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Copolymerization behavior of 2-vinylselenophene

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Summary

2-Vinylselenophene was synthesized and its copolymerization 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 these preliminary experiments indicate that 2-vinylselenophene is a very reactive monomer, approximately as reactive as 2-vinylthiophene in copolymerizations with methyl methacrylate and n-butyl acrylate.

Introduction

The first synthesis of and the initial investigation of the polymerization behavior of 2-vinylselenophene was by Yurev, et. al. (1-3). However, no work on the copolymerization behavior of 2-vinylselenophene has been reported, and since wa have recently been engaged in studying the copolymerization behavior of vinyl heterocycles (4-8), it was thought that it would be of interest to investigate the copolymerizatiion of 2-vinylselenophene, particularly in order to more fully evaluate the effect of the heteroatom on the copolymerization behavior of a vinyl heterocycle (8). This paper reports our initial results concerning the copolymerization of 2-vinylselenophene with the commonly available monomers methyl methacrylate (MMA) and n-butyl acrylate (BA).

Experimental

General

All solvents were reagent grade and were used as received. The MMA and BA were purified by distilling three times from CaH_2. The monomers were stored in tightly capped flasks under nitrogen and kept in a refrigerator at -5^oC until used. The ^1H-nmr spectra were recorded at 90 MHz on $CDCl_3$ solutions of polymer (5-7% w/v) at ambient temperature using a Perkin-Elmer R32 spectrometer operating in the CW mode. The molecular weights were measured with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. A polystyrene calibration curve was employed to obtain numerical values for the molecular weights.

Monomer Synthesis

The monomer was synthesized from selenophene (Aldrich) via a Vilsmeier-Haack formylation and a Wittig reaction (9,10). The carboxaldehyde was synthesized in 52% yield and was purified by distillation b.p. = 50-52°/2.0 mm (lit b.p. 60-61°/m mm) (11). ^{1}H-Nmr, $CDCl_3$; δ7.20 (t, 1H); δ7.76 (d, 1H); δ8.25 (d, 1H); δ9.50 (s., 1H). A Wittig reaction on the aldehyde gave 2-vinylselenophene in 43% yield. The 2-vinylselenophene was purified by distillation (3 times) and was 99%+ pure by GC analysis. B.p. = 59-60°/25 mm (lit. b.p. = 69-70°/26 mm) (1). ^{1}H-Nmr, $CDCL_3$; δ 4.90-5.45 (AB quartet, 2H); δ6.45-6.75 (4 s.s., 1H); δ 6.95 (m, 2H); δ7.55 (d, 1H).

Polymer Synthesis

Polymers were synthesized by employing a feed concentration ladder as summarized in Table 1. Typically, the desired amounts of comonomers were weighed into a clean, dry screw cap vial and 0.8 wt % recrystallized (CH_3OH) Vazo-67 was added. The monomer mixture was sparged with dry nitrogen while cold (-50°C) to minimize evaporation losses ($<$ 1%), and the vials were tightly capped with teflon lined caps. The vials were then placed in a thermostated water bath for the desired length of time. The polymerizations were terminated by removing the vials from the bath and adding 4-5 ml of cold CH_3OH to the contents. The copolymers were purified by reprecipitaiton from $CHCl_3$ solution into excess CH_3OH (2 times). The polymers were dried in vacuo at room temperature for 48h. The conversions were determined gravimetrically.

Results and Discussion

The results obtained are summarized in Table 2.

The results presented in Table 2 are the average of duplicate measurements. The copolymer composition data was obtained from the ^{1}H-nmr spectra of the copolymers. The composition was determined by comparing the areas of signals at δ6.60-8.00 with signals at δ0.70-4.50 for the MMA copolymers and signals at δ6.10-7.90 with signals at δ0.75-4.45 for the BA copolymers. Peak areas were determined by tracing on high quality paper, then cutting and weighing the tracings.

The copolymer composition data was then analyzed using a nonlinear least squares error-in-variables method (4-8, 12, 13). This method accounts for the errors in the measured values in a copolymerization experiment and treats the subsequent error in the reactivity ratio values as a joint error. The error in determining feed concentration was estimated as 1.5% for both the BA and MMA copolymers. For the MMA copolymers the error in determining composition was estimated as 8.0%; for the BA copolymers the error in determining co-

TABLE 1

Summary of Polymerization Conditions

Polymer[a]	M_f[b] of Vinyl Selenophene	M_f of MMA in Feed	M_f of BA in Feed	Pzn Time (h)	Convers. (wt %)
VSEM 1	0.115	0.885	-	5.5	1.0
VSEM 2	0.169	0.831	-	5.5	1.5
VSEM 3	0.184	0.816	-	5.5	2.0
VSEM 4	0.521	0.479	-	5.5	3.6
VSEM 5	0.681	0.319	-	5.5	5.9
VSEM 6	0.734	0.266	-	5.5	4.1
VSEB 1	0.189	-	0.811	6.5	1.8
VSEB 2	0.243	-	0.747	6.5	2.7
VSEB 3	0.364	-	0.636	6.5	3.3
VSEB 4	0.439	-	0.561	6.5	5.0
VSEB 5	0.676	-	0.324	5.6	3.0
VSEB 6	0.822	-	0.178	6.5	5.4

[a] VSEM = 2-vinylselenophene/MMA copolymers; VSEB = 2-vinylselenophene/BA copolymers.

[b] M_f = mole fraction.

TABLE 2

Copolymer Compositions and Molecular Weights

Polymer	M_f VSEL[a] in Polymer	M_f MMA in Polymer	M_f BA in Polymer	M_n	M_w	M_w/M_n
VSEM 1	0.511	0.489	-	3200	5900	1.89
VSEM 2	0.579	0.421	-	3600	6400	1.78
VSEM3	0.585	0.415	-	3500	6500	1.86
VSEM 4	0.776	0.224	-	2900	5600	1.93
VSEM 5	0.846	0.154	-	5100	8700	1.71
VSEM 6	0.872	0.128	-	6900	12600	1.83
VSEB 1	0.563	-	0.437	4400	7900	1.80
VSEB 2	0.573	-	0.427	4600	8000	1.74
VSEB 3	0.713	-	0.287	3800	7000	1.84
VSEB 4	0.728	-	0.272	3200	6800	2.12
VSEB 5	0.880	-	0.120	5400	9900	1.83
VSEB 6	0.941	-	0.059	5900	12000	2.03

a. VSEL = 2-Vinylselenophene

polymer composition was estimated as 10.0%.

Figure 1 shows the joint confidence intervals at the 95% confidence level for the reactivity ratios. Table 3 summarizes the point estimates for r_1 and r_2[(+) symbol in the Figure].

TABLE 3

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
VSEL	MMA	2.09	0.0180	0.0380
VSEL	BA	3.16	0.1120	0.3540

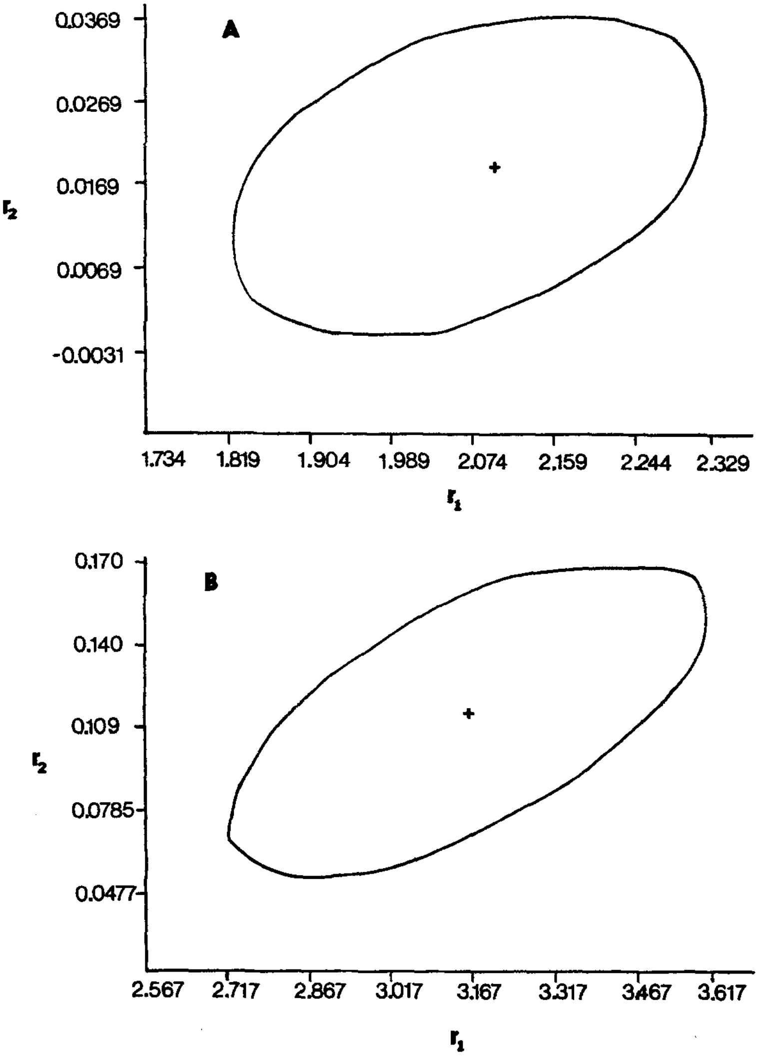

Figure 1: 95% joint confidence intervals for: A) VSel/MMA and B) VSel/BA copolymers.

Conclusions

Like most of the heterocyclic monomers studied to date (4-8), 2-vinylselenophene is a very reactive monomer. The growing chain end, no matter it's identity, prefers to add 2-vinylselenophene. The joint confidence intervals are somewhat large, reflecting the degree of error involved in determining copolymer composition, however, the values of the reactivity ratios are believed to be reasonable estimations. More reliable values can be obtained through designed experiments (4-8, 13) and such experiments are currently in progress.

The molecular weights of the polymer obtained are low in general, increasing with increasing feed concentration of 2-vinylselenophene. This may reflect chain transfer or termination phenomena of some kind, possibly involving the selenium atom, but more detailed experiments will be necessary before any explaination can be advanced with certainty.

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