Polymer Bulletin 28, 555–560 (1992)

Polymer Bulletin

Copolymerization behavior of 3-vinylbenzothiophene

David L. Trumbo

The Glidden Company, 16651 Sprague Rd., Strongsville, OH 44136, USA

Summary

3-Vinylbenzothiophene was synthesized and its copolymerization with methyl methacrylate and n-butyl acrylate was investigated. The copolymerizations were performed according to an experimental design scheme and the results were analyzed using a nonlinear error-in-variables method. The 3-vinylbenzothiophene was found to be a reactive monomer with reactivity ratio values similar to those of 2-vinyl thiophene.

Introduction

As part of an ongoing investigation into the polymerization and copolymerization behavior of vinyl heterocycles, we have synthesized and evaluated several unsubstituted and substituted vinyl thiophenes and vinyl furans. (1-6) We have found that, in general, vinyl heterocycles are quite reactive in copolymerization reactions with ring substituted species being the most reactive. In order then to study the effect of a fused ring structure on the copolymerization behavior of a vinyl thiophene, we synthesized 3-vinylbenzothiophene and examined its copolymerization behavior with methyl methacrylate and n-butyl acrylate comonomers.

Experimental

General

All solvents used in this study were reagent grade and were used without further purification. ^{1}H-Nmr spectra were recorded on 5-7% w/v solutions of polymer in $CDCl_3$ at ambient temperature using a Perkin-Elmer R32 instrument operating at 90 MHz in the CW mode. Spectral resonance areas were determined by electronic integration and by cutting and weighing tracings of the signals in the spectra. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100A ultrastyragel columns. A polystyrene calibration curve was used to calculate molecular weights.

Monomer Synthesis

Benzo[b]thiophene-3-carboxaldehyde was synthesized form 3-methylbenzo-[b]thiophene (Lancaster) by the method of Campaigne and Niess (7). After distillation, b.p. = 105-107^{o}/0.8 mm (lit. b.p. = 125-128^{o}/2.0 mm), the aldehyde was isolated as white crystals in 40% yield. M.p. = 56-57^{o}, (lit. m.p. = 58^{o}) (8).

The 3-vinylbenzothiophene (3VBZT) monomer was synthesized by a Wittig reaction (9) in 55% yield. B.p. = 82-84^{o}/1 mm. ^{1}H-Nmr, CDCl$_3$; 5.25-5.85 (2H, AB quartet); 6.75-7.10 (1H, 4 s.s.); 7.25-7.46 (2H m); 7.60-7.95 (2H, m). The monomer was purified by two distillations from CaH$_2$ (99% purity by GC).

Copolymer Synthesis

Copolymer syntheses were performed using an experimental design scheme as previously described (1-6). Conventional 'concentration ladder' type experiments were performed first in order to obtain feed concentration values for the experimental design scheme (10). The feed concentration values so obtained are summarized in Table 1.

TABLE 1

Feed Concentrations of Monomer for Experimental Design Copolymer Synthesis

Monomer 1	Monomer 2	$f_1{}'^{a}$	$^{a}f_1{}''$	$^{a}f_1{}''^{*}$
3VBZT	MMA	0.615	0.1800	-
3VBZT	BA	0.625	0.0458	0.115

a. $f_1{}'$, $f_1{}''$, $f_1{}''^{*}$ = mole fraction of monomer one in the feed

Normally in this design scheme only two different concentrations are required. However, the f_1'' value in the BA case is very low, and because it is known (11) that low concentrations of reactive monomers can inhibit polymerization, i.e. no polymer may be formed, a third feed concentraiton was chosen as a precaution. The $f_1''^{*}$ value chosen is based on experience gained in performing the concentration ladder experiments. It is a cencentration at which copolymer was obtained and it is reasonably close to the f_1'' value.

Four polymerizaitons were performed at each feed concentration given in Table 1. The polymerizations were accomplished by weighing the required amounts of comonomer into clean, dry vials using a five-

TABLE 2

Polymerization Conditions, Conversions, Molecular Weights and Polymer Compositions

Polymers	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 Copolymer
3VBZTMMA 1-4	3VBZT	MMA	0.6150	1.0	2.6	11600	20300	1.75	0.689
3VBZTMMA 5-8	3VBZT	MMA	0.1800	1.0	2.9	24000	39400	1.64	0.333
3VBZTBA 1-4	3VBZT	BA	0.6290	2.5	5.1	8300	14000	1.69	0.776
3VBZTBA 5-8	3VBZT	BA	0.0458	3.5	4.0	9500	17900	1.88	0.219
3VBZTBA 9-12	3VBZT	BA	0.1150	2.5	5.0	13200	19600	1.48	0.392

place analytical balance. Vazo-67 (recrystallized, CH_3OH), 0.8 wt %, was then added. The monomer mixture was then sparged with nitrogen while cold (-50°C) to minimize evaporation losses (1.0 %). The vials were sealed with teflon lined screw caps and placed in a thermostated water bath at 65°C for the desired length of time. The polymerizations were terminated by removal from the water bath and addition of 3-4 ml of cold methanol. The polymers were purified by reprecipitating three times from $CHCl_3$ solution into CH_3OH. The polymers were dried in vacuo for 72h at ambient temperature and the conversions were determined gravimetrically.

Results and Discussion

Table 2 summarizes the polymerization conditions and results obtained. The conversion, molecular weight and composition data presented in the Table are the averages of the four polymers obtained at each feed composition. For reactivity ratio calculations however, each polymerization was regarded as an individual result.

As previously stated, the results were analyzed using a nonlinear error-in-variables method. (1-6, 12) The method accounts for the errors in the measured variables in a copolymerization experiment and considers the error in r_1 and r_2 as a joint error.

The error in weighing the monomers into the polymerization vials was estimated as 1.5%. The error in determination of copolymer composition was estimated as 8% for the 3VBZT/MMA copolymers and as 6% for the 3VBZT/BA copolymers.

The joint confidence limits for r_1 and r_2 at the 95% confidence level are shown in Figure 1. The (+) symbol represent the point estimates of r_1 and r_2 and these are summarized in Table 3.

TABLE 3

Reactivity Ratios for 3VBZT Copolymers

M_1	M_2	r_1	r_2	r_1r_2
3VBZT	MMA	1.08	0.317	0.342
3VBZT	BA	1.66	0.131	0.217

Based on literature values for MMA and BA (13), Q and e values for 3VBZT were calculated. The values obtained are summarized in Table 4.

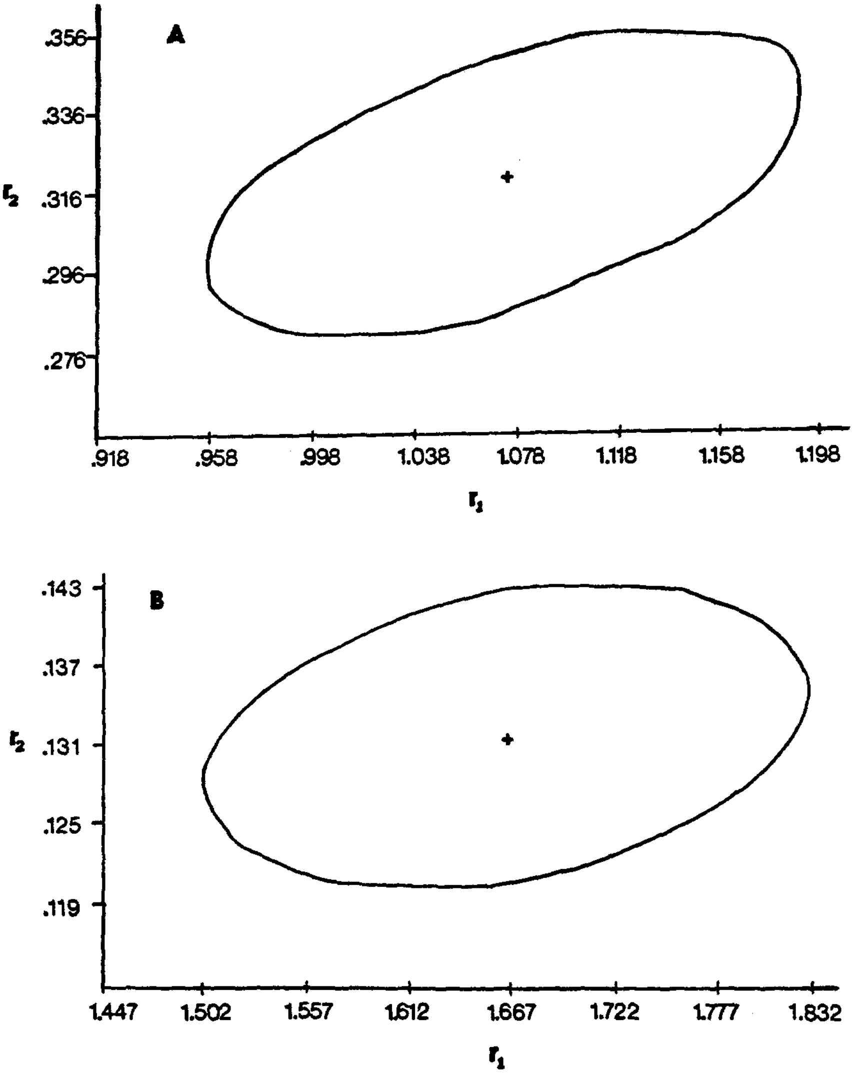

Figure 1 Joint confidence limits, 95% confidence level for: A) Vinylbenzothiophene/MMA and B) Vinylbenzothiophene/BA

TABLE 4

Q and e Values for 3-Vinylbenzothiophene

M_1	M_2	Q	e
3VBZT	MMA	3.77	1.44
3VBZT	BA	8.42	2.09

Conclusions

3-Vinylbenzothiophene has been synthesized and copolymerized with MMA and BA. The copolymerizations were conducted according to the experimental design scheme of Mortimer and Tidwell and the results were analyzed and reactivity ratios calculated through the use of a non-linear error-in-variables method. The joint confidence intervals are of reasonable size indicating relatively good accuracy for r_1 and r_2. The 3VBZT is a reactive monomer with values of r_1 and r_2 approximating those of 2-vinyl thiophene (3) in copolymerizations with MMA and BA.

References

1. D. L. Trumbo, Polym. Bull., 24, 215 91990).
2. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 357 (1991).
3. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 603 (1991).
4. D. L. Trumbo, Polym. Bull., 26, 271 (1991).
5. D. L. Trumbo. J. Appl. Polym. Sci., 44, 185 (1992).
6. D. L. Trumbo, Polym. Bull., 19, 217 (1988).
7. E. Campaigne and E. S. Neiss, J. Heterocyclic Chem., 3(1), 46 (1966).
8. W. J. King and F. F. Nord, J. Org. Chem., 13, 635 (1948).
9. A. Maelecker, Org. React., 14, 395 (1965).
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. K. F. O'Driscoll and P. M. Reilly, Makromol. Chem. Macromol. Symp., 10/11, 355 (1987).
13. J. Brandup and E. H. Immergut Eds., The Polymer Handbook, 3rd Ed., Wiley, New York, 1989.

Accepted May 1, 1992 K