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Copolymerization behavior of 5-methyl-2-vinyl thiophene

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Summary

The copolymerization of 5-methyl-2-vinyl thiophene with methyl methacrylate and n-butyl acrylate was investigated. The copolymerization data was analyzed by a nonlinear least squares error-in-variables method. The results of this preliminary study show that the 5-methyl-2-vinyl thiophene is a very reactive monomer, although less so than other 5- substituted -2-vinyl thiophenes.

Introduction

We have been engaged for some time in the study of the polymerization and copolymerization behavior of vinyl heterocycles (1-5). Recently we have begun investigating the effect of ring substitution on the copolymerization behavior of 2-vinyl thiophenes (6). We have found, in some cases, that ring substitution of 2-vinyl thiophene increases the reactivity of the monomer relative to unsubstituted 2-vinyl thiophene. In this communication we wish to report our preliminary findings concerning the copolymerization behavior of 5-methyl-2-vinyl thiophene.

Experimental

General

All chemicals used in this study were reagent grade and were used, unless otherwise noted, without further purification. The monomers were distilled 3 times from CaH_2 and were stored in the refrigerator at 0^oC in tightly sealed containers until used. ^1H-Nmr spectra were obtained on 5-10% w/v solutions in $CDCl_3$ at ambient temperature using a Perkin-Elmer R-32 spectrometer operating at 90 MHz in the CW mode. Molecular weight measurements were obtained with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. Tetrahydrofuran was used as the eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from 5-methyl-2-thiophenecarboxaldehyde (Aldrich) via a Wittig reaction as previously described (6,7). Mon-

TABLE 1

Conversions, Feed Charges, Molecular Weights and Reaction Times for 5-Methyl-2-Vinyl Thiophene

Polymer	M_1[a]	M_2[b]	M_f of M_1 in Feed	Pzn Time (h)	Conv. (wt %)	M_w	M_n	M_w/M_n
MeTM1	5MeVT	MMA	0.100	6.5	5.0	5900	4800	1.23
MeTM2	5MeVT	MMA	0.246	6.5	7.0	6400	4700	1.36
MeTM3	5MeVT	MMA	0.350	6.5	2.0	6800	4900	1.39
MeTM4	5MeVT	MMA	0.500	6.5	2.0	8100	5600	1.45
MeTM5	5MeVT	MMA	0.600	6.5	3.0	9100	6000	1.52
MeTB1	5MeVT	BA	0.165	5.5	5.1	14700	9950	1.48
MeTB2	5MeVT	BA	0.257	5.5	7.0	16000	10200	1.58
MeTB3	5MeVT	BA	0.363	5.5	7.5	16200	9200	1.76
MeTB4	5MeVT	BA	0.450	5.5	8.2	16600	8600	1.93
MeTB5	5MeVT	BA	0.542	5.5	10.0	18200	10200	1.78
MeTB6	5MeBT	BA	0.662	5.5	10.8	21900	11500	1.90
MeTB7	5MeVT	BA	0.857	5.5	9.8	16700	8800	1.90

a. 5MeVT = 5-Methyl-2-vinyl thiophene

b. MMA = Methylmethacrylate,
BA = Butyl acrylate

omer boiling point = 49-50^{o}C at 12 mm Hg. ^{1}H-Nmr ($CDCl_3$) δ 2.43 (s.s., 3H) δ 5.00-5.57 (AB quartet, 2H); δ 6.65 (m, 1H); δ6.75 (m, 2H).

Polymer Synthesis

Copolymers were synthesized by weighing the desired amounts of the comonomers into clean, dry vials. The initiator, AIBN (0.8 wt %), was then charged into the vial. The contents of the vial were sparged with dry nitrogen while cold (-30^{o}C) to minimize evaporation losses ($<$ 1.0 wt %). The vials were sealed with a teflon lined cap and placed in a thermostated water bath at 60^{o}C for the desired length of time. The vials were removed from the bath, cooled with cold water and the polymerizations terminated by the addition of 3-4 ml of cold methanol. The polymers were purified by dissolution into $CHCl_3$ and precipitation into methanol, a process that was repeated 3 times. The polymers were dried for 72h in a vacuum oven at 35^{o}C and conversions were determined gravimetrically.

Results and Discussion

The monomer feed charges, polymerization times, conversions and molecular weights obtained are summarized in Table 1.

Copolymer compositions were calculated from the ^{1}H-nmr spectra by comparing the areas at 6.00-6.70 ppm (thiophene ring proton resonance) with those at 0.5-3.20 ppm (aliphatic proton resonances) for the 5MeVT/MMA copolymers, and the areas at 5.90-6.55 ppm and 0.75-4.10 ppm for the 5MeVT/BA copolymers. The compositions obtained are given in Table 2.

The copolymer composition data was analyzed using a nonlinear least squares error-in-variables method (8,9). The joint confidence limits for the reactivity ratios, at the 95% confidence level, are shown in Figure 1. The error in weighing the monomers into the vials was estimated at 1.5%, while the error in determining copolymer composition was estimated at 10% (1-5). The point estimates for the reactivity ratios are given in Table 3 (the + symbols in Fig. 1).

The results show that in both cases, 5-methyl-2-vinyl thiophene is quite reactive as a monomer, with the growing polymer chains much prefering to add it (5MeVT) no matter what their terminus.

The results presented here encompass only a limited range of feed compositions and must be regarded as preliminary. However, these results follow much the same pattern as results previously obtained for vinyl thiophene and substituted vinyl thiophenes (1-5). Design experiments are currently in progress to confirm the results presented here.

Conclusions

Copolymers of 5-methyl-2-vinyl thiophene with MMA and BA have been synthesized and analyzed. While the results cover a limited range, the conclusion that 5-methyl-2-vinyl thiophene is the most reactive monomer in both cases is regarded as valid.

TABLE 2

Copolymer Compositions

Polymer	M_1	M_2	$M_f{}^a$ of M_1 in Copolymer	M_f of M_2 in Copolymer
MeTM1	5MeVT	MMA	0.324	0.676
MeTM2	5MeVT	MMA	0.479	0.521
MeTM3	5MeVT	MMA	0.603	0.397
MeTM4	5MeVT	MMA	0.796	0.294
MeTM5	5MeVT	MMA	0.805	0.195
MeTB1	5MeVT	BA	0.488	0.512
MeTB2	5MeVT	BA	0.562	0.438
MeTB3	5MeVT	BA	0.595	0.405
MeTB4	5MeVT	BA	0.706	0.293
MeTB5	5MeVT	BA	0.717	0.282
MeTB6	5MeVT	BA	0.800	0.200
MeTB7	5MeVT	BA	0.095	0.095

TABLE 3

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
5MeVT	MMA	2.08	0.200	0.42
5MeVT	BA	1.52	0.072	0.11

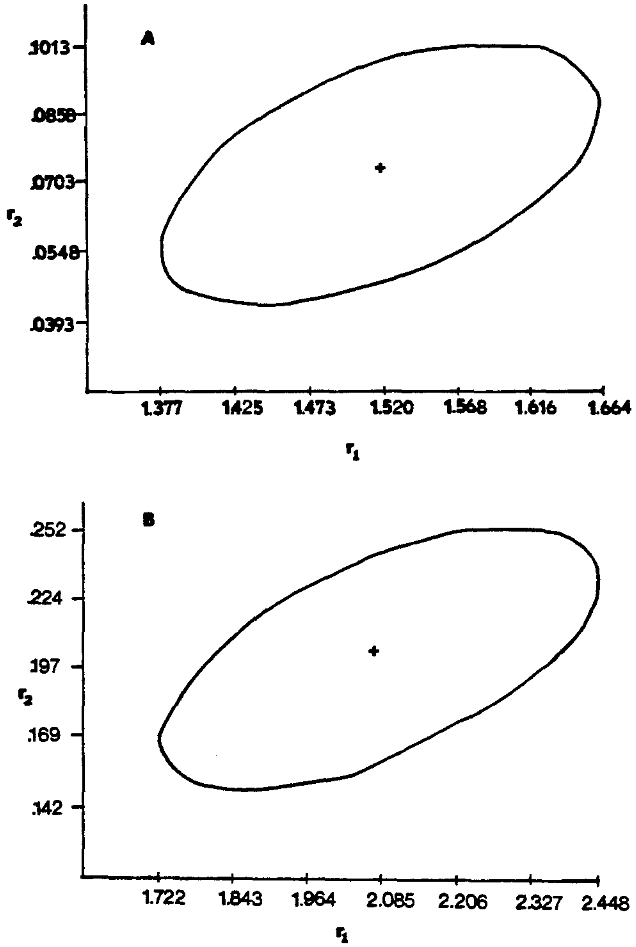

Figure 1 The 95% confidence level joint confidence limits for r_1 and r_2 of A) 5-methyl-2-vinyl thiophene/butyl acrylate[1] copolymers B) 5-methyl-2-vinyl thiophene/methyl methacrylate copolymers.

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