Polymer Bulletin 29, 171–176 (1992)

Polymer Bulletin

Synthesis and copolymerization behavior of 2-thienyl vinyl ketone

David L. Trumbo

The Glidden Company, 16651 Sprague Road, Strongsville, OH 44136, USA

Summary

2-Thienyl vinyl ketone was synthesized via a Hoffman elimination reaction and its copolymerization behavior was examined. Comonomers chosen were methyl methacrylate (MMA) and n-butyl acrylate (BA). The copolymers were synthesized according to an experimental design scheme and the results were analyzed by using a nonlinear error-in-variables method. The 2-thienyl vinyl ketone and MMA have approximately equal reactivity, while the 2-thienyl ketone is much more reactive than BA.

Introduction

As part of our ongoing investigation of the polymerization and copolymerization behavior of vinyl heterocyclic monomers (1-6) we noted the work of Labidi, et al.(7) concerning the polymerization of 2-furyl vinyl ketone. From that work it is obvious that a thiophene analog could be synthesized. Since there was no published data on such a monomer we decided it would be of interest to examine its polymerization and copolymerization behavior. The results obtained from copolymerization of 2-thienyl vinyl ketone with the commonly available monomers MMA and BA are the subject of this report.

Experimental

General

All solvents were reagent grade and were used without further purification. The monomers were purified by twice distilling from CaH_2 and were stored under nitrogen in tightly capped bottles at -5°C until they were used. ^{1}H-Nmr spectra were obtained on 7% w/v solutions in $CDCl_3$ with TMS added as an internal standard. The spectra were recorded at ambient temperature on a Perkin Elmer R32 spectrometer operating at 90 MHz in the CW mode. Molecular weight measurements were made with a Waters 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 the molecular weights.

weights.

Monomer Synthesis

The monomer was synthesized from the ethylamine hydrochloride by a Hoffmann elimination (7,8). 2-Thienyl methyl ketone (200g, 1.59 mol) was reacted with paraformaldehyde (204g) and dimethylamine hydrochloride (270.9g, 1.66 mol) in 530 ml of ethanol, 2 or 3 drops of concentrated HCl were added as a catalyst. The reaction mixture was refluxed for 4h and then allowed to cool overnight in a refrigerator, during which time a white crystalline solid was deposited. The solvent was decanted and the solid was washed with several portions of cold diethyl ether. Purification of the solid was by recrystallization from acetonitrile. Yield of N,N-dimethyl-2-(2-thienyl) ethylamine hydrochloride was 76%, m.p. = 171-173°C with some decomposition. ^{1}H-Nmr (CD_3OD); δ 2.45 (d, 6H), δ2.10 (m, 4H), δ3.70 (s, 1H), δ6.75 (m, 1H), δ7.45 (m, 2H). An aqueous solution of the salt (100g/250 ml) was steam distilled until no more organic material evolved. The distillate was extracted with 3 x 200 ml portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried with Na_2SO_4 and the CH_2Cl_2 was removed on a rotovap. The residue was subjected to vacuum distillation and 2-thienyl vinyl ketone was collected at 74-76°C/6 mm. ^{1}H-Nmr ($CDCl_3$) δ 5.75-6.50 (AB quartet, 2H); δ 7.20 (m, 2H); δ 7.65 (m, 2H). The yield of monomer was 32%.

Polymer Synthesis

The polymers were synthesized according to an experimental design scheme as previously described (1-6). In the design scheme concentration ladder experiments are first performed in order to obtain feed concentrations of monomer 1 to be used in the experimental design (9, 10) scheme. The feed concentrations used in this work are summarized in Table I.

TABLE I

Feed Concentrations, f_1', f_1'' and $f_1''*$, of 2-Thienyl Vinyl Ketone in Experimental Design Scheme

M_1	M_2	$f_1'^{b}$	f_1''	$f_1''*$
2TVK[a]	MMA	0.830	0.140	-
2TVK	BA	0.550	0.036	0.11

a. 2TVK = 2-Thienyl Vinyl Ketone
b. f values are Mole Fractions

TABLE II

Feed Ratios, Conversions, Molecular Weights and Copolymer Compositions for 2TVK Copolymers

Polymer	M_1	M_2	M_f of M_1 in Feed[a]	Pzn Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f of M_1 in Copolymer
2TVKMMA 1-5	2TVK	MMA	0.830	0.75	4.2	14000	23400	1.67	0.7620
2TVKMMA 6-10	2TVK	MMA	0.140	0.75	7.2	65900	107000	1.62	0.2100
2TVLBA 1-5	2TVK	BA	0.550	1.33	2.6	10800	20700	1.92	0.7490
2TVKBA 6-10	2TVK	BA	0.036	1.33	9.3	134000	239000	1.92	0.0610
2TVKBA 11-15	2TVK	BA	0.108	1.33	4.7	12300	22600	1.84	0.1550

[a] M_f = Mole Fraction.

Normally, only two different concentrations are used, but it is well known that low concentrations of very reactive monomers can have an inhibitory effect on polymerization i.e. no polymer may be formed at all (11). The f_1'' value for the BA comonomer is very low and so to insure that polymer would be obtained an $f_1''*$ value, at which it was known polymer was obtained (from the ladder experiments) and which was reasonably close to the f_1'' value was used as a third concentration. Five polymerizations were then performed at each feed concentration value. The copolymers were synthesized and purified as previously described (1-6, 9).

Results and Discussion

The results obtained are summarized in Table II. The results presented in the Table are the average values obtained for the five copolymers synthesized at each feed concentration. However, for application of the error-in-variables analysis each copolymerization was treated as an individual datum. The nonlinear error-in-variables method (9, 10) used 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 (5-place balance) was estimated as 1.5%. The error in determining copolymer composition was estimated as 7% for the 2TVK/MMA copolymers and as 8% for the 2TVK/BA copolymers.

The joint confidence limits for r_1 and r_2 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 III.

TABLE III

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
2TVK	MMA	0.603	0.5080	0.306
2TVK	BA	2.870	0.0660	0.190

From the data given in Table III and from literature values of Q and e for MMA and BA (12), Q and e values for 2TVK were calculated. These are presented in Table IV.

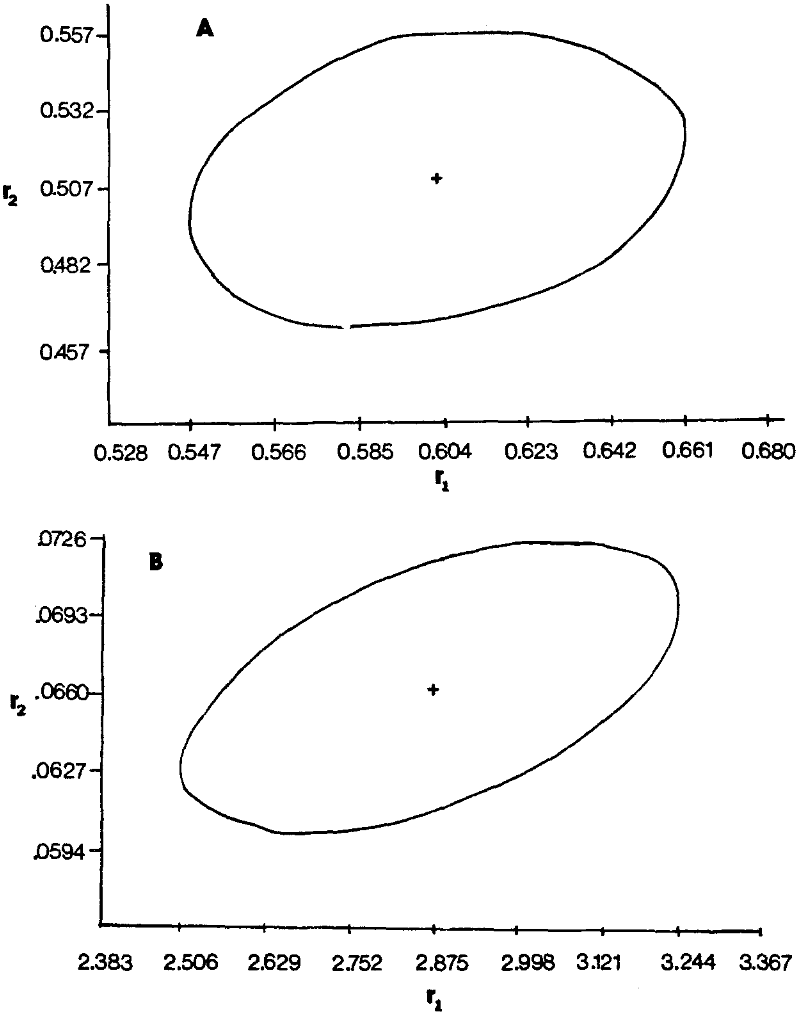

Figure 1: 95% joint confidence intervals for; A) 2TVK/MMA and B) 2TVK/BA copolymers.

TABLE IV

Q and e Values

M_1	M_2	Q	e
2TVK	MMA	2.34	1.48
2TVK	BA	16.80	2.13

Conclusions

2-Thienyl vinyl ketone was synthesized and its copolymerization behavior was explored. The copolymerizations were performed according to an experimental design scheme and the results were analyzed using a nonlinear error-in-variables method. The joint confidence limits of the r_1 and r_2 values calculated from the analysis are relatively small, indicating that the values obtained are reasonably accurate. The r_1 and r_2 values obtained show that 2TVK has approximately the same reactivity as MMA but is much more reactive than BA. The reason(s) for this may be due to steric requirements in the BA copolymerization.

References

1. D. L. Trumbo, Polym. Bull., 24, 215 (1990).
2. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 35 (1991).
3. D. L. Trumbo, J. Appl. Polym. Sci., 44, 185 (1992).
4. D. L. Trumbo and R. A. Zander, J. Polym. Sci., Polym. Chem. Ed., 29, 1053 (1991).
5. D. L. Trumbo, Polym. Bull., 26, 271 (1991).
6. D. L. Trumbo, J. Polym. Sci., Polym. Chem. Ed., 29, 603 (1991).
7. A. Labidi, m. C. Salon, A. Gandini and H. Cheradame, Polym. Bull., 14, 271 (1985).
8. J. Sam and J. R. Mozingo, J. Pharm. Sci., 58, 1030 (1969).
9. K. F. O'Driscoll and P. M. Reilly, Makromol. Chem. Macromol. Symp., 10/11, 355 (1987).
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. J. Brandup and E. H. Immergut, Eds., "The Polymer Handbook", 3rd Ed., Wiley, NY, 1989.

Accepted June 24, 1992 K