Polymer Bulletin 19, 217–221 (1988)

Polymer Bulletin

Copolymerization of 5-vinyl-2,2'-bithiophene with methyl methacrylate and n-butyl acrylate

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Summary

Copolymers of 5-vinyl-2,2'-bithiophene with methyl methacrylate or n-butyl acrylate were synthesized. Copolymer compositions were analyzed by nuclear magnetic resonance spectroscopy and reactivity ratios were calculated using the Kelen-Tüdõs method. 5-Vinyl-2,2'-bithiophene proved to be a very reactive monomer with a reactivity ratio value of greater than 3 in copolymerization reactions with methyl methacrylate and a value of greater than 4 in copolymerization reactions with n-butyl acrylate.

Introduction

Gipstein *et al* (1) have previously reported the synthesis, polymerization and select copolymerization of 5-vinyl-2,2'-bithiophene. The comonomers chosen were N-vinylindole and 4-vinyldibenzofuran and while 5-vinyl-2,2'-bithiophene was shown to be quite reactive, no reactivity ratios were calculated. In order then to more fully evaluate the reactivity of 5-vinyl-2,2'-bithiophene regarding copolymerization reactions and because the polymerization behavior of vinyl heterocycles has been a continuing research interest of ours (2,3) we undertook the study of the copolymerization behavior of 5-vinyl-2,2'-bithiophene with the commonly available monomers methyl methacrylate and n-butyl acrylate. The results of this study are reported herein.

Experimental

5-Formyl-2,2'-Bithiophene

The Vilsmeier formylation method of Silverstein *et al* (4) was used. Reagent grade dimethyl formamide (0.12 mol) was charged into a 500 ml flask equipped with a magnetic stirrer, thermometer, addition funnel and reflux condenser. The flask and contents were cooled to 10°C by immersion in an ice bath and phosphorus oxychloride (0.12 mol) was added dropwise from the addition funnel over a period of 25 min. while maintaining a temperature of 10-15°C for the flask contents.

After addition of all the phosphorus oxychloride the flask contents solidified. 1,2-Dichloroethane (60 ml) was added and the mixture was gently warmed until all the solid dissolved, yielding a pale yellow solution. This solution was cooled to 5°C and a solution of 2,2'-bithiophene (0.12 mol) in 140 ml of 1,2-dichloroethane was added over the course of 1 h while the internal temperature was maintained at 5-10°C. After all of the bithiophene solution was added the reaction mixture was warmed to room temperature. After 20 min. at room temperature a large amount of a bright yellow material precipitated from solution. The reaction mixture was then heated at the reflux temperature of 1,2-dichloroethane for 30 min. to ensure complete reaction. During this reflux a mild evolution of HCl vapor was evident. The precipitated yellow solid did not dissolve in the refluxing 1,2-dichloroethane. The reaction mixture was cooled to room temperature and 150 ml of a saturated sodium acetate solution was added. The reaction mixture was then heated at reflux for 15 min., cooled to room temperature and the precipitated solid removed by filtration. The remaining liquid was transfered to a seperatory funnel and the organic layer was removed. The water layer was extracted with three 75 ml portions of diethyl ether. The organic layers were then combined and washed with three 100 ml portions of a saturated sodium carbonate solution. The organic layer was dried over sodium sulfate and the solvents were then removed under reduced pressure. The solid residue was combined with the previously removed solid and recrystallized from benzene/petroleum ether (1/10) to yield 14.2 g (61%) of 5-formyl-2,2'-bithiophene. Liquid chromatographic and nmr analysis showed 97% purity with no trace of the disubstituted product, 5,5'-diformyl-2,2'-bithiophene. M.p. = 59-60°C (lit. (1) m.p. = 58-59°C).

5-Vinyl-2,2'-Bithiophene

The monomer was synthesized via a Wittig reaction. (5) Sodium hydride (0.061 mol, 1.83 g of an 80% dispersion in mineral oil) was charged into a 300 ml three-neck flask equipped with a reflux condenser, magnetic stirrer, nitrogen inlet and pressure equallizing addition funnel. Eighty milliliters of dry 1,2-dimethoxyethane was added to the flask and vigorous stirring was commenced. Methyltriphenylphosphonium bromide (0.052 mol) was then added under nitrogen. The mixture was stirred vigorously under nitrogen at room temperature for 3 h to generate the ylide. The mixture becomes intensly yellow during this period. A solution of 5-formyl-2,2'-bithiophene (0.052 mol) in 50 ml of dry 1,2-dimethoxyethane was then added dropwise from the addition funnel over a period of 1 h. The resulting mixture was refluxed for 3 h under nitrogen to complete the formation of olefin. The reaction mixture was cooled to room temperature and 50 ml of water was cautiously added to decompose any remaining sodium hydride. The reaction mixture was transfered to a separatory funnel and extracted with diethyl ether (4 x 200 ml) the combined ether extracts were then dried over anhydrous sodium sulfate and the diethyl ether was removed under reduced pressure at room temperature. The remaining residue is a semi-solid slush consisting of triphenylphosphine oxide, the desired olefin and some dimethoxyethane. This slush is triturated with several portions of reagent grade cyclohexane to extract the vinyl compound. The cyclohexane was removed under reduced pressure on a rotary evaporator and the residue was chromatographed on a silica gel column using benzene as eluent. The crude vinyl compound was collected in the first fraction and was further purified by twice passing it through columns of neutral alumina using benzene as eluent each time. The monomer was isolated as a light yellow-orange oil. Yield = 7.90 g (79%); ^{1}H-nmr ($CDCl_3$), δ 5.03-5.58 (AB quartet, 2H), 6.55-6.79 (m, 1H), 6.85-7.05 (m, 5H).

Copolymerization

The requisite amounts of the comonomers were weighed into clean, dry glass vials using a five place analytical balance (Mettler AE-163). AIBN (0.5 wt %) was added as the initiator and the mixtures were sparged with dry nitrogen while being cooled in an ice-bath to minimize evaporation losses. The vials were tightly sealed with teflon-lined screw caps and placed in a thermostated water bath at 65°C for a period of 7 h. Polymerizations were terminated by the addition of a quantity (1-2 ml) of cold methanol. The copolymers were isolated by dissolving this mixture in chloroform and precipitating it into an eight-fold excess of methanol. The copolymers were collected by filtration and purified by reprecipitating three times from chloroform solution into methanol. The copolymers were thoroughly washed with hot cyclohexane and then with hot ethanol-water (50/50) to remove the vinyl bithiophene and methyl methacrylate or butyl acrylate homopolymers respectively. In all cases only trace amounts of homopolymer were isolated from these washings and GPC revealed only one peak for all the copolymers.

Polymer Characterization

Polymer molecular weights were measured using a Waters 150 ALC/GPC chromatograph equipped with 1×10^6, 1×10^5, 1×10^4, 1×10^3, 500 and 100Å microstyragel columns. Tetrahydrofuran was used as the eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve. Copolymer compositions were measured by ^{1}H-nmr spectroscopy using a Perkin-Elmer R-12B spectrometer operating at 60 MHz in the CW mode. The spectra were obtained at ambient temperature on $CDCl_3$ solutions of the copolymers with TMS added as an internal reference. Peak areas were determined by electronic integration and by cutting and weighing. The copolymer compositions were calculated by comparing the intensities of the aromatic proton signals (δ = 6.03-7.40) and the aliphatic proton signals (δ = 0.65-3.75). Reactivity ratios were calculated using the Kelen-Tüdõs method. (6)

Results and Discussion

The results obtained are summarized in Tables 1 and 2.

TABLE 1

Monomer Feed Ratios and Copolymer Analysis Data

Polymer Designation	M_f[a] of Vinyl Bithiophene in Feed	M_f of **MMA**[b] in Feed	M_f of **n−BA**[b] in Feed	M_f of **Vinyl-**Bithiophene in Copolymer	% Conversion	M_n[b]	M_w[b]	M_w/M_n
PBT-1	0.10	0.90	-	0.57	3.1	28000	34200	1.22
PBT-2	0.25	0.75	-	0.66	1.9	17400	32800	1.89
PBT-3	0.40	0.60	-	0.76	5.4	16900	33500	1.98
PBT-4	0.50	0.50	-	0.82	7.6	16200	32000	1.89
PBT-5	0.75	0.25	-	0.90	11.0	14300	29400	2.06
PBT-6	0.10	-	0.90	0.45	1.7	12300	24900	2.02
PBT-7	0.25	-	0.75	0.71	2.6	13300	30000	2.26
PBT-8	0.40	-	0.60	0.79	3.4	17400	36700	2.11
PBT-9	0.50	-	0.50	0.83	6.7	13100	26100	1.99
PBT-10	0.75	-	0.25	0.94	9.1	12300	24800	2.02

a. M_f = mole fraction.

b. The values presented are the average of duplicate runs at each of the feed compositions listed.

TABLE 2

Monomer Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
5-Vinyl-2,2'-Bithiophene	MMA	3.42 ± .47	0.017 ± .003	0.058
5-Vinyl-2,2'-Bithiophene	n-BA	4.48 ± .60	0.059 ± .008	0.26

The results show that in copolymerizations wtih methyl methacrylate and n-butyl acrylate, 5-vinyl-2,2'-bithiophene is a very reactive monomer. In both cases r_1 is much greater than 1 and r_2 is much less than 1, meaning that the growing chain end, no matter what its terminus, much prefers to add 5-vinyl-2,2'-bithiophene monomer. (7)

Many previous studies on the copolymerization behavior of vinyl heterocyclic monomers have shown similar results (8,9,10) i.e. that compared to the more "usual" monomers, such as the acrylates, methacrylates and many styreneics, vinyl hetrocycles are much more reactive. So, it is not suprising that 5-vinyl-2,2'-bithiophene is much more reactive than either methyl methacrylate or n-butyl acrylate in copolymerization reactions.

Conclusions

5-Vinyl-2,2'-bithiophene's copolymerization behavior with methyl methacrylate and n-butyl acrylate has been examined and reactivity ratios have been calculated. The values obtained showed 5-vinyl-2,2'-bithiophene to be a very reactive monomer. The high reactivity of the vinyl bithiophene monomer is not surprising, however, considering the results obtained for other vinyl heterocycles by other investigators.

Acknowledgements

The author is grateful to Dr. L. R. Ross for the molecular weight measurements.

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Accepted December 10, 1987 K