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The copolymerization of 2-vinylfuran with methyl methacrylate and *n*-butyl acrylate

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Summary

2-Vinylfuran (2VF) was copolymerized with methyl methacrylate and n-butyl acrylate according to an experimental design scheme. The results were analyzed with a nonlinear error-in-variables method. The values obtained for the reactivity ratios using this approach were much different than reactivity ratios obtained from conventional copolymerization experiments. The r_1 and r_2 values obtained in the present case indicate that 2VF has approximately the same reactivity as methyl methacrylate, but is much more reactive than n-butyl acrylate.

Introduction

For some time we have been engaged in the study of the copolymerization behavior of vinyl heterocycles (1-5). Most of our work has been with sulfur containing heterocycles and we have shown that, in general, such monomers are very reactive in copolymerizations involving comonomers like methyl methacrylate and n-butyl acrylate. In order to more fully investigate the role fo the heteroatom in copolymerization reactivity, we have begun to examine the copolymerization behavior of monomers such as 2VF with methyl methacrylate (MMA) and n-butyl acrylate (BA). This paper summarizes some of our results.

Experimental

General

All solvents were reagent grade and were used as received. The monomers were purified by distilling three times from CaH_2. The monomers were stored under N_2 in tightly sealed flasks at -10^{o}C until used. The ^{1}H-nmr spectra and molecular weight measurements were obtained as previously described (1-5).

Monomer Synthesis

2-Vinylfuran was synthesized from 2-furyl acrylic acid by decarboxylation according to the procedure of Hachikana and Imoto (6). The yield was 61%, b.p. = 100-109^{o}/760 mm (lit. b.p. = 99-100^{o}/760 mm) (7). The 2-furyl acrylic acid itself was synthesized from furfural

(Aldrich) and malonic acid by the method of Rajogopalan and Ramen (8). The yield obtained was 82% and the melting point was 139-140°C after recrystallization (lit. m.p. = 140-141°) (8). The ^{1}H-nmr spectra of the acid and the 2VF monomer matched those of authentic samples of each material (9).

Polymer Synthesis

The polymerizations were performed according to the experimental design of Tidwell and Mortimer (10). Basically, concentration 'ladder' experiments (1-3) are first performed in order to calculate the mole fraction of M_1 to be used in the feed (M_f of M_2 = 1 - M_1). The mole fractions of M_1 used in this work are summarized in Table 1.

TABLE 1

Feed Concentrations of M_1 for Design Copolymerization

M_1	M_2	f'_1 [a]	f_1''	f_1^*	f_1^{**}
2VF	MMA	0.604	0.0260	0.100	-
2VF	BA	0.694	0.0654	0.200	0.330

a. All f_1 values refer to the mole fraction of M_1 in the feed.

Normally only two different feed concentrations of M_1 are used and four or five copolymerizations are performed at each of these concentrations. However, in both cases above the value of f_1'' is very low, and since it is well known (11) that low concentrations of reactive monomers can have an inhibitory effect on polymerization, i.e. no polymer may be formed; additional feed concentrations were chosen which were greater than the f_1'' values. The additional values were chosen so as to be reasonably close to the f_1'' value and because they were the lowest feed concentrations of M_1 at which polymer had been obtained in the preliminary concentration ladder experiments. In the case of BA an additional value was chosed (F_1**) because previous work had shown that at a feed concentration of 2VF of 20 mol % only very small amounts of polymer had been obtained. A feed concentration of 2VF of 33 mol % represents a concentration at which a reasonable amount of polymer is obtained, also, the value is relatively close to the f_1* value.

The polymerizations were performed and the polymers treated as previously described (1-5).

Results and Discussion

The results obtained are summarized in Table 2. Four copolymerizations were performed at each feed concentration given in Table 1. The values presented in Table 2 are the average values for the four copolymers obtained at each feed concentration, however for the purpose of the error-in-variables analysis each copolymer was treated as an individual datum.

The error-in-variables method accounts for the errors in the measured variables in a copolymerization experiment. The error in determining the monomer feed concentrations was estimated as 2.0%. The error in determining the copolymer composition was estimated as 12% for both the MMA and BA copolymers. The joint confidence limits of the reactivity ratios at the 95% confidence level are shown in Figure 1. The (+) symbols represent the point estimates of r_1 and r_2 and these are summarized in Table 3.

TABLE 3

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
2VF	MMA	0.211	0.124	0.262
2VF	BA	1.760	0.105	0.185

The values for r_1 and r_2 given in Table 3 differ considerably from the corresponding values obtained from more traditional concentration ladder experiments. In our hands such experiments yield values of $r_1 = 1.31 \pm .5$ and $r_2 = 0.053 \pm 0.21$ for 2VF/MMA and $r_1 = 0.88 \pm .45$, $r_2 = 0.14 \pm .08$ for 2VF/BA, in both cases 2VF is M_1.

There is a considerable amount of error in the r_1 and r_2 values obtained from the ladder experiments, reflecting a high degree of data scatter. There was also some data scatter in the design copolymerizations, which is reflected in the larger than usual (1-5) joint confidence limits. Despite the large error limits there is no overlap of error speces of the ladder experiments with the error spaces of the design experiments i.e. the differences in reactivity ratio values is a real difference.

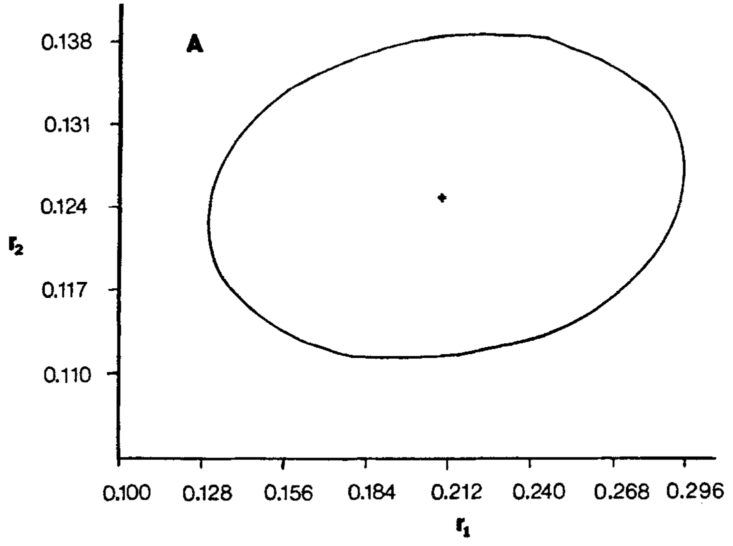
While the joint confidence intervals are larger than usual they are not huge and many authors have pointed out the superiority of a nonlinear least squares analysis for data of this type (10,12-14). Therefore, it is believed that the values for r_1 and r_2 obtained from the experimental design are the most accurate. The r_1 and r_2 values

TABLE 2

Results of 2-Vinylfuran Copolymerizations

Polymer	M_1	M_2	M_f of M_1 in Feed	Polymerization Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f of M_1 in Copolymer
2VFM 1-4	2VF	MMA	0.604	5.5	3.7	17000	30000	1.76	0.577
2VFM 5-8	2VF	MMA	0.260	5.5	6.6	19300	28700	1.48	0.174
2VFM 9-12	2VF	MMA	0.100	5.5	2.5	13500	17000	1.26	0.262
2VFB 1-4	2VF	BA	0.694	6.5	3.1	14800	23000	1.55	0.823
2VFB 5-8	2VF	BA	0.654	5.6	0.0[a]	-	-	-	-
2VFB 9-12	2VF	BA	0.200	6.5	1.7	10000	18000	1.80	0.519
2VFB 13-16	2VF	BA	0.330	6.5	2.6	12500	19000	1.52	0.588

a. No methanol insoluable polymer could be isolated from these polymerizations.



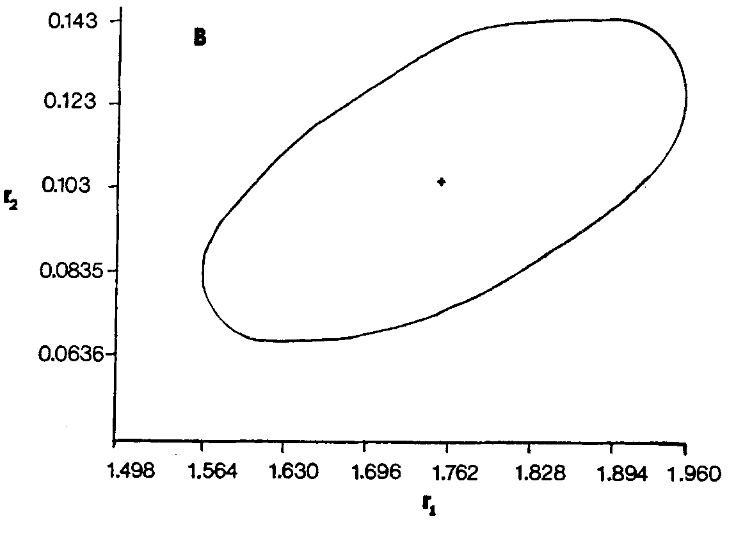


Figure 1: The 95% joint confidence intervals for: A) 2VF/MMA monomer pair and B) 2VF/BA monomer pair

show that 2VF and MMA have approximately equal reactivity. In fact, for 2VF/MMA r_1r_2 is a very small number, indicating a tendency toward alternation in copolymerizations involving this monomer pair. The values obtained for 2VF/BA show that 2VF is a much more reactive monomer than butyl acrylate, which is the same behavior as observed in the sulfur containing vinyl heterocycle copolymerizations.

Conclusions

Design copolymerizations of 2-vinylfuran with methylmethacrylate and n-butyl acrylate have been performed. The results were analyzed using a nonlinear least squares error-in-variables method. The reactivity ratios calculated were significantly different than those obtained from more traditional experiments, but are believed to be more reliable than the reactivity ratios obtained from concentration ladder experiments.

In the 2VF/BA copolymerizations no copolymer was formed at the feed concentration (f_1'') dictated by the experimental design scheme. This feature may contribute in some manner to the differences in r_1 and r_2 values observed between the concentration ladder experiments and the design experiments. However, the differences in reactivity ratio values between the two kinds of experiments is large enough so that it is not the only reason for the observed difference. It is believed that differences in the accuracy of the methods used to analyze the data accounts, in large part, for the differences in r_1 and r_2 values.

References

1. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 35 (1991).
2. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 603 (1991).
3. D. L. Trumbo, J. Appl. Polym. Sci., 44, 185 (1992).
4. D. L. Trumbo, Polym. Bull., 26, 271 (1991).
5. D. L. Trumbo, Polym. Bull., 24, 215 (1990).
6. Y. Hachikama and M. Imoto, J. Soc. Chem. Inc. Jap., 190B (1942).
7. A. P. Dunlop and F. N. Peters, "The Furans", Reinhold Pub. Co., New York, NY, 1953.
8. S. Rajogopalan and P. V. A. Ramen, Org. Syn. Col. Vol. 3, 425 (1955).
9. D. L. Trumbo, Ph.D. Thesis, The Univ. of Akron, Akron, OH 1984.
10. P. W. Tidwell and G. A. Mortimer, J. Polym. Sci., A3, 369 (1965).
11. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, NY, 1953.
12. P. M. Reilly and H. Patino-Leal, Technometrics, 23, 221 (1981).
13. K. F. O'Driscoll and P. M. Reilly, Makromol. Chem. Macromol. Symp., 10/11, 355 (1987).
14. D. J. Hill and J. H. O'Donnell, Makromol. Chem. Macromol. Symp., 10/11, 375 (1987).

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