The Copolymerization of 3-Vinyl Pyridine

INTRODUCTION

For some time we have been engaged in a study of the polymerization behavior of vinyl heterocycles, particularly in regard to polymer stereochemistry.[1-5] During these investigations we have discovered that little data has been published concerning the copolymerization behavior of certain of these vinyl heterocycles. We have therefore undertaken a study of the copolymerization behavior of these monomers, some of the results of which have previously appeared.[6,7] In the case of 3-vinyl pyridine, we discovered that while a relatively large body of literature concerning the polymerization and copolymerization behavior of 2-vinyl and 4-vinyl pyridine existed,[8-11] virtually no published information existed concerning the copolymerization behavior of 3-vinyl pyridine.[12] We decided then to investigate the copolymerization behavior of 3-vinyl pyridine with the commonly available monomers, methyl methacrylate and n-butyl acrylate.

EXPERIMENTAL

General

All solvents and the methyl methacrylate and butyl acrylate were purified twice by distilling from the appropriate drying agent. The monomers and solvents were then stored under nitrogen in tightly sealed containers at $-5°C$ until used. The AIBN used was purified by recrystallization from methanol. ^{1}H-Nmr spectra were obtained at 90 MHz using a Perkin-Elmer R-32 CW instrument. The polymers were dissolved in 7–10% w/v concentration in $CDCl_3$ and the spectra were recorded at ambient temperature. 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 A ultrastyragel columns. Tetrahydrofuran was used as the eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized from the aldehyde via a Wittig reaction.[13] Purification was effected by twice distilling from CaH_2, b. p. = 64–65°C/20 mm Hg (lit b. p. = 62°C/20 mm Hg).[12] ^{1}H-Nmr in $CDCl_3$; δ 5.10–5.78 (AB quartet, 2H); δ 6.36–6.77 (m, 1H); δ 7.00–7.78 (m, 2H); δ 8.25–8.55 (m, 2H). Gas chromatography showed a monomer purity of >99% (the methyl methacrylate and butyl acrylate also showed this level of purity).

Polymer Synthesis

The copolymers were synthesized according to an experimental design scheme recommended by Tidwell and Mortimer.[14] In this scheme, eqs. (1) and (2) were used to define two initial feed levels for monomer 1; 3-vinyl pyridine in the present case, and then four or five copolymerizations are performed at each feed composition.

$$f'_1 = \frac{2}{2 + r_1} \qquad (1)$$

$$f''_1 = \frac{r_2}{2 + r_2} \qquad (2)$$

This method required initial estimates of r_1 and r_1. These estimates can be rough and can be obtained from the literature, or preliminary "ladder"-type copolymerizations can be performed. Ladder-type experiments are those wherein the feed concentration of M_1 is varied in a systematic fashion, for example, mole fraction of M_1 in the feed = 0.1, 0.2, 0.3, 0.4, etc. In the present case such experiments were performed and the results were analyzed using linear least squares techniques.[15] The estimates obtained for r_1 and r_2, and the calculated values for f'_1 and f''_1 are summarized in Table I.

Five polymerizations were performed at each of the feed compositions given in Table I, that is, five at each f'_1 value and five at each f''_1 value. The required amounts of monomer were weighed into clean, dry vials and AIBN (1.0 wt %) was added. The monomer mixture was then sparged with dry nitrogen while cold ($-20°C$) to minimize evaporation losses (< 0.7%). The vials were tightly capped with teflon lined caps and placed in a thermostated waterbath at $60 \pm 1°C$ for the desired length of time. Polymerizations were terminated by removing the vials from the bath, cooling with cold water, then adding 2–3 mL of cold diethyl ether. Polymers were purified by reprecipitation from $CHCl_3$ solution into 8–10 fold excesses of di-

Table I   Initial Estimates of r_1 and r_2 and Calculated f'_1 and f''_1 Values

Monomer 1	Monomer 2	r_1	r_2	f'_1	f''_1
3VP[a]	BA[b]	0.69 ± 0.14	0.61 ± 0.13	0.743	0.233
3VP	MMA[b]	0.45 ± 0.08	0.48 ± 0.07	0.816	0.195

[a] 3VP = 3-Vinyl pyridine.
[b] BA = Butyl acrylate, MMA = Methyl methacrylate.

Table II   Summary of Results

Polymer	M_f 3VP Feed	Pzn. Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f 3VP Polymer
3VP BA 1–5	0.743	1.0	8.25	27,200	47,500	1.73	0.707
3VP BA 6–10	0.233	2.0	8.75	54,000	82,300	1.52	0.400
3VP MMA 1–5	0.195	0.5	5.56	55,900	92,200	1.65	0.243
3VP MMA 6–10	0.816	0.5	7.74	24,300	46,200	1.90	0.705

ethyl ether, a process that was repeated three times. The polymers were collected by filtration and dried *in vacuo* at 35°C for 72 h. Conversion was determined gravimetrically.

RESULTS AND DISCUSSION

The results obtained are summarized in Table II. The results in the Table are the average of the five copolymerizations performed at each feed composition listed in Table I. Copolymer compositions were determined by comparing the area of the aromatic resonances ($\delta = 6.60$–8.45) to the area of the aliphatic resonances ($\delta = 0.55$–3.70).

In order to obtain reactivity ratios, the data was analyzed using a nonlinear least squares error-in-variables method.[16,17] This method accounts for the errors in all the measured variables in the copolymerization experiments. The error involved in weighing the monomers into the vials was estimated as 1.5%. The error involved in determining copolymer composition from the ^{1}H–nmr spectra was estimated as 7.0%. The values obtained for r_1 and r_2 are given in Table III. The 95% confidence level joint confidence limits are given in Figure 1. The values in Table III are the point estimates of r_1 and r_2 represented by the ($+$) symbol in the Figure.

The values for r_1 and r_2 obtained from the designed experiment methodology are significantly different from the values obtained from the ladder experiments, although for the 3VP–MMA monomer pair there is considerable overlap of the error limits. The joint confidence intervals are relatively small, indicating that the values of r_1 and r_2, obtained from design methodology and nonlinear least squares data analysis, are quite reliable, more so than the values obtained from the ladder-type experiments.

The values of r_1 and r_2 indicate that for both the 3VP–BA and 3VP–MMA systems, there is some tendency towards alternation (particularly for the 3VP–BA pair) but the tendency is not pronounced, that is, the copolymers are essentially random.

From the values of r_1 and r_2 obtained from design methodology and the literature Q and e values[18] for BA and MMA, Q and e values for 3VP were calculated. For 3VP–BA, Q = 6.39, e = 2.32, and for 3VP–MMA, Q = 2.08, e = 1.60.

CONCLUSIONS

The copolymerization of 3VP with BA and MMA was investigated using experimental design methodology. The data was analyzed using a nonlinear, least squares, error-in-variables method. The values of r_1 and r_2 obtained in this manner were significantly different from those values obtained from more traditional ladder-type copolymerizations. The joint confidence intervals obtained for the designed experiments are relatively small and the values obtained for r_1 and r_2 can be regarded as more reliable than the corresponding values garnered from ladder-type experiments.

Table III   Reactivity Ratios for 3-Vinyl Pyridine Copolymers

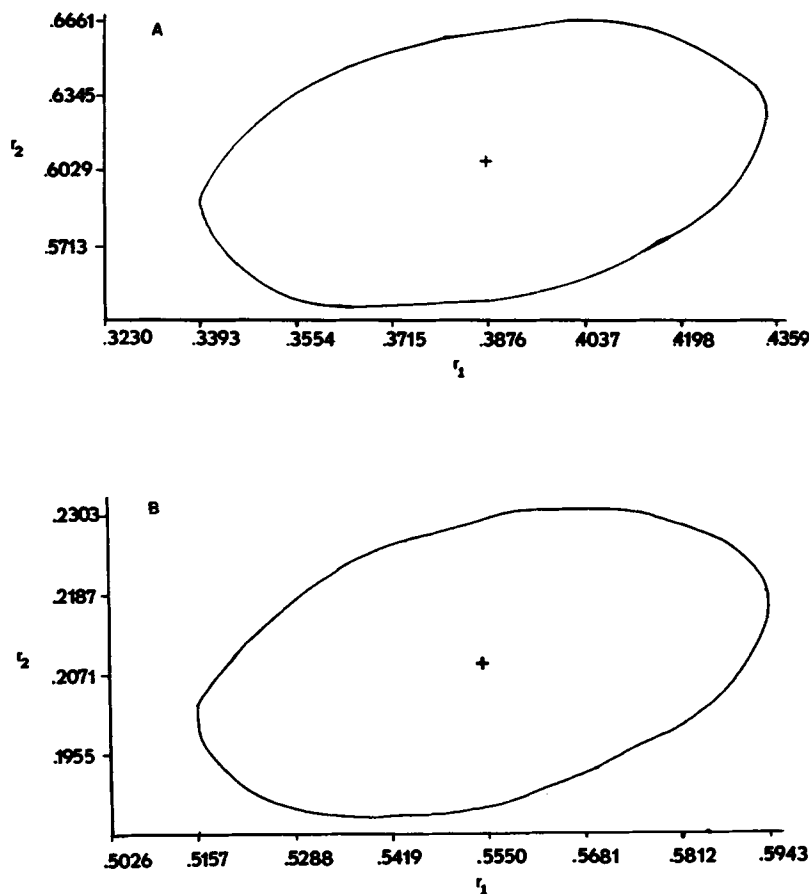| Monomer 1	Monomer 2	r_1	r_2	$r_1 r_2$
3VP	BA	0.554	0.208	0.115
3VP	MMA	0.387	0.606	0.235

Figure 1 95% joint confidence intervals for r_1 and r_2 in (A) 3VP–MMA copolymerization and (B) 3VP–BA copolymerization.

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