffusion capacities owing to the difference in the size of the molecules. The rate of diffusion of the bulkier vinylsilane molecules will probably be lower than that of the acrylonitrile, and the copolymers prepared in bulk will therefore have fewer silane units compared with copolymers prepared under homogeneous conditions where the role of diffusion is less important, and the composition of the copolymers is mainly dependent on the reactivity of the comonomers. In view of this we used the data regarding the composition of copolymers prepared in DMFA solution (Table 2) in order to calculate the copoly-

merization constants. The constants in question obtained using the Finemann–Ross method [7] have been tabulated (see Table 3).

TABLE 3. COPOLYMERIZATION CONSTANTS FOR
VINYLSILANES WITH ACRYLONITRILE ($M_1$)

| Vinylsilane ($M_2$) | $r_1$ | $r_2$ | $Q_2$ | $e_2$ |
|---|---|---|---|---|
| VTMS | 3·85 | 0·08 | 0·035 | −0·10 |
| VPDMS | 3·84 | 0·18 | 0·055 | 0·60 |

The found constants show that the type of substituent at the Si atom has some effect on the reactivity of vinylsilanes in radical processes. The replacement of a methyl group in the VTMS molecule by the phenyl group doubles the reactivity of VPDMS. The introduction of an electron acceptor substituent, i.e. the phenyl group, into the vinylsilane molecule apparently changes the electron density of the double bond of the vinyl group in such a way that the polymerization of VPDMS proceeds more readily compared with VTMS. The $Q$ and $e$ values obtained using the Alfrey–Price equation (Table 3) also indicate that the vinylsilanes differ as to polarity. The quantity $e_2 = −0·10$ for VTMS shows that the electron density at the double bond of the vinyl group is greater compared with VPDMS, for which $e_2 = 0·60$. The introduction of an electron acceptor substituent ($C_6H_5$ group) into the silane molecule apparently reduces the inductive effect of the trisubstituted silyl group, so that the electron density at the double bond is reduced.

The low $Q$ values for vinylsilanes shows that the ⟶$CH_2$—$CH$—$SiR_3$ radical cannot be stabilized to any appreciable extent as a result of the delocalization of unpaired electrons accompanying the depletion of the $d$-orbitals of silicon.

The second comonomer has a major effect on the copolymerizability of vinylsilanes: the latter copolymerize preferentially with acrylonitrile rather than with styrene, where $r_1$ (styrene) $= 26·0$, and $r_2 = 0·01$ [4]. It seems that the acrylonitrile macroradical is more active than the styrene macroradical in the copolymerization with vinylsilanes. Using the values obtained for $r_1$ and $r_2$ and the copolymer composition equation we calculated the quantitative dependence of the copolymer composition on the composition of the reaction mixture at the initial moment of time (Fig. 3). The curves obtained correspond to a case where the acrylonitrile is more active than the vinylsilanes in the propagation reaction with both polymeric radicals.

## CONCLUSIONS

(1) A study has been made of the copolymerization of vinyltrimethylsilane and vinylphenyldimethylsilane with acrylonitrile in the presence of benzoyl peroxide.

(2) The copolymerization constants are $r_1$ (acrylonitrile)$=3\cdot85$; $r_2$ (vinyl-trimethylsilane)$=0\cdot08$; $r_1'$ (acrylonitrile)$=3\cdot84$; $r_2''$ (vinylphenyldimethylsilane) $=0\cdot18$.

(3) It has been shown that the structure of vinylsilanes has a marked effect on their relative activity during radical copolymerization with acrylonitrile.

*Translated by* R. J. A. Hendry

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# STRUCTURE AND CONFORMATION OF POLY-*p*-METHACRYLYLPHENYL ESTERS OF *p*-ALKOXYBENZOIC ACIDS*

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In a study of polyalkylmethacrylates [1] it was found that lengthening of the side group of the molecule was accompanied by a marked rise in the negative anisotropy. This fact was interpreted as evidence that orientational ordering takes place in side chain radicals, and that the degree of orientational ordering in this case is higher than in the main chain of flexible molecules.

To obtain direct proof that the observed effect is due to the interaction of side radicals we studied some polymeric esters of alkoxybenzoic acids having