Copolymerization of 3-methyl-2-vinylthiophene with methyl methacrylate and ethyl acrylate

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Summary
The copolymerization behavior of 3-methyl-2-vinylthiophene with methyl methacrylate or ethyl acrylate in bulk, using free radical initiation was investigated. The copolymerizations were performed according to the experimental design scheme of Mortimer and Tidwell (1). The experimental results were analyzed by using a nonlinear least squares error-in-variables method. In both cases the 3-methyl-2-vinylthiophene proved to be the more reactive monomer.

Introduction
For some time we have been investigating the copolymerization behavior of vinyl heterocycles with common acrylate and/or methacrylate monomers (2-7). We have found in all cases that the vinyl heterocycle is the more reactive monomer. We have also found that substituents on the heterocyclic ring enhance the reactivity of these monomers relative to the unsubstituted vinyl heterocycles. Our data shows (3-5) that electron withdrawing substituents on the ring yield more reactive monomers than electron releasing substituents, although both types are more reactive than the unsubstituted parent heterocycle. The data also shows that the position of the substituent relative to the vinyl group also plays a role in determining relative reactivity. We recently (7) published the results of a study of the copolymerization behavior of 5-methyl-2-vinylthiophene, and we thought it would be interesting to examine the copolymerization behavior of 3-methyl-2-vinylthiophene (3MVT) for comparison purposes.

Experimental

General
All solvents and reagents used in this study were reagent grade and, unless otherwise noted, were used without further purification. The 3-methylthiophene-2-carboxaldehyde was obtained from Aldrich and used as received. The AIBN was also obtained from Aldrich and
was recrystallized from CH$_2$OH. Copolymer compositions were determined by $^1$H-nmr spectroscopy on 70% w/v solutions of polymer in CDCl$_3$ with TMS added as an internal standard. The spectrometer was a Varian Gemini 300 FT NMR. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 10$^5$, 10$^6$, 10$^7$, 500 and 100A microstyragel columns. Numerical values for the molecular weights were obtained from a polystyrene calibration curve.

Monomer Synthesis
The monomer was synthesized from the carboxaldehyde via a Wittig reaction as previously described (8). The monomer was purified by distillation from CaH$_2$, b.p. = 73-75$^\circ$ mm Hg. All monomers were purified by distillation from CaH$_2$ immediately before use.

Polymer Synthesis
The copolymers were synthesized according to the experimental design scheme of Mortimer and Tidwell. The required amount of 3MVT was weighed into a clean, dry screw cap vial followed by the required amount of comonomer. The AIBN (0.8 wt %) was then added and the mixture was sparged with dry N$_2$ while cool to minimize evaporation losses (1%). The vials were then tightly sealed with a teflon lined screw cap and placed in a thermostated water bath at 70$^\circ$C for the desired length of time. The polymerizations were terminated by removing the vials from the bath, cooling and adding CH$_2$OH to the MMA copolymerizations and hexane to the EA copolymerizations. The copolymers were purified by reprecipitating them twice from CHCl$_3$ solution into either CH$_2$OH (MMA) or hexane (EA). The polymers were dried in vacuo for 72h at 28$^\circ$C and then weighed to determine conversion.

Results and Discussion
As previously stated these copolymerizations were performed under the experimental design scheme of Mortimer and Tidwell. Briefly, the method involves doing ladder polymerizations first to obtain approximate values of $r_1$ and $r_2$. These values of $r_1$ and $r_2$ are then used to calculate two different feed compositions at which 4 or 5 copolymerizations are performed. For the 3MVT-MMA monomer pair the values were $f'_1 = 0.49$ and $f''_1 = 0.052$. The $f$ values are the mole fractions of 3MVT in each of the two feed compositions. For the 3MVT-EA monomer pair the values were $f'_1 = 0.82$ and $f''_1 = 0.065$. Five copolymerizations were performed at each feed composition given. The data obtained are summarized in Table 1.

The values presented in Table 1 (MW's, Conversion, and M$_f$ of 3MVT in copolymer) are the average of the values obtained for each individual copolymer. However, for the calculation of reactivity ratios, the composition of each copolymer was considered as an individual data point. The reactivity ratios were calculated using an error-in-variables method as previously described (3-6).