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Copolymerization of 6-vinyl-1,4-benzodioxane with methyl methacrylate and *n*-butyl acrylate

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Summary

6-Vinyl-1,4-benzodioxane was synthesized and its copolymerization with methyl methacrylate and n-butyl acrylate was investigated. In this work concentration ladder type copolymerizations were performed. The results of copolymerization were analyzed using a nonlinear least squares method and reactivity ratios were calculated from the analysis. The 6-vinyl-1,4-benzodioxane was found to be a more reactive monomer than either the mehtyl methacrylate or butyl acrylate, but only slightly so in the methyl methacrylate case.

Introduction

We have previously investigated the homo- and copolymerization behavior of ring substituted polystyrenes (1-3), in order to study the effect of such substitution on the nmr (^{1}H and ^{13}C) spectrum of the resultant polymers and on the reactivity ratios of the ring substituted monomers. In addition, we are interested in the copolymerization of ring substituted styrenes as a route to the production of functional polymers. Therefore, we decided to investigate the copolymerization behavior of 6-vinyl-1,4-benzodioxane (VBD) with methyl methacrylate (MMA) and n-butyl acrylate (BA). This paper summarizes our results to date.

Experimental

General

All solvents used in this study were reagent grade and were used as received. ^{1}H-Nmr spectra were recorded at ambient temperatures on 5-7% w/v solutions of polymer in $CDCl_3$. The spectrometer was a Perkin-Elmer R-32B operating at 90 MHz in the CW mode. Molecular weights were obtained using a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. Tetrahydrofuran was used as the eluent and numerical values for the molecular weights were obtained by ccmparison to a polystyrene calibration curve.

Monomer Synthesis

The VBD was synthesized from 1,4-benzodioxane-6-carboxaldehyde (Aldrich) via a Wittig reaction (4). The VBD was purified by distillation b.p. = 84-85°/a mm Hg. ^{1}H-Nmr, $CDCl_3$; δ 4.80 (s.s., 4H); δ 5.30-5.80 (AB quartet, 2H); δ 6.85 (m. 2H); δ 7.40 (m. 1H).

Polymer Synthesis

The copolymers were synthesized by weighing the desired amounts of monomers into a clean, dry screw cap vial. Recrystallized AIBN (0.7 wt %) was added and the monomer mixture was sparged with dry nitrogen while cold (-50^{o}) to minimize loss by evaporation (<1%). The vials were then tightly capped with teflon lined caps and placed in a thermostated waterbath at 65^{o} for the desired length of time. Polymerizations were terminated by removing the vials from the bath and adding 4-5 ml of cold CH_3OH to the contents. The polymers were purified by twice reprecipitating them from $CHCl_3$ solution into excess CH_3OH. The polymers were dried in vacuo at 30^{o} for 72h. Conversions were determined gravimetrically.

Results and Discussion

The monomer feed charges used, conversions, molecular weights and copolymer compositions obtained are summarized in Table 1.

The copolymer composition data in Table 1 was analyzed and reactivity ratios calculated using a nonlinear least squares error-in-variables method (5-7). This method accounts for the errors in the measured variables in a copolymerization experiment. The errors in r_1 and r_2 are considered as joint errors and the confidence interval is given in the form of an ellipse as shown in Figure 1. The error in weighing the monomers into the polymerization vials i.e. the error in determining feed compositions was estimated as 2.0% for both the MMA and BA copolymer series. The error in determining polymer composition was estimated at 7.0% for the MMA copolymers and 8.0% for the BA copolymers. The point estimates for r_1 and r_2 are given in Table 2.

TABLE 2

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
VBD	MMA	0.476	0.312	.149
VBD	BA	0.629	0.322	.203

TABLE 1

Feed Ratios, Conversions, Molecular Weights and Copolymer Compositions

Polymer	M_1	M_2	M_f M_1 Feed[a]	M_f M_2 Feed	Pzn Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f of M_1 Copolymer
VBDM1	VBD	MMA	0.050	0.950	2.67	8.0	37000	72000	1.95	0.128
VBDM2	VBD	MMA	0.116	0.884	2.67	6.2	40900	84500	2.07	0.239
VBDM3	VBD	MMA	0.274	0.726	2.67	5.2	39000	76000	1.95	0.399
VBDM4	VBD	MMA	0.541	0.459	2.67	3.3	54300	107000	1.97	0.548
VBDM5	VBD	MMA	0.650	0.350	2.67	7.0	32000	62000	1.94	0.616
VBDM6	VBD	MMA	0.774	0.226	2.67	3.9	42000	84400	2.01	0.696
VBDM7	VBD	MMA	0.800	0.200	2.67	6.8	55000	109000	1.98	0.741
VBDB1	VBD	BA	0.050	0.950	2.25	13.0	94000	183000	1.95	0.122
VBDB2	VBD	BA	0.150	0.850	2.25	13.1	61000	108000	1.77	0.306
VBDB3	VBD	BA	0.250	0.750	2.25	8.0	78000	136000	1.74	0.374
VBDB4	VBD	BA	0.316	0.684	2.25	9.7	128000	250000	1.95	0.416
VBDB5	VBD	BA	0.397	0.603	2.25	8.0	106000	208000	1.96	0.486
VBDB6	VBD	BA	0.495	0.505	2.25	12.5	108000	220000	2.04	0.555
VBDB7	VBD	BA	0.750	0.250	2.25	6.5	84000	161000	1.92	0.724

[a] M_f = Mole fraction.

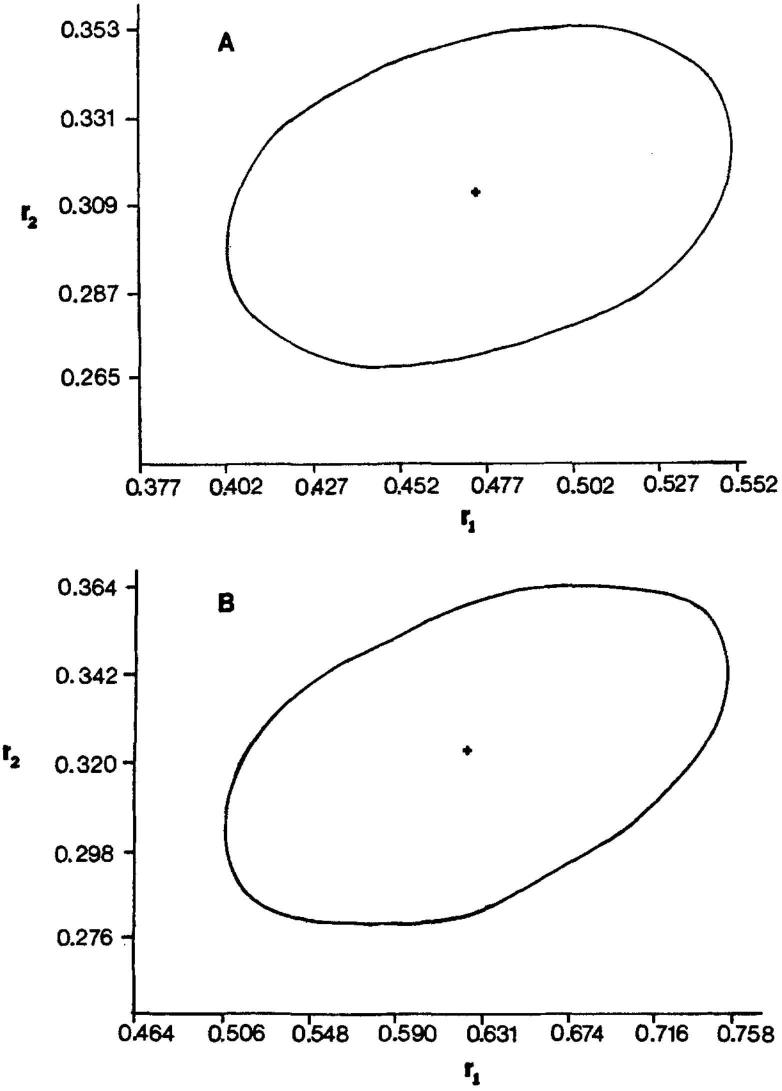

Figure 1: Joint confidence intervals for r_1 and r_2 at the 95% confidence level for A) VBD/MMA comonomers and B) VBD/BA comonomers.

The values obtained for r_1 and r_2 show that in each case VBD is the more reactive monomer although not dramatically so. Using Pyun's equations (8) average sequence lengths can be estimated. These estimates are summarized in Table 3.

TABLE 3

Average Sequence Lengths

Polymer	M_1	M_2	1^a	2^a
VBDM1	VBD	MMA	1.07	3.13
VBDM4	VBD	MMA	1.58	1.26
VBDM7	VBD	MMA	2.36	1.11
VBDB1	VBD	BA	1.09	3.32
VBDB4	VBD	BA	1.44	1.45
VBDB7	VBD	BA	2.65	1.12

a. $_1$ $_2$ = mean sequence lengths for M_1 and M_2 respectively.

The mean sequence lengths given in Table 3 show that while there might be a slight alternating tendence at certain feed compositions, predominately, the VBD/MMA and VBD/BA copolymers are random copolymers.

Conclusions

Copolymerization of 6-vinyl-1,4-benzodioxane with methyl methacrylate or butyl acrylate has been accomplished using a concentration ladder technique. The results were analyzed using a nonlinear least squares error-in-variables method. The reactivity ratios show that the 6-vinyl-1,4-benzodioxane is the more reactive monomer in each case, but not dramatically so. More complete experimentation, involving experimental design methodology, is currently being pursued in order to determine the reactivity ratio values with a higher degree of certainty.

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