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Bulk Copolymerization of Styrene and Methyl Methacrylate at Elevated Temperatures

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Reactivity ratios and full conversion range data (conversion, copolymer composition, molecular weight averages, glass transition temperature) are presented for styrene (STY)/methyl methacrylate (MMA)/copolymerization at elevated temperatures (130 and 150°C), a region where polymerization studies are scarce for the system, both for purely thermal polymerization and for peroxide-initiated ones.

Keywords bulk, copolymerization, thermal, styrene, methyl methacrylate

Introduction

Styrene (STY)-methyl methacrylate (MMA) copolymerization has been studied extensively for the conventional temperature range (40–80°C) (1); however, studies at elevated temperatures are scarce, specifically for the full conversion range. This kinetic study of copolymerization of STY/MMA at elevated temperatures is part of a larger project to study the terpolymerization of STY/MMA and acrylonitrile (AN) for optical applications.

STY/MMA copolymer is transparent and used in optical applications. Adding acrylonitrile as a termonomer improves several desired chemical and mechanical properties, such as solvent resistance and toughness of the product (2, 3).

In principle, in order to study the terpolymerization of STY/MMA and AN in a comprehensive way, the three copolymer pairs of STY/MMA, STY/AN and MMA/AN should be investigated (4) at regular and elevated temperatures, with and without initiator. The STY/AN copolymer has been well studied at conventional temperatures and there is some work in the literature at higher temperatures (1). Copolymerization of MMA/AN was recently studied (5, 6, 7) at a wide temperature range (60–140°C) with different initiators and under thermal initiation conditions. Reactivity ratios were evaluated and in addition, full conversion studies examined conversion vs. time profiles, average molecular weights, copolymer composition and glass transition temperatures of products for this copolymerization.

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STY/MMA copolymerization has received much literature attention compared to other copolymer systems, and a comprehensive literature review can be found in Gao and Penlidis (1). However, in spite of numerous important applications of STY/MMA, information at elevated temperatures is scarce, both with and without initiator.

Experimental

Styrene and methyl methacrylate (Aldrich) were purified by classical methods (8). Di-tert-butyl peroxide (Trigonox B (TgB), Akzo Chemicals) was used without purification. Experiments were carried out in borosilicate glass ampoules, as described in McManus and Penlidis (9) and Khesareh et al. (5). Conversion was measured based on total polymer by gravimetry. Copolymer compositions of samples were determined by ^{1}H-NMR (10) for samples dissolved in deuterated methylene chloride. A Bruker 300 MHz NMR spectrometer with Avance software was used to record the spectra. Molecular weights were measured by gel permeation chromatography (GPC). Further details on molecular weight and other polymer characterization have also been given in Khesareh et al. (6).

The Tidwell-Mortimer experimental design (11) was employed for preliminary experiments. According to the criterion, the initial mole fractions of the monomer designated as monomer 1 are given by:

$$f'_{1o} = 2/(2 + r_1) \tag{1}$$

and

$$f''_{1o} = r_2/(2 + r_2) \tag{2}$$

Initial guesses for the reactivity ratios r_1 and r_2 needed in the above equations were obtained from Lewis et al. (12) at 130°C. Table 1 cites information for concentrations/initial mole fractions used in the experiments (both with and without initiator (thermal)).

Table 1

Polymerization conditions for reactivity ratio estimation and full conversion range experiments (1 = STY, 2 = MMA)

Temperature (°C)	[I] (mol/L)	Initial feed (mole fraction) f'_{10}	f''_{10}	Conversion (%)	Reactivity ratios r_1	r_2
130	0.001	0.77	0.21	<4	0.586	0.54
150	0.003	0.70	0.20	<5	0.616	0.543
130	Thermal	0.77	0.21	<3	0.592	0.538
150	Thermal	0.70	0.20	<3	0.615	0.534
130	0.01	0.71		Full conversion, Tg = 99–104°C		
130	0.0025	0.71		Full conversion, Tg = 97–104°C		
130	Thermal	0.69		Full conversion, Tg = 96–102°C		
150	Thermal	0.70		Full conversion, Tg = 97–100°C		

Results and Discussion

The conversion levels were controlled below 5% for all runs (see Table 1). The Error in Variables Model (EVM) method was employed to calculate reactivity ratios based on the Mayo-Lewis equation. The RRVEM program, which works based on the EVM method, was run to estimate reactivity ratios (3, 14). The reactivity ratio point estimates are presented in Table 1 and the 95% posterior probability contours are shown in Figure 1. The feed composition and the copolymer composition errors, used in the EVM program to calculate the 95% probability contours, were 0.5% and 5%, respectively, based on previous studies (14). As shown in Figure 1, the point estimates for reactivity ratios with initiator at 130 and 150°C are close and their 95% probability contours strongly overlap. Therefore, for all practical purposes, the reactivity ratios of STY/MMA at these two temperatures are the same.

Reactivity ratio estimation experiments without initiator were also conducted at 130 and 150°C (purely thermal polymerization). The monomer feeds for experiments were designed by the Tidwell-Mortimer approach and presented in Table 1. The reactivity ratio point estimates are also presented in Table 1 and the 95% posterior probability contours are shown in Figure 1 (T denotes thermal polymerization). As shown in the figure, the point estimates for the thermal polymerization are very close to those estimated in polymerization with initiator. Also, the 95% posterior probability contours for reactivity ratios with and without initiator for both temperatures strongly overlap. The Arrhenius model was fitted to our reactivity ratio data and data from 60°C obtained from the literature (1). The Arrhenius plot is shown in Figure 2. Experimental conditions

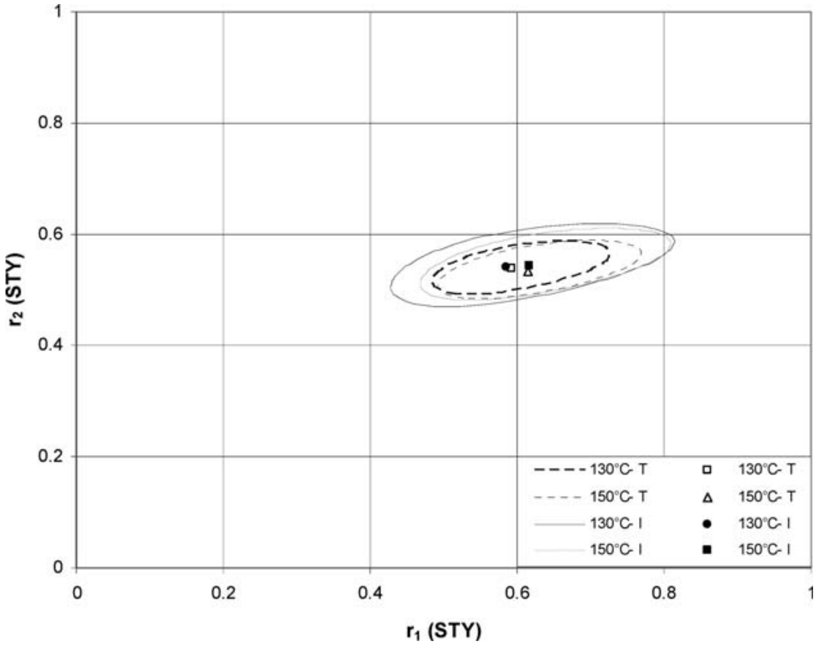

Figure 1. 95% posterior probability contours and point estimates for reactivity ratios estimated by EVM for copolymerization of STY/MMA at 130 and 150°C (with initiator (I) and without initiator (T)).

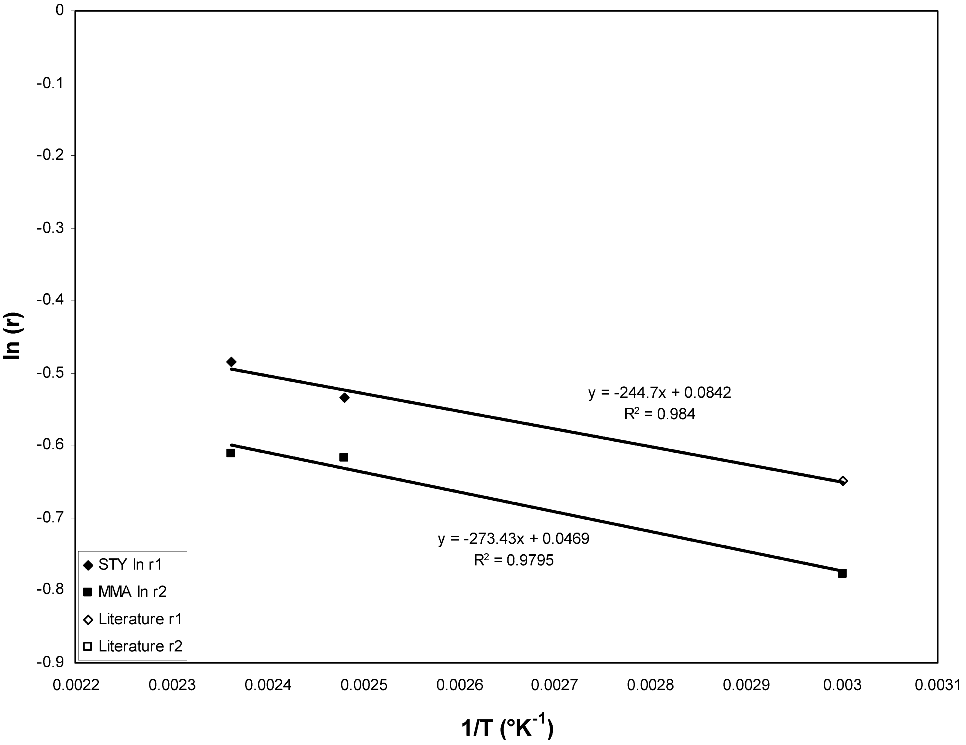

Figure 2. Arrhenius plots for reactivity ratios obtained in this work and from previous literature (data with initiator).

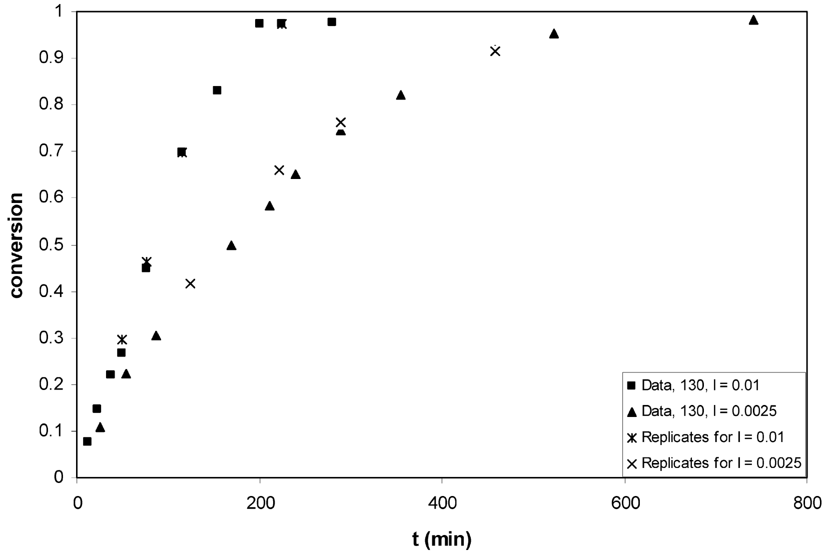

Figure 3. Conversion vs. time for STY/MMA with initiator at 130°C, showing experimental and replicate data.

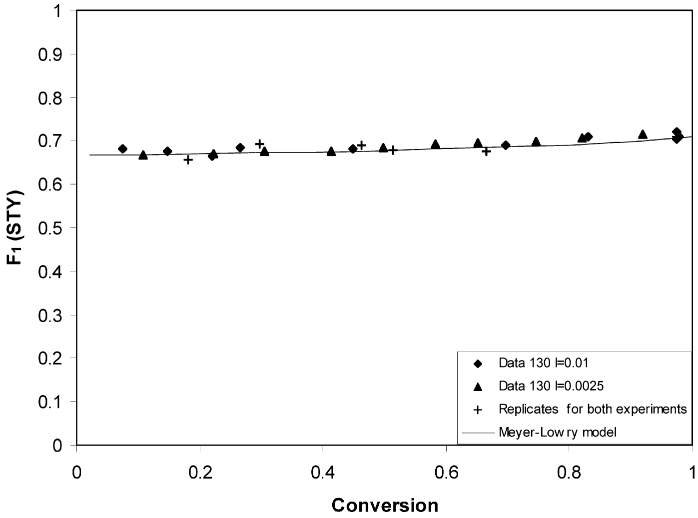

Figure 4. Cumulative copolymer composition for STY vs. conversion for STY/MMA with two levels of initiator at 130°C, showing experimental data and model.

for several full conversion range experiments are summarized in Table 1. The monomer conversion versus time results from experiments at 130°C using two initiator concentrations are plotted in Figure 3. The cumulative copolymer composition vs. conversion results for the runs at 130°C are plotted in Figure 4. The reproducibility is very good.

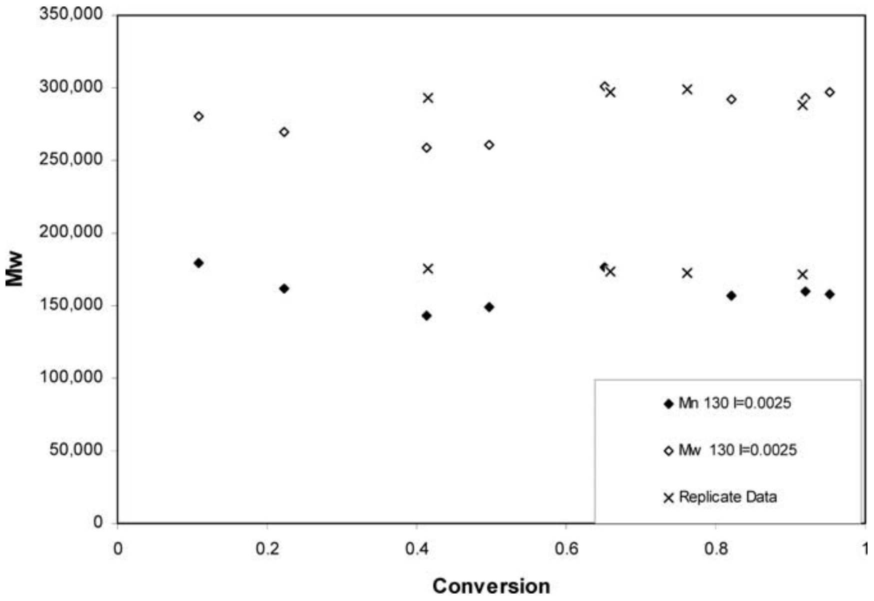

Figure 5. Cumulative number and weight average molecular weights of STY/MMA produced at 130°C with 71 mol% STY and 0.0025 mol/l TgB.

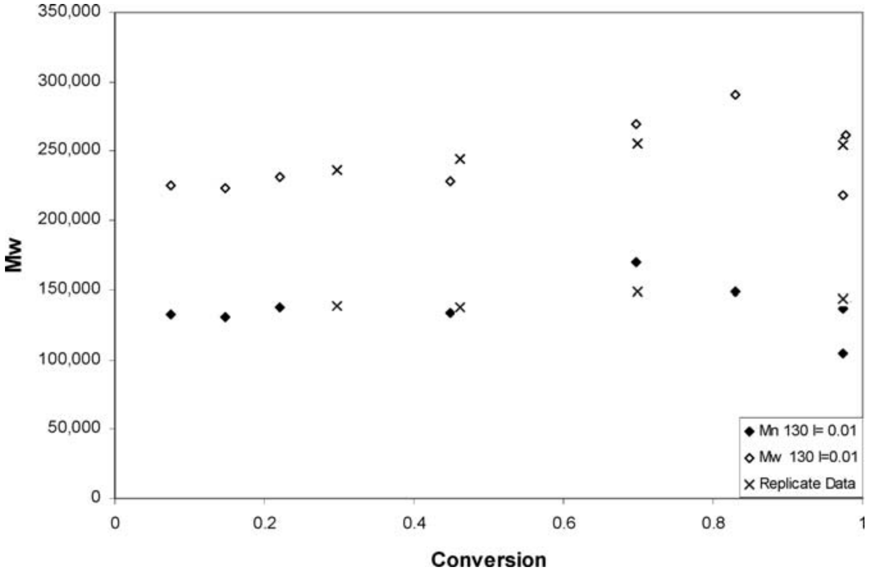

Figure 6. Cumulative number and weight average molecular weights of STY/MMA produced at 130°C with 71 mol% STY and 0.01 mol/l TgB.

The cumulative copolymer composition calculated by the Meyer-Lowry model (15), using the estimated reactivity ratios, is also shown in Figure 4. The agreement between experimental data and model is very good.

The cumulative number and weight average molecular weights are plotted for experiments at 130°C with 0.0025 mol/l and with 0.01 mol/l initiator in Figures 5 and 6, respectively.

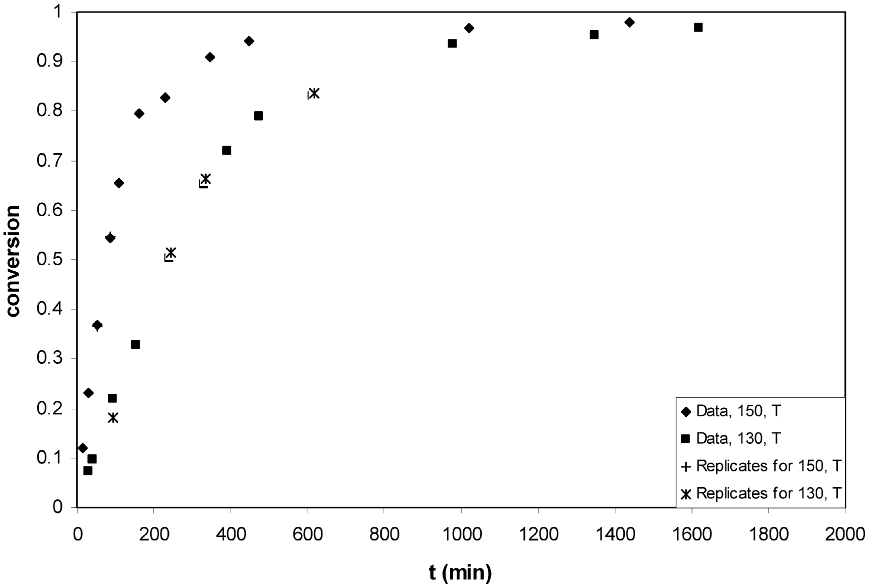

Figure 7. Conversion vs. time for STY/MMA without initiator at 130 and 150°C.

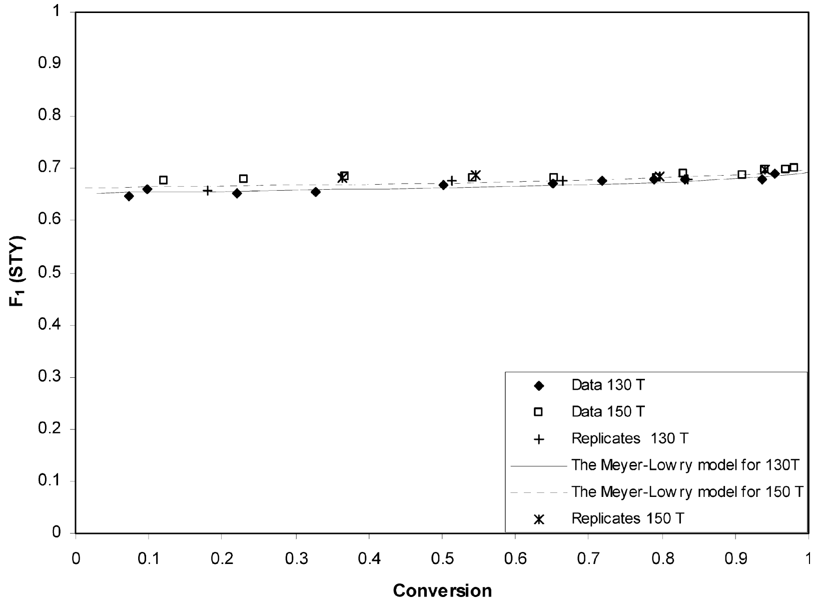

Figure 8. Cumulative copolymer composition for STY vs. conversion for STY/MMA with thermal initiation at 130 and 150°C, showing experimental data and model.

Table 1 cites the experimental conditions. The monomer conversion vs. time results are plotted in Figure 7. The cumulative copolymer composition vs. conversion results for the runs at 130 and 150°C are plotted in Figure 8. The overall picture is similar to that of Figure 4.

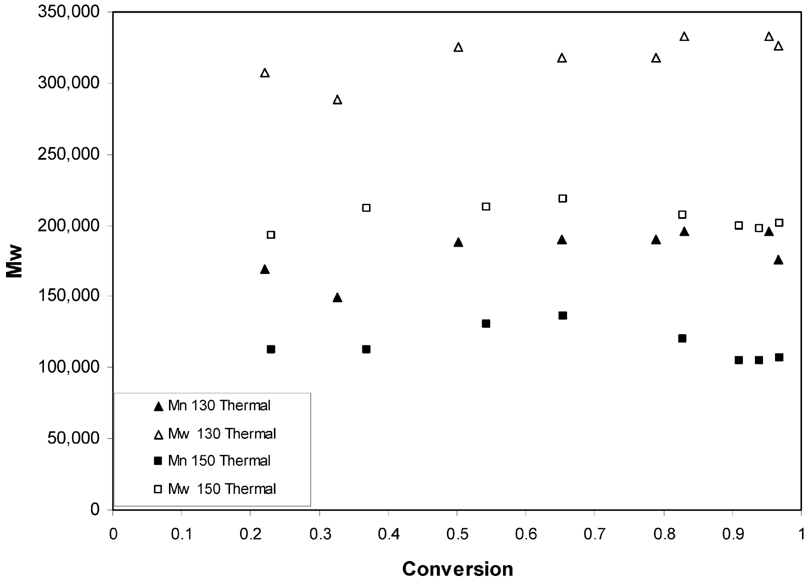

Figure 9. Cumulative number and weight average molecular weights of STY/MMA produced at 130 and 150°C.

Molecular weight averages for the thermal polymerizations at 130 and 150°C are presented in Figure 9. Finally, glass transition temperatures for selective samples are also cited in Table 1. Given typical errors for Tg values, samples at different conversion levels exhibit the same Tg.

Acknowledgements

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