

## **Copolymerization of 4-bromo-2-vinyl thiophene with methyl methacrylate and *n*-butyl acrylate**

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### Summary

The copolymerization behavior of 4-bromo-2-vinyl thiophene with the commonly available monomers methyl methacrylate and *n*-butyl acrylate was investigated. The copolymerizations were performed under an experimental design scheme and the results were analyzed by employing a nonlinear least squares error-in-variables method. The 4-bromo-2-vinyl thiophene was found to be a very reactive monomer.

### Introduction

Recently we have been involved in investigation of the copolymerization behavior of vinyl heterocycles (1-6). In general we have found these materials to be quite reactive in copolymerization reactions and the present case is no exception. Preliminary ladder copolymerizations were performed in order to generate feed ratios for use in the experimental design scheme suggested by Tidwell and Mortimer (7). The results of subsequent copolymerizations were analyzed by using a nonlinear least squares error-in-variables method (8,9), a method which accounts for the errors in all the measured variables in a copolymerization experiment.

### Experimental

#### General

All solvents used in this study were reagent grade and were used without further purification.  $^1\text{H-Nmr}$  spectra were obtained on 7-10 wt % solutions of polymer in  $\text{CDCl}_3$ . The spectra were recorded at ambient temperature using a Perkin-Elmer R32 spectrometer operating in the CW mode. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ , 500 and 100 A ultrastyrigel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

#### Monomer Synthesis

The 4-bromo-2-vinyl thiophene was synthesized from the corresponding aldehyde (Aldrich) via a Wittig reaction (6,10). The yield was 56%. The vinyl compound was purified by distilling three times from  $\text{CaH}_2$ ; b.p. = 54-56°C at 3 mm of Hg.  $^1\text{H-Nmr}$ ,  $\text{CDCl}_3$ ;  $\delta$  5.10-5.63 (2H, AB

quartet);  $\delta$  6.50-6.70 (1H, m);  $\delta$  6.83 (1H, s);  $\delta$  7.00 (1H, s).

#### Copolymer Synthesis

The copolymers were synthesized by weighing, using a five-place analytical balance, the desired amounts of monomer into clean, dry screw cap vials. Vazo-67 (recrystallized,  $\text{CH}_3\text{OH}$ ) was added as the initiator (0.7 wt %) and the monomer mixture in the vial was sparged with dry nitrogen while cold ( $-40^\circ\text{C}$ ) in order to minimize evaporation losses ( $<1$  wt %). The vials were tightly capped with teflon lined caps and were placed in a thermostated water bath at  $65^\circ\text{C}$  for the desired length of time. Polymerizations were terminated by removing the vials from the bath, cooling them in cold water, then adding 4 ml of cold methanol to the vial contents. Polymers were purified by dissolving in  $\text{CHCl}_3$  and precipitating in methanol, a process that was repeated three times. The polymers were dried to a constant weight at  $25^\circ\text{C}$  in a vacuum oven. Conversions were determined gravimetrically.

In order to obtain feed charges for the Tidwell-Mortimer experimental design scheme, initial estimates of the reactivity ratios must be made. To make these estimates ladder copolymers, in which the feed concentration of 4-bromo-2-vinyl thiophene is gradually increased, were synthesized. In all cases conversions were kept low ( $<6\%$ ) and the Kelen-Tudos (11) method was used to analyze the results. For the 4-bromo-2-vinyl thiophene ( $M_1$ )/methyl methacrylate system,  $r_1 = 1.73 \pm .5$  and  $r_2 = 0.095 \pm .03$ . For the 4-bromo-2-vinyl thiophene ( $M_1$ )/butyl acrylate system,  $r_1 = 3.99 \pm .6$  and  $r_2 = 0.045 \pm .02$ . Equations 1 and 2 were then used to calculate the feed charges (in mole fractions) of 4-bromo-2-vinyl thiophene.

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

$$f_1'' = \frac{r_2}{2+r_2} \quad 2)$$

The values obtained for  $f_1'$  and  $f_1''$  are given in Table 1.

TABLE 1  
 $f_1'$ ,  $f_1''$  and  $f_1'^*$  Values for  
 4-Bromo-2-Vinyl Thiophene Copolymers

$M_1$	$M_2$	$f_1'$	$f_1''$	$f_1'^*$
4BVT <sup>a</sup>	MMA	0.536	0.0453	~
4BVT	BA	0.334	0.0220	0.0500

a. 4BVT = 4-bromo-2-vinyl thiophene

Five copolymerizations are conducted at each individual feed concentration of 4BVT. For the BA copolymers a third feed concentration ( $f_1'^*$ ) was added because of the low value of  $f_1''$  and the uncertainty of obtaining polymer at this low feed concentration. It is known (12) that low concentrations of very reactive monomers can have inhibitory effects.

#### Results and Discussion

The results obtained are presented in Table 2. The values in the Table are the average of the five copolymerizations performed at each feed charge. For calculation of  $r_1$  and  $r_2$  values each individual result was included.

TABLE 2  
 Copolymerization Results

Polymer	$M_1$	$M_2$	$M_f^a$ of $M_1$ in Feed	Pzn Time (h)	Conv. (wt %)	$M_n$	$M_w$	$M_w/M_n$	$M_f$ of $M_1$ in Co-polymer
4BVTM 1-5	4BVT	MMA	0.536	2	9.0	13000	24500	1.88	0.858
4BVTM 6-10	4BVT	MMA	0.0153	2	9.1	15000	23000	1.53	0.236
4BVTB 1-5	4BVT	BA	0.334	3	10.1	10000	17000	1.70	0.634

(Continued)

TABLE 2  
(Continued)

Polymer	M <sub>1</sub>	M <sub>2</sub>	M <sub>f</sub> <sup>a</sup> of M <sub>1</sub> in Feed	Pzn Time (h)	Conv. (wt %)	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>f</sub> of M <sub>1</sub> in Co- polymer
4BVTB 6-10	4BVT	BA	0.0220	3	9.2	33700	62000	1.84	0.076
4BVTB 11-15	4BVT	BA	0.0500	3	11.0	13400	22000	1.64	0.242

As previously stated the error-in-variables method accounts for the error in all the measured variables in a copolymerization experiment. In the present case the error involved in weighing the monomer feed charges was estimated as 1.5% based on repeated weighings and the stated accuracy of the balance. The error in determining copolymer composition was estimated as 10% for the BA copolymers and 7% for the MMA copolymers based on repeated signal integration and the signal-to-noise ratio of the nmr instrument.

The values calculated for  $r_1$  and  $r_2$  are given in Table 3. The 95% confidence level joint confidence limits are shown in Figure 1. The (+) sign indicates the point estimates for  $r_1$  and  $r_2$  and these are the values recorded in Table 3.

TABLE 3  
Reactivity Ratios

M <sub>1</sub>	M <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>	r <sub>1</sub> r <sub>2</sub>
4BVT	MMA	5.05	0.141	0.712
4BVT	BA	2.83	0.181	0.512

The values show that the growing chain ends much prefer to add the 4BVT monomer. This is particularly true in the MMA case, a fact which is a reverse of the trend seen in previous copolymerizations involving vinyl heterocycles and MMA and BA. It is possible that steric factors are responsible for this seeming reversal, however more detailed work will be necessary to more fully elucidate any possible

explanation. At this point it is sufficient to note that 4-bromo-2-vinyl thiophene is a very reactive monomer, as have been all the vinyl heterocycles investigated to date.

Based on the  $r_1$  and  $r_2$  values obtained in this study, and literature values for MMA and BA (13),  $Q$  and  $e$  values were calculated for 4BVT. The results are summarized in Table 4.

TABLE 4  
 $Q$  and  $e$  Values

$M_1$	$M_2$	$Q$	$e$
4BVT	MMA	6.96	0.98
4BVT	BA	4.21	1.67

#### Conclusions

Copolymers of 4-bromo-2-vinyl thiophene with methyl methacrylate and n-butyl acrylate have been synthesized according to an experimental design scheme. The copolymers were analyzed by a nonlinear least squares error-in-variables method and values for the reactivity ratios were calculated. The reactivity ratios show the 4BVT is a very reactive monomer. The results also show that the butyl acrylate is more reactive in copolymerization with 4BVT than is methyl methacrylate, a result opposite of those previously obtained in vinyl heterocycle polymerizations and opposite the values obtained from the ladder polymerization experiments. The values for  $r_1$  and  $r_2$  obtained from the nonlinear least squares analysis are quite different from those obtained from the linear analysis of the ladder copolymerizations. This is not uncommon (8,9,14) as nonlinear methods are regarded as yielding more accurate values and error-in-variables methods that recognize errors in these types of experiments as joint errors further increase accuracy.

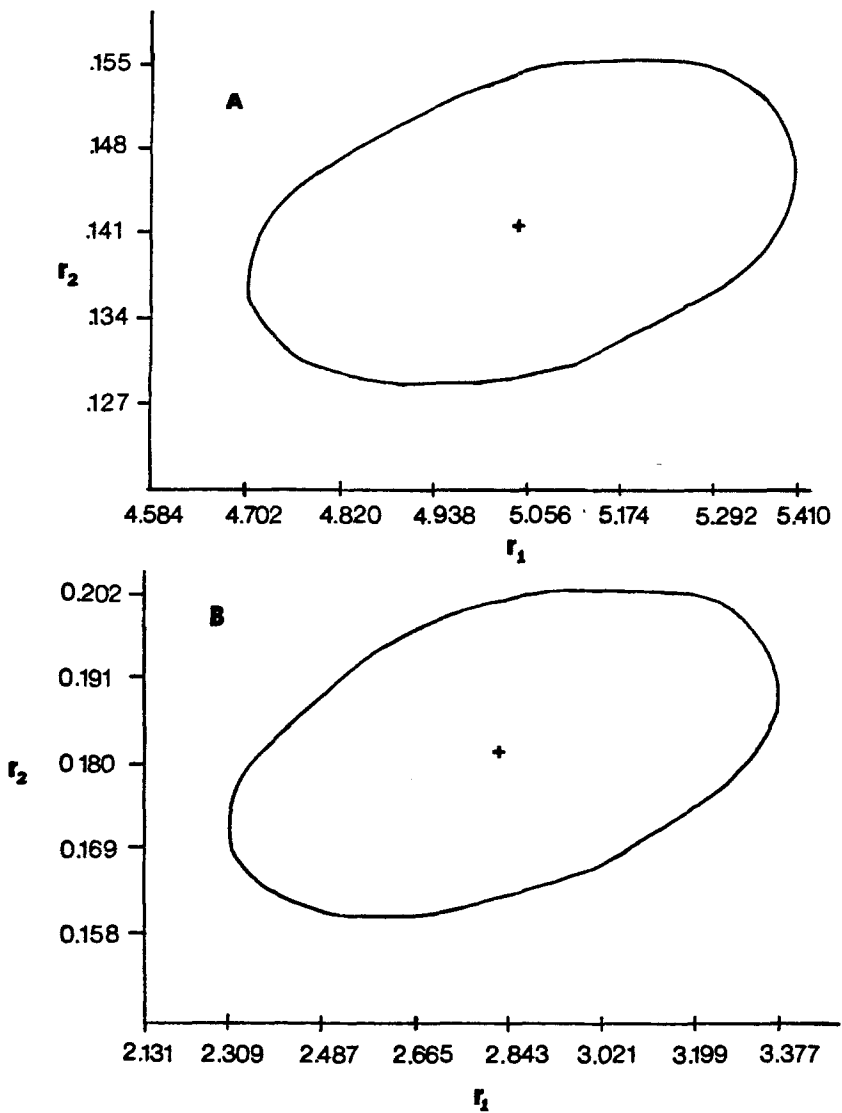


Figure 1 The 95% confidence level joint confidence limits for  $r_1$  and  $r_2$ : A) 4-bromo-2-vinyl thiophene/MMA copolymers; B) 4-bromo-2-vinyl thiophene/BA copolymers.

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