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A re-evaluation of the reactivity ratios of 3-vinyl thiopene in copolymerization with butyl acrylate and methyl methacrylate

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Summary

The reactivity ratios of 3-vinyl thiophene in copolymerization with n-butyl acrylate and methyl methacrylate were determined by using a nonlinear least squares error-in-variables method coupled with an experimental design scheme. The values obtained were found to be significantly different than those previously reported.

Introduction

Recently, some authors (1-5) have argued that performing ladder type copolymerization experiments and analyzing the data obtained with linear least squares techniques to determine reactivity ratios can lead to values that are in error. Ladder type experiments and linear least squares analyses do not consider that the error in the reactivity ratios is a joint error, the character of which may be poorly understood (3). Thus, the use of reactivity ratios obtained by such methods to predict polymer structure can lead to large errors. In order to obtain more statistically valid values for reactivity ratios Tidwell and Mortimer (6) recommended the use of designed experiments coupled with a nonlinear least squares analysis of the data. O'Driscoll et al, (2,3) have advanced this concept by analyzing copolymerization data with a nonlinear least squares error-in-variables method. This method accounts for the errors inherent in all the measured variables in a copolymerization experiment.

We recently reported the reactivity ratios for 3-vinyl thiophene (3VT) in binary copolymerizations with methyl methacrylate and butyl acrylate (7). The values of the reactivity ratios were obtained via ladder type experiments and linear least squares analysis of the data. However, given the arguments quoted above, it was decided to re-evaluate the reactivity ratios of 3-vinyl thiophene using experimental design methodology and nonlinear least squares error-in-variables data analysis.

Experimental

Monomer Synthesis and Purifications

The 3-vinyl thiophene was synthesized as previously reported (7). Purification was effected by twice distilling from CaH_2 immediately before use. The n-butyl acrylate and methyl methacrylate were also purified by twice distilling from CaH_2. The purity of all the monomers was 99.5% as determined by gas chromatography.

Copolymer Synthesis

The copolymers were synthesized using the design methodology of Tidwell and Mortimer. Equations 1 and 2 were used to calculate the feed mole fractions of 3-vinyl thiophene to be used.

$$f_1' = \frac{2}{2+r_1} \tag{1}$$

$$f_1'' = \frac{r_2}{2+r_2} \tag{2}$$

Here r_1 and r_2 represent initial guesses of the reactivity ratios, these guesses can be quite rough and in the present case the values for r_1 and r_2 obtained from the ladder type experiments were used as initial estimates. Four copolymerizations were then performed at each of the feed concentrations obtained from equations 1 and 2. The values obtained for f_1' and f_1'' are summarized in Table 1.

Table 1

Values of f_1' and f_1''

Monomer 1	Monomer 2	f_1'	f_1''
3VT	MMA	0.962	0.248
3VT	BA	0.855	0.237

The required amounts of monomer were weighed into clean, dry vials using a five-place analytical balance. Recrystallized (methanol) AIBN (0.8 wt %) was then added. The monomer mixture was then sparged with dry nitrogen while cold (-15°C) to minimize losses due to evaporation. Weighing of the vials before and after sparging showed that weight loss was less than 0.5%. The vials were then tightly sealed with teflon lined screw caps and placed in a water bath at 65°C for the desired time. The vials were periodically agitated to insure good mixing. Polymerizations were terminated by cooling the vials in cold water, then adding 2-3 ml of cold methanol. The polymers were purified by reprecipitation from chloroform solution into methanol, a process that was repeated three times. Polymer was collected by filtration, dried in vacuo at 30°C for 72h, then weighed to determine conversion. Copolymer composition was determined by 90 MHz ^{1}H-nmr spectroscopy performed on 7-9% w/v solutions of copolymer in $CDCl_3$ using a Perkin-Elmer R-32B instrument operating in the CW mode. Tetramethylsilane was used as an internal reference and the spectra were recorded at room temperature. The intensities of the aromatic proton resonances were compared with the aliphatic proton resonances to determine composition (7). Polymer molecular weights were determined using a Waters 150 ALC/GPC equipped with 1 x 10^6, 1 x 10^5, 1 x 10^4, 1 x 10^3, 500 and 100Å ultrastyragel columns. THF was used as eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Results and Discussion

Table 2 summarizes the conversions, polymerization times, molecular weights and copolymer compositions. The results given are the average of the four copolymers obtained at each feed composition.

Table 2

Conversions, Molecular Weights and Polymer Compositions

Polymer	$M_f{}^a$ 3VT in Feed	PZN Time (h)	Conv (wt %)	M_n	M_w	M_w/M_n	M_f 3VT in Copolymer	M_f Comonomer in Copolymer
3VT-BA1-4	0.237	4.0	8.1	41000	60500	1.48	0.341	0.659
3VT-BA5-8	0.855	4.0	5.8	16800	26000	1.55	0.790	0.210
3VT-MMA1-4	0.248	2.0	7.8	48800	77500	1.59	0.285	0.715
3VT-MMA5-8	0.962	5.0	6.8	7700	13200	1.71	0.869	0.131

a. M_f = Mole Fraction

While the results presented in the Table above are averages, each individual result was used in the calculation of r_1 and r_2. This is done in order to provide an idea of the scatter in the data and thus derive full benefit from the method employed (8). The error involved in weighing the monomers was determined as 2.0%, while the error in measuring the copolymer composition from the nmr resonance areas was determined, from a consideration of instrument signal to noise ratio and repeated integration of the signals, as 5.0%. The data was then analyzed through the use of a computer program (9) and the values obtained are given in Table 3. The joint confidence intervals, obtained at the 95% confidence level, are shown in Figure 1. The (+) represents the point estimates for r_1 and r_2 and it is these values which are given in Table 3.

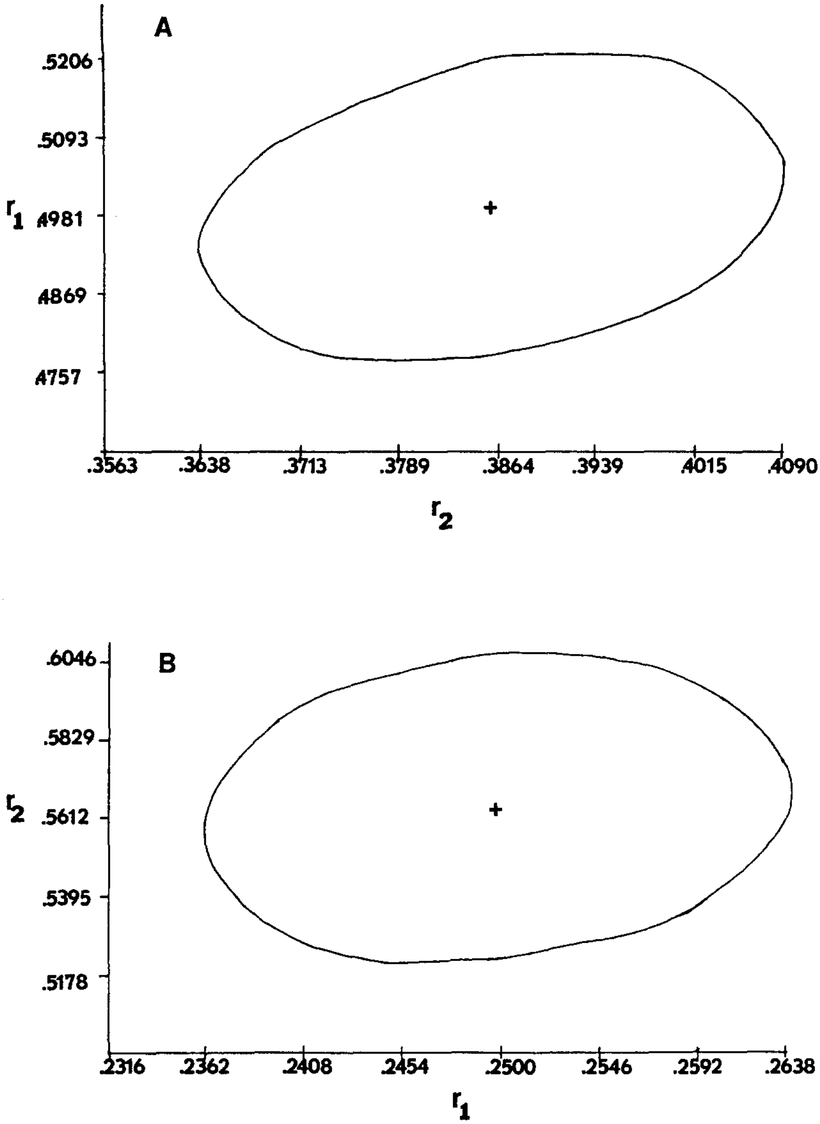

Figure 1: Joint confidence intervals for the reactivity ratios of A) the 3VT monomer pair and B) the 3VT-MMA monomer pair.

Table 3

Reactivity Ratios

Monomer 1	Monomer 2	r_1	r_2	r_1r_2
3VT	BA	0.499	0.386	0.193
3VT	MMA	0.250	0.563	0.141

The values obtained for r_1 and r_2 in the present study differ considerably from those previously obtained. The values previously obtained were $r_1 = 0.34 \pm .13$, $r_2 = 0.62 \pm .14$ for the 3VT-BA monomer pair (3VT = M_1) and $r_1 = 0.08 \pm .06$, $r_2 = 0.66 \pm .08$ for the 3VT-MMA monomer pair (3VT = M_1). The error limits for these previously obtained values were recalculated for this present work and hence are different than those reported in reference (7).

Note that not only are the values for r_1 and r_2 significantly different in the present case from those obtained previously, but, despite recalculation, there is very little overlap of the error limits with the joint confidence intervals established for r_1 and r_2 in the present case.

These joint confidence intervals are relatively small, which justifies more confidence in the accuracy of the values for r_1 and r_2 obtained in the present case than in those previously obtained. However, the values of r_1 and r_2 still indicate that the 3VT radical has a preference for adding the acrylate or methacrylate comonomer only somewhat less so than originally thought. Also, it seems that the butyl acrylate radical shows much more of an affinity for 3VT monomer than originally thought, giving the polymer a slightly more alternating character. But, for both monomer pairs essentially random copolymers are produced. Using literature values for the Q and e's of butyl acrylate and methyl methacrylate (10) and the reactivity ratios obtained in this study, the Q and e values for 3VT can be calculated. The values are e = 2.34, Q = 5.04 for 3VT-BA and e = 1.80, Q = 2.30 for 3VT-MMA.

Conclusions

Revised reactivity ratios, obtained using more statistically valid methods, have been calculated for 3VT in copolymerizations with BA and MMA. The values of r_1 and r_2 are very different from the values previously obtained, but the size of the joint confidence limits obtained in the present case shows that the use of the r_1 and r_2 values previously obtained as initial estimates is justified. While more confidence in the r_1 and r_2 values obtained in the present case can be had, the tendencies r_1 and r_2 reflect are the same. It should be pointed out that while in the present case dramatic differences in the values obtained for r_1 and r_2 were evident when nonlinear least squares data analysis coupled with experimental design methodology was employed versus ladder-type experiments and linear least squares data analysis, this is not always the case. In many cases ladder methodology and linear least squares analysis give values for r_1 and r_2 which are comparable with nonlinear analysis-experimental design methodology values (11). Also, the accuracy and reliability of linear least squares data analysis can be improved if it is coupled with design methodology (3).

References

1. H. Patino-Leal, P. M. Reilly and K. F. O'Driscoll, J. Polym. Sci., Polym. Lett. Ed., 18, 219(1980).
2. R. C. McFarlane, P. M. Reilly and K. F. O'Driscoll, J. Polym. Sci., Polym. Chem. Ed., 18, 251(1980).
3. K. F. O'Driscoll and P. M. Reilly, Makromol. Chem. Makromol. Symp. 10/11, 355(1987).
4. D. J. Hill, J. H. O'Donnell and P. W. O'Sullivan, Macromolecules, 15, 950(1982).
5. D. J. Hill and J. H. O'Donnell, Makromol. Chem. Makromol. Symp., 10/11, 375(1987).
6. P. W. Tidwell and G. A. Mortimer, J. Polym. Sci., A3, 369(1965).
7. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 26, 3127(1988).
8. P. M. Reilly and H. Patino-Leal, Technometrics, 23, 221(1981).
9. M. A. Dube, R. A. Sanaayi, P. M. Reilly and K. F. O'Driscoll, Univ. of Waterloo, Waterloo, Ontario, Canada. A copy of the program may be obtained from K. F. O'Driscoll at the University of Waterloo.
10. The Polymer Handbook, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975.
11. T. Kelen, F. T. Tudos and B. Turcsanyi, Polym. Bull., 2, 71(1980).

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