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Copolymerization behavior of 2-vinyl-5-methyl furan

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Summary

The title monomer was copolymerized with methyl methacrylate, isobutyl methacrylate n-butyl acrylate. The results of the copolymerization experiments were analyzed using a nonlinear least squares error-in-variables method in order to obtain reactivity ratios for each monomer pair. In all cases the 2-vinyl-5-methyl furan proved to be the more reactive monomer, although this monomer is not as reactive as some other vinyl heterocycles have proved to be in copolymerizations with these same or similar comonomers.

Introduction

Recently, we have been studying the effect of ring substitution on the copolymerization behavior and nmr spectra (relative to polymer stereochemistry assessment) of some vinyl heterocycles (1-6). We have found that ring substitution can have a significant effect on polymer nmr spectra and also can have an effect on monomer copolymerization behavior. We have recently summarized our studies of vinyl heterocycles in which the substituent was the methyl group in different positions on the heterocyclic ring relative to the vinyl group (7,8). We found that both the nmr spectra of the polymers and the copolymerization behaviors of the monomers is significantly different from the spectra and copolymerization behavior of the unsubstituted vinyl heterocycle. As these previous studies dealt primarily with thiophene based monomers, we thought it would be of interest to extend our studies to other vinyl heterocycles. In this paper we report results obtained using a substituted vinyl furan as the heterocyclic monomer.

Experimental

General

All solvents and reagents used in this study were purified by distillation from the appropriate drying agent (9). The AIBN was purified by recrystallization from CH_3OH. All the monomers used were purified by distillation from CaH_2. Polymer ^1H-NMR spectra were recorded at ambient temperature on $CDCl_3$ (5-8% w/v) solutions of polymer employing TMS as an internal standard. The spectrometer was a Varian Gemini 300 FT NMR. Copolymer compositions were determined by comparison of the appropriate peak areas which were measured by electronic integration and by tracing the signals on high quality paper, cutting out the tracings and weighing them on a five place analytical balance. The polymer molecular weights were measured with a GPC equipped with a Waters 510 pump, two Polymer Labs linear columns (total length = 180 cm), and a Waters 410 RI detector. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The 2-vinyl-5-methyl furan (2VFM) was synthesized and purified as previously described (7).

Polymer Synthesis

The copolymers were synthesized by weighing the desired amounts of the comonomers into a clean, dry screw cap vial. The monomer mixture was sparged with dry N_2 while cold (-15°C) to minimize loss by evaporation ($<1\%$). The initiator, AIBN, 0.8%, was then added and the vial was tightly sealed with a teflon lined screw cap. The vial(s) were placed in a thermostated waterbath at 65°C for the desired length of time. The polymerizations were terminated by the addition of 4 ml of cold CH_3OH to the contents of the vial. The copolymers were purified by reprecipitating them twice from $CHCl_3$ solution into excess CH_3OH. The copolymers were dried in vacuo at 25°C for 72-96hr and then weighed to determine conversions.

Results and Discussion

The polymerization conditions used and results obtained are summarized in Table 1.

The results were analyzed by employing a nonlinear least squares error- in-variables method (9,10). Briefly, this method accounts for all the errors in the measured variables and treats the error in r_1 and r_2 as joint error. The error in determining monomer feed compositions (weighing error) was estimated as 1.5% for the 2VFM-MMA monomer pair, the error in determining copolymer compositions for this pair was estimated as 15%. For the 2VFM-IBMA pair the weighing error was estimated as 1.5% and the error in determining copolymer composition was estimated as 10%. The weighing error for the 2VFM-BA pair was estimated as 2.0% while the composition error was estimated at 20%. Table 2 summarizes the point values of r_1 and r_2 obtained for each monomer pair. Figures 1 and 2 show the 95% joint confidence regions for each reactivity ratio pair.

TABLE 1

Polymerization Condition and Polymer Analysis Results

Polymer	M_1	M_2	$M_f M_1$ in Feed	$M_f M_2$ in Feed	Pzn Time (h)	Conv. (%)	M_n	M_w	$M_f M_1$ Copolymer	$M_f M_2$ Copolymer
5MVFM1	2VFM	MMA	0.33	0.67	6.5	7.2	11700	20100	0.48	0.52
5MVFM2	2VFM	MMA	0.48	0.52	6.5	7.8	5700	8200	0.59	0.41
5MVFM3	2VFM	MMA	0.62	0.38	6.5	6.6	10000	16700	0.71	0.29
5MVFM4	2VFM	MMA	0.71	0.29	6.5	10.3	9900	18500	0.76	0.24
5MVFM5	2VFM	MMA	0.80	0.20	6.5	1.9	7700	9600	0.79	0.21
5MVFI1	2VFM	IBMA[a]	0.22	0.78	6.0	6.9	5400	9500	0.46	0.54
5MVFI2	2VFM	IBMA	0.33	0.67	6.0	1.1	7700	14200	0.50	0.50
5MVFI3	2VFM	IBMA	0.45	0.55	6.0	8.2	3800	7400	0.59	0.41
5MVFI4	2VFM	IBMA	0.51	0.49	6.0	10.0	4500	7900	0.64	0.36
5MVFI5	2VFM	IBMA	0.63	0.37	6.0	9.7	20700	31100	0.66	0.34
5MVFI6	2VFM	IBMA	0.80	0.20	6.0	9.9	9800	20000	0.79	0.21
5MVFB1	2VFM	n-BA	0.24	0.76	6.0	7.1	12300	20400	0.45	0.55
5MVFB2	2VFM	n-BA	0.33	0.67	6.0	9.1	6700	12200	0.49	0.51
5MVFB3	2VFM	n-BA	0.39	0.61	6.0	9.9	25200	37100	0.50	0.50
5MVFB4	2VFM	n-BA	0.50	0.50	6.0	8.1	12400	23900	0.56	0.44
5MVFB5	2VFM	n-BA	0.86	0.14	6.0	1.1	7400	10300	0.77	0.23

a. IBMA = isobutyl methacrylate

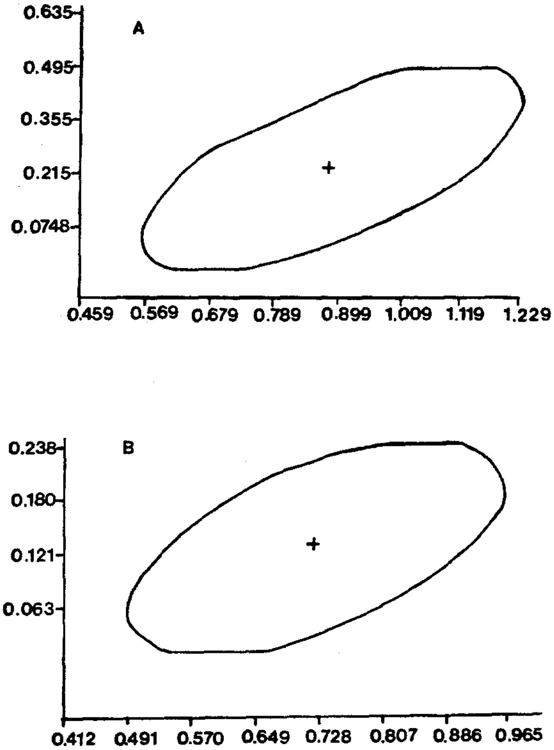

Figure 1

Joint confidence limits, 95% confidence level for
A) 2VFM-MMA monomer pair; B) 2VFM-IBMA monomer pair

TABLE 2

Reactivity Ratios

m_1	m_2	r_1	r_2	r_1r_2
2VFM	MMA	0.89	0.23	0.20
2VFM	IBMA	0.72	0.13	0.094
2VFM	n-BA	0.39	0.12	0.047

In all the cases the 2VFM is the more reactive monomer however, the 2VFM is significantly less reactive than its thiophene analog. For example, in copolymerization with MMA and BA the reactivity ratios of 2-vinyl-5-methyl thiophene (r_1) are 2.08 and 1.52 respectively (8).

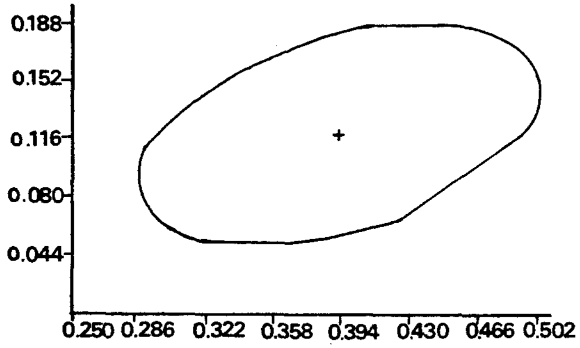

Figure 2

Joint confidence limit, 95% confidence level for the 2VFM-BA monomer pair

However, values of r_1 for 2-vinyl furan (2VF) in copolymerizations with MMA and BA are 0.21 and 1.76 respectively (11). So, while the values of r_1 might be considered to be generally low for 2VFM, the values obtained for 2VF and 2VFM in copolymerization with MMA are somewhat comparable. The values obtained for copolymerization with n-BA on the other hand are significantly different. At present there is no reasonable explaination for this result. Possibly the electronic character of the vinyl group in 2VFM is altered in such a way by the presence of the methyl group so as to be closer in reactivity to the double bond of butyl acrylate. The value of r_1r_2 for both the 2VFM-IBMA and 2VFM-BA monomer pair indicate some degree of alternation. To estimate the magnitude of this tendency some average sequence lengths were calculated using Pyun's equations (12). The results are summarized in Table 3.

As expected the 2VFM-BA monomer pair showed the most tendency toward alternation with 2/1 ratios of 2VFM-BA only being obtained at the highest feed ocncentration of 2VFM. In contrast this ratio is approximately obtained for low to moderate feed concentrations of 2VFM in the 2VFM-MMA copolymerization.

TABLE 3

Average Sequence Lengths

Polymer	r_1	r_2	μ_1[a]	μ_2
5MVFM1	0.89	0.23	1.82	1.25
5MVFM3	0.89	0.23	3.17	1.09
5MVFM5	0.89	0.23	4.35	1.06
5MVFI1	0.72	0.13	1.61	1.15
5MVFI3	0.72	0.13	2.04	1.09
5MVFI6	0.72	0.13	3.71	1.03
5VFFB1	0.39	0.12	1.32	1.15
5VFFB3	0.39	0.12	1.39	1.12
5VFFB5	0.39	0.12	2.30	1.04

a. μ_1 = aver. sequence length of monomer 1; μ_2 aver. sequence length of monomer 2

Conclusions

Copolymerization of 2-vinyl-5-methyl furan with MMA, IBMA or BA has been carried out and the reactivity ratios have been calculated using a nonlinear least squares error-in-variables method. In all cases the 2VFM was found to be the more reactive monomer, though it is somewhat less reactive than the corresponding thiophene based monomer. The data sets evaluated in the present case are somewhat limited, but the results obtained are not expected to vary significantly when broader or more complete data sets are used.

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