Preparation of Well-Defined Block Copolymer Having One Polystyrene Segment and Another Poly(styrene-*alt*-maleic anhydride) Segment with RAFT Polymerization

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ABSTRACT: Block copolymers, polystyrene-*b*-poly(styrene-*co*-maleic anhydride), have been prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization technique using three different approaches: 1-phenylethyl phenyldithioacetate (PEPDTA) directly as RAFT agent, mediated polystyrene (PS) block as the macromolecular PS-RAFT agent and mediated poly(styrene-maleic anhydride) (SMA) block with alternating sequence as the macromolecular SMA-RAFT agent. Copolymers synthesized in the one-step method using PEPDTA as RAFT agent possess one PS block and one SMA block with gradient structure. When the macromolecular RAFT agents are employed, copolymers with one PS block and one alternating SMA block can be produced. However, block copolymers with narrow molecular weight distribution (MWD) can only be obtained using the PS-RAFT agent. The MWD deviates considerably from the typical RAFT polymerization system when the SMA is used as the RAFT agent. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1740–1746, 2011

Key words: RAFT polymerization; diblock copolymer; poly(styrene-*co*-maleic anhydride); poly(styrene-*alt*-maleic anhydride); polystyrene

INTRODUCTION

The molecular weight (MW) and sequence structure of styrene (St) and maleic anhydride (MAn) copolymer (SMA) prepared by traditional free radical copolymerization processes are not well-defined,[1–4] especially in the aspects of molecular weight distribution (MWD) and composition drift. Synthesis of SMA with designed structure using controlled free radical polymerization technique has received considerable amount of interest. Rizzardo and coworkers had investigated the RAFT polymerization of styrene and polar vinyl monomers such as (meth)acrylate and obtained block copolymers with narrow molecular weight distribution.[5–7] You et al. copolymerized St and MAn using dibenzyl trithiocarbonate as RAFT agent at 22°C.[8] The ^{13}C NMR spectra confirmed that the produced SMA possessed alternating structure. Chernikova et al. found that polymerization was faster and quality of control was poorer in the presence of RAFT agent when the proportion of MAn in the monomer feed was high.[9] Davies et al. carried out the study on RAFT copolymerization of substituted St and MAn.[10] Recently, block SMA has also been synthesized by various researchers. Benoit et al.[11] and Park et al.[12] independently obtained copolymers with one PS block and one SMA block (PS-*b*-Poly(St-*co*-MAn)) by nitroxide-mediated living free radical polymerization (NMP). However, random sequence structure instead of alternating structure was observed in the SMA block. More recently, Lessard and Maric synthesized SMA with exclusively alternating structure using NMP technique at 90°C due to the relatively low temperature.[13] Furthermore, this SMA was used as a macro-nitroxide-mediated agent for a fresh batch of St polymerization. The diblock copolymers PS-*b*-Poly(St-*alt*-MAn) with a PS block and another alternating SMA block was obtained. Lessard and Maric also used the simple one-step method to synthesis PS-*b*-Poly(St-*co*-MAn), which had both random and alternating structure. However, both the resultant diblock copolymers using the one-step and two-step methods had rather broad MWD (the ratio between weight average molecular weight, M_w, and number average molecular weight, M_n) over 1.6. Zhu et al. claimed that PS-*b*-Poly(St-*co*-MAn) was prepared in the one-step method using RAFT polymerization.[14] They only used ^{1}H NMR to analyze St content in the

produced copolymer. ^{13}C NMR analysis was not presented to confirm the alternating structure in the SMA block. In this work, PS-b-Poly(St-co-MAn) have been prepared using RAFT polymerization technique in three different approaches: directly using PEPDTA as the RAFT agent with one-step method, copolymerization of St and MAn using PS as the macromolecular RAFT agent (PS-RAFT) and polymerization of St using alternating SMA as the macromolecular RAFT agent (SMA-RAFT). The aim is to obtain uniform diblock copolymer PS-b-Poly(St-alt-MAn) with both narrow molecular weight and strictly alternating SMA segment.

EXPERIMENTAL

Materials

St was washed with 10 wt % NaOH aqueous solution, dehydrated with 5 Å zeolites, and distilled in vacuum with anhydrous CaCl$_2$ before being used. MAn was recrystalized in CHCl$_3$. PEPDTA was synthesized according to Quinn et al.'s work.[15] Tetrahydrofuran (THF), butanone, and methanol were purchased from Sinopharm Chemical Reagent and used as received.

Polymerization

All polymerization runs were conducted in the flowing nitrogen atmosphere with thermal initiation. No external initiator was used. St (0.9615 mol) and PEPDTA (0.00321 mol) were mixed at the molar ratio of 300 : 1. Polymerization was carried out at 110°C for a specified period (223 min). The crude products were precipitated in methanol, and alternatively dissolved in THF and precipitated with methanol for three times to obtain the pure products, PS-RAFT. The purified polymers were dried at 60°C in vacuum for 24 h.

St (0.2885 mol), MAn (0.2885 mol), and PEPDTA (0.00289 mol) were dissolved in butanone at the molar ratio of 100 : 100 : 1. The weight fraction of monomers was 40%. Copolymerization was carried out at 75°C for a specified period (223 min). The products, SMA-RAFT, were purified using the same procedure as PS-RAFT.

The block copolymers were synthesized using three different methods:

1. PS-RAFT method: St (0.1442 mol), MAn (0.1442 mol), and PS-RAFT (0.00144 mol) were mixed at the molar ratio of 100 : 100 : 1. Butanone was used as the solvent. The weight fraction of monomers was 20%. Copolymerization was taken place at 75°C.
2. SMA-RAFT method: St (0.2885 mol) and SMA-RAFT (0.00096 mol) were mixed at the molar

ratio of 300 : 1. Polymerization was taken placed at 110°C.
3. One-step method: St (0.9615 mol), MAn (0.1068 mol), and PEPDTA (0.00321 mol) were mixed at the molar ratio of 270 : 30 : 1. Copolymerization was carried out at 110°C.

All crude products were purified using the same method as the macromolecular RAFT agents. Scheme 1 presents the details of the reactions involved in this work.

Characterization

The molecular weight distribution of the purified samples were measured by PL-50 Gel Penetration Chromatography (GPC) with refractive index detector, light scattering detector, and viscosity detector. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} at 30°C. Two PLgel 10 μm MIX-B LS 300 × 7.5 linear columns and one PLgel 5 μm 500E 300 × 7.5 column were linked by serials.

The average fraction and the sequence of MAn in the copolymer chain were determined by ^{13}C NMR spectrum recorded in a Bruker Avance 500M superconducting nuclear magnetic resonance meter with d_6-acetone as the solvent (30%$_{w/v}$) and TMS as the internal reference. The molecular fraction of MAn in PS-b-Poly(St-co-MAn) and SMA-RAFT can be calculated from eqs. (1) and (2), respectively.

$$M\% = \frac{2A_{MSM} + A_{SSM+MSS}}{4A_{MSM} + 3A_{SSM+MSS} + 2A_{SSS}} \quad (1)$$

$$M\%_{SMA} = \frac{M\% \times Mn_{PS-b-SMA}}{Mn_{SMA}} \quad (2)$$

Here, A_{MSM}, A_{SSM}, A_{MSS}, and A_{SSS} are the area of the resonances representing MSM (δ: 136–138 ppm), SSM/MSS(δ: 138–144 ppm), and SSS (δ: 144–147 ppm) triad, respectively. $Mn_{PS-b-SMA}$ and Mn_{SMA} are the number-average molecular weight of block copolymer and its SMA block.

Polymerization conditions and characterization results of the typical polymers synthesized in this work are shown in Table I.

RESULTS AND DISCUSSION

The plots of ln([M]$_0$/[M]) vs. time and M_n vs. conversion are shown in Figure 1 for the St homopolymerization using PEPDTA as RAFT agent with thermal initiation. The first-order kinetics curve (ln([M]$_0$/[M]) vs. time) for the St homopolymerization is found to be linear. The conversion increases from 0 to 16% during a 223-min period of the polymerization. The relationship between M_n and conversion is

PS-RAFT method

SMA-RAFT method

One-step method
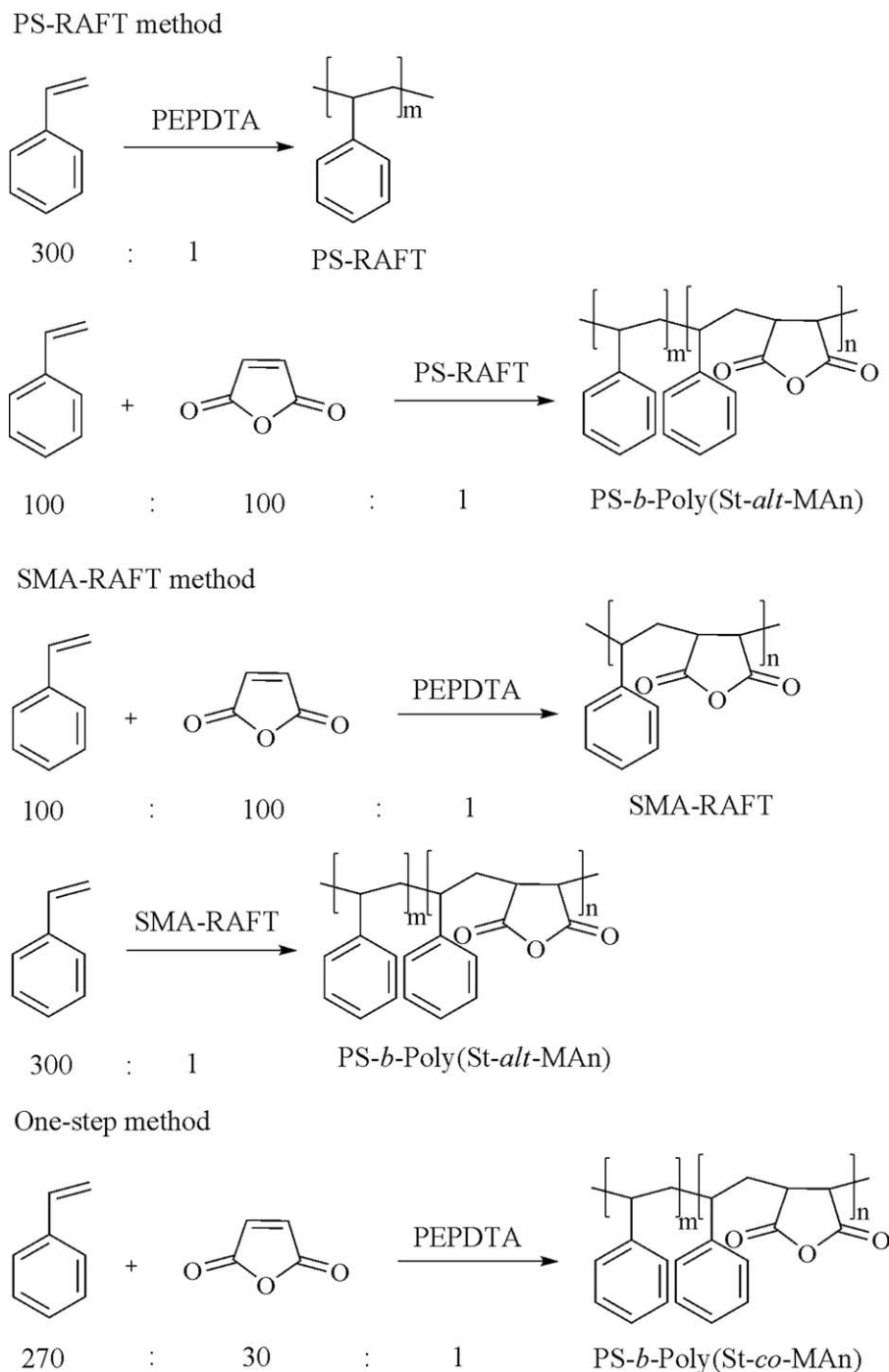
Scheme 1 The reactions involved in this work.

also linear. The deviations between the theoretic M_n and experiment data are negligible. The M_n of the PS-RAFT produced at 223 min is 5700. PS-RAFT with various chain lengths can be obtained by varying the polymerization time. Figure 2 shows that the peak of MWD curves shift to the direction of higher molecular weight when conversion is increased. It can also be seen that all MWD are very narrow with M_w/M_n in the range of 1.02–1.05.

Seen from Figure 3, the copolymerization of St and MAn with PEPDTA as RAFT agent also shows the characteristics of typical controlled radical polymerization, such as linear first-order kinetics curve and linearly increased M_n with the conversion. The reaction rate of St-MAn copolymerization is faster than that of St homopolymerization. The conversion increases from 0 to 26% in 50 min. The SMA-RAFT produced at 50 min has a M_n of 5100. The small

TABLE I
Polymerization Conditions and Characteristic Results of the Obtained Polymers

Sample	PS-RAFT	SMA-RAFT	Block copolymer-1	Block copolymer-2	Block copolymer-3
$f_{MAn,0}$[a]	0	0.5	0.1	0.5	0
$f_{St,0}$[a]	1	0.5	0.9	0.5	1
RAFT agent[b]	PEPDTA	PEPDTA	PEPDTA	PS-RAFT	SMA-RAFT
T (°C)[c]	110	75	110	75	110
T (min)[d]	223	50	195	90	265
X (%)[e]	16	26	36	62	36
F_{Man}[f]	0	0.49	0.28	0.34	0.11
$F_{MAn(SMA)}$[g]	–	0.49	–	0.49	0.49
Mn_{PS}[h]	5700		–	5700	18,300
Mn_{SMA}[i]	–	5100	–	13,200	5100
$Mn_{PS-b-SMA}$[j]			11,000	18,900	23,400
MWD	1.02	1.17	1.18	1.05	1.80

[a] Initial feed ratio.
[b] RAFT agent.
[c] Polymerization temperature.
[d] Polymerization time.
[e] Conversion.
[f] MAn molar fraction in the block copolymer.
[g] MAn molar fraction in the SMA block.
[h] M_n of the PS block.
[i] M_n of the SMA block.
[j] M_n of the block copolymer.

deviations between the theoretic M_n and experiment data can be attributed to experimental error. PS-RAFT with other specified molecular weight can be obtained with different polymerization time. The MWD curve at various conversion are shown in Figure 4. All MWD are relatively narrow. The M_w/M_n is reduced from 1.18 to 1.06 when conversion is increased from 16 to 37%.

To synthesis PS-b-Poly(St-alt-MAn), St, and MAn are copolymerized in the presence of the macromolecular RAFT agent, PS-RAFT. Figure 5 shows good
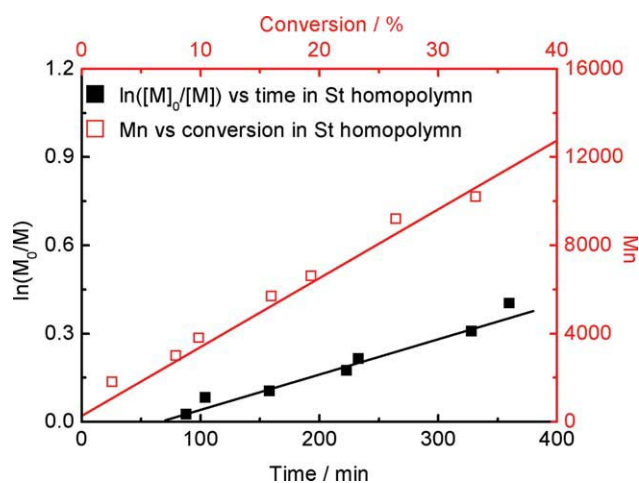
linear relationship between $\ln([M]_0/[M])$ and time. The M_n follows a good linear relationship with respect to conversion and fits the theoretic line well. Figure 6 presents the MWD curves of polymers produced at various conversions. With increasing conversion, the molecular weight is increased and its distribution stays narrow. The M_w/M_n of the produced polymers range from 1.02 to 1.06, which is very close to the M_w/M_n of the PS-RAFT (1.02).

Figure 1 Time evolution of $\ln([M]_0/[M])$ and conversion versus M_n in styrene polymerization using PEPDTA as RAFT agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
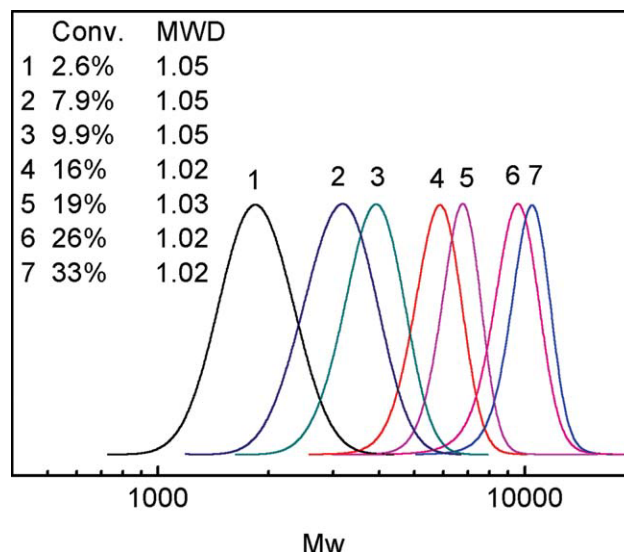

Figure 2 The molecular weight distribution curves of the obtained polystyrene block. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
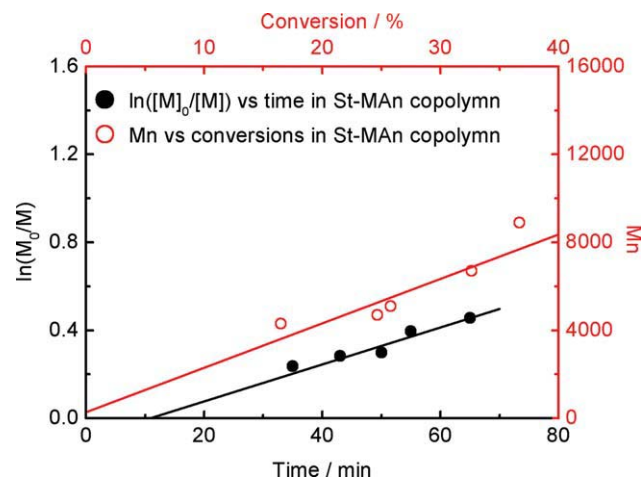
Figure 3 Time evolution of $\ln([M]_0/[M])$ and conversion versus M_n in the copolymerization of styrene and maleic anhydride using PEPDTA as RAFT agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These results indicate that the St and MAn are incorporated into the existing PS chains and form the two block copolymers, PS-*b*-Poly(St-*alt*-MAn) instead of generating new copolymers, Poly(St-*alt*-MAn).

Another approach for producing PS-*b*-Poly(St-*alt*-MAn) is the homopolymerization of St using the alternating SMA-RAFT agent. As shown in Figure 7, $\ln([M]_0/[M])$ versus time still appear to be linear. However, M_n versus conversion is considerably higher than the theoretic line. As shown in Figure 8, the peak of the MWD curves shift to the direction of higher molecular weight when conversion is increased. But the part of MWD curves accounting for the low molecular weight does not change signif-
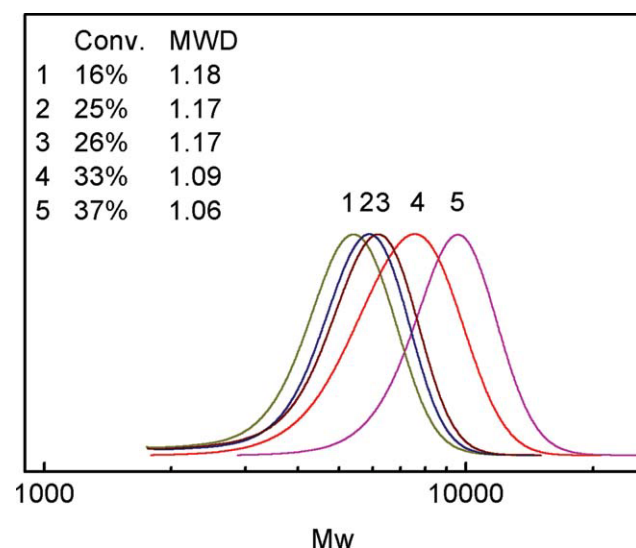

Figure 5 Time evolution of $\ln([M]_0/[M])$ and conversion versus M_n in the copolymerization of styrene and maleic anhydride using the PS-RAFT. [Color figure can be viewed in the online issue, which is available at wiley onlinelibrary.com.]

icantly until the conversion is over 50%. This means that part of the SMA-RAFT agent does not grow at the beginning of the polymerization process. Compared with the PS-RAFT agent, the MWD of the produced polymers is much broader with a M_w/M_n range of 1.5–1.8. It is unclear whether these products are diblock copolymers with broad MWD or the mixture of SMA, PS, and diblock copolymers.

In the one-step method, St and MAn are copolymerized directly using PEPDTA as RAFT agent with the molar ratio of 270 : 30 : 1(St : MAn : PEPDTA) at 110°C. Seen from Figure 9, the total monomer conversion increases rapidly in the first 75 min and successive change is slowed. The experimental data

Figure 4 The molecular weight distribution curves of the resultant SMA block. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
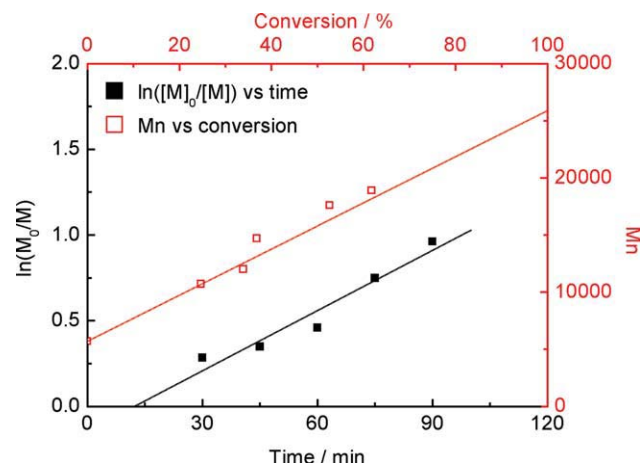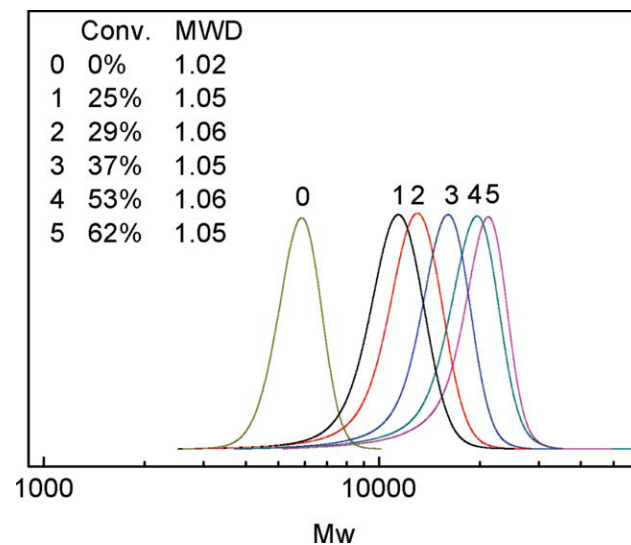

Figure 6 The molecular weight distribution curves of the produced diblock copolymers. [Color figure can be viewed in the online issue, which is available at wiley onlinelibrary.com.]
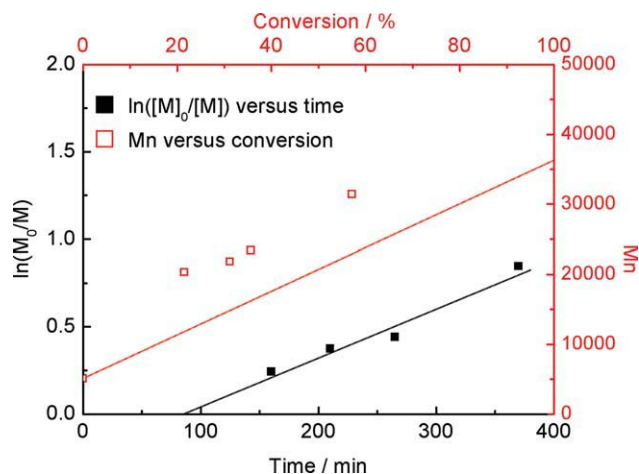
Figure 7 Time evolution of $\ln([M]_0/[M])$ and conversion versus M_n in the styrene polymerization using the SMA-RAFT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9 Time evolution of $\ln([M]_0/[M])$ and conversion versus M_n in the copolymerization of styrene and maleic anhydride using PEPDTA as RAFT agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows that the ratio between the MAn and St incorporated into the copolymers is 1 : 1.23, 1 : 2.08, 1 : 2.38, and 1 : 2.56 at 30, 75, 120, and 240 min, respectively. The corresponding MAn fraction in the residual monomers is 0.025, 0.004, 0.003, and 0. This indicates that MAn is continuously incorporated into macromolecular chain in the first 240 min. However, the ratio between St and MAn in the copolymer changes as the polymer chain propagates. The formed SMA block possesses a "gradient" structure instead of the alternating structure. After 240 min, MAn is completely consumed. Subsequently, polymer chain continues to propagate for forming a PS block. Moreover, the M_n develops nearly linearly with increasing conversion. The deviations between
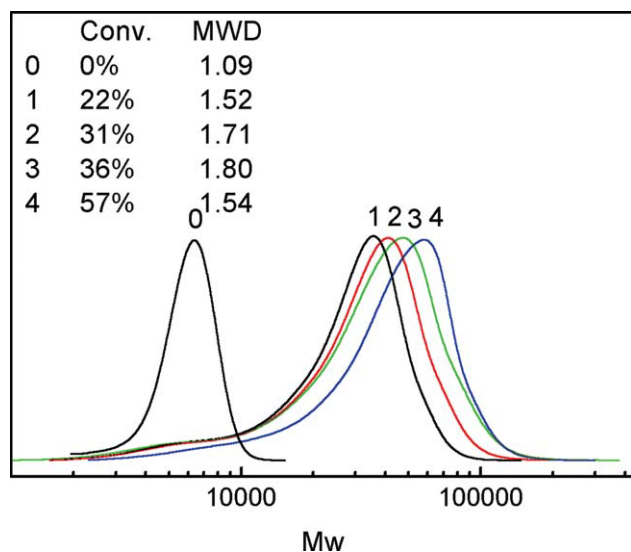
theoretic M_n and experiment data are small. As shown in Figure 10, the molecular weight of produced copolymers increase and the MWD become narrower with the development of conversions. The M_w/M_n data are in the range of 1.35–1.16.

The sequence structure of obtained polymers using various methods are confirmed by the ^{13}C NMR spectra shown in Figure 11. It can be seen that only the chemical shift representing MSM are found in the spectrum for SMA-RAFT. The chemical shift for SSS, MSM, SSM, and MSS triad can all be observed in the ^{13}C NMR analysis for the products of the one-step method. Therefore, this polymer has

Figure 8 The molecular weight distribution curves of the produced diblock copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
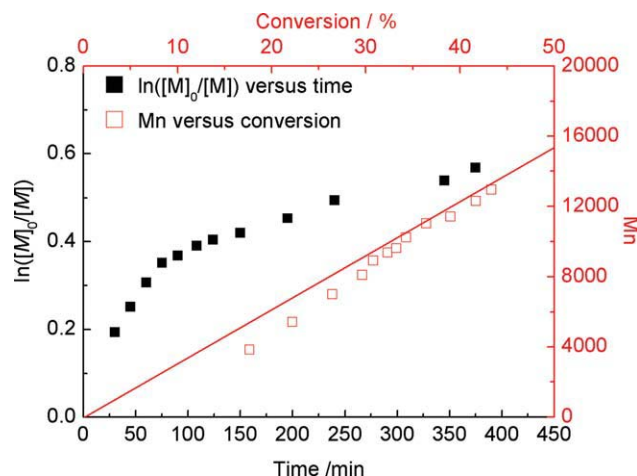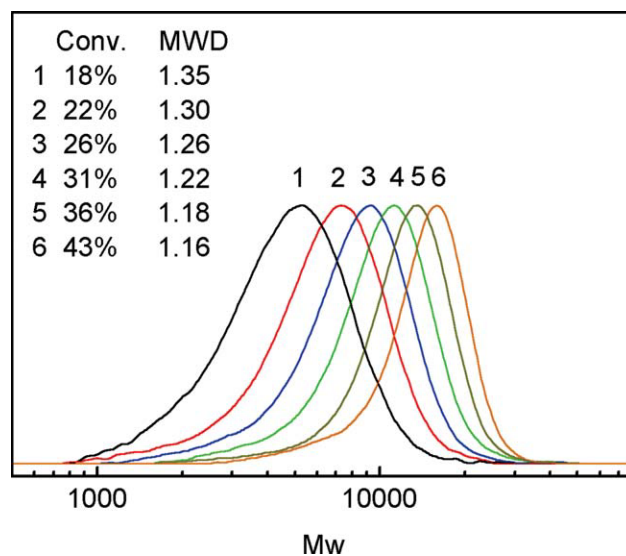

Figure 10 The molecular weight distribution curves of the produced copolymers in one-step method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
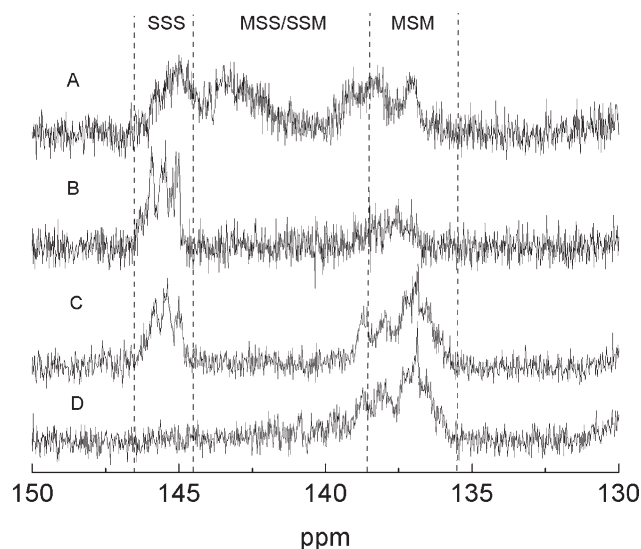
Figure 11 ^{13}C NMR spectra of the resulting SMA with different microstructure.

the blocks with PS, St-MAn alternating structure, and St-MAn random structure. In the spectra for the polymers produced using PS-RAFT or SMA-RAFT, both chemical shift for the SSS and MSM triad are found and the chemical shift for the SSM and MSS triad can not be observed. Therefore, these two polymers possess PS block and Poly(St-*alt*-MAn) block but do not have St-MAn random structure.

CONCLUSIONS

Block copolymers of St and MAn have been prepared using three different methods. When PS-RAFT is used, PS-*b*-Poly(St-*alt*-MAn) with narrow MWD is obtained. PS-*b*-Poly(St-*alt*-MAn) can also be synthesized using SMA-RAFT. However, the MWD of this product is more than 1.5, deviated considerably from the typical RAFT polymerization system. In the one-step method, copolymer with one PS block and one SMA block is produced. The SMA block in this copolymer possesses gradient structure instead of the required alternating structure. In summary, well-defined copolymer with one PS block and one alternating SMA block can only be synthesized using PS-RAFT agent at the moderate temperature.

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