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Vinyltrimethoxysilane-*co*-2-vinylpyridine copolymer

Synthesis and monomer reactivity ratios

Nicolás Gatica, Ligia Gargallo, D. Radić[*]

Facultad de Química Pontificia Universidad Católica de Chile, Casilla.306, Santiago 22, Chile

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Summary

Copolymers containing vinyltrimethoxysilane (VTMOS) and 2-vinylpyridine (2VPy) at different compositions were synthesized and characterized. The monomer reactivity ratios r_1 and r_2 were estimated by using the classical Fineman-Ross and Kelen Tudos linear fitting procedures. Moreover, these parameters were also estimated using a nonlinear computational fitting known as Reactivity Ratios Error in Variable Method (RREVM). Attempts to obtain the corresponding copolymer with vinyltrimethylsilane (VTMS) were performed but only hompolymerization 2VPy is observed due to the non-reactivity of VTMS under this conditions. The results were analysed in terms of the relative comonomeric structures and compared with similar related systems. The reactivities are interpreted in terms of the resonance and stabilization effects together with the chemical structure.

Introduction

The increasing interest in silicon-containing polymers and copolymers applicable as electronic, optical and semiconducting materials, precursors of β-silicon carbide, ceramic precursors etc., has promoted the development of silicon-containing polymers with a well controlled molecular weight and molecular weight distribution as well as controlled microstructure and monomer sequences in the case of copolymers. The reactivity of vinyl silane and related monomers in radical copolymerization with different other monomers is strong dependent on the position of the Si atom relative to the vinyl group (1-6). If the Si atom is close to the vinyl group the reactivity ratio for the silane monomer is zero due to the dπ-pπ interactions between the Si atom and the vinyl group as it has been pointed out by Rao et al (2). On the other hand, the chemical structure of the comonorner should play some role on the reactivity behaviour of vinyl silane through the stabilization of the intermediate radical. Comonomers with poor reactivity with themselves should enhance the reactivity of silane derivatives, taking into account the low electron-attracting inductive effect of silicon atom (7). In fact, vinyl silanes (8-10) have been copolymerized with styrene, acrylonitrile and other monomers using radical initiators. Babu et al. (2) have reported the copolymerization of styrene with various vinyl silanes. Copolymers containing Si show great improvement in the physical properties of silicone rubbers which can be vulcanized at room temperature when they are blended. In order to improve the properties of this kind of copolymers it is desirable to control the amount of silane derivative and the comonomer in

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[*] Corresponding author

order to change the hydrophilic/hydrophobic ratio. However, this is a unfavourable process due to the low copolymerizability of vinylsilicon compounds because their relative reactivities in copolymerization are nearly zero (1, 11).

The aim of this work is the copolymerization of vinyltrimethoxysilane (VTMOS) and vinyltrimethyl silane with 2-vinylpyridine in order to compare their relative reactivities and therefore to be able to synthesize copolymers with controlled amount of silicon atoms in the polymer chain.

Experimental

Monomer and copolymer preparation

Commercial samples of 2-vinylpyridine (2VPy), vinyltrimethylsilane (VTMS) and vinyltrimethoxysilane (VTMOS) from Aldrich had been previously distilled under vacuum for use in copolymerization. Copolymerization of the monomers was carried out in bulk at 323 K under nitrogen, using (α,α'-azobisisobutyronitrile (AIBN) (0.4 % mol). The monomer feed ratio was varied in a series of copolymerizations of both comonomers in each series, as shown in Table 1. Polymerization time was varied to obtain a conversion of monomer to polymer about 10%. Purification of the copolymers was achieved by repeated dissolution in methanol and reprecipitation with ethyl ether before vacuum drying at 313 K.

Copolymer characterization

Copolymers were characterized by ^{1}H-NMR in a Bruker AC-200 spectrometer using TMS as an internal standard and deuterated chloroform as solvent. FTIR spectra in KBr were performed using a Bruker IFS 25 instrument. Copolymer composition was determined by elementary analysis following the nitrogen content of the resulting copolymers from different feed compositions.

Results and Discussion

Table 1 summarizes the copolymerization parameters at different feed compositions (M_1). This Table also shows the resulting copolymer compositions (dM_1). Data are presented considering VTMOS as monomer 1 (top) or 2VPy as monomer 1 (bottom). According to these results the resulting copolymer incorporates a larger amount of 2VPY than VTMOS as a consequence of the different monomer reactivities. Monomer reactivity ratios (MRR) was estimated using the classical straight-line intersection methods such as Fineman-Ross (12) and Kelen Tüdos (13). Figures 1-a and 1-b show both representations, i.e., G vs F and η vs ξ where:

$$G = Fr_1 - r_2 \qquad (1)$$

according to Fineman-Ross with $G = \frac{x(y-1)}{y}$,$F = \frac{x^2}{y}$, $x = M_1/M_2$ and $y = dM_1/dM_2$ and

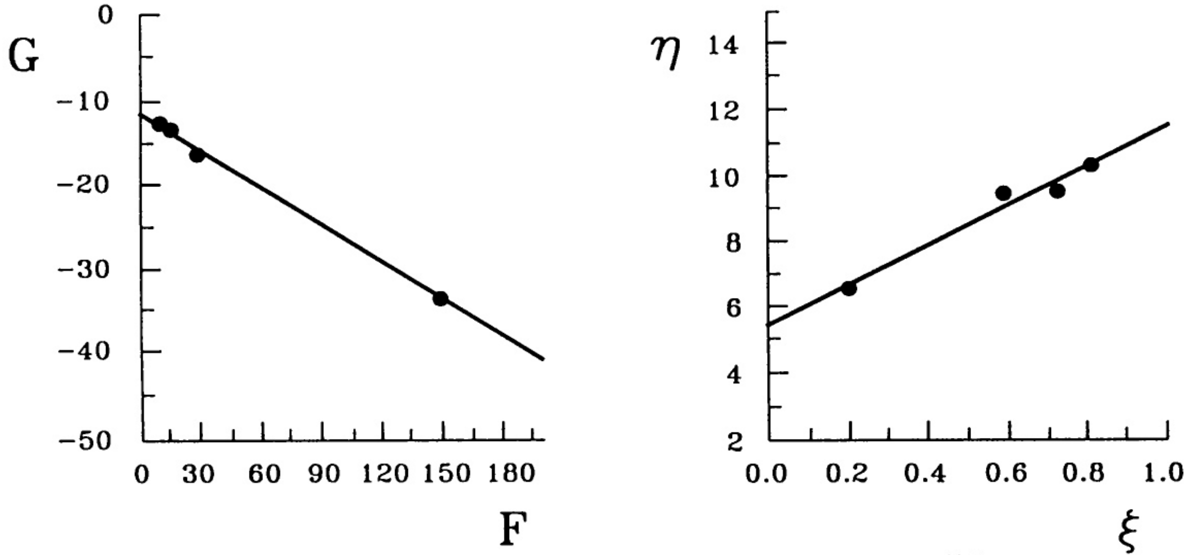
$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (2)$$

according to Kelen-Tüdos with $\eta = \frac{G}{\alpha + F}$ and $\xi = \frac{F}{\alpha + F}$. where η and ξ are mathematical functions of the mole ratios of monomers in the feed and in the copolymer, $\alpha = (F_l\ F_h)^{½}$ where F_l and F_h are the lowest and higher value of the calculated F from the series of measurements (1, 13).

Table 1: Copolymerization data for copolymer (VTMOS-co-2VPy): composition in feed (M_1), resulting composition in the copolymer (dM_1), ratio of monomer concentration (x), concentration ratio of the copolymer components (y), Fineman and Ross parameters G and F and Kelen-Tüdos parameters η, ξ and α.

Monomer 1	M_1	dM_1	x	y	F	G	η	ξ
VTMOS (α =36.47)	40	4.65	0.6667	0.0498	8.9255	-12.721	-0.2803	0.2522
	50	6.52	1.0000	0.0698	14.3267	-13.327	-0.2624	0.2821
	60	7.71	1.5000	0.0835	26.9461	-16.464	-0.2596	0.4249
	80	9.70	4.0000	0.1074	148.978	-33.244	-0.1793	0.8034
2VPy (α= 0.027)	20	90.0	0.2500	9.3093	0.0067	0.2232	6.6036	0.1982
	40	92.9	0.6667	11.9702	0.0371	0.6110	9.5171	0.5779
	50	93.8	1.0000	14.3374	0.0698	0.9303	9.6006	0.7203
	60	95.5	1.5000	20.5054	0.1097	1.4269	10.4306	0.8019

Table 1 also summarizes the different parameters corresponding to both linear procedures which allow to obtain Figures 1-a and 1-b. From these Figures the monomer reactivity ratios r_1 and r_2 can be determined.Table 2 compiles the r_1 and r_2 values determined by both procedures and good agreement is found. Nevertheless, these linear methods are not enough reliable because they use statistically invalid assumptions (14), but their results are useful as starting values for nonlinear procedures. In fact, monomer reactivity ratios can be estimated using procedures based on the statistically valid error-in-variables model EVM) which are currently used nowadays (14-16). Figure 2 shows the 95% posterior probability contour for estimated r_1 and r_2 for VTMOS-co-2VPy copolymer starting from



(a) (b)

Figure 1. Fineman Ross (a) and Kelen Tüdos (b) plots of the copolymerization parameters for (VTMOS-co-2VPy)

the r_1 and r_2 values obtained from the Kelen Tüdos procedure as starting values. These values were generated using errors of 1 % for the monomer feed composition and 5% for the copolymer composition. The r_1 and r_2 values obtained by this nonlinear procedure are also summarized in Table 2. The probability contour determined by this way, usually show an elliptical shape, but in this case (VTMOS-co-2VPy) is only a line of probability because r_2 is always zero in this copolymer.

Table 2: Monomer reactivity ratios r_1 and r_2 obtained by Fineman-Ross, Kelen-Tudos and RREVM methods for P(VTMOS-co-2VPy).

Method		r	
		VTMOS	2VPy
FR	1=2VPy	0.0*	11.5
	2=VTMOS	0.0*	11.7
KT		0.0*	11.7
RREVM		0.0*	15.7

* Low values of MRR which are approximately zero.

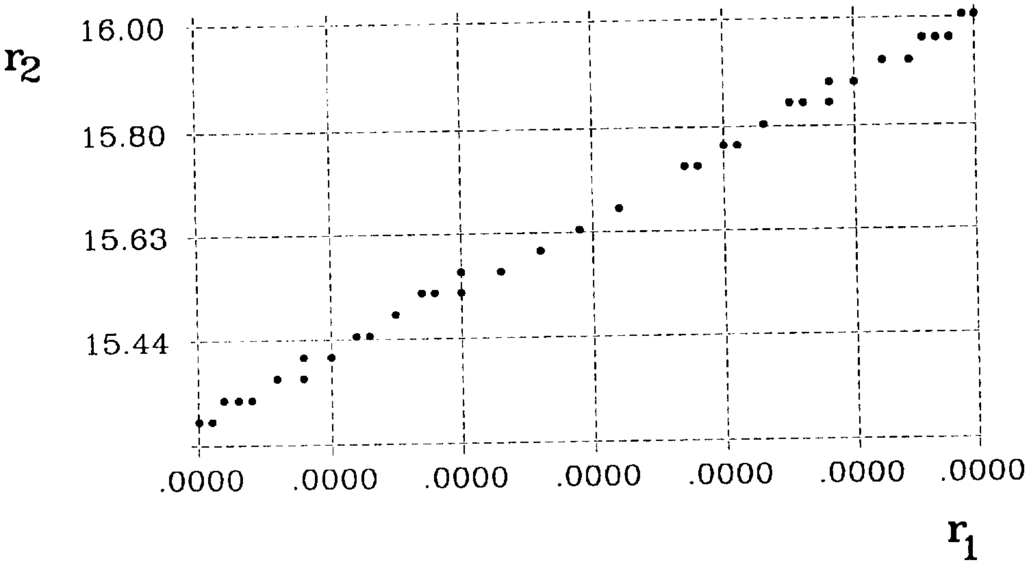


Figure 2. The 95% posterior contour for estimated r_1 and r_2 for VTMOS-co-2VPy copolymer.

The values of the monomer reactivity ratios are in good agreement irrespective of the procedure followed. The resonance effect in 2VPy is reflected in these values. In fact, among the factors that influence the monomer reactivity, the stabilization of the radical during the growing process plays an important role (17). As the stabilization of the intermediate radical increases, the reactivity with itself also increases and therefore the other comonomer is less reactive. In this case the stabilization of the intermediate in 2-vinylpyridine radical, is favoured due to the stabilization by resonance. The reaction between both monomers is kinetically unfavoured process and the formation of small blocks of the more reactive monomer is favoured. Therefore the copolymer sequence should be composed of isolated VTMOS units (r_{VTMOS}=0) between small blocks of 2VPy. In order to analyze this peculiar behaviour, copolymerization of vinyltrimethylsilane (VTMS) with

2VPy was attempted. Only homopolymerization of 2VPy is observed irrespective of the feed composition. However, the behaviour of copolymers containing VTMOS radicals is different due to the presence of oxygen atoms. Therefore, some stabilization of VTMOS radicals takes place, because the electron attracting effect of the substituent. It is interesting to compare these results with those previously reported for VTMS and VTMOS with vinylpyrrolidone (VP) (1). Those systems show reactivities of VTMS and VTMOS relative to 2VPy follow the same trend than both monorners with VP. However, there is an important difference between both systems, which is that the reactivity of 2VPy with VTMS and VTMOS is notably larger than the reactivity of both monomers with VP. In the former system, the stabilization by resonance of the 2VPy radical is higher than the corresponding stabilization of the VP radical. In fact, 2VPy homopolymerizes, against VTMS and give rise to small blocks of 2VPy with isolated units of VTMOS. In the second case the stabilization by resonance of the VP radical is minor than 2VPy and therefore a larger reactivity of VTMS and VTMOS against VP giving a copolymer with small blocks of VP with VTMS and a perfectly random copolymer with VTMOS.

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