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VINYLTRIMETHYLSILANE-CO-METHYLMETHACRYLATE COPOLYMERS. SYNTHESIS AND REACTIVITY RATIOS

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NOTE

VINYLTRIMETHYLSILANE-CO-METHYLMETHACRYLATE COPOLYMERS. SYNTHESIS AND REACTIVITY RATIOS

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ABSTRACT

In order to obtain information about the copolymerization process of vinyltrimethyl silane with comonomers of different chemical structure, copolymers containing vinyltrimethylsilane and methyl methacrylate at different compositions were synthesized and characterized. Comparison of the reactivity ratios of the resulting copolymers with those containing N-vinyl-2-pyrrolidone and 2-vinylpyridine previously reported and other related comonomers with different chemical structure allows us to establish some reactivity structure relationship and a generalization for these systems. The monomer reactivity ratios r_1 and r_2 (MRR) were estimated by using the classical linear fitting procedures and also through a computer program based on a nonlinear minimization algorithm, starting from the r_1 and r_2 values obtained by the former procedures.

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INTRODUCTION

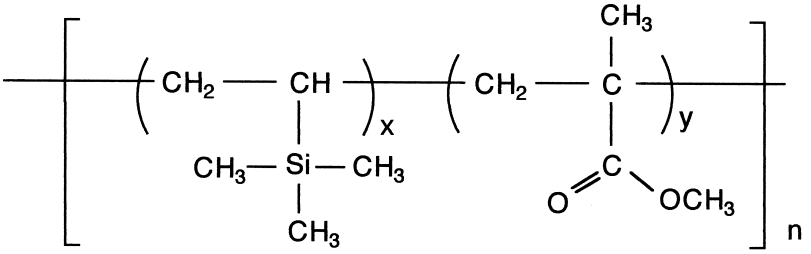
It has been previously reported that the polymerization of vinyltrimethylsilane (VTMS) by radical polymerization is not a favorable process [1-5]. However, the copolymerization of this monomer with other vinyl monomers gives rise to interesting results dealing with the relative reactivities of the monomers. In fact, copolymerization of VTMS with N-vinyl-2-pyrrolidone (VP) shows that resulting copolymers have a clear trend to VP units block formation and a tendency of VTMS to cross propagation is also observed [6]. This result is in good agreement with results previously reported dealing with the reactivity of pure vinyltrimethylsilane [7]. On the other hand, the reaction of VTMS with 2-vinylpyridine (2VPy) produces 2VPy homopolymer [8] and no copolymer is obtained. The particular behavior of VTMS is generally analyzed in terms of the position of the Si atom. If the Si atom is close to the vinyl group the reactivity ratio for the silane monomer was found to be zero or close to zero, which has been attributed to the $d\pi$-$p\pi$ interactions between the Si atom and the vinyl group [1]. The reactivity of VTMS could be enhanced during the copolymerization processess depending on the chemical structure of the comonomer. Recently, (8) we have reported results dealing with the reactivity of vinyltrimethoxysilane (VTMOS) with 2-vinylpyridine (2VPy) and the non-reactivity of VTMS with 2VPy. These results were interpreted in terms of the differences in the chemical structure of the comonomers and on the stabilization of VTMOS due to the electron attracting effect of the substituent, which apparently plays an important role in the copolymerization process depending on the chemical structure of the another comonomer.

The aim of the present work is the copolymerization of vinyltrimethylsilane with methylmethacrylate to obtain VTMS-co-MMA copolymer (see Scheme 1) in order to compare the reactivity ratio of these copolymers with those of related copolymers with different chemical structures, to obtain information about the effect of the monomer structure on the reactivity of VTMS.

EXPERIMENTAL

Monomer and Copolymer Preparation

Vinyltrimethylsilane (VTMS) from Aldrich Chemical, previously distilled under vacuum was used for copolymerization. Commercial methyl methacrylate previously distilled under vacuum was used. Copolymerization of



Scheme 1.

the monomers was carried out in bulk at 323 K under nitrogen, using α,α'-azobisisobutyronitrile (AIBN) (0.3 mol%) according to procedures previously reported [6, 8]. The monomer feed ratio was varied in a series of copolymerizations of both comonomers, 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 toluene and reprecipitation with ethyl alcohol 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 ^{1}H-NMR.

RESULTS AND DISCUSSION

Copolymer composition was determined by ^{1}H-NMR using the ratio between the normalized integral of the methyl group of the ester group of MMA, i.e. one proton, that is 1/3 of the integration, and the normalized integral of the methyl groups linked to the silicon atom of VTMS, i.e., 1/9 of the integration. In this way, it was possible to determine the MMA/VTMS proportion obtained in the resulting copolymer corresponding to each feed composition. Table 1 summarizes the feed composition M_1, the value of the normalized integral in ^{1}H-NMR in terms of MMA and VTMS, the mole ratio MMA/VTMS, and the resulting copolymer composition dM_1. According to these results, the resulting copolymers are rich in MMA. This result can be attributed to the different reac-

TABLE 1. Copolymerization Data for VTMS-co-MMA Copolymer: Composition in Feed (M_1) Normalized Integral of ^{1}H-NMR Spectra at Different Copolymer Compositions, Mole Ratio of n_{MMA}/n_{VTMS} and Resulting Composition in the Copolymer (dM_1).

Copolymer	M_1 (mol % VTMS)	Normalized Integral		n_{MMA}/n_{VTMS}	dM_1 (mol % VTMS)
		MMA	VTMS		
I	80	100/3	12.5/9	16.9/1	5.6
II	70	100/3	6.19/9	32.6/1	3.0
III	60	100/3	4.71/9	63.7/1	1.5
IV	50	100/3	3.29/9	91.2/1	1.1
V	40	100/3	4.34/9	69.1/1	1.4
VI	20	100/3	0.91/9	330/1	0.3

tivity of both monomers. In order to determine the monomer reactivity ratios, the classical straight line intersection methods of Fineman and Ross (FR) [9] and Kelen Tüdos (KT) [10] were used following procedures previously reported [6, 8, 11]. A Nonlinear Minimization Algorithm (NLMA) using a computer program [12] which is known as Reactivity Ratios Error-in-Variable Model (RREVM), were also used, starting from the r_1 and r_2 values of the straight line methods.

Figure 1 (a) and (b) represents the FR and KT plots for VTMS-co-MMA. In this way, it is possible to obtain the monomer reactivity ratios r_1 and r_2, dealing with the different reactivities of the comonomers using the different extrapolation procedures. Table 2 compiles the r_1 and r_2 values obtained by both linear procedures, respectively. Good agreement between both procedures is found, although slight differences in the values of r_{MMA} are observed, which is very common [11, 12], because the main disadvantage and weaknesses of these methods is the use of statistically invalid assumptions [12]. The most useful procedures to obtain good r_1 and r_2 values is that based on statistically valid Error-in-Variable Model (EVM).

For this reason, in order to obtain information about the reactivity ratios of VTMS-co-MMA copolymers, r_1 and r_2 values were also determined using a computer program based on the nonlinear minimization algorithm. Starting from the r_1 and r_2 values obtained by the KT procedure which can be considered as good initial r_1 and r_2 estimation [8]. Table The r_1 and r_2 values estimated by this

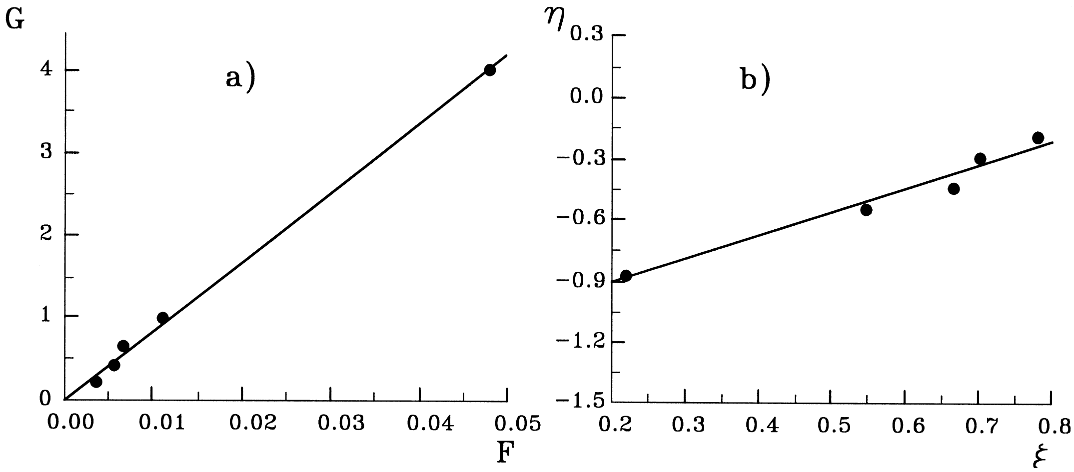


Figure 1. **(a)** F.R. representation of the copolymerization parameters for VTMS-co-MMA and **(b)** K.T. representation of the copolymerization parameters for VTMS-co-MMA.

TABLE 2. Monomer Reactivity Ratios r_1 and r_2 for VTMS-co-MMA Copolymer, Determined by FR, KT and RREVM Procedures.

		r	
		VTMS	MMA
FR	1 = VTMS	0.09	93.7
	1 = MMA	0.0	83.1
KT		0.03	85.8
RREVM		0.0	84.2

nonlinear procedure are also in good agreement with those previously described using linear methods. According to the definition of MRR:

$$r_{MMA} = \frac{k_{MMA\text{-}MMA}}{k_{MMA\text{-}VTMS}} \quad \text{and} \quad r_{VTMS} = \frac{k_{TMS\text{-}VTMS}}{k_{VTMS\text{-}MMA}} \tag{1}$$

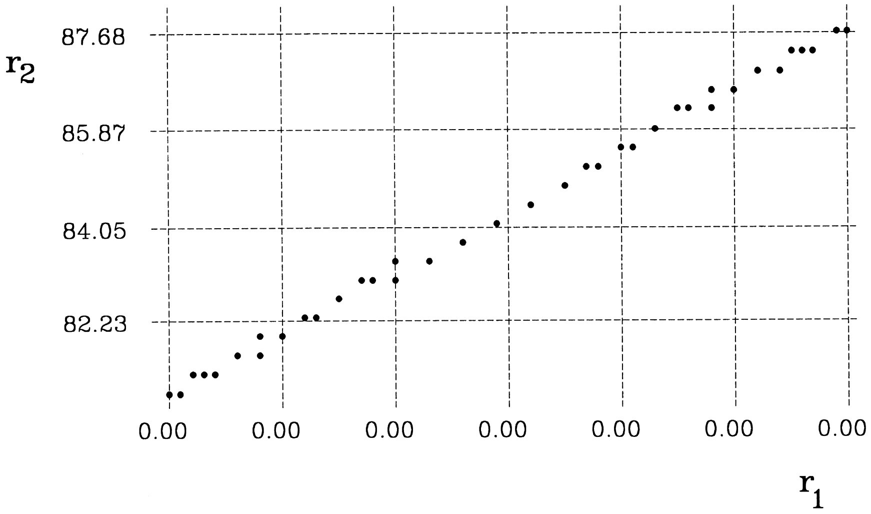


Figure 2. The 95% posterior contour for estimated r_1,r_2 for VTMS-co-MMA copolymers.

where $\mathbf{k}_{ii}$ and $\mathbf{k}_{ij}$ represent the self-propagating and cross-propagation rate constant, respectively. Therefore, irrespective of the method for determining r_1 and r_2, this copolymer, in general, presents a marked tendency to methyl methacrylate units blocks formation ($\mathbf{r}_{MMA}$ = 84.2) and a tendency to vinylsilane monomer to cross propagation ($\mathbf{r}_{VTMS}$ = 0). This result is in qualitative agreement with the results previously reported dealing with the reactivity of pure vinyltrimethylsilane [1] and related copolymers [1-8]. These results are rather different to those usually expected for a radical copolymerization in the sense that no random copolymers are obtained. Among the factors which influence the monomer reactivity, the stabilization of the radical during the growing process plays an important role as Cowie [14] pointed out. As the stabilization of the macroradical (M_1) generated *in situ* increases, the reactivity with itelf also increases relative to the other monomer (M_2) which will be less reactive. Therefore, the reaction between M_1 and M_2 is a kinetically unfavorable process and the formation of small blocks of the more reactive monomer is favored [6, 14]. On the other hand, the effect of the substituent on the stabilization of the radical is another factor to take into account. In this case the MMA units can stabilize the radical by electronic delocalization through the ester group. In VTMS no stabilization is expected due to their structure. For this reason, in this copolymer the presence of isolated VTMS units between blocks of MMA are postulated and according to the specific value obtained for $\mathbf{r}_{VTMS}$.

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