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The copolymerization of 2- and 3-vinyl thiophene with α-methylene-γ-butyrolactone

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Summary

Binary copolymers of 2- and 3-vinyl thiophene were synthesized via free-radical initiated bulk polymerization. The copolymerizations proceeded readily at 65°C to yield copolymers of reasonable molecular weight. The 2-vinyl thiophene monomer was found to be more reactive than the α -methylene-γ-butyrolactone, while the 3-vinyl thiophene was found to be less reactive than the lactone.

Introduction

In previous papers (1-3) we have reported on the copolymerization behavior of 2- and 3-vinyl thiophene with various comonomers. In all cases the 2-vinyl isomer has proved to to the more reactive isomer. In order to investigate this trend further, as well as to investigate the synthesis of unique copolymers through the use of novel combinations of comonomers, we undertook the study that is the subject of this preliminary communication. As in our previous work the data was analyzed by using a nonlinear error-in-variables method which has proven useful for analysis of data of the type generated in copolymerization studies (4,5).

Experimental

General

All solvents employed in this study were reagent grade and were used as received. The AIBN was purified by recrystallization from methanol. ^{1}H-Nmr spectra were recorded on 10-15% w/v solutions of polymer in $CDCl_3$ or d_6-DMSO using a Perkin-Elmer R-32B 90 MHz spectrometer operating in the CW mode. TMS was used as an internal standard. Molecular weights were measured with a Waters 150/ALC GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A ultrastyragel columns. THF was used as eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis and Purification

The 2- and 3-vinyl thiophene were synthesized by previously reported methods (1-3). The α-methylene-γ-butyrolactone was purchased from the Aldrich Chemical Company. All monomers were distilled three times from CaH_2 immediately before use, purity was 99+% by GC analysis.

Polymer Synthesis

The polymers were synthesized in bulk using the feed charges and conditions summarized in Table 1. The monomers were weighed into clean, dry vials followed by the stated amount of AIBN. The monomer mixture was sparged with nitrogen while cold (-25°C) and the vials were sealed with teflon lined caps. The vials were then placed in a thermostated water bath for the time given in Table 1.

TABLE 1

Polymer Synthesis Conditions

Polymer	Mole Fraction 2VT[a] in Feed	Mole Fraction 3VT[b] in Feed	Mole Fraction MBL[c] in Feed	AIBN (wt %)	Polymerization Temp. °C	Polymerization Time (hr)
2BTMBL1	0.126	-	0.874	0.7	65	1.0
2BTBML2	0.204	-	0.796	0.7	65	1.0
2VTMBL3	0.363	-	0.637	0.7	65	1.0
2VTMBL4	0.448	-	0.556	0.7	65	1.0
2VTMBL5	0.551	-	0.449	0.7	65	1.0
2VTMBL6	0.729	-	0.271	0.7	65	1.0
3VTBML1	-	0.122	0.878	0.9	65	0.75
3VTMBL2	-	0.189	0.811	0.9	65	0.75
3VTMBL3	-	0.289	0.711	0.9	65	0.75
3VTMBL4	-	0.364	0.636	0.9	65	0.75
3VTMBL5	-	0.709	0.291	0.9	65	0.75
3VTMBL6	-	0.810	0.190	0.9	65	0.75

a: 2VT = 2-vinyl thiophene
b: 3VT = 3-vinyl thiophene
c: MBL = α-methylene-γ-butyrolactone

The polymerizations were terminated by removing the vials from the polymerization bath, cooling them in cold water and adding 3 ml of cold methanol. The polymers were purified by dissolution in $CDCl_3$ or DMSO (2VTMBL 1-3 and 3VTMBL 1-3) and precipitation into an 8-9 fold excess of methanol, a process that was repeated three times. The polymers were collected by filtration and dried in vacuo at 35°C for 72h.

Results and Discussion

The results obtained are summarized in Table 2. The copolymer composition data and monomer feed data were then used to calculate the reactivity ratios via a nonlinear least squares error-in-variables method. The details of this method have been given previously (1-5); briefly, the method accounts for the errors inherent in the measured variables in a copolymerization experiment. In the present case the error in weighing the monomers into the polymerization vials, i.e. the error involved in determining the mole ratios of monomers in the feed, was estimated at 2.0%. The error involved in determining copolymer composition from ^{1}H-nmr data was estimated as 8.0%.

TABLE 2

Copolymer Composition, Converison and Molecular Weight

Polymer	Conv. (wt %)	M_n	M_w	M_w/M_n	Mole Fraction of 3VT in Copolymer	Mole Fraction of 2VT in Copolymer
2VTMBL1	1.0	11500	15900	1.38	-	0.24
2VTMBL2	1.1	11000	14600	1.33	-	0.33
2VTMBL3	5.8	15900	23100	1.48	-	0.45
2VTMBL4	4.0	18000	26700	1.49	-	0.50
2VTMBL5	5.8	17400	26200	1.50	-	0.55
2VTMBL6	6.6	14600	23400	1.61	-	0.69
3VTMBL1	5.8	25400	35800	1.41	0.17	-
3VTMBL2	6.5	28300	37900	1.34	0.23	-
3VTMBL3	8.9	37000	50600	1.37	0.27	-
3VTMBL4	7.2	35300	48000	1.36	0.35	-
3VTMBL5	4.8	50000	73600	1.47	0.54	-
3VTMBL6	1.6	38000	55000	1.45	0.57	-

The point estimates of the reactivity ratios and the joint confidence intervals for the 95% confidence level, are given in Figure 1. The point estimates are summarized in Table 3.

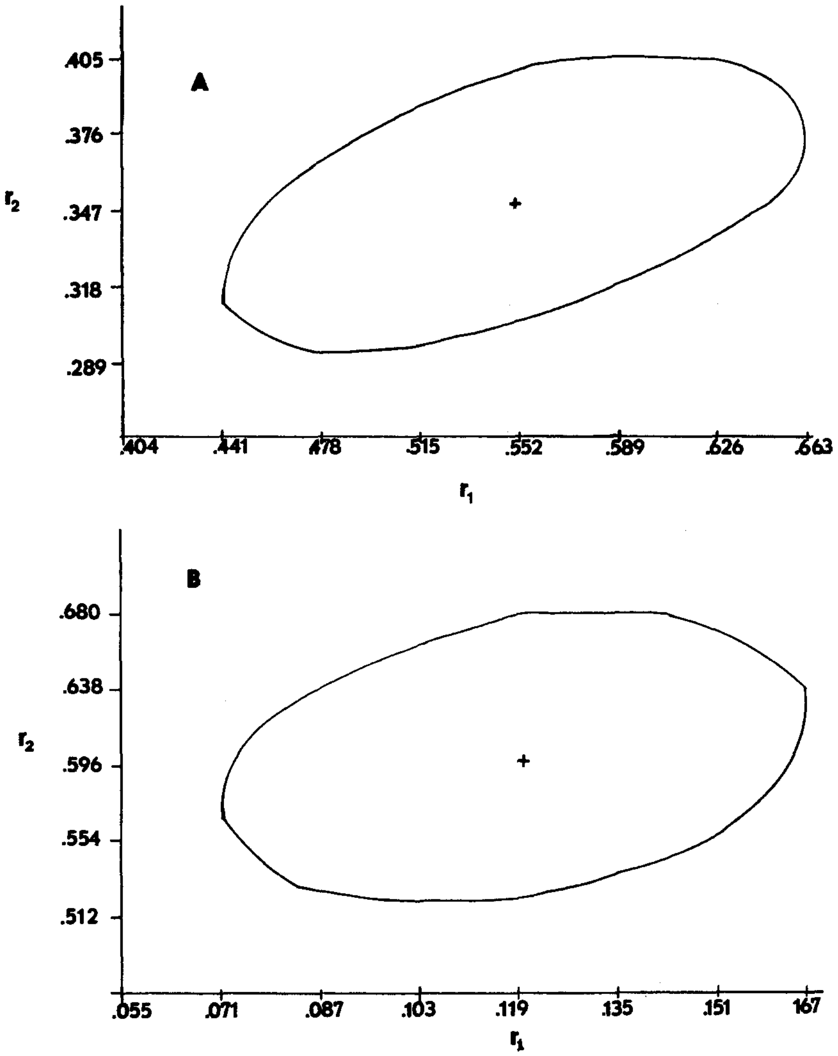

Figure 1 Joint confidence intervals for: A) 2VT/MBL monomer pair and B) 3VT/MBL monomer pair

TABLE 3

Point Estimate Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
2VT	MBL	0.55	0.35	0.19
3VT	MBL	0.12	0.60	0.07

The confidence intervals, while not narrow, are not extraordinarily large. So, the reactivity ratios determined have a reasonable degree of accuracy. More experimentation, involving the use of experimental design methodology (6-8) is currently underway to more completely characterize these copolymer systems and will be the subject of a future communication. In any case, the current data shows that while the copolymers produced have some tendency towards alternation, with the trend being more pronounced in the 3VT case, the polyemr also prossess a good amount of random character. Also, the 2VT seems to be more reactive than 3VT in copolymerization with MBL. This is not unexpected as it (2VT) has proven to be in other copolymerizations as well (2,3).

Conclusions

The reactivity ratios of 2- and 3-vinyl thiophene in copolymerization with α-methylene-γ-butyrolactone have been evaluated in a preliminary fashion. The values obtained indicate that 2VT is a more reactive monomer than 3VT in these copolymerizaitons. The results also indicate that MBL is a reactive monomer (9). Also, it should be noted, that while 2VT is relatively the more reactive monomer, the 3VT copolymers were all higher molecular weight than the 2VT copolymers. This would be somewhat consistent with the lower reactivity of 3VT in that perhaps the chains have more of a chance to grow before a termination event occurs.

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