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Copolymerization of 2,5-dimethyl-3-vinylthiophene with methyl methacrylate, styrene and isobutyl methacrylate

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Summary

The title vinyl thiophene monomer was synthesized by dehydration of the corresponding secondary alcohol. Free radical initiated copolymerizations with methyl methacrylate, styrene or isobutyl methacrylate were performed and the copolymer compositions were used in the calculation of reactivity ratios. The data was analyzed via a nonlinear least squares error-in-variables method. The 2,5-dimethyl-3-vinylthiophene was shown to have equal or slightly less reactivity than each of the monomers chosen as comonomers.

Introduction

We have been investigating the copolymerization of vinyl heterocycles for quite some time (1-4), attempting to ascertain the effect of the heteroatom and various ring substituents on the activity, in terms of copolymerization, of vinyl heterocycles. In some cases we have found that the position and type of ring substituent has a significant effect on the reactivity of the vinyl heterocycle in question. Also, the position of the vinyl group relative to the heteroatom can have a significant effect on vinyl heterocycle reactivity (5,6). In general 3-vinyl heterocycles are less reactive than 2-vinyl heterocycles and electron withdrawing or releasing groups enhance the reactivity dependent on which type of comonomer is chosen (i.e. these with electron rich double bond or electron poor double bonds). Recently, we have found that alkyl substitution of the ring of 3-vinyl heterocycles enhances the ease (rate) of homopolymerization of these materials relative to the unsubstituted parent vinyl heterocycle. In fact, in some cases, such substitution results in materials that polymerize with more facility than unsubstituted 2-vinyl heterocycles (5-7). In order to investigate further the effect of substitution on the copolymerization of vinyl heterocycles we synthesized 2,5- dimethyl-3-vinylthiophene (DMVT) and investigated its copolymerization with such commonly available monomers as methyl methacrylate, styrene and isobutyl methacrylate. The following is an account of our work to date.

Experimental

General

All solvents and chemicals used in this work were reagent grade and were utilized without further purification unless otherwise noted. Spectra were recorded on $CDCl_3$ solutions (5-10% w/v) of polymer at ambient temperature with a Varian Gemini 300 FT NMR. Peak areas were determined by electronic integration and by tracing on high quality paper, cutting out and weighing the tracings on a 5-place analytical balance. Molecular weights were measured as previously described (1-4).

Monomer Synthesis

The monomer was synthesized by dehydration of the alcohol formed from the $NaBH_4$ reduction of 3-acetyl-2,5-dimethylthiophene. The dehydration was by the method of Brooks (8). The monomer was purified by distillation from CaH_2, (b.p. = 58-60° at 10 mm) ^1H-NMR, $CDCl_3$; δ5.33 (s. 1H); δ 6.14 (m. 1H); δ 4.98-4.64 (2H, AB quartet); δ 1.92 (s. 3H); δ 1.88 (s. 3H).

Copolymer Synthesis

The copolymers were synthesized by weighing the desired amounts of comonomers into clean, dry screw cap vials followed by 0.5% AIBN. The monomer initiator solutions were sparged with dry N_2 while cold (evaporation loss 0.5%) and the vials were sealed with teflon lined screw caps. The vials were then placed in a thermostated water bath at 65°C for the desired length of time. The vials were removed from the bath and 5 ml of cold CH_3OH was added to precipitate any polymer formed. The copolymers were purified by reprecipitating from $CHCl_3$ solution into CH_3OH three times.

Results and Discussion

Polymerization conditions and copolymerization results are summarized in Table 1.

The composition data in Table 1 was analyzed using a nonlinear least squares error-in-variables method as previously described (1-4,9,10). Briefly, this method considers all errors in the measured variables as joint errors and yields reactivity ratios as point values with joint confidence areas, as shown in Figures 1 and 2. The point values for the reactivity ratio (represented by the '+' symbol in the Figures) are given in Table 2. The error in measuring feed compositions was estimated at 1.2% in each case. The error in determining copolymer composition was estimated as 15% for DMVT/MMA, 20% for DMVT/styrene and 20% for DMVT/IMBA.

TABLE 1

Copolymerization Conditions and Results

Polymer	M_1[a]	M_2	M_f of M_1 in Feed	M_f of M_2 in Feed	PZN Time (h)	% Conv. (wt%)	M_n	M_w	M_f of M_1 in Copolymer
DMVM1	DMVT	MMA	0.09	0.91	0.5	5.0	118000	211000	0.17
DMVM2	DMVT	MMA	0.19	0.81	0.5	6.4	78000	141000	0.27
DMVM3	DMVT	MMA	0.26	0.74	0.5	3.8	67000	119000	0.32
DMVM4	DMVT	MMA	0.35	0.65	0.5	6.9	58000	100000	0.41
DMVM5	DMVT	MMA	0.41	0.59	0.5	4.5	58000	104000	0.45
DMVM6	DMVT	MMA	0.49	0.51	0.5	4.2	54000	101000	0.48
DMVM7	DMVT	MMA	0.56	0.44	0.5	5.0	52000	92000	0.54
DMVM8	DMVT	MMA	0.71	0.29	0.5	4.2	50000	87000	0.63
DMVM9	DMVT	MMA	0.79	0.21	0.5	3.1	44000	81000	0.69
DVTS1	DMVT	Styrene	0.12	0.88	0.75	3.6	46000	80000	0.15
DVTS2	DMVT	Styrene	0.20	0.80	0.75	1.9	43000	75000	0.22
DVTS3	DMVT	Styrene	0.28	0.72	0.75	3.3	43400	74000	0.28
DVTS4	DMVT	Styrene	0.38	0.62	0.75	3.5	40500	73000	0.36
DVTS5	DMVT	Styrene	0.44	0.56	0.75	3.7	40000	72000	0.42
DVTS6	DMVT	Styrene	0.52	0.48	0.75	3.6	36000	61000	0.50
DVTS7	DMVT	Styrene	0.72	0.28	0.75	2.7	35000	62000	0.68
DVTS8	DMVT	Styrene	0.80	0.20	0.75	3.7	28200	54000	0.77
DVMI1	DMVT	IBMA	0.17	0.83	0.75	5.2	68000	120000	0.35
DVMI2	DMVT	IBMA	0.27	0.73	0.75	1.7	55300	102000	0.37
DVMI3	DMVT	IBMA	0.35	0.65	0.75	3.6	51000	89000	0.43
DVMI4	DMVT	IBMA	0.43	0.57	0.75	2.9	47000	82000	0.48
DVMI5	DMVT	IBMA	0.53	0.47	0.75	5.9	55000	95000	0.57
DVMI6	DMVT	IBMA	0.81	0.19	0.75	2.0	32000	63000	0.71
DVMI7	DMVT	IBMA	0.85	0.15	0.75	3.8	41000	75000	0.74

TABLE 2

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
DMVT	MMA	0.40	0.45	0.18
DMVT	Styrene	0.71	0.81	0.58
DMVT	IBMA	0.38	0.25	0.095

The reactivity ratio values obtained show that both styrene and MMA are more reactive than DMVT while DMVT is more reactive than IBMA. However, in all cases the differences in reactivity are relatively small. The r_1r_2 values for DMVT/MMA and DMVT/IBMA are small indicating some tendency toward alternation. As a further gauge of this tendency, Pyun's equations (11) were used to estimate average sequence lengths for some of the copolymers evaluated in this study. The results obtained are listed in Table 3.

TABLE 3

Average Sequence Lengths

Polymer	r_1	r_2	μ_1[a]	μ_2
DMVM1	0.40	0.45	1.08	3.19
DMVM3	0.40	0.45	1.19	1.96
DMVM6	0.40	0.45	1.54	1.58
DMVM9	0.40	0.45	1.89	1.20
DVTS1	0.71	0.81	1.13	5.59
DVTS4	0.71	0.81	1.40	2.44
DVTS7	0.71	0.81	2.51	1.38
DVTS8	0.71	0.81	3.38	1.24
DVMI1	0.38	0.25	1.20	1.46
DVMI3	0.38	0.25	1.29	1.33
DVMI5	0.38	0.25	1.50	1.19
DVMI7	0.38	0.25	2.08	1.09

μ_1 = average sequence length of M_1
μ_2 = average sequence length of M_2

The average sequence length show the DMVT/IBMA copolymers to be the most alternating, followed by DMVT/MMA and DMVT/Styrene.

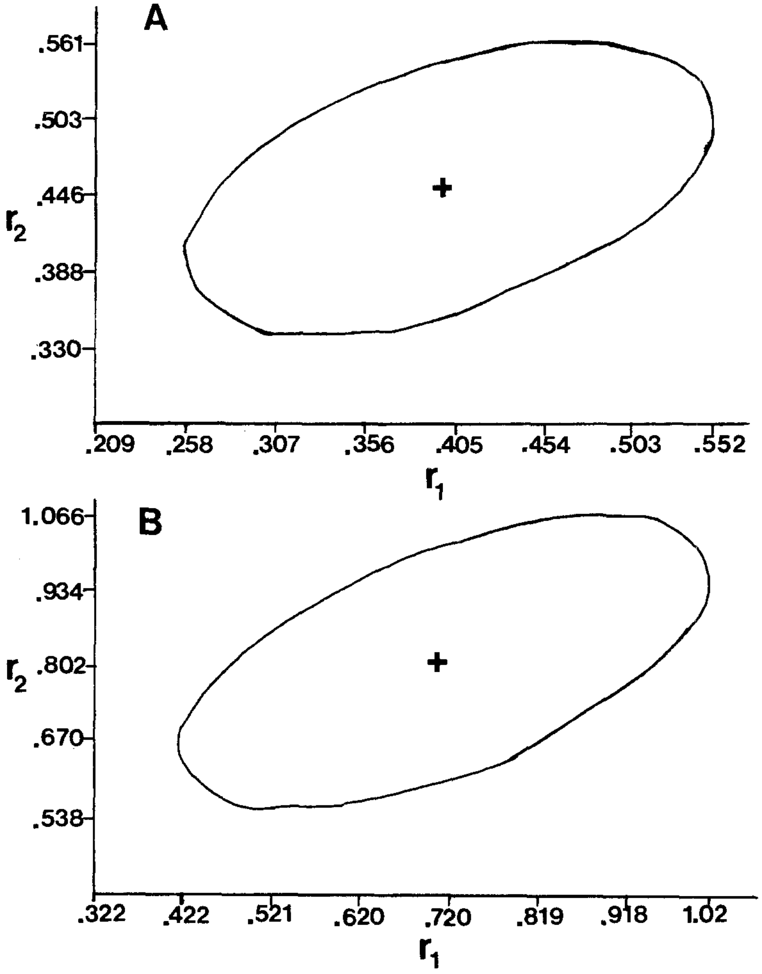

Figure 1

Joint confidence intervals, 95% confidence level for:
A) DMVT/MMA; B) DMVT/Styrene

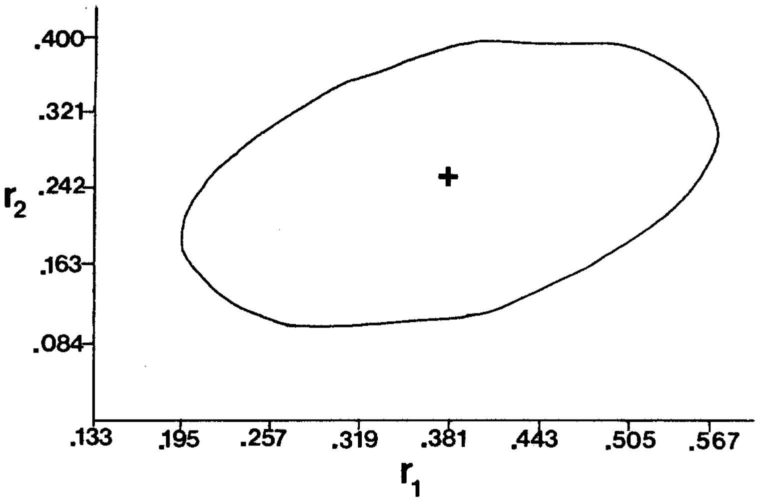

Figure 2

Joint confidence interval, 95% confidence level for DMVT/IBMA

Conclusions

A dimethyl-3-vinylthiophene monomer was synthesized and copolymerized with some commonly available monomers. The reactivity ratios show DMVT to be approximately equal in reactivity to all the comonomers used in this study. This is in contrast to unsubstituted 2- and 3-vinyl heterocycles which are typically more reactive, sometimes much more reactive, than most acrylate and styrene monomers (1-4). However, DMVT copolymerizations proceed to higher conversions in shorter reaction times. This behavior is expected for monomers of nearly equal reactivities, as in copolymerizations of two monomers with significantly different reactivities, the more reactive monomer can actually serve as an inhibitor at certain feed concentrations (12).

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