Living Radical Copolymerization of Styrene/Maleic Anhydride

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ABSTRACT: Styrene/maleic anhydride (MA) copolymerization was carried out using benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Styrene/MA copolymerization proceeded faster and yielded higher molecular weight products compared to styrene homopolymerization. When styrene/MA copolymerization was approximated to follow the first-order kinetics, the apparent activation energy appeared to be lower than that corresponding to styrene homopolymerization. Molecular weight of products from isothermal copolymerization of styrene/MA increased linearly with the conversion. However products from the copolymerization at different temperatures had molecular weight deviating from the linear relationship indicating that the copolymerization did not follow the perfect living polymerization characteristics. During the copolymerization, MA was preferentially consumed by styrene/MA random copolymerization and then polymerization of practically pure styrene continued to produce copolymers with styrene-*co*-MA block and styrene-rich block. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2239–2244, 2000

Keywords: styrene; maleic anhydride; copolymerization; TEMPO

INTRODUCTION

The ability to synthesize macromolecules with complex and controlled architecture is becoming an increasingly important aspect of polymer science. Traditionally, control of polymer molecular weight distribution and structure has been achieved using living polymerization techniques such as anionic[1] or cationic polymerization.[2]

Recent studies[3,4,7] reported that narrow polydispersity resins could be synthesized by a stable free-radical polymerization (SFRP) process by using nitroxide free radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[5] Subsequently a large number of publications have appeared confirming the " living" nature of this new technique and demonstrating the preparation of well-defined macromolecular architecture.[13,14] However, long reaction time and low molecular weight limited the usefulness of this reaction for industrial applications.

It has been reported that the rate of the SFRP could be enhanced by performing the reaction in the presence of polar additives, such as camphorsulfonic acid,[4] 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (FMPTS),[8] and acetic anhydride.[12] The strong organic acids have been known to reduce the autopolymerization of styrene, which took place concomitantly with the SFRP at high temperatures.[9]

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Benoit et al.[13] performed the SFRP using a new type of nitroxide, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy and obtained polyisoprene and poly(1,3-butadiene) with low polydispersity.

A series of styrene/MA copolymerizations were performed, using BPO and TEMPO with varying amounts of MA. Interestingly enough, MA boosted up the rate of the SFRP significantly and made the SFRP realizable even below 110 °C. In this article, effects of MA concentration on the SFRP for styrene/MA copolymerization are reported.

EXPERIMENTAL

Styrene (Junsei) was purified by two times of vacuum distillation. BPO (Acros organics) was purified by precipitation from chloroform into methanol, and recrystallized in methanol at 0 °C. TEMPO (Aldrich) and maleic anhydride (MA) (Showa Chemical Inc.) were used as received

Styrene was copolymerized with MA in the presence of TEMPO and BPO([TEMPO]/[BPO] = 1.8) at 120 °C. The product was precipitated in methanol and dried in vacuum oven at 60 °C until constant weight was attained.

Molecular weight and its distribution were measured using GPC [Waters 410, RI detector, THF eluent, 1.0 mL/min, 30 °C, column (porosity: 10 μm, Stragel® HR 1, HR 2, HR 4, Linear)] employing polystyrene (Showadenko SL-105) as a standard.

The thermal properties of the polymers were determined by DSC (PerkinElmer DSC 7). Thermal history of the products was removed by scanning to 200 °C with the heating rate of 20 °C/min. After cooling down the sample at the rate of 20 °C/min to room temperature, it was reheated at 20 °C/min to 200 °C and the second scan DSC thermogram was obtained.

Styrene/MA copolymer was characterized by ^{1}H NMR spectra recorded at room temperature on a Bruker AC-250 FT NMR spectrometer. Ten milligrams of the copolymer was dissolved in 0.5 mL of $CDCl_3$ (20 wt/vol %) and was subjected to the ^{1}H NMR measurements.

RESULTS AND DISCUSSION

Styrene/MA copolymers produced from the reaction medium containing 0.2 mol % of MA and 17.5 mol % of MA by BPO/TEMPO at 120 °C exhibited ^{1}H NMR spectra as shown, respectively, in Figure 1(a,b). The peak at 0.8 ppm in Figure 1(a) is ascribed to the methyl protons in TEMPO.

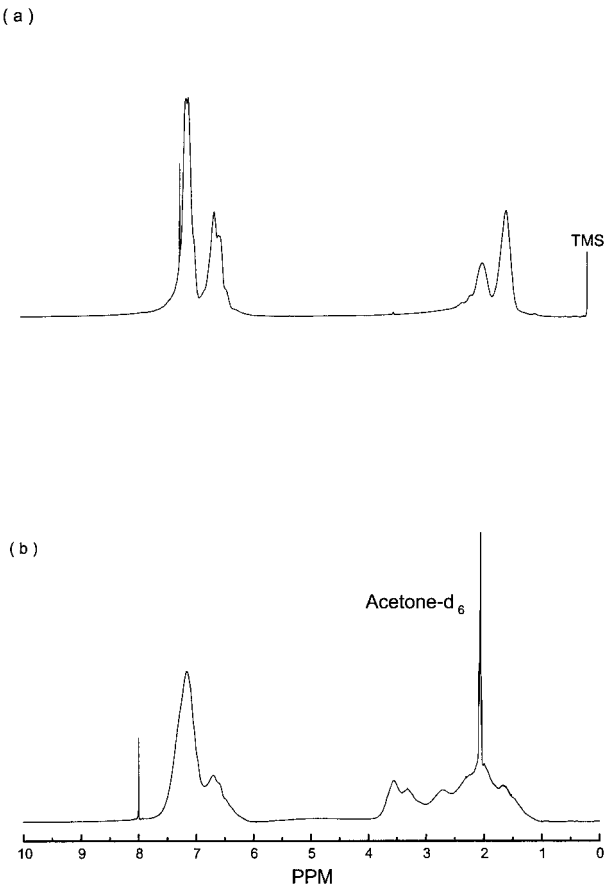

Figure 1. ^{1}H NMR spectra of copolymer (a) TPSM01 and (b) TPSM07.

As the MA concentration in the reaction increased to 17.5 mol %, methine peaks of MA units in the copolymer were observed at 3.0–3.7 ppm as in Figure 1(b).

Conversion, molecular weight and its distribution are collected in Table I for copolymers synthesized from the reaction medium composed of 0.2–17.5 mol % of MA with [TEMPO]/[BPO] fixed at 1.8, where the conversion was defined as weight of the produced copolymers divided by weight of the initial monomers.

Bulk polymerization of styrene for 20 h reached 42% of conversion with weight average molecular weight of 9,100. In comparison, conversions after 20 h copolymerization of reaction medium containing 2.6, 3.8, and 5.0 mol % of MA in styrene increased, respectively, to 82, 86, and

Table I. Effect of Maleic Anhydride Concentration on the Behavior of the Styrene–Maleic Anhydride Copolymerization

Sample Code	Polymerization Time (hours)	[MA] (mol %)	Conversion (%)	M_n	M_w	M_w/M_n
TPS01	20	0.0	42	7,500	9,100	1.21
TPS02	48	0.0	77	14,600	17,600	1.20
TPSM01	20	0.2	64	14,300	18,900	1.32
TPSM02	40	0.2	77	17,100	21,100	1.23
TPSM03	20	2.6	82	19,500	27,500	1.41
TPSM04	20	3.8	86	20,700	29,400	1.42
TPSM05	20	5.0	91	23,500	31,500	1.34
TPSM06	20	9.6	92	22,500	35,000	1.56
TPSM07	20	17.5	93	22,900	37,100	1.62

Polymerization temperature: 120 °C, [BPO] = 0.033 M, [TEMPO]/[BPO] = 1.8.

91%. Thereafter a further increase in MA concentration did not increase the rate of copolymerization considerably. Similarly molecular weight of the copolymers increased with MA concentration up to 5.0 mol % and then leveled off. Molecular weight distribution broadened to M_w/M_n of 1.6 as the MA content in the reaction medium increased to 17.5 mol %.

Table II and Table III list conversion, molecular weight, and molecular weight distribution of copolymers synthesized at different temperatures and at different polymerization times, respectively, with [TEMPO]/[BPO] of 1.8 and MA concentration of 2.6 mol %. Contrary to the conventional radical copolymerization, molecular weight increased as the copolymerization temperature went up.

Figure 2 shows good linear relationship between $\ln\{\ln(1 - x)^{-1}\}$ and 1/T for styrene homopolymerization with an activation energy of 82.4 kJ/mol indicating that styrene homopolymerization by BPO/TEMPO follows the first-order kinetics.

For copolymerization, the kinetics appears to be quite complicated due to different reaction rate constants and cross terminations. However $\ln\{\ln(1 - x)^{-1}\}$ versus 1/T plot appeared to be linear for styrene/MA copolymerization by BPO/TEMPO except the copolymerization at 90 °C when conversion was defined as previously.

The apparent activation energy was determined to be 64.7 kJ/mol from the slope of the plot. Thus it can be said that addition of MA in the reaction medium increased the copolymerization rate, and reduced its temperature dependence.

Polymer was not produced at all below 110 °C for styrene homopolymerization. However, curiously enough, copolymer was formed from styrene/MA (97.4 mol %/2.6 mol %) mixture at 90 °C even though reaction temperature should be higher than 110 °C in order to reactivate the bond blocked by TEMPO.

Table II. Effect of Polymerization Temperature on the Behavior of the Styrene–Maleic Anhydride Copolymerization

Sample Code	Polymerization Temperature (°C)	Conversion (%)	M_n	M_w	M_w/M_n
TPSM08	90	7	5,300	8,100	1.51
TPSM09	100	44	13,000	17,200	1.33
TPSM10	110	50	16,500	23,000	1.39
TPSM11	120	82	19,500	27,500	1.41
TPSM12	130	91	21,900	31,400	1.43

Polymerization time: 20 h, [BPO] = 0.033 M, [TEMPO]/[BPO] = 1.8, [MA] = 2.6 mol %.

Table III. Effect of Polymerization Time on the Behavior of the Styrene–Maleic Anhydride Concentration

Sample Code	Polymerization Time (hours)	Conversion (%)	M_n	M_w	M_w/M_n
TPSM13	1	15	4,300	5,200	1.21
TPSM14	3	38	9,700	12,800	1.32
TPSM15	4	46	11,700	15,500	1.32
TPSM16	5	59	13,600	18,100	1.33
TPSM17	7	70	15,700	21,300	1.35
TPSM18	14	91	21,400	28,700	1.34
TPSM19	20	92	23,500	31,500	1.34

Polymerization temperature: 120 °C, [ST] = 0.48 mol, [TEMPO]/[BPO] = 1.8, [MA] = 5.0 mol %.

Malmstrom et al.[12] also observed that addition of a small amount of acetic anhydride accelerated greatly the nitroxide-mediated free radical polymerization. They suggested acylation of the alkoxyamine nitrogen leading to an increase in the lability of the C—ON bond as a possible explanation for the effect.

It has been reported[10] that styrene/MA copolymerization above 80 °C proceeds randomly rather than in alternating manner, because the charge-transfer complex of styrene and MA could not be formed. In this study, copolymerization of styrene/MA was carried out well above 90 °C, excluding the possibility of the copolymerization in the form of the styrene-MA charge-transfer complex.

In Figure 3 the initial slope of the plots for $\ln(1-x)^{-1}$ versus time goes up with increase in MA concentration. Random copolymerization of styrene/MA took place in the initial stage of the reaction followed by polymerization of practically pure styrene after almost complete exhaustion of MA molecules in the reaction medium (in this stage the polymerization rate fell sharply as in Fig. 3) to produce copolymers with styrene-*co*-MA block and styrene-rich block.

Figure 4(a,b) corresponds to DSC thermograms, respectively, for TPSM06 (MA 9.6 mol %) and TPSM07 (MA 17.5 mol %). Glass-transition temperature of TPSM06 was 105.1 °C, which was slightly higher than that of polystyrene homopolymer (100 °C).

On the other hand, two T_g's appeared on DSC thermogram of TPSM07 at 105.1 °C and 178.2 °C, respectively. As the copolymer was Soxhlet extracted with boiling cyclohexane for 24 h, residual

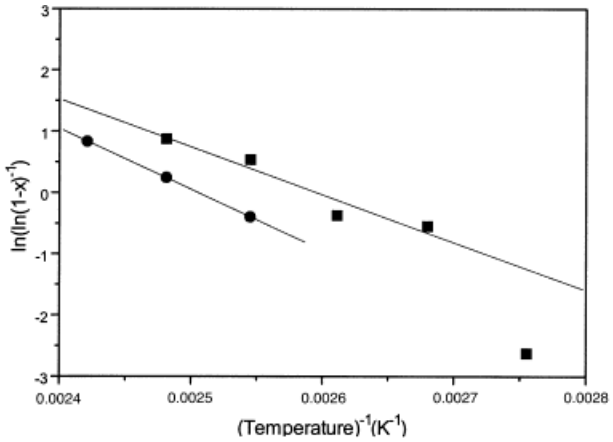

Figure 2. Relationship between $\ln\{[\ln(1-x)^{-1}]\}$ and 1/T for styrene/maleic anhydride copolymerization by BPO/TEMPO system. ■, styrene/maleic anhydride copolymerization; ●, styrene homopolymerization.

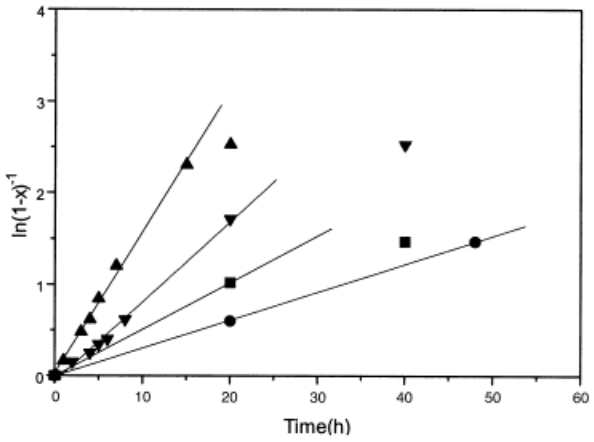

Figure 3. Representation of the copolymerization of styrene/maleic anhydride by the first-order kinetics [MA] = 5.0 mol %: ▲; [MA] = 2.6 mol %: ▼; [MA] = 0.2 mol %: ■; [MA] = 0.0 mol %: ●.

polystyrene homopolymer in the copolymer would not exhibit any detectable glass transition.

A literature[11] reports T_g's of styrene/MA copolymers containing 5.0 mol % of MA and 33 mol % of MA were 106 °C and 155 °C, respectively. Therefore it can be said that the results in Figure 4(a,b) supports the conclusion that TPSM07 is composed of styrene-*co*-MA block and styrene-rich block.

It should be noted that the high T_g of TPSM07 (178.2 °C) is much higher than T_g of styrene/MA copolymers having 33 mol % of MA made by the conventional radical copolymerization (155 °C).

This is because MA reacts with styrene-ended radical faster than styrene. Addition of MA to MA-ended radical should be difficult due to the steric hindrance of MA. Hence MA molecules wait until another styrene molecule reacts with MA-ended radical. Therefore, it can be said that styrene-*co*-MA block in TPSM07 resembles styrene-*alt*-MA rather than styrene-*ran*-MA.

Figure 5 shows number-average molecular weight (M_n) and weight-average molecular weight (M_w) as a function of conversion. As was previously reported,[6] M_n and M_w of styrene homopolymer follow a good linear relationship with respect to conversion.

When styrene/MA concentration was carried out isothermally M_n and M_w of styrene/MA copolymer also increased linearly with conversion.

However, M_n and M_w of styrene/MA copolymer produced at different temperatures deviated considerably from the linear relationship indicating that the copolymerization was not a perfect living system.

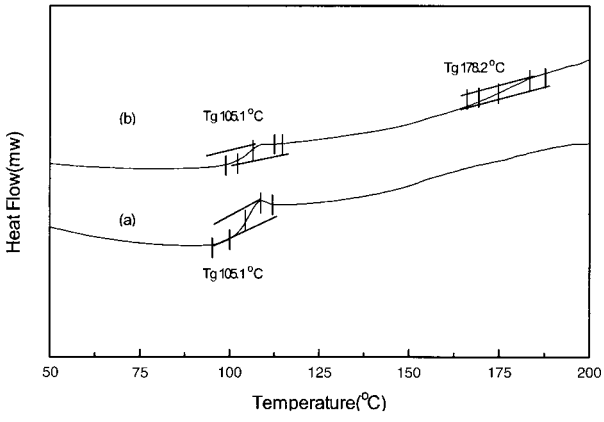

Figure 4. DSC thermograms of poly(styrene-*co*-maleic anhydride): (a) styrene/maleic anhydride copolymer produced from a reaction medium containing 90.4 mol % of styrene and 9.6 mol % of maleic anhydride (TPSM06); (b) styrene/maleic anhydride copolymer produced from a reaction medium containing 82.5 mol % of styrene and 17.5 mol % of maleic anhydride (TPSM07).

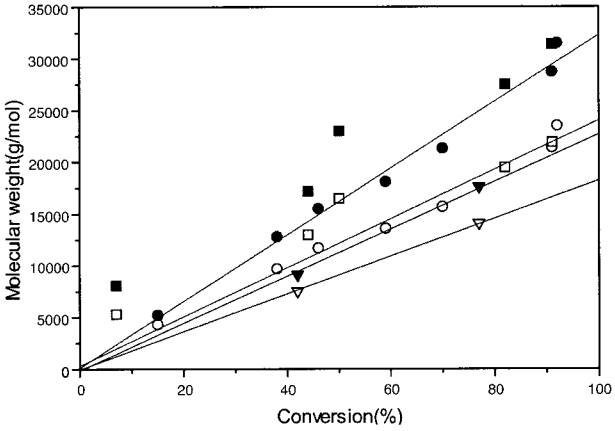

Figure 5. Molecular weight as a function of conversion for styrene homopolymerization and for styrene/maleic anhydride copolymerization. ▽, ▼: M_n and M_w for isothermal polymerization of styrene; ○, ●: M_n and M_w for isothermal copolymerization of styrene and maleic anhydride; □, ■: M_n and M_w for copolymerization of styrene and maleic anhydride at different temperatures.

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