Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization of Acrylonitrile with Functional Silanes

V. Lakshmana Rao[a]; G. N. Babu[a]
[a] Polymer Research Laboratory Department of Chemistry, Indian Institute of Technology Powai, Bombay, India

To cite this Article Rao, V. Lakshmana and Babu, G. N.(1983) 'Copolymerization of Acrylonitrile with Functional Silanes', Journal of Macromolecular Science, Part A, 20: 5, 527 — 537

To link to this Article: DOI: 10.1080/00222338308061789

URL: http://dx.doi.org/10.1080/00222338308061789

J. MACROMOL. SCI.–CHEM., A20(5&6), pp. 527-537 (1983)

Copolymerization of Acrylonitrile with Functional Silanes

V. LAKSHMANA RAO and G. N. BABU*

Polymer Research Laboratory
Department of Chemistry
Indian Institute of Technology
Powai, Bombay 400076, India

ABSTRACT

Acrylonitrile (AN) has been copolymerized with vinyltriethoxysilane (VTES) and vinyltris(methoxy ethoxy)silane (VTMES) in bulk at 60°C using benzoyl peroxide. The copolymer composition has been determined from elemental analysis. The reactivity ratios of AN (M_1) copolymerizations with VTES ($r_1 = 4.72$, $r_2 = 0$) and VTMES ($r_1 = 2.45$, $r_2 = 0$) have been determined. Mechanistic explanations of the monomer reactivities are presented. The structure-property relationship of AN-vinylsilane copolymers has been discussed.

INTRODUCTION

Functional silanes [1-6] have been copolymerized with organic monomers such as acrylonitrile (AN) and styrene to impart thermal stability and electrical properties. In our previous studies we reported the reactivity ratios of AN and alkyl methacrylates with vinyl silanes

---

*To whom all correspondence should be addressed.

0022-233X/83/2005-0527$3.50/0

[7, 8]. In this work we report the copolymerizabilities of the two vinylsilanes with AN and the crystallinity and thermal stability of these structurally related copolymers.

EXPERIMENTAL

AN, vinyltriethoxysilane (VTES), and vinyltris(methoxy ethoxy)-silane (VTMES) (all Fluka) monomers were distilled under reduced pressure prior to use.

Benzoyl peroxide (BDH) was purified by recrystallization from methanol.

Copolymerization

Comonomers and initiator were mixed and freed of air by freeze-evacuation-thaw cycles. Copolymerization was carried out at 50°C. After the requisite time the polymers were precipitated in a rapidly stirred large excess of methanol. The polymers were filtered and then dried in vacuo at 40°C to constant weight. The compositions of the copolymers were calculated from elemental analyses.

The infrared spectra of the copolymers were recorded in Nujol between 400 and 4000 cm^{-1} on a Perkin-Elmer Spectrophotometer.

X-ray diffraction patterns were obtained on powdered specimens by using a Debye-Scherrer diffractometer with Ni-filtered radiation.

The thermogravimetric analyses were carried out with a Stanton Redcroft ST-780 thermobalance in static air from room temperature to 900°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The reaction conditions and results are summarized in Tables 1 and 2. The radical copolymerizations of AN with VTES and VTMES proceeded normally with a decrease in the rate of copolymerization with an increase in the proportion of silane in the feed. The general observation that silane monomers will not homopolymerize may be explained in terms of the low reactivity of the monomers themselves rather than possible inhibition by impurities.

The copolymerizations were terminated at low conversions in order to use the differential form of the copolymerization equation. The monomer reactivity ratios (r_1 and r_2) obtained by the Kelen-Tüdös linear method [9] are

VTES: $r_1 = 4.72$, $r_2 = 0$

VTMES: $r_1 = 2.45$, $r_2 = 0$

TABLE 1. Copolymerization of AN (M_1)-VTMES (M_2)

Mole fraction of M_2 in feed	% Conversion	Mole fraction of m_2 in copolymer
0.9	6.7	0.958
0.8	8.6	0.954
0.7	4.5	0.863
0.6	3.9	0.794

TABLE 2. Copolymerization of AN (M_1)-VTES (M_2)

Mole fraction of M_2 in feed	% Conversion	Mole fraction of m_2 in copolymer
0.9	10.4	0.988
0.8	9.8	0.951
0.7	6.5	0.919
0.6	5.9	0.869

The value of $r_2 = 0$ for VTES and VTMES means that these monomers do not self-propagate ($k_{22} = 0$) under the experimental conditions. The dependence curves for AN-VTES and AN-VTMES are presented in Fig. 1.

The low polymerizability of these silane monomers seems to be consistent with our earlier studies [8]. Similar observations have also been made by other workers [2, 10].

In contrast to the examples above, trimethylsilylbutadiene monomer in which the silyl moiety is far away from the reactive site do exhibit radical polymerizability.

The poor reactivity of silane monomers might be explained, at least in part, by the electron-deficient nature of the monomers. This implies that the electron density at the double bond is reduced due to delocalization of the electron cloud to the vacant d-orbitals of the silicon. It is therefore difficult for the electron-deficient VTES and VTMES radicals to add to the electron-deficient monomer ($k_{22} = 0$).

By comparing the r_1^{-1} values of the two copolymerization systems, it is revealed that VTMES is about two times more reactive than VTES toward the PAN radical, which is consistent with the greater polarity of the former.

The IR spectra of AN-VTES and AN-VTMES copolymers exhibited

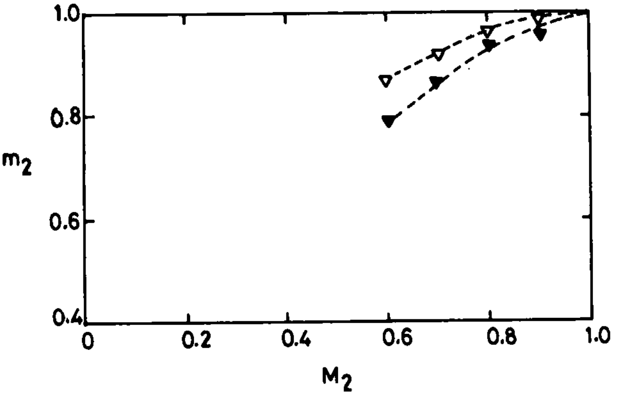

FIG. 1. Initial copolymer composition vs composition of monomer feed (▽) AN-VTES and (▼) AN-VTMES.

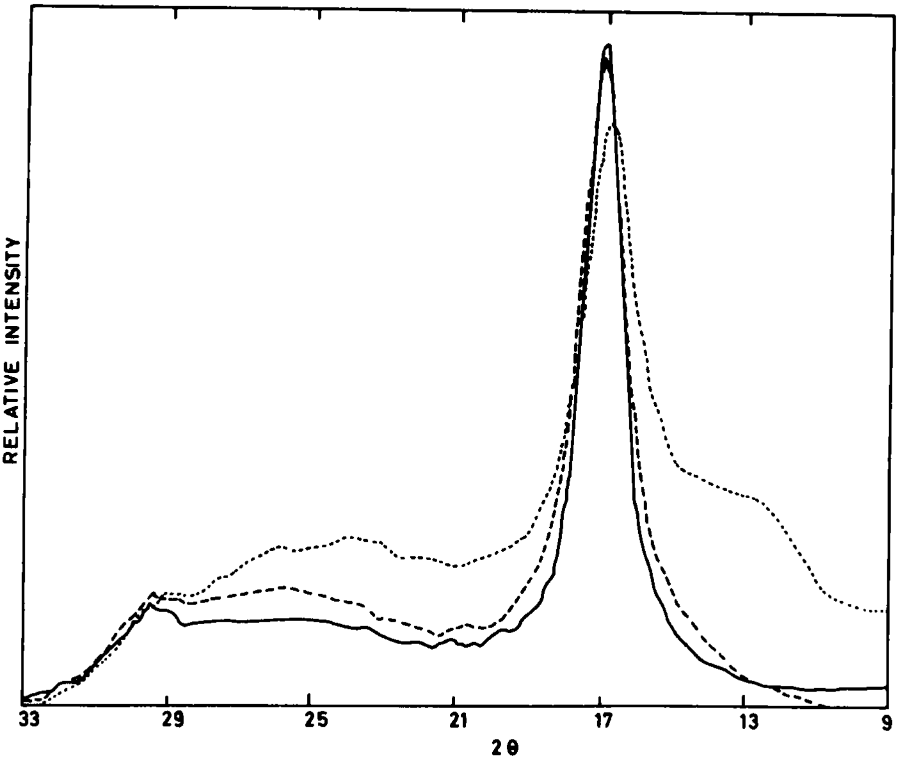

FIG. 2. Intensity vs angle of diffraction (2θ): (—) PAN, (– –), AN-VTES copolymer (m_2 = 4.9 mol%), and (- -) AN-VTES copolymer (m_2 = 13.1 mol%).

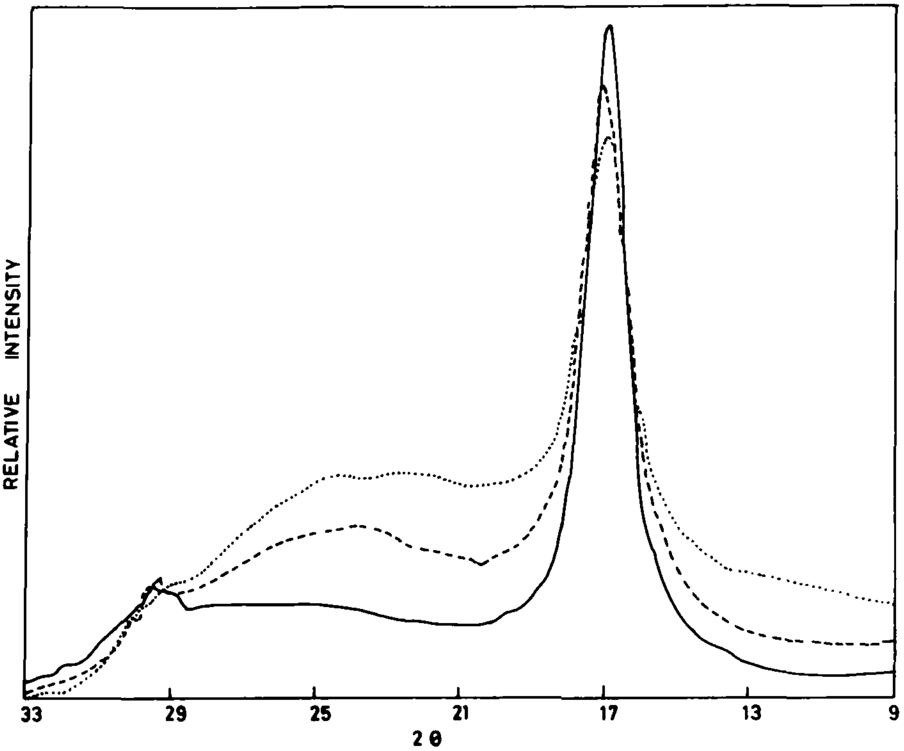

FIG. 3. Intensity vs angle of diffraction (2θ): (—) PAN, (- -) AN-VTMES copolymer (m_2 = 4.2 mol%), and (···) AN-VTMES copolymer (m_2 = 13.7 mol%).

characteristic absorption bands at 2252 and 1493 cm^{-1} due to nitrile groups, 1026 and 1260 cm^{-1} due to ν_{as}(Si–O–C), and the region 940-970 cm^{-1} due to ethoxysilanes.

The wide-angle x-ray diffractograms showing the radical scans of the intensity vs angle of diffraction (2θ) for PAN, AN-VTES, and AN-VTMES systems are presented in Figs. 2 and 3. The presence of sharp and diffuse patterns for PAN and copolymers shows the characteristic of the semicrystalline polymers. The PAN curve shows a sharp reflection at 2θ = 17° (Peak 1), a diffuse reflection at 2θ = 26.5° (Peak 2), and another sharp but low intensity peak at 2θ = 29.5° (Peak 3). Similar observations were made by Imai et al. [11] for various types of PAN structures. Further, there is diffuse scattering between the Peak 1 and Peak 3 region, indicating the presence of the disordered phase which is distributed throughout the region. The interesting observation is that the positions of sharp reflections (Peaks 1 and 2) re-

TABLE 3. Bragg Spacing and the Degree of Crystallinity of PAN and AN-Vinylsilane Copolymers

Polymer	m_2 (mol%)	2θ (degrees)			Bragg spacing (Å)			Degree of crystallinity (%)
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3	
PAN	-	17	26.5	29.5	5.27	3.45	3.13	42.8
P(AN-VTES)	4.9	16.9	26.2	29.5	5.30	3.49	3.13	37.6
P(AN-VTES)	13.1	17.2	-	29.0	5.21	-	3.18	26.4
P(AN-VTMES)	4.2	17.0	-	29.2	5.27	-	3.16	33.5
P(AN-VTMES)	13.7	17.0	-	-	5.27	-	-	22.9

main undisturbed in the copolymer and are independent of copolymer composition. In other words, comonomer incorporation has no effect on the crystalline lattice. Further, Peak 3 becomes diffuse with an increase in silane content. The increase in silane content also results in a decrease of peak heights and an increase in the intensity of the diffuse region between 17 and 30°. The positions of the peaks, the corresponding Bragg spacings, and the percentage crystallinity are summarized in Table 3. The degree of crystallinity was calculated from the areas under the amorphous and crystalline regions according to the method of Bell and Dumbelton [12].

Bragg spacing for Peak 1 in PAN was found to be 5.4 Å which is consistent with earlier reports [11]. Peak 3 in PAN has been attributed to the second-order reflection of Peak 1. The disappearance of the peak in the copolymer may be due to the weak intensities of the first-order reflections of Peak 1. The diffuse reflection of Peak 2 is overshadowed by the large amorphous region. It may, therefore, be inappropriate to comment on the nature of the peak and the changes associated with it with an increase in comonomer content.

Perusal of the data of Table 3 reveals that the introduction of silane reduces the degree of crystallinity while it has little influence on the crystalline structure. This means that the copolymer contains some blocks of AN units of reasonable length that form a crystalline structure interspersed with silane units. Surprisingly, 27 mol% of VTMES introduction in PAN does not change the crystalline structure. In summary, it may be said that PAN has two well-defined phases–crystalline and amorphous.

The TGA results for the polyacrylonitrile homopolymer and the copolymers are presented in Table 4. The threshold degradation temperature of the copolymers is lowered compared to PAN (Figs. 4 and 5). However, all the copolymers show increased stability beyond 325°C. One would have expected the silane monomers to exert a blocking effect on the nitrile groups, leading to poor stability of the copolymers. The greater stability of copolymers may be due to crosslinking of tertiary carbons, or ethoxy radicals in the system may react with nitrile groups to initiate the polymerization of nitrile groups. Thus the higher rate of oligomerization of nitrile groups in copolymers may lead to a more cyclized structure and so to higher thermal stability of the copolymers.

The relative thermal stabilities of copolymers were also assessed by considering the decomposition temperature for a particular weight loss. The higher stabilities of copolymers have also been reflected from maximum decomposition temperature (T_{max}) and integral procedural decomposition temperature (IPDT) (Table 4).

TABLE 4. Thermal Behavior of AN (M_1)-Vinylsilanes (M_2)

Polymer	Mol% in copolymer	DT at different weight loss 10%	30%	70%	T_{max}[a]	IPDT[b]
PAN	-	311	400	604	425	511
P(AN-VTES)	1.2	321	453	630	422	541
P(AN-VTES)	4.9	329	475	737	495	603
P(AN-VTES)	13.9	321	446	620	427	533
P(AN-VTMES)	4.2	362	493	755	568	636
P(AN-VTMES)	13.7	371	480	909	622	667
P(AN-VTMES)	20.6	398	449	838	600	626

[a] T_{max} = maximum decomposition temperature.

[b] IPDT = integral procedural decomposition temperature.

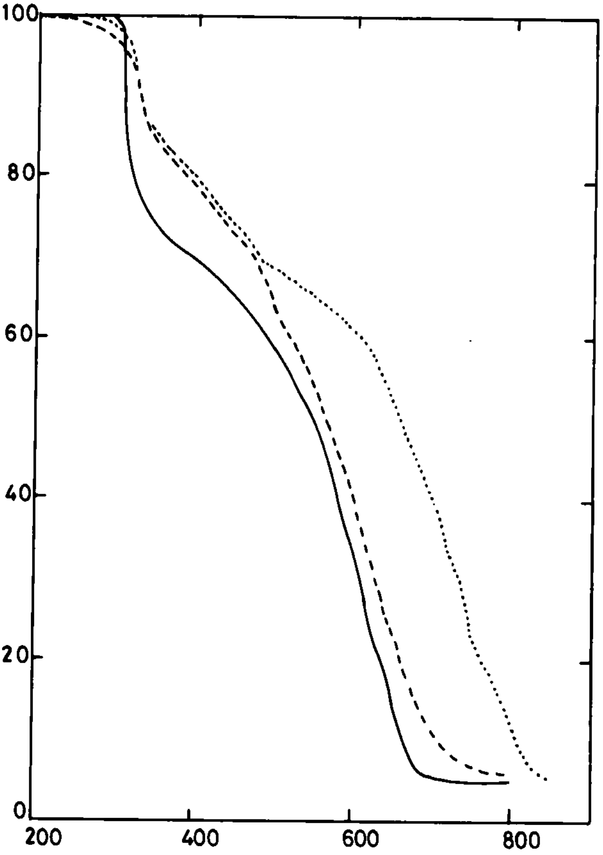

FIG. 4. Thermogravimetric analysis of (—) PAN, (- -) AN-VTES copolymer (m_2 = 1.2 mol%), and (··) AN-VTES copolymer (m_2 = 4.9 mol%).

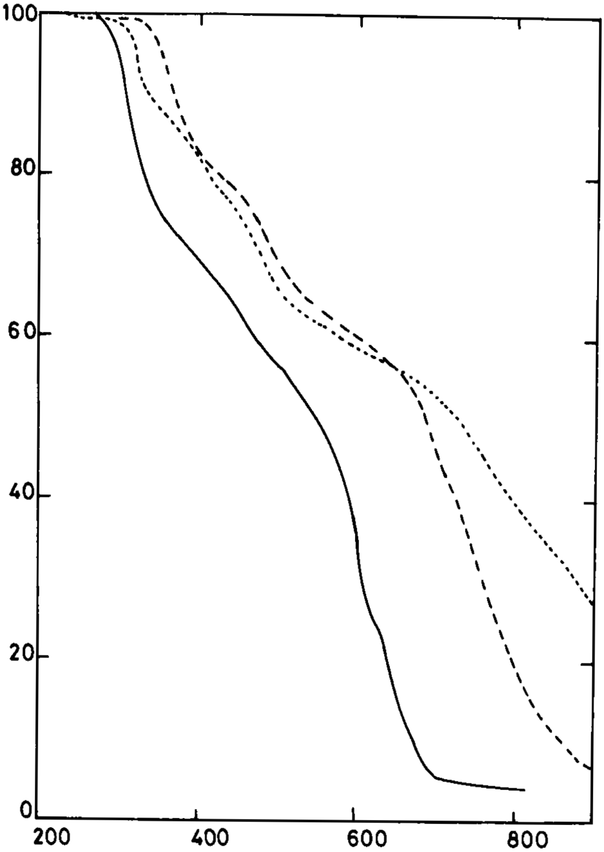

FIG. 5. Thermogravimetric analysis of (—) PAN, (- -) AN-VTMES copolymer (m_2 = 4.6 mol%), and (···) AN-VTMES copolymer (m_2 = 20.6 mol%).

ACKNOWLEDGMENTS

The authors thank the Council of Scientific and Industrial Research (CSIR), New Delhi, for awarding a Junior Research Fellowship to V.L.R. Thanks are also due to Dr Deshpande for his keen interest in the work.

REFERENCES

[1] G. Greber and E. Reese, Makromol. Chem., 77, 13 (1964).

[2] C. E. Scott and C. C. Price, J. Am. Chem. Soc. 81, 2670 (1959).

[3] N. S. Nametkin, I. N. Kozhukhova, S. G. Durgaryan, and V. G. Filippova, Vysokomol. Soedin., Ser. A, 13, 2085 (1971).

[4] Z. M. Rzayev, L. V. Brykoina, Sh. K. Kyazimov, and S. I. Sadykh-Zade, Ibid., 14, 287 (1972).

[5] Y. Iwakura, F. Tada, and K. Hattori, J. Polym. Sci., Part A-1, 6, 1633 (1968).

[6] P. Bajaj, Y. P. Khanna, and G. N. Babu, J. Polym. Sci., Polym. Chem. Ed., 14, 465 (1976).

[7] G. N. Babu and P. Bajaj, Angew. Makromol. Chem., 64, 211 (1977).

[8] G. N. Babu, D. R. Atodaria, and A. Deshpande, Eur. Polym. J., 17, 427 (1981).

[9] T. Kelen and F. Tüdős, J. Macromol. Sci.–Chem., A9, 1 (1975).

[10] Yu. A. Sangalov and I. I. Gorbachevskaya, Vysokomol. Soedin., Ser. B, 14(6), 406 (1972).

[11] Y. Imai and S. Minami, J. Polym. Sci., Part B, 8, 281 (1970).

[12] J. P. Bell and J. H. Dumbleton, Text. Res. J., 41, 196 (1971).

Accepted by editor February 15, 1983
Received for publication March 17, 1983