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Copolymerization of 3-methyl-2-vinylthiophene with methyl methacrylate and ethyl acrylate

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Summary

The copolymerization behavior of 3-methyl-2-vinylthiophene with methyl methacrylate or ethyl acrylate in bulk, using free radical initiation was investigated. The copolymerizations were performed according to the experimental design scheme of Mortimer and Tidwell (1). The experimental results were analyzed by using a nonlinear least squares error-in-variables method. In both cases the 3-methyl-2-vinylthiophene proved to be the more reactive monomer.

Introduction

For some time we have been investigating the copolymerization behavior of vinyl heterocycles with common acrylate and/or methacrylate monomers (2-7). We have found in all cases that the vinyl heterocycle is the more reactive monomer. We have also found that substituents on the heterocyclic ring enhance the reactivity of these monomers relative to the unsubstituted vinyl heterocycles. Our data shows (3-5) that electron withdrawing substituents on the ring yield more reactive monomers than electron releasing substituents, although both types are more reactive than the unsubstituted parent heterocycle. The data also shows that the position of the substituent relative to the vinyl group also plays a role in determining relative reactivity. We recently (7) published the results of a study of the copolymerization behavior of 5-methyl-2-vinylthiophene, and we thought it would be interesting to examine the copolymerization behavior of 3-methyl-2-vinylthiophene (3MVT) for comparison purposes.

Experimental

General

All solvents and reagents used in this study were reagent grade and, unless otherwise noted, were used without further purification. The 3-methylthiophene-2-carboxaldehyde was obtained from Aldrich and used as received. The AIBN was also obtained from Aldrich and was recrystallized from CH_3OH. Copolymer compositions were determined by ^{1}H-nmr spectroscopy on 10% w/v solutions of polymer in $CDCl_3$ with TMS added as an internal standard. The spectrometer was a Varian Gemini 300 FT NMR. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100A microstyragel columns. Numerical values for the molecular weights were obtained from a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from the carboxaldehyde via a Wittig reaction as previously described (8). The monomer was purified by distillation from CaH_2, b.p. = 73-75°/40 mm Hg. All monomers were purified by distillation from CaH_2 immediately before use.

Polymer Synthesis

The copolymers were synthesized according to the experimental design scheme of Mortimer and Tidwell. The required amount of 3MVT was weighed into a clean, dry screw cap vial followed by the required amount of comonomer. The AIBN (0.8 wt %) was then added and the mixture was sparged with dry N_2 while cold to minimize evaporation losses (1%). The vials were then tightly sealed with a teflon lined screw cap and placed in a thermostated water bath at 70°C for the desired length of time. The polymerizations were terminated by removing the vials from the bath, cooling and adding CH_3OH to the MMA copolymerizations and hexane to the EA copolymerizations. The copolymers were purified by reprecipitating them twice from $CHCl_3$ solution into either CH_3OH (MMA) or hexane (EA). The polymers were dried in vacuo for 72h at 28°C and then weighed to determine conversion.

Results and Discussion

As previously stated these copolymerizations were performed under the experimental design scheme of Mortimer and Tidwell. Briefly, the method involves doing ladder polymerizations first to obtain approximate values of r_1 and r_2. These values of r_1 and r_2 are then used to calculate two different feed compositions at which 4 or 5 copolymerizations are performed. For the 3MVT-MMA monomer pair the values were $f_1' = 0.49$ and $f_1'' = 0.052$. The f values are the mole fractions of 3MVT in each of the two feed compositions. For the 3MVT-EA monomer pair the values were $f_1' = 0.82$ and $f_1'' = 0.065$. Five copolymerizations were performed at each feed composition given. The data obtained are summarized in Table 1.

The values presented in Table 1 (MW's, Conversion, and M_f of 3MVT in copolymer) are the average of the values obtained for each individual copolymer. However, for the calculation of reactivity ratios, the composition of each copolymer was considered as an individual data point. The reactivity ratios were calculated using an error-in-variables method as previously described (3-6).

TABLE 1

Copolymerization Conditions and Results

Polymer	^aM_f 3MVT in feed	Pzn Time (hr)	Conv. Wt. %	M_n	M_w	M_w/M_n	M_f 3MVT in Copolymer
3MVT-MMA 1-5	0.49	4.0	6.0	7400	10500	1.42	0.58
3MVT-MMA 6-10	0.052	5.5	8.0	6600	11000	1.67	0.26
3MVT-EA 1-5	0.82	2.5	7.8	7600	13400	1.76	0.86
3MVT-EA 6-10	0.065	4.5	6.3	7700	12600	1.64	0.34

Briefly, the method calculates reactivity ratios and a joint error confidence limit by taking the errors in all the measured variables into account. The error in weighing the monomer into the polymerization vials was estimated as 1.5% for both the 3MVT-MMA monomer pair and the 3MVT-EA monomer pair. The error in measuring copolymers composition was estimated as 8.0% for the 3MVT-MMA copolymers and 7.0% for the 3MVT-EA copolymers. The values obtained for r_1 and r_2 are listed in Table 2. The joint confidence intervals at the 95% confidence level are shown in Figure 1.

TABLE 2

Reactivity Ratios

M_1	M_2	r_1	r_2
3MVT	MMA	0.58	0.11
3MVT	EA	1.16	0.078

The reactivity ratios show that 3MVT is the more reactive monomer in both cases. As was the case for other vinyl heterocycles the difference in the reactivity of 3MVT and MMA was less that the difference between 3MVT and EA. However, the values of r_1 and r_2 obtained for the 3MVT-MMA monomer pair are significantly different than the r_1 and r_2 values obtained for the 5-methyl-2-vinylthiophene-MMA monomer pair (7) which were $r_1 = 2.08$ and $r_2 = 0.20$ (5-methyl-2-vinylthiophene = M_1). The exact reason for this dramatic difference is unknown at the present time, but could be due to a number of factors, the most significant of which may be steric. The position of the methyl group on thiophene ring may serve to lessen the preference of the 3MVT for itself versus the MMA, i.e. the 3MVT and

MMA become less distinguishable to the growing polymer chain due to steric compresion about the vinyl group of 3MVT.

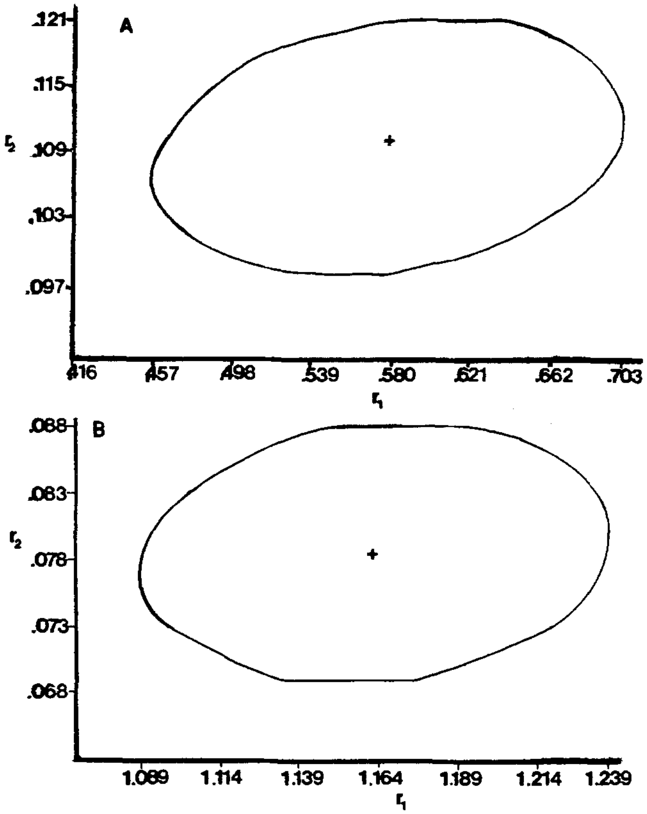

Figure 1

95% Joint confidence intervals for: A) MMA-3MVT monomer pair; B) EA-3MVT monomer pair. The + symbols are the values of r_1 and r_2 given in Table 2

Another factor could be electronic; the position of the methyl group changes the electron density around the double bond, hence its reactivity. The reactivity ratios for 3MVT-EA while comparable to reactivity ratios obtained for other vinyl heterocycle and BA or MA copolymers, are also lower than most of these other values particularly the value obtained for 3MVT in the present case.

Molecular orbital calculations might help to answer this question of differential reactivity. Such calculations are underway and will be the subject of future communications.

Conclusions

The copolymerization of 3-methyl-2-vinylthiophene was performed with methyl methacrylate or ethyl acrylate according to the experimental design scheme of Mortimer and Tidwell. The copolymer composition data was analyzed using a nonlinear least squares error-in-variables method. The 3-methyl-2-vinylthiophene proved to be the more reactive monomer in each case, but the differences in reactivity between the vinyl heterocyclic monomer and the MMA or EA were not as pronounced in the present case as the differences in copolymerizations of other vinyl heterocycles with MMA and acrylate monomers.

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