Polymer Bulletin 40, 707–713 (1998)

Polymer Bulletin
© Springer-Verlag 1998

Vinyltrimethylsilane-*co*-*N*-vinyl-2-pyrrolidone and vinyltrimethoxysilane-*co*-*N*-vinyl-2-pyrrolidone copolymers

Synthesis and reactivity ratios*

Nicolás Gatica, Fernando R. Díaz, Ligia Gargallo, Deodato Radić**

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

Received: 18 February 1998/Revised version: 11 March 1998/Accepted: 16 March 1998

Summary

Copolymers containing vinyltrimethylsilane and vinyltrimethoxysilane with N-vinyl-2-pyrrolidone at different compositions were synthesized and characterized. The reactivity ratios was estimated by using the classical Fineman-Ross and Kelen Tüdos linear fitting procedures. These parameters were also estimated through a computer program based on nonlinear minimization algorithm, starting from the r_1 and r_2 values obtained by the former procedures. The analysis of the results allow us to interpret the reactivity behaviour of these polymers in terms of the relative reactivity of the substiuents. The effect of the chemical structure of the polymer side group is discussed in terms of the different contributions to the stabilization of the radical intermediates.

Introduction

Polymerization of vinyltrimethylsilane (VTMS) by radical polymerization is rather difficult (1-5). Nevertheless, copolymerization of this monomer with other vinyl monomers can be performed succesfully. In free radical polymerization the reactivity of these monomers depends gratly from the position and substitution of the Si atom (1). 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 what has been attributed to the dπ-pπ interactions between the Si atom and the vinyl group (1). However, it should be possible to enhance the reactivity of VTMS and related structures by copolymerization with monomers with poor reactivity with themselves. Several attempts to copolymerize silane monomers with different comonomers has been reported (3,6-8). These copolymers should be of interest in order to introduce silane units to a macromolecule due to the hydrophobicity of this kind of chains. The copolymerization of vinyltriethoxysilane and vinyltrimethoxysilane with styrene and acrylonitrile show very low resonance factors due to the small conjugation (9). However, due to low copolymerizability of vinylsilicon compounds, their relative reactivities in copolymerization reactions with styrene were found to be usually zero or extremely low (10).

The aim of the present work is the copolymerization of viniltrimethylsilane and vinyltrimethoxysilane with vinylpyrrolidone (VTMS-co-VP) and VTMOS-co-VP)

---

* Dedicated to the memory of Prof. Irmina Hernandad-Fuentes

** Corresponding author

respectively, in order to check the reactivity of VP with the corresponding silane derivatives and to get confidence about the effect of the chemical structure on the reactivity ratios.

Experimental

Monomer and copolymer preparation

Commercial samples of N-vinyl-2-pyrrolidone (VP), vinyltrimethylsilane (VTMS) and vinyltrimethoxysilane (VTMOS) from Aldrich had been previously distillated under vacuuum for use in copolymerization, Copolymerization of the monomers was carried out in bulk at 323 K under nitrogen, using α,α'-azobisisobutyronitrile (AIBN) (0.1 and 0.4% mol, for VTMS and VTMOS respectively). 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 ethanol and reprecipitation with petroleum benzine 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 compiles the feed composition (Ml) and copolymer composition (dM_1) for different feed compositions. The incorporation of vinylpyrrolidone units (VP) clearly is favoured over the VTMS and/or VTMOS units. This result can be attributed to the diferent reactivity of both monomers. In order to determine the monomer reactivity ratios, the Fineman and Ross (FR) (11), Kelen Tüdos (KT) (12) and a Nonlinear Minimization Algorithm (NLMA) using a computer program (13) which is known as reactivity ratios error-in-variable model (RREVM), were used.

According to Fineman-Ross the monomer reactivity ratios can be obtained by plotting the G parameter against F according to:

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

with $F = \frac{x^2}{y}$ and $G = \frac{x(y-1)}{y}$ and

$x = \frac{M_1}{M_2}$, and $y = \frac{dM_1}{dM_2}$

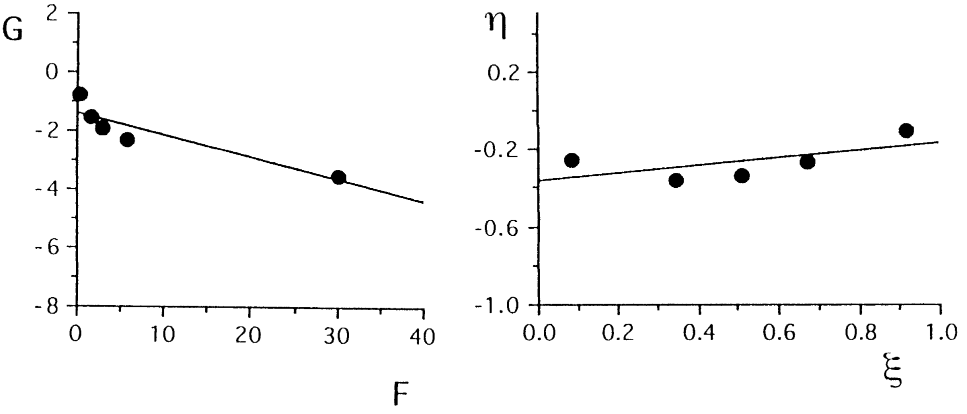
where M_1 and M_2 are the monomer compositions in feed and dM_1 and dM_2 correspond to the compositions of monomer units in the resulting copolymer. The r_1 and r_2 values obtained by this method are summarized in Table 2 using the feed and copolymer composition in terms of VTMS, VTMOS and/or VP. These values are slightly different what is very common (14,15) which is one of the weaknesses of the method. Alternatively r_1 and r_2 values were obtained using the Kelen-Tüdos (KT) method (13) according to the equation:

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

where η and ξ are mathematical functions of the mole ratios of monomers in the feed and in the copolymer, defined as:

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \tag{3}$$

α denotes an arbitrary constant, which best value is $\alpha = (F_1\ F_h)^{1/2}$ where F_1 and F_h are the lowest and highest value of the calculated F from the series of measurements. From the plots of η as function of ξ and extrapolating to $\xi = 0$ and $\xi = 1 - \frac{r_2}{\alpha}$ and $- r_1$ are obtained. Figure 1 (a) and (b) represent the FR and KT plots for VTMS-co-VP as an example of this kind of representation.



(a) **(b)**

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

Table 1 also compiles the FR and KT parameters for these copolymers. These methods correspond to the so-called straight-line intersection methods and poor agreement is found in the determination of r_1 and r_2. The main disadvantage of these linear methods is the use of statistically invalid assumptions (13). Procedures based on the statistically valid error-in-variables model (EVM) are nowadays frequently used (13,14). For this reason, in order to gain confidence about the reactivity ratio of VTMS-co-VP and VTMOS-co-VP 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 2 summarizes the r_1 and r_2 values obtained using the linear and nonlinear procedures. Figure 2 is a representation of the 95% posterior probability contour for estimated r_1, r_2 for (VTMS-co-VP) and (VTMOS-co-VP) copolymers. These r_1 and r_2 values were generated using errors of 1% for the monomer feed composition and 5% for the copolymer composition. It is interesting to remark that this kind of procedure gives an elliptical probability contour but in the case of (VTMS-co-VP) we obtain only a line of probability because r_2 is always zero in this copolymer (see Figure 2-a). A normal behaviour is observed for (VTMOS-co-VP) copolymers as shown in Figure 2-b.

Table 1. Copolymerization data for copolymers of VTMS and VP: 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.

	M_1	dM_1	x	y	F	G	η	ξ
VTMS								
	20	19.98	0.250	0.2389	0.2616	-0.7965	-0.2594	0.0852
	40	23.34	0.667	0.3045	1.4597	-1.5228	-0.3567	0.3420
a)	50	25.68	1.000	0.3455	2.8944	-1.8944	-0.3322	0.5075
	60	28.19	1.500	0.3926	5.7310	-2.3207	-0.2718	0.6711
	80	34.66	4.000	0.5305	30.160	-3.5401	-0.1074	0.9148
α = 2.8088								
	20	65.34	0.250	1.8852	0.0332	0.1174	0.3015	0.0853
	40	71.81	0.667	2.5474	0.1745	0.4050	0.7631	0.3288
b)	50	74.32	1.000	2.8941	0.3455	0.6545	0.9327	0.4924
	60	76.66	1.500	3.2845	0.6850	1.0433	1.0020	0.6579
	80	80.72	4.000	4.1867	3.8216	3.0446	0.7288	0.9147
α = 0.3562								
VTMOS								
	20	24.40	0.250	0.3228	0.1936	-0.5245	-0.3851	0.1421
	40	39.01	0.667	0.6396	0.6950	-0.3757	-0.2016	0.3730
c)	50	44.50	1.000	0.8018	1.2472	-0.2472	-0.1023	0.5163
	60	50.90	1.500	1.0367	2.1704	0.0531	0.0159	0.6501
	70	59.15	2.333	1.4480	3.7599	0.7219	0.1465	0.7629
	80	69.41	4.000	2.2690	7.0516	2.2371	0.2722	0.8579
α = 1.1684								
	20	30.59	0.2500	0.4407	0.1418	-0.3173	-0.3181	0.1422
	30	40.85	0.4286	0.6906	0.2660	-0.1920	-0.1925	0.2667
d)	40	49.10	0.6667	0.9646	0.4608	-0.0245	-0.0246	0.4692
	50	55.50	1.0000	1.2472	0.8018	0.1982	0.1987	0.8038
	60	60.99	1.5000	1.5635	1.4391	0.5406	0.5428	1.4415
	80	75.60	4.0000	3.0984	5.1640	2.7090	2.7158	5.1769
α = 1.1684								

a) VTMS = monomer 1; b) VP = monomer 1; c) VTMOS = monomer 1. d) VP = monomer 1

The results shown in Table 2 indicate a quantitative discrepancy among the different methods used to obtain r_1 and r_2. Nevertheless irespective of the method for determining r_1 and r_2 in general the copolymer shows a clear trend to vinylpyrrolidone units blocks formation. Moreover, a tendency of vinylsilane monomers to cross propagation is observed. This result is in qualitative agreement with the results previously reported, dealing with the reactivity of pure vinyltrimethylsilane. In the case of copolymers containing vinyltrimethoxysilane, the reactivity ratios are rather different than the former. The results for these copolymers are typically the values obtained for radical polymerization and random copolymers are obtained. The difference in the reactivity ratios between VTMS and VTMOS can be attributed to the presence of the oxygen atom in VTMOS which can contribute to the stabilization of the intermediate radical during the

Table 2. Monomer reactivity ratios r_1 and r_2 and the product r_1r_2 obtained by Fineman-Ross, Kelen-Tüdos for VTMS-co-VP and VTMOS-co-VP.

		r		r_1r_2
Method		VTMS	VP	
FR	1=VTMS 2=VP	0.074	1.414	0.105
	1=VP 2=VTMS	0.0	0.725	0.0
KT	1=VTMS 2=VP	0.0	1.016	0.0
	1=VP 2=VTMS	0.0	1.016	0.0
RREVM	1= VTMS 2= VP	0.0	1.074	1.074
	1=VP 2=VTMS	0.0	1.391	1.391

		r		r_1r_2
Method		VTMOS	VP	
FR	1=VTMOS 2=VP	0.407	0.714	0.290
	1=VP 2=VTMS	0.329	0.591	0.194
KT	1=VTMOS 2=VP	0.361	0.626	0.226
	1=VP 2=VTMS	0.361	0.626	0.226
RREVM	1=VTMOS 2= VP	0.157	0.405	0.064
	1=VP 2=VTMOS	0.792	0.361	0.286

polymerization process due to the high electronegativity. In fact, among the factors which influence the monomer reactivity, the stabilization of the radical during the growing process, plays an important role as Cowie (16) pointed out. As the stabilization of the macroradical (M_1) generated in situ increases, the reactivity with himself 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 unfavourable process and the formation of small blocks of the more reactive monomer is favoured. On the other hand the effect of the substituent on the stabilization of the radical is another factor to take into account. In the case of (VTMS-co-VP) the VP units can stabilize the radical by electronic delocalization through the amide group. In VTMS less stabilization is expected due to their structure. For this reason in these copolymers the presence of isolated VTMS units between blocks of VP are postulated. For VTMOS the situation is quite different where a clear effect of the oxygens is observed. The stabilization of the radical by the oxygen atoms is clearly reflected in the reactivity of this monomer with VP relative to VTMS. Therefore. accordira, to the monomer reactivity ratios for (VTMOS-co-VP) the copolymer can be considered as random which is quite different to the copolymer containing VTMS units.

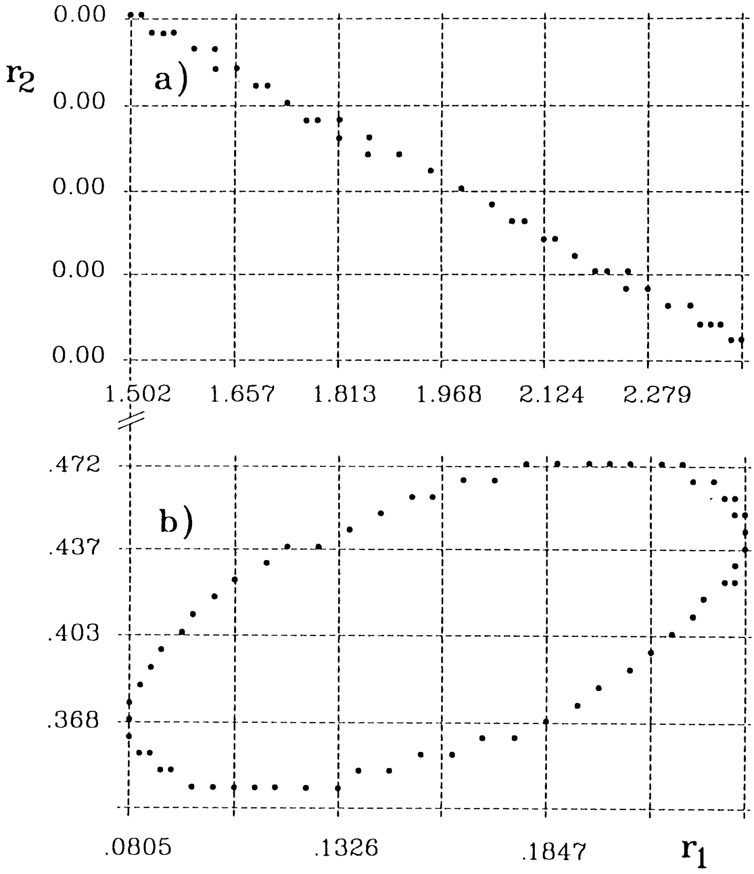


Figure 2. The 95% posterior contour for estimated r_1, r_2 for (a) (VTMS-co-VP) and (b) (VTMOS-co-VP) respectively.

Acknowledgements: We express our thanks to **Fondecyt,** Grant 8970011 for partial financial support. N.G. thanks to **Conicyt** for Doctoral Felowship and to **Fondecyt** project 2960022 for partial financial support. D.R. acknowledges to **Catedra Presidencial en Ciencias’95** for financial help.

References

1. Rao V.L, Babu G.N, (1989) Eur. Polym. J.25: 609 and references therein.
2. Babu G.N, Atodaria D.R, Desphande (1981) Eur. Polym. J., 17: 427
3. Bajaj P, Gupta D.C. Babu G.N, (1983) J. Macromol. Sci. A 20: 527
4. Bajaj P, Gupta D.C. (1979) Eur. Polym. J., 15: 271
5. Stefanac,T.M, Brook M.A, Stan R, (1996) Macromolecules 29: 4549
6. Bajaj P, Gupta D.C, (1983) J. Polym. Sci. Polym. Chem. Edn. 21:1347
7. Bajaj P, Babu G.N (1976) Eur. Polym. J. 12:601
8. Bajaj P, Gupta D.C, Gupta A.K (1980)J. Appl. Polym. Sci., 25:1673

9. Scott Ch, Price Ch, (1959). J. Am. Chem. Soc., 81: 2670
10. Bajaj, P, Khanna, Y.P, Babu, G.N, (1976) J. Polym. Sci., Polym. Chem. Ed., 14:465
11. Fineman, M, Ross, S.D, (1950) J. Polym. Sci. 5:259
12. Kelen, T, Tüdos, F. (1975) J. Macromol. Sci-Chem. A9:11
13. Dube, M. Sanayei, R.A, Penlidis, A, O'Driscoll, K.F, Reilly, (1991), P.M, J. Polym. Sci., Polym. Chem-Ed. 29:703
14. O'Driscoll, K.F, Reilly, P.M, (1987) Makromol Chem., Macromol. Symp., 10/11: 355
15. Radic' D, Gargallo L, (1997) Macromolecules 30:817
16. 16 Cowie, J.M.G., "Polymers: Chemistry and Physics of Modern Materials" International Texbook Company Limited, London, 1973, p 90