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The copolymerization behavior of *N*-methyl-2-vinylpyrrole

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Summary

N-Methyl-2-vinylpyrrole was copolymerized with methyl methacrylate and n-butyl acrylate according to an experimental design scheme. The results of the experiment were analyzed by, and reactivity ratios calculated from, a nonlinear least squares error-in-variables method. The N-methyl-2-vinylpyrrole (NMVP) proved to have reactivity approximately equal to that of methyl methacrylate (MMA) but was much more reactive than n-butyl acrylate (BA).

Introduction

For some time we have been investigating the polymerization and copolymerization behavior of vinyl heterocycles. Most of our work has concerned heterocycles based on sulfur as the heteroatom (1-4). Recently, we have begun to investigate vinyl heterocycles with O or Se as the heteroatom (5,6). The selenium materials have reactivities similar to vinylthiophenes in copolymerizations with MMA and BA while the oxygen containing material (2-vinylfuran) is somewhat less reactive than the vinylthiophenes, particularly in copolymerizations with MMA. In order to more fully evaluate the effect of the heteroatom on copolymerization activity, we decided to investigate the copolymerization behavior of a N containing heterocycle. Specifically, we were interested in a five-membered ring, so we decided to synthesize a vinylpyrrole and chose N-methyl-2-vinylpyrrole. Previous experience with 2-vinylpyrrole and its polymer (7) indicated a sensitivity to air and light that produced an insoluable material relatively rapidly. Since it was thought that the hydrogen atom attached to the ring nitrogen played some role in the crosslinking reaction, we decided to synthesize an N-substituted vinylpyrrole for our copolymerization studies.

Experimental

General

All solvents were reagent grade and were used without further purification. The MMA and BA were distilled three times from CaH_2 and were stored under nitrogen in tightly stoppered flasks at $-5^{o}C$ until used.

The ^{1}H-nmr spectra and GPC measurements were made as previously described (1-6).

Monomer Synthesis

The N-methyl-2-vinylpyrrole was synthesized from the corresponding 2-carboxaldehyde (Aldrich) via a Wittig reaction (7). The monomer was purified by distillation, b.p. = 60-61^o/10 mm. ^{1}H-Nmr $CDCl_3$; δ 1.78 (s., 3H); δ 4.90-5.50 (AB quartet, 2H); δ 6.30 (m., 2H); δ 6.72 (m, 2H).

Polymer Synthesis

The polymers were synthesized according to the design scheme proposed by Tidwell and Mortimer (8). First, copolymers are synthesized according to a feed concentration 'ladder' i.e. the feed concentrations of M_1 and M_2 are varied in a systematic manner. Reactivity ratios are then calculated from analysis of copolymer composition. The values of r_1 and r_2 are then used to calculate monomer feed concentrations for the experimental design scheme. The feed concentrations of M_1 (NMVP) so obtained are given in Table 1.

TABLE 1

Monomer Feed Concentrations

M_1	M_2	$f_1{}'^a$	f_1''	f_1^{**}
NMVP	MMA	0.904	0.0520	0.104
NMVP	BA	0.752	0.2330	-

a. f values are mole fractions of M_1 in the feed.

Four polymerizations were performed at each feed concentration of M_1. Normally, only two different values are used (f_1' and f_1'') but for the NMVP/MMA copolymerizations a third value, f_1^{**} was included. The f_1'' value is quite low, and it is well known that low concentrations of very reactive monomers can inhibit polymerizations to the point where no polymer is formed (9). In this case an f_1^{**} value was chosen at which, as was known from previous experience, that a reasonable quantity of polymer would be formed. Additionally, the value chosen is relatively close to the value of f_1'' dictated by the experimental design scheme and so could be used in place of f_1'' should no polymer be formed at that feed concentration of M_1. If polymer is formed at all three feed concentrations then the f_1^{**} copolymers provide an additional measure of accurracy for the design scheme.

The polymerizations were performed by weighing the desired amounts of comonomer into clean, dry, screw cap vials. Vazo-67 (0.8 wt %) was then added and the monomer mixture was sparged with dry N_2 while cold (-50^oC) to minimize evaporation losses (1%). The vials are then tightly capped with teflon lined caps and placed in a thermostated water bath (65^o) for the desiged length of time. Polymerizations were terminated by removing the vials from the water bath and adding 3-4 ml of cold CH_3OH to the contents of the vial. The polymers were purified by reprecipitation from $CHCl_3$ solution into an 8-fold excess of CH_3OH, a process that was repeated 3 times. The polymers were dried in vacuo at ambient temperature and conversions were determined gravimetrically.

Results and Discussion

The results obtained are summarized in Table 2. The results presented in Table 2 are the average values obtained for the 4 copolymerizations performed at each feed concentration of M_1. However, for the purpose of calculating r_1 and r_2 through the error-in-variables analysis method, each copolymerization was treated as an individual datum.

The values obtained for r_1 and r_2 are given in Table 3. The joint confidence intervals for r_1 and r_2 at the 95% confidence level are shown in Figure 1. The point estimates for r_1 and r_2 are represented by the (+) symbols and these are the values given in Table 3.

TABLE 3

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
NMVP	MMA	0.385	0.1060	0.0302
NMVP	BA	0.695	0.0348	0.0242

The results for the NMVP/MMA copolymerization show that these monomers possess approximately equal reactivity. The low values for r_1, r_2 and r_1r_2 indicate that NMVP/MMA copolymers have a strong tendency towards alternation. For the NMVP/BA copolymerization the results show NMVP

TABLE 2

Copolymerization Results

Polymer	M_1	M_2	M_f[a] of M_1 in Feed	Polymerization Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f of M_1 in Copolymer
NMVPM 1-4	NMVP	MMA	0.9040	4.0	5.80	14000	26000	1.86	0.770
NMVPM 5-8	NMVP	MMA	0.0520	4.0	8.99	34900	52000	1.49	0.265
NMVPM 9-12	NMVP	MMA	0.1040	4.0	5.90	25400	37300	1.47	0.335
NMVPB 1-4	NMVP	BA	0.7520	4.5	10.00	16000	26000	1.63	0.755
NMVPB 5-8	NMVP	BA	0.233	4.5	7.00	37900	6000	1.58	0.521

a. M_f = mole fraction.

to be much more reactive than BA, a result similar to what has been obtained in other vinyl heterocycle/BA copolymerizations. However, in the present case the difference is somewhat less pronounced than for other vinyl heterocycles, particularly sulfur containing vinyl heterocycles. The low value of r_1r_2 indicates a tendency toward alternation. Using Pyun's (10) equations average sequence lengths of the comonomers for each group of copolymers were calculated and the results are summarized in Table 4.

TABLE 4

Average Monomer Sequence Lengths

Polymer	M_1	M_2	μ_1[a]	μ_2
NMVPM 1-4	NMVP	MMA	1.95	1.03
NMVPM 5-8	NMVP	MMA	1.10	1.29
NMVPM 9-12	NMVP	MMA	1.14	1.21
NMVPB 1-4	NMVP	BA	3.14	1.01
NMVPB 5-8	NMVP	BA	1.75	1.03

a. μ_1 and μ_2 = average sequence lengths of M_1 and M_2 respectively.

The values presented in Table 4 confirm the strong alternating tendency of NMVP/MMA copolymers, with sequence lengths of less than two being obtained for NMVP even at very high feed concentrations. For the NMVP/BA copolymers the alternation tendence is less pronounced, but still evident as even at feed concentrations of 75 mol % NMVP the average sequence length for NMVP is only 3.

Using literature values of Q and e for MMA and BA (11), Q and e values for NMVP were calculated and these are summarized in Table 5.

TABLE 5

Q and e Values for NMVP

M_1	M_2	Q	e
NMVP	MMA	15.6	2.27
NMVP	BA	56.5	2.78

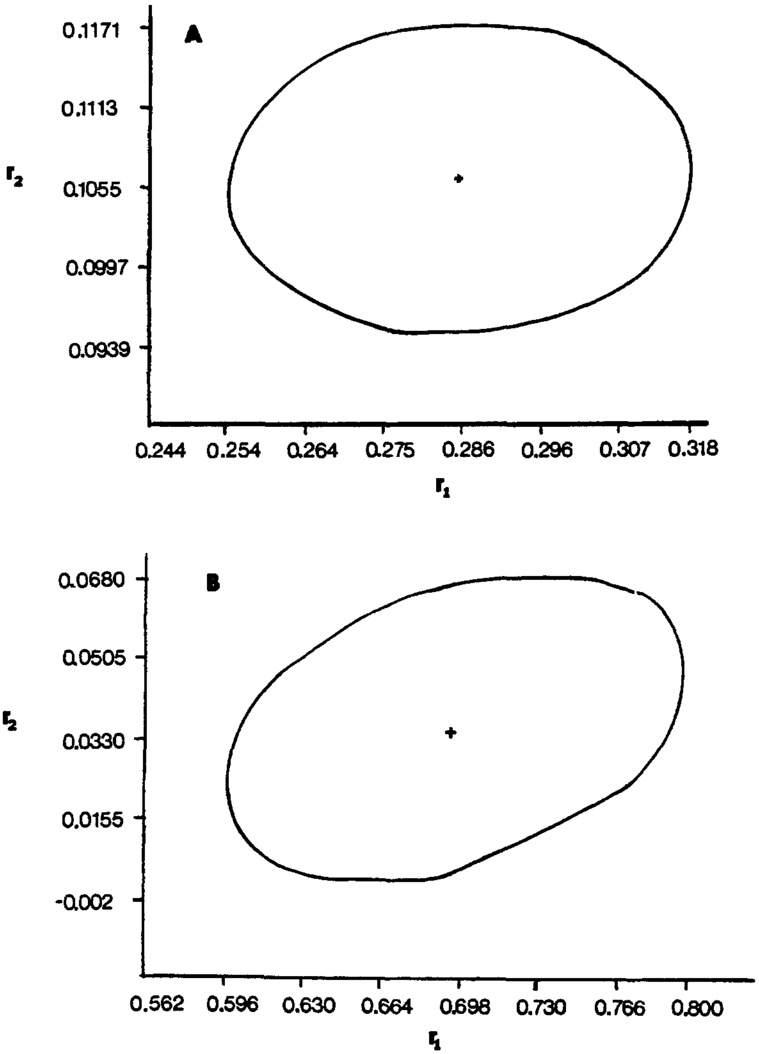

Figure 1: The joint confidence intervals for r_1 and r_2 of: A) the NMVP/MMA monomer pair and, B) the NMVP/BA monomer pair.

Conclusions

Copolymers of N-methyl-2-vinylpyrrole with methyl methacrylate or butyl acrylate have been synthesized according to an experimental design scheme. The data collected was analyzed by and reactivity ratios calculated with, a nonlinear least squares error-in-variables method. The values obtained for r_1 and r_2 indicate that NMVP and MMA have approximately equal reactivity and their copolymers have a strong tendency to alternate, even at high feed concentrations of NMVP or MMA. This result is similar to our earlier results obtained with 3-vinylthiophene/MMA copolymers (3), but contrasts with results obtained for 2-vinylthiophene/MMA copolymers (4), which show the vinyl heterocycle to be significantly more reactive than MMA. The NMVP/BA results follow the trend of results obtained to date for vinyl heterocycle/BA copolymerizations, i.e. the vinyl heterocycle is much more reactive than BA.

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