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Copolymerization of 5-vinyl-1,3-benzodioxole with n-butyl acrylate and methyl methacrylate

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Summary

Copolymers of 5-vinyl-1,3-benzodioxole (VBD) with n-butyl acrylate and methyl methacrylate were synthesized. The copolymers were synthesized according to a designed experiment methodology and reactivity ratios were estimated using a nonlinear least squares error-in-variables procedure. The values of r_1 and r_2 obtained show that VBD is slightly less reactive than styrene in similar copolymerization reactions.

Introduction

Because catechol has proven to be a very versatile reagent in organic chemistry, several investigators have attempted to include this functionality in polymeric supports (1,2). Direct polymerization of a vinyl monomer with blocked hydroxyl groups is the preferable synthesis technique, as a broader range of final polymer properties could be obtained through copolymerization with appropriate comonomers. To this end Daly and Chotiwana (3) synthesized VBD and studied its polymerization behavior and the synthesis of polymer reagents containing VBD. However, the copolymerization of VBD with commonly available comonomers to produce soluable copolymers was not evaluated. Given the potential of catechol chemistry, we thought it would be of value to assess the reactivity of VBD in copolymerization with n-butyl acrylate and methyl methacrylate.

Experimental

General

All solvents and reagents used in this study were reagent grade and were used as received. ^{1}H-Nmr spectra were recorded on 10% w/v solutions in $CDCl_3$ at ambient temperature using a Perkin-Elmer R-32B spectrometer operating at 90 MHz in the CW mode. Tetramethylsilane was used as an internal standard. Molecular weights were measured using a Waters 150 ALC/GPC equipped with 1×10^6, 1×10^5, 1×10^4, 1×10^3, 500 and 100Å columns. Tetrahydrofuran was used as an eluent and numerical values were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The VBD was synthesized from 3,4-methylenedioxybenzaldehyde (piperonal) via a Wittig reaction (4). The monomer was purified by disstillation b.p. = 90-92°C/14.0 mm Hg (lit b.p. = 122-124°C/25 mm Hg).

The ^{1}H-nmr spectrum matched that previously reported (3).

Polymer Synthesis

The copolymerizations were performed using the experimental design methodology of Tidwell and Mortimer (5) as recommended by several authors (6-9). The details of the methodology employed have previously been given (6,7,10). Briefly, four or five copolymerizations are performed at each of two different feed compositions. The feed ratios used are given in Table 1.

TABLE 1

Monomer Feed Charges

Polymer	Comonomer	M_f[a] VBD in Feed	M_f Comonomer in Feed
VBDM 1-5	MMA	0.353	0.647
VBDM 6-10	MMA	0.749	0.251
VBDBA 1-5	BA	0.275	0.725
VBDBA 6-10	BA	0.813	0.187

a. M_f = Mole fraction

Five polymerizations were performed at each of the feed charges given above. The appropriate amounts of purified monomers were weighed into clean dry vials using a five place analytical balance and 0.9 wt % recrystallized (methanol) AIBN was added. The mixture was sparged with nitrogen while cold (-15°C) in order to minimize evaporation losses, which were determined to be less than 1.0%. The vials were tightly capped with teflon lined caps and placed in a thermostated water bath at 65°C for the desired length of time. The vials were periodically agitated to ensure good mixing. Polymerizations were terminated by removing the vials from the bath, cooling to room temperature and adding 3 ml of cold methanol. The polymers were purified by dissolution in $CHCl_3$ and precipitation in methanol. This process was repeated three times. The polymers were collected by filtration, dried in vacuo at 35°C for 72h and weighed to determine conversion.

Results and Discussion

The results obtained are presented in Table 2. The values presented are the average values for the five copolymerizations performed at each feed concentration.

TABLE 2

Molecular Weights, Conversions and Polymer Compositions

Polymer	M_f VBD in Feed	Pzn Time (h)	Conv. (wt %)	M_n	M_w	M_w/M_n	M_f VBD in Copolymer
VBDM 1-5	0.353	2.0	3.4	35700	71000	1.99	0.474
VBDM 6-10	0.749	2.0	4.0	36400	69500	1.91	0.669
VBDBA 1-5	0.275	2.5	6.8	62200	99400	1.60	0.461
VBDBA 6-10	0.813	2.5	8.0	53700	96300	1.79	0.755

The data in Table 2 were analyzed using a nonlinear least squares error-in-variables method in order to obtain values for r_1 and r_2. This method (6,8,9) accounts for the errors inherent in the measured variables in the copolymerization experiment. The errors in r_1 and r_2 are considered as joint errors and the confidence intervals are given in the form of ellipses as shown in Figure 1. The point estimates for r_1 and r_2, depicted as the (+) sign in the Figure, are given in Table 3.

TABLE 3

Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
VBD	MMA	0.409	0.197	0.0806
VBD	BA	0.555	0.171	0.0949

The joint confidence intervals (95% confidence level) are of relatively small size, indicating that the values given for r_1 and r_2 may be considered fairly accurate. What the r_1 and r_2 values show is that no matter which monomer radical forms the chain terminus the preference is for the addition of the other monomer, i.e. VBD radical prefers to add either BA or MMA and vice versa. Therefore, VBD copolymers have some tendency towards alternation. Using Pyun's equations (11) average sequence lengths can be estimated. These values are summarized in Table 4.

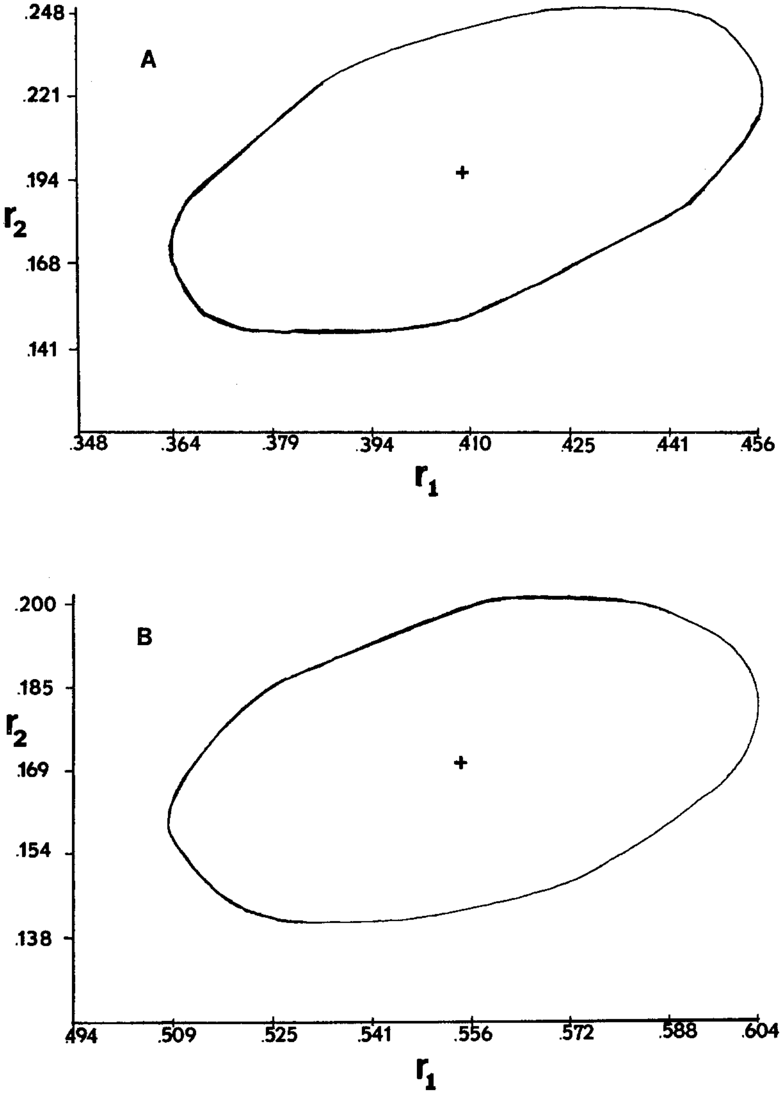

Figure 1: Joint confidence intervals for: A) VBD-MMA monomer pair and B) VBD-BA monomer pair.

TABLE 4

Average Sequence Lengths

Polymer	M_1	M_2	μ_1[a]	μ_2[b]
VBDM 1-5	VBD	MMA	1.37	1.22
VBDM 6-10	VBD	MMA	1.83	1.10
VBDBA 1-5	VBD	BA	1.47	1.20
VBDBA 6-10	VBD	BA	2.71	1.06

a. μ_1 = Average sequence length of monomer 1.

b. μ_2 = Average sequence length of monomer 2.

The values in Table 4 show that even at high feed concentrations the average sequence length of VBD rarely exceeds three and that the average sequence length of the comonomer farely exceeds two in all cases. The values support the tendency towards alternation of the VBD copolymes.

Using literature values of Q and e for BA and MMA (12), Q and e values for VBD may be calculated. The values are Q = 6.91, e = 1.98 for the VBD-MMA monomer pair and Q = 14.81, e = 2.59 for the VBD-BA monomer pair.

Conclusions

Copolymers of VBD with MMA and BA have been synthesized employing designed experiment methodology. Reactivity ratios were calculated using a nonlinear least squares error-in-variables technique. The copolymers were found to have some tendency towards alternation.

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