

Copolymerization Behavior of 2-Vinylbenzofuran: Copolymers of Ethyl Acrylate, *n*-Butyl Acrylate, and Methyl Methacrylate

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SYNOPSIS

The reactivity of 2-vinylbenzofuran in copolymerization reactions with *n*-butyl acrylate, ethyl acrylate, and methyl methacrylate was investigated. The vinylbenzofuran was found to be a very reactive monomer with the growing chain preferring to react with this monomer no matter what its terminus. Reactivity ratios were calculated using a nonlinear least squares error-in-variables method, which gives more reliable values of r_1 and r_2 .

INTRODUCTION

In the course of investigations into the stereochemistry of polyvinyl heterocycles¹⁻³ we discovered that little work had been done on the copolymerization behavior of these monomers. Accordingly, we undertook an investigation into the copolymerization behavior of several vinyl heterocycles,^{4,5} one of which was 2-vinylbenzofuran (2VBzF). 2-Vinylbenzofuran, while known as a monomer for more than four decades,^{6,7} has had, as far as could be ascertained by us, very little work of a quantitative nature done on its copolymerization behavior. 2-Vinylbenzofuran has been reported to copolymerize with butadiene, styrene, and 9-vinyl carbazole in emulsion polymerizations,^{8,9} but no values for reactivity ratios were given. We therefore undertook a study of the copolymerization behavior of 2VBzF with commonly used acrylate and methacrylate monomers. This paper summarizes some of our results.

EXPERIMENTAL

General

All solvents used in this study were reagent grade and were used without further purification. All the

monomers used were purified by three distillations from CaH_2 , with the last distillation performed immediately prior to use. AIBN was purified by recrystallization from methanol. ^1H -NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer operating at 90 MHz in the CW mode. The spectra were recorded at room temperature on 7% w/v solutions of the copolymers in CDCl_3 . Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 1×10^6 , 1×10^5 , 1×10^4 , 1×10^3 , 500, and 100 Å ultrastaygel columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The detector employed was the refractive index detector. Numerical values for the polymer molecular weights given in this article were determined by comparison with a calibration curve constructed using narrow molecular weight distribution polystyrene standards. Glass transition temperature measurements were made with a DuPont 2100 Thermal Analyzer at a scan rate of $15^\circ\text{C}/\text{min}$.

Monomer Synthesis

2-Vinylbenzofuran was synthesized via a published procedure^{10,11} and purified by distillation; bp $76\text{--}78^\circ\text{C}$ at 2.0 mm (lit. bp = $74^\circ\text{C}/1.8$ mm). Yield = 66%.

Copolymerization

Copolymer synthesis was accomplished by charging desired quantities of freshly distilled monomers into

clean, dry glass vials. AIBN (0.9 wt %) was added and the solution was sparged with nitrogen while cooling the vials in a dry-ice-acetone bath. The weight of the monomer(s) lost was less than 1.0% as determined by before and after weighings on a five place analytical balance. The vials were then tightly sealed with teflon lined caps and placed in a thermostated water bath at 65°C for the desired length of time. The feed ratios and reaction times are summarized in Table I. The polymerizations were terminated by removing the vials from the bath, quickly cooling to room temperature, and adding 2–3 mL of cold methanol. The polymers were purified by dissolution in CHCl_3 and precipitation into an eight-fold excess of methanol, a process that was repeated three times. The polymers were collected by filtration and dried *in vacuo* for 72 h at room temperature and then the polymers were weighed to determine conversions.

RESULTS AND DISCUSSION

The conversions, molecular weights, glass transition temperatures, and copolymer compositions are summarized in Table II. The polymer compositions

were calculated from $^1\text{H-NMR}$ data by comparing the areas of the aromatic proton resonances ($\delta = 6.5\text{--}7.5$) with the areas of the aliphatic proton resonances ($\delta = 0.7\text{--}4.0$). The areas were determined by electronic integration and by tracing the resonances on high quality paper, cutting out, and then weighing these tracings. Each of these area measurement techniques was repeated three times for each copolymer evaluated. The values summarized in Tables I and II are the average of three repetitions at each feed composition given. The data presented in Table II show that even at low feed concentrations the amount of 2VBzF in the copolymers is quite high. Also, increasing the 2VBzF feed concentration has the effect of gradually increasing the copolymer molecular weight and the polydispersity. Conversion, on the other hand, while sometimes increased with high 2VBzF feed concentration, does not generally seem that much affected by increasing 2VBzF feed concentrations.

The glass transition temperature also increases with increasing 2VBzF content in the copolymer. This is not surprising as the glass transition temperature of 2VBzF homopolymer was determined to be $115^\circ\text{C} \pm 2^\circ\text{C}$ (all glass transition temperatures

Table I. Monomer Feed Ratios and Reaction Times

Polymer	M_f^a 2VBzF in Feed	M_f EA ^b Feed	M_f BA ^b Feed	M_f MMA ^b Feed	Reaction Time (h)	Reaction Temperature (°C)
VBzFB1	0.10	—	0.90	—	5.0	65
VBzFB2	0.20	—	0.80	—	5.0	65
VBzFB3	0.25	—	0.75	—	5.0	65
VBzFB4	0.40	—	0.60	—	5.0	65
VBzFB5	0.55	—	0.45	—	5.0	65
VBzFB6	0.70	—	0.30	—	5.0	65
VBzFB7	0.85	—	0.15	—	5.0	65
VBzFM1	0.10	—	—	0.90	3.5	65
VBzFM2	0.15	—	—	0.85	3.5	65
VBzFM3	0.25	—	—	0.75	3.5	65
VBzFM4	0.35	—	—	0.65	3.5	65
VBzFM5	0.40	—	—	0.60	3.5	65
VBzFM6	0.43	—	—	0.57	3.5	65
VBzFM7	0.50	—	—	0.50	3.5	65
VBzFM8	0.60	—	—	0.40	3.5	65
VBzFM9	0.70	—	—	0.30	3.5	65
VBzFE1	0.12	0.88	—	—	4.0	65
VBzFE2	0.20	0.80	—	—	4.0	65
VBzFE3	0.32	0.68	—	—	4.0	65
VBzFE4	0.43	0.57	—	—	4.0	65
VBzFE5	0.52	0.48	—	—	4.0	65
VBzFE6	0.73	0.27	—	—	4.0	65

^a M_f = mole fraction.

^b EA = ethyl acrylate; BA = butyl acrylate; MMA = methyl methacrylate.

Table II. Copolymer Molecular Weights, Conversions, T_g , and Compositions

Polymer	Conversion (wt %)	M_n	M_w	M_w/M_n	M_f VBzF Polymer	T_g (°C)
VBzFB1	3.0	5700	6800	1.19	0.549	—
VBzFB2	6.0	5800	7400	1.28	0.728	67
VBzFB3	3.0	5800	7900	1.36	0.742	—
VBzFB4	4.0	7200	11200	1.56	0.849	91
VBzFB5	6.0	7100	11360	1.60	0.910	101
VBzFB6	5.0	15600	29000	1.86	0.937	106
VBzFB7	10.0	11000	18370	1.67	0.980	109
VBzFM1	2.0	5200	6200	1.19	0.498	105.8
VBzFM2	3.5	7400	10900	1.48	0.634	—
VBzFM3	2.5	5450	7250	1.33	0.699	106.6
VBzFM4	4.0	6800	9600	1.41	0.714	—
VBzFM5	3.0	6500	9400	1.45	0.789	—
VBzFM6	6.6	11500	18500	1.62	0.822	107
VBzFM7	3.0	10000	15600	1.56	0.840	—
VBzFM8	6.0	11500	18400	1.60	0.856	107.8
VBzFM9	7.5	13500	22000	1.63	0.902	108.9
VBzFE1	2.6	5500	6900	1.25	0.598	—
VBzFE2	3.5	5100	7700	1.35	0.703	69
VBzFE3	4.2	7000	10300	1.47	0.767	79
VBzFE4	4.0	9500	15000	1.58	0.838	85
VBzFE5	4.4	10400	17600	1.69	0.877	93
VBzFE6	7.2	17000	29800	1.75	0.940	—

in Table II are $\pm 2^\circ\text{C}$) and as the copolymers become richer in 2VBzF, the T_g approaches that of the homopolymer. In all cases the DSC showed a single transition.

The data in Table II were used to calculate reactivity ratios using a nonlinear least squares error-in-variables method.¹²⁻¹⁴ This method accounts for the error inherent in all the measured variables on which reactivity ratio calculations are based. For the cases considered in the present study the monomer weighing error was determined as 1.5% and the error in determining copolymer composition was determined as 3.0%. The values of r_1 and r_2 obtained for the monomer pairs evaluated in this study are summarized in Table III. The joint confidence intervals obtained are shown in Figures 1 and 2. The joint confidence intervals shown are those for the 95% confidence level. The confidence intervals are reasonably small, indicating that a reasonable amount of trust may be placed in the accuracy of the values

Table III. Reactivity Ratios

M_1	M_2	r_1	r_2	$r_1 r_2$
2VBzF	BA	6.718	0.0229	0.154
2VBzF	MMA	3.934	0.0238	0.0936
2VBzF	EA	5.669	0.0232	0.132

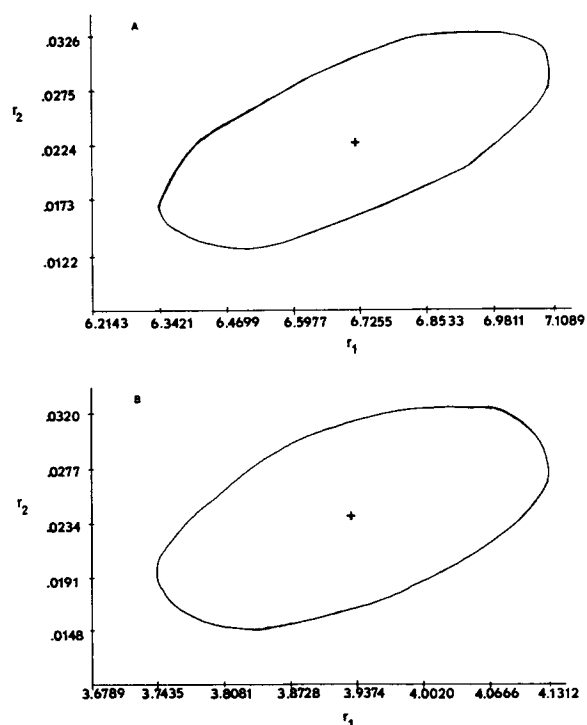


Figure 1. Joint confidence intervals for: (A) 2-vinylbenzofuran/*n*-butyl acrylate monomer pair; (B) 2-vinylbenzofuran/methyl methacrylate monomer pair. The (+) represents the point estimate of r_1 and r_2 which are values recorded in Table III.

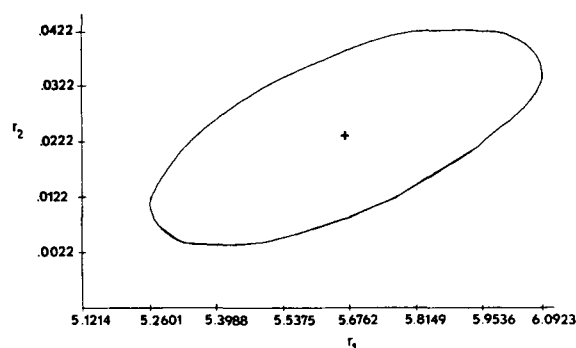


Figure 2. Joint confidence interval for the 2-vinylbenzofuran/ethyl acrylate monomer pair. The (+) represents the point estimate for r_1 and r_2 .

obtained for r_1 and r_2 . What these reactivity ratios show is that in all cases the growing polymer chain end much prefer to react with 2VBzF. The average sequence lengths for some of the copolymers were estimated using Pyun's equations,¹⁵ the results are summarized in Table IV.

CONCLUSION

A nonlinear least squares error-in-variables method has been used to evaluate the reactivity ratios for some 2VBzF copolymers. It is accepted that nonlinear least squares methods are more accurate than linear least squares methods for the determination of reactivity ratios^{13,14,16} and coupling a nonlinear least squares method with an error-in-variables method should increase the confidence in the values determined to an even greater extent.^{14,17}

In the cases of methyl methacrylate and ethyl acrylate comonomers the highest feed concentrations were 70 and 73 mol %, respectively. While it may be argued that higher concentrations in the feed

would produce a more accurate picture of copolymerization behavior, in the present case the concentration of 2VBzF in the copolymer is very high at these feed concentrations (> 90% in both cases) and it is doubtful that higher feed concentrations would significantly alter the results obtained.

The values of the reactivity ratios and the mean monomer sequence lengths show that 2VBzF is a very reactive monomer and that the copolymers formed are quite "blocky" in nature with long runs of 2VBzF being evident. Further work, including designed experimentation is in progress, in order to more thoroughly explore the reactivity of 2VBzF.

The author would like to thank Ms. M. Pack for the NMR spectra, Dr. C. Y. Kuo for the molecular weight measurements, and Mr. C. M. Neag for the glass transition temperature measurements.

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Table IV. Mean Monomer Sequence Lengths

Polymer	M_1 2VBzF Polymer	μ_1^a	μ_2^b
VBzFB1	0.549	9.17	1.02
VBzFB3	0.742	20.30	1.01
VBzFB6	0.937	99.80	1.00
VBzFM1	0.498	4.90	1.03
VBzFM3	0.699	10.13	1.01
VBzFM7	0.840	21.63	1.00
VBzFM9	0.907	39.33	1.00
VBzFE1	0.598	9.43	1.01
VBzFE3	0.767	19.66	1.01
VBzFE5	0.877	41.43	1.00

^a μ_1 = Mean sequence length of M_1 (2VBzF).

^b μ_2 = Mean sequence length of M_2 .

Received April 24, 1990

Accepted August 7, 1990