

A Novel Polymer Chain Growing Mode and Styrene Copolymer Prepared with Low Molecular Weight Copolymer of α -Methylstyrene and Styrene as Macroinitiator

Qian Liu,¹ Lianying Liu,¹ Yuhong Ma,¹ Changwen Zhao,^{1,2} Wantai Yang^{1,2}

¹College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

²State Key Laboratory of Chemical Resource Engineering, College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Correspondence to: Y. H. Ma (E-mail: mayh@mail.buct.edu.cn) and W. T. Yang (E-mail: yangwt@mail.buct.edu.cn)

ABSTRACT: A new polymer chain growth mode, having multiple potential chain propagation sites, initiated by oligomer of α -methylstyrene (AMS) and styrene (St) (PAS) is presented in this article. The effects of PAS content, AMS fraction in PAS and reaction temperature on bulk polymerization of St have been investigated. It is demonstrated that the PAS performed as macroinitiator in the polymerization of St. The average molecular weights of products increase significantly with the evolution of the polymerization, which is different from conventional free radical polymerization. With 20 wt % macroinitiator, the molecular weights increase from 1.21×10^5 to 3.00×10^5 with the monomer conversion increasing from 15.3 to 83.0%. This unique feature is tentatively attributed to both the reversible polymerization–depolymerization of AMS segments at high temperature which could generate more than one propagation sites in a polymer chain and the combination termination of St free radical polymerization. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41460.

KEYWORDS: copolymers; monomers; oligomers and telechelics; polystyrene; radical polymerization

Received 11 April 2014; accepted 25 August 2014

DOI: 10.1002/app.41460

INTRODUCTION

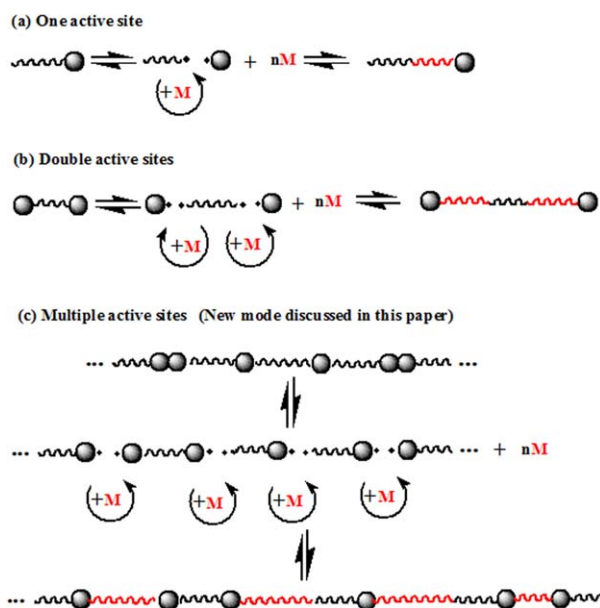
The controllability of structure, composition, and molecular weight in polymer synthesis is of importance in developing high performance polymer materials. The controlled free radical polymerization technologies, such as atom-transfer radical polymerization,^{1,2} reversible addition-fragmentation chain transfer process,^{3–5} nitroxide-mediated radical polymerization^{6,7} and so forth are robust tools to tailor polymer structures. However, there are still some challenges of these controlled polymerization technologies, such as unpleasant product color (and/or smell) and residues of catalysts. In addition, the controlled polymerizations always have slow polymerization rates and cost inefficiency. Thus it is necessary to develop new technologies to balance the controllability and the cost of the polymerization process. Nuken et al.⁸ reported that the nonpolymerizable monomer, 1,1-diphenylethylene (DPE), could mediate the conventional free radical polymerization to a controlled system. In the presence of DPE, the molecular weights increased almost linearly with the monomer conversions and the molecular weight distribution was much lower than that of the control runs. Moreover, the semiquinone structure formed in the presence of DPE in the copolymerization

could generate macroradicals when heated.⁹ The DPE mediated free radical polymerization has been applied to prepare block copolymers, such as, PMMA-*b*-PS,⁸ PMMA-*b*-PBA¹⁰, and PMMA-*b*-PVAc.¹¹ However, when the propagation chain incorporated a DPE molecule, the chain could no longer to add new monomer molecules. The chain free radical (active chain) ended with DPE unit could be terminated only by free radical combination. Thus, each oligomer chain with DPE unit bears only one initiating site maximum. As a result, the efficiency of the macroinitiator is limited.

As a derivative of styrenic monomers, α -methylstyrene (AMS), has low free radical homopolymerization reactivity due to the low enthalpy.¹² There have been intensive studies on the copolymerization of AMS with other vinyl monomers. It was showed that the AMS copolymerization cannot be inhibited or retarded although the enthalpy of AMS polymerization is low.¹³ However, the free radical copolymerization of AMS with other vinyl monomers always showed slow reaction rate and yielded low molecular weight products. There are different explains, for example, the steric restrictions on the placement of successive AMS units (penultimate effect),^{14,15} reversibility of

polymerization,^{16–18} degradative chain transfer to AMS monomer^{19,20} and the kinetic factor^{14,21–23} to address the observations. These studies also revealed that the degradation of AMS segments occurred in the copolymerization of AMS with other monomers when the reaction temperature was higher than the ceiling temperature of AMS polymerization. The chain degradation in the copolymerization tends to form a new AMS unit radical from the AMS-containing copolymer chain at the temperature above the ceiling polymerization temperature of AMS.

Recently, our laboratory has found that the copolymerization behavior in the presence of AMS was similar with that in the presence of DPE.²⁴ The copolymer of AMS and glycidyl methacrylate (GMA) can be performed as macroinitiator to initiate the polymerization of MMA or St to prepare block polymers.²⁵ With *N*-*t*-butyl- α -phenylnitron as radical scavenger, the generation of free radicals by heating AMS/GMA copolymers was supported by ESR.²⁶ Then the copolymers of AMS and other (meth)acrylates have been prepared and studied. The AMS mediated free radical copolymerization was applied to prepare AMS/butyl acrylate (BA)/acrylic acid (AA) copolymers and AMS/AA/MMA copolymers by emulsion-free process.²⁷ Furthermore, the AMS/BA/AA copolymer could be used to initiate the emulsion-free polymerization of St to prepare the core-shell nanoparticle of which the core was PS and the shell was AMS/BA/AA copolymer.²⁸ With the AMS copolymer as macroinitiator, a series of block copolymers as dispersant agents has been prepared. The technology is very competitive for industrial scale up.²⁹ The studies showed that AMS-mediated free radical polymerization can be widely suitable for various monomers. Except for application in initiating the monomer polymerization, the oligomers of AMS copolymers have also been exploited to form grafting chains in polymer molten blending and graft onto the carbon nanotubes. When the AMS/GMA oligomer was added to a blend of PP and Ny66, the crystallinity degree of Ny66 decreased due to the *in situ* compatibilization.³⁰ When the AMS/GMA or AMS/St oligomer was heated with multiwalled carbon nanotubes (MWCNTs) in a solvent, the modified MWCNTs could be dispersed stably in both *N,N*-dimethylformamide and acetone.³¹ It was explained that the oligomers generated free radicals and then grafted onto the MWCNTs when heated. Very recently, we have reviewed the mechanism and application of the AMS mediated free radical polymerization.²⁴ So far, the investigations have been focused on the copolymerization of AMS and (meth)acrylates and the performance of the copolymers as macromolecular initiators. However, there are also some limitations caused by the great difference of the monomer reactivity ratios as follows: (1) the monomer conversion, the molar fraction of AMS unit in the copolymer (oligomer) and the molecular weight of the copolymer strongly depend on the fraction of AMS in monomer feed; and (2) the AMS unit incorporated into the copolymer chain is much less than that in the monomer feed. As a result, there are also some unfavorable effects of the AMS-containing copolymers on the reactions using the copolymers as macroinitiators. The termination of the chains growth will be caused by the disproportionation termination of (meth)acrylates, which might lead to the low molecular weights. To suppress this effect, we launched a project to examine if it is helpful to get higher molecular weight copolymers by AMS-mediated copolymerization in preparing copolymers



Scheme 1. Proposed chain growth modes of the AMS/St copolymer-initiated radical polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the AMS-containing copolymers as macroinitiators. This project is based on the following thoughts: (1) styrene is expected to get a copolymer with higher AMS fraction in the polymer chains and a higher monomer conversion,³² and (2) compared with the DPE mediated free radical polymerization which has only one likely initiating site per polymer chain, high incorporation of the AMS unit could form more AMS-containing weak bonding sites in the copolymer chains which might have multiple potential initiating sites; and (3) because combination termination is main termination mode of St polymerization, there would be more molecular chains keeping active in the polymerization initiated by the AMS-containing copolymer. With the understanding of the AMS mediated copolymerization and the mechanism of the AMS-containing copolymer as macroinitiator, we thought it is possible to develop a novel polymer chain growth mode with the AMS/St copolymer as initiator. There were one or two initiation groups in the polymerization initiated by traditional small molecular initiators, as shown in Scheme 1(a) and (b). Different from the small molecular initiators, there could be more than one active center in the macroinitiator in the same time, as shown in Scheme 1(c). The molecular chains in the polymerization have multiple potential active sites. It is possible to achieve high polymerization rate and get the polymer with high molecular weight.

In this contribution, the bulk polymerizations of St initiated by copolymers of AMS and styrene (abbreviated as PASs) with different AMS contents were investigated. The effects of PAS content, AMS content in PAS and reaction temperature on the monomer conversions, molecular weights and $\ln([M_0]/[M])$ were revealed. The molecular weights of products increased significantly with the evolution of polymerization. This behavior is different from the conventional free radical polymerization. This unique chain growth mechanism has been proposed and discussed. The results offered a new insight in polymer synthesis methodology.

Table I. The Structure Parameters of AMS/St Copolymers Used as Macroinitiators

Entry	Molar fraction of AMS in the monomer mixture (%)	Molar fraction of AMS in the copolymer ^a (%)	Mn ^b (g/mol)	PDI
PAS1	30	0.22	6400	2.97
PAS2	40	0.31	5000	2.22
PAS3	50	0.42	4400	1.76

^a Values measured by ¹H NMR, referenced to TMS.^b Values measured by GPC.

EXPERIMENTAL

Materials

Styrene (St, Beijing Chemical Reagent Corp.) was distilled under reduced pressure before use. Tetrahydrofuran (THF) and methanol were purchased from Beijing Chemical Reagent Corp. were used as received. AMS/St copolymer (PAS) was prepared by free radical polymerization with azodiisobutyronitrile (AIBN) as initiator at 70°C. The PASs were dried under vacuum at room temperature for 48 h and stored in a desiccator. The structure parameters of PAS with different AMS content were summarized in Table I.

Instruments

NMR spectra were obtained in CDCl₃ at room temperature with a Bruker AV600 spectrometer. ¹H chemical shifts were referenced to tetramethylsilane and the residual nondeuterated solvent signal at $\delta = 7.23$ ppm. Molecular weights and polydispersities (PDI, Mw/Mn) of the products were determined by a gel permeation chromatography (GPC) (Waters 1515-717-2414 system with Styragel® HT3, 4, and 5 in series). The GPC was calibrated using polystyrenes (PSs) as standards and THF as an eluent.

Bulk Polymerization of St Initiated by PASs

Bulk polymerization of St was performed at 90–100°C using PASs as macroinitiator without addition of conventional radical initiator under nitrogen atmosphere in a tube reactor. When the polymerization time was ended, the crude products were dissolved in THF and precipitated in excess methanol to remove the residual monomer. This solve/precipitation process was repeated thrice for each run. The final product was dried under vacuum at room temperature for 48 h and stored in a desiccator. The conversion of the monomer was determined gravimetrically. The products were characterized by GPC, differential scanning calorimetry (DSC), ¹H and ¹³C NMR spectroscopy.

Bulk Polymerization of St Without any Initiator

The synthesis and purification of the PS reference polymer followed the same procedure as described above but without PAS or any other initiator (Table II).

RESULTS AND DISCUSSION

The Effects of PAS Content on Bulk Polymerization of St

The bulk polymerizations of St were performed with different amount of PAS1 (Mn = 6400 g/mol, PDI = 2.97) as the macroinitiators at 100°C. The resulting polymers were designated as PASS. Figure 1(a) showed the monomer conversions of the poly-

merizations as reaction time. The monomer conversion was defined by an equation as following:

$$C = \frac{m - m_0}{M} \times 100\% \quad (1)$$

In Eq. (1), *C* is the monomer conversion; *M* is the total mass of the sample at different time; *m* is the mass of the dried sample at different time; and *m*₀ is the mass of macroinitiator in the sample at different time. The reaction times were 12 h without PAS1 (controlled run), 12 h with 20 wt % PAS1, 10 h with 30 wt % PAS1 and 8 h with 40 wt % PAS1, respectively. Without PAS and the final monomer conversion was under 20% (control run of bulk styrene polymerization, denoted as RBS). Conversely, the final monomer conversions of other three runs were 83.0% (PASS1-1), 87.2% (PASS1-2), and 91.5% (PASS1-3). It was revealed that the polymerization was hardly performed when no PAS was added, which supported that the PAS performed as the initiator in the polymerization of St. Moreover, the reaction rates increased with the amount of PAS1 loaded. As showed in Figure 1(b), the average molecular weights of products decreased with the increase of the amount of PAS1. These observations supported that the PAS played the role as the initiator in polymerization. Furthermore, it was also found that the molecular weight increased significantly with the evolution of the polymerization, which was quite different from the conventional free radical polymerization. Using 20 wt % PAS1 as macroinitiator, the molecular weights of the polymers increased from 121,000 (conversion at 15.3%) to 301,000 (conversion at 83.0%), which was caused by the presence of chain radical ended with AMS. The $\ln([M_0]/[M])$, which represents concentration of radical, was defined by eq. (2).

$$\ln \left(\frac{[M_0]}{[M]} \right) = \ln \frac{1}{1-C} \quad (2)$$

In eq. (2), *C* is the monomer conversion; [M₀] = concentration of the monomer at time *t* = 0 h and [M] = concentration of the monomer at the corresponding time, wherein the concentration of monomer in bulk polymerization was calculated by eq. (3).

$$[M] = \frac{M - m}{M} \quad (3)$$

Table II. Summaries of Experiments of St in Bulk Initiated by PASs

Entry	Reaction temperature (°C)	Macroinitiator	Weight fraction of macroinitiator ^a (%)
RBS	100	/	/
PASS1-1	100	PAS1	20
PASS1-2	100	PAS1	30
PASS1-3	100	PAS1	40
PASS2	100	PAS2	40
PASS3	100	PAS3	40
PASS1-4	90	PAS1	20

^a values measured based on the St monomer.

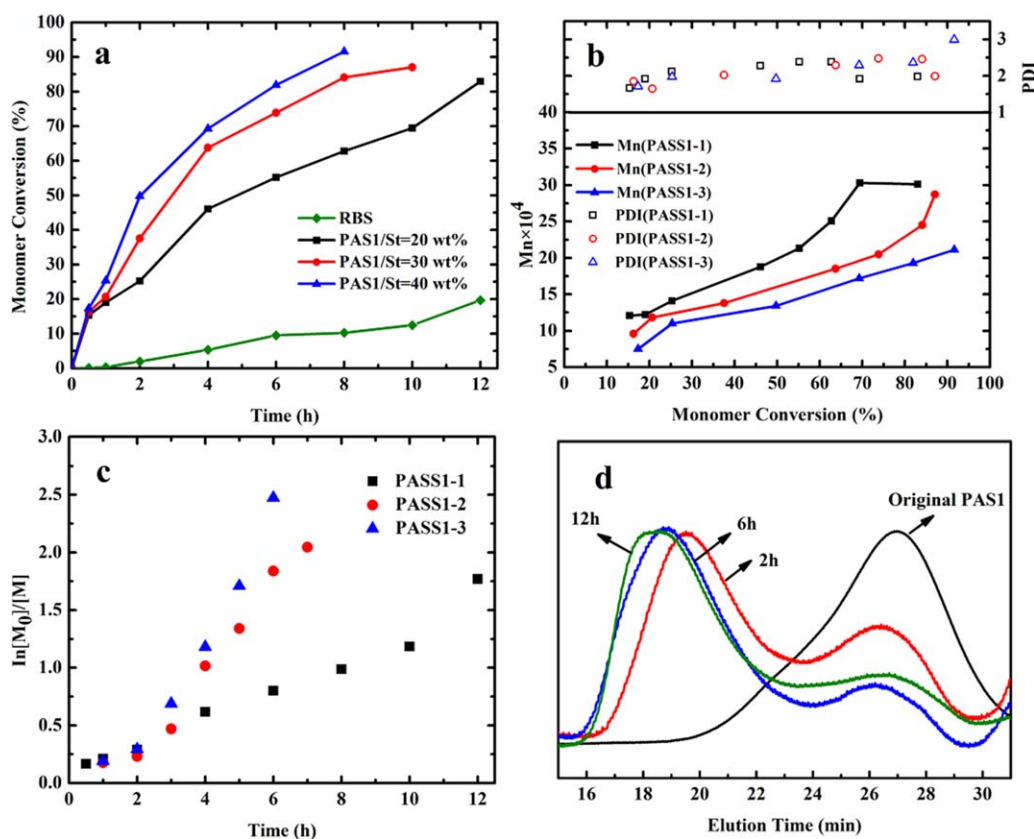
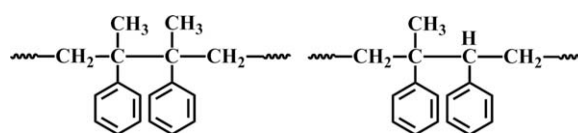


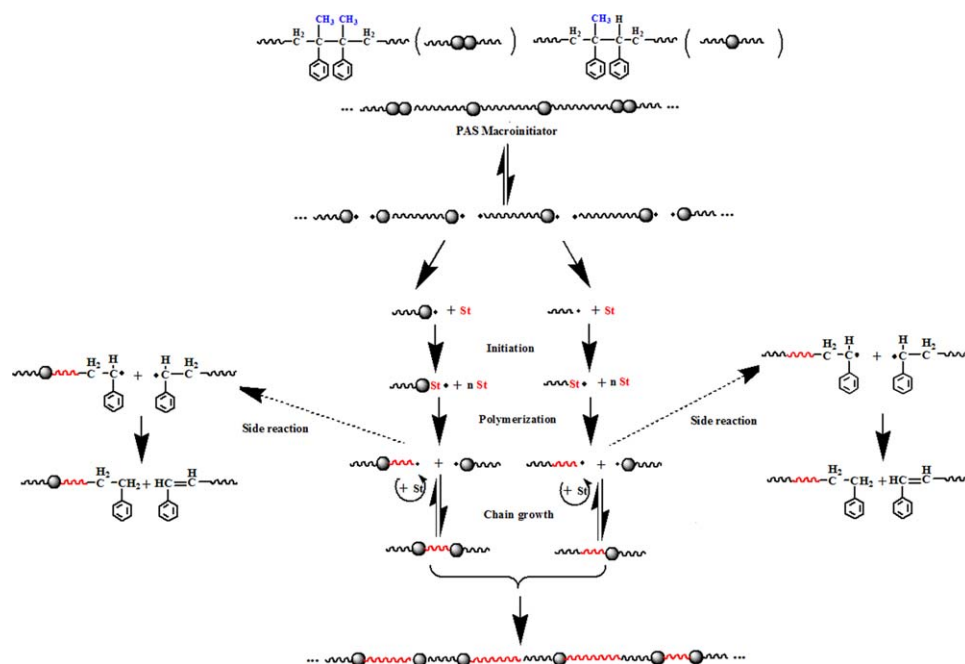
Figure 1. (a) Dependence of monomer conversions as function of time in the bulk polymerization initiated by different content of PAS1; (b) dependence of average molecular weight (M_n) and polydispersity (PDI) as function of monomer conversion; (c) plots of $\ln([M_0]/[M])$ (where $[M_0]$ = concentration of the monomer at time $t = 0$ h and $[M]$ = concentration of the monomer at the corresponding time) as function of time; and (d) GPC curves for original PAS1 and samples obtained during bulk polymerization of St initiated by PAS1 macroinitiator (weight fraction of PAS1 = 20 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In eq. (3), M is the total mass of the sample at different time and m is the mass of the dried sample at different time. As showed in Figure 1(c), the $\ln([M_0]/[M])$ also increased almost linearly with the reaction time, and the slopes increased with the amounts of PAS1 macroinitiator added. The phenomena implied that the concentration of radicals was almost constant in the polymerization process. Combined with the fact of the molecular weights of the polymers increased significantly with the monomer conversions, it might be concluded that there might be polymer chains keeping active during the St polymerization initiated by PAS macroinitiator. In previous reports, it was demonstrated that weak bonds in AMS copolymer macroinitiators, such as -AMS-AMS- (head-head) and -AMS-M- (head-head), could give the birth of new chain radicals when heated.^{25,26} In the polymerization of St, the AMS-containing weak bonds (as illustrated in Scheme 2) in PAS macroinitiator could generate chain radicals to initiate the polymerization at the reaction temperature. In the polymerization of St, new weak bonds would form due to the combination termination of chain radicals ended with AMS with other radicals, such as other AMS radical and St radical. These new weak bonds could generate new chain radicals again to initiate the polymerization of new monomers to keep the growth of polymer chains at reaction temperature. As the degradation of PAS always existed dur-

ing the polymerization, there would be always chain radicals. Moreover, when PAS content increased, the radical concentration increased. As the combination termination is the main termination mode of St polymerization, there would always be active sites in the polymer chains. Moreover, as more than one AMS-containing weak bond existed in PAS, there were multiple initiating sites in a molecular chain of PAS. The unique structure of the PAS macroinitiator made the polymerization showed a different mode of polymer chain growth from that of conventional radical polymerization. This novel initiating and chain growth mode of St polymerization was illustrated in Scheme 3. However, when the content of weak bonds was low [as showed at curve of PASS1-1 molecular weights in Figure 2(b)], the change of molecular weights were leveling off at the latter stage of the polymerization. That was because the polymer chain propagation in the polymerization got weak when content of



Scheme 2. The possible structures of AMS-containing units in PAS macroinitiator.



Scheme 3. The proposed mechanism of molecular chain growth in the St bulk polymerization initiated by PAS macroinitiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

active sites was low, especially at the later stage of polymerization with the decrease of the monomer concentration. To further figure out the initiation mechanism of PAS, the typical GPC curves of original PAS1 and the samples obtained during the polymerization initiated by 20 wt % PAS1 were showed in Figure 1(d). The PASS peaks shifted to higher molecular weight with the extension of the polymerization time. The GPC traces at different polymerization times showed that the molecular weights of PASS increased steadily. Conversely, the oligomer peaks slightly shifted to lower molecular weight end with the extension of polymerization times. This change indicated the degradation of PAS during the polymerization. The phenomena suggested that the PAS could be used to initiate polymerization of St. However, the peaks corresponding to the oligomer did not completely disappear at the end of the polymerization. Thus we calculated the integral areas of the high molecular weight peak and the remaining oligomer peak to further understand the initiating efficiency and mechanism. An equation was introduced to define the relationship between AMS-containing oligomer content in the product and the theoretical possible max AMS-containing oligomer at different reaction time.

$$R = \frac{\frac{Ax}{Ao}}{\frac{20\%}{20\%+C}} \quad (4)$$

In eq. (4), Ax is the integral area of the remaining oligomer peak; Ao is the total integral area of the high molecular weight peak and the remaining oligomer peak and C is the monomer conversion of polymerization at different time. Both Ax and Ao were obtained from separating overlapped GPC curve showed in Figure 1(d). The values of R were shown in Table III. It was shown that the values of R at different reaction time were lower than 1. The results implied the PAS can act as the initiator in the polymerization. However, the value of R at 12 h, when the

polymerization ended, was close to 1. The behavior might be caused by two factors. It is well known that the disproportionation termination (side reaction) in the polymerization of St increases due to the high reaction temperature.³³ Some primary chain radicals (formed by the thermolysis of the PAS) were terminated by the disproportionation or chain transfer but no longer reacting with monomer. This is the main reason of the existence and shift of the PAS peaks. Conversely, when monomer concentration decreased at the latter stage of the polymerization, the effects of degradation of AMS units got strong. The degradation of AMS-containing copolymer might cause the decrease of the molecular weight at high temperature.²⁶ As a result, there were AMS-containing oligomers in the resulting products, which would also cause the existence of the peaks at low molecular weight in the GPC traces.

As shown in Figure 2, the structure and composition of the resulting PASS polymers were determined by ¹H NMR and ¹³C NMR. According to the ¹H NMR spectra, the molar fractions of AMS in the resulting polymers could be determined by comparing the integral areas of the chemical shifts assigned to the methyl in AMS [H8, Figure 2(a)] with the integral areas of aromatic protons in the polymers [H1–H5, Figure 2(a)].¹³ The results were shown in Table IV. Figure 2(b) showed the ¹³C NMR spectrum of resulting PASS1-1. According to literature, the methyl of the AMS [C8, Figure 2(b)] is the most sensitive carbon of the copolymer and its chemical shift is within the range of ca. 22.8 ppm.³⁴ The ¹³C NMR results showed the resulting products were AMS-containing polymer.

The Effects of AMS Content in PAS on Bulk Polymerization of St

To further understand the effects of AMS-containing weak bonds in PAS on the polymerization, the bulk polymerizations

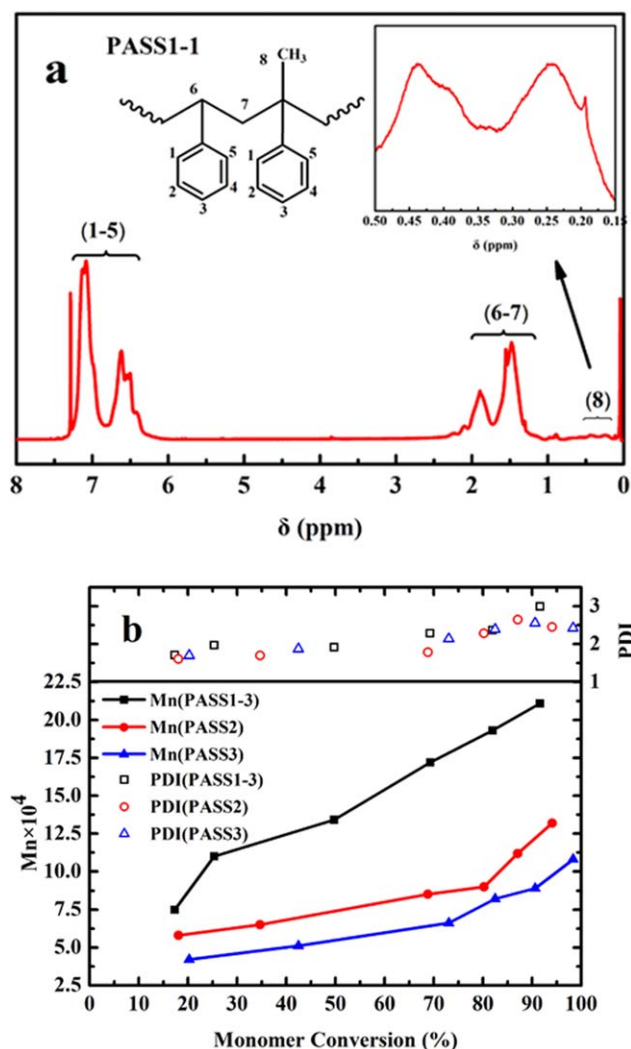


Figure 2. (a) ^1H NMR spectra of resulting PASS1-1 in CDCl_3 at room temperature and (b) ^{13}C NMR spectra of resulting PASS1-1 in CDCl_3 at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of St were initiated by different PASs with different AMS fractions, namely PAS1 with 22 mol % AMS, PAS2 with 31 mol % AMS and PAS3 with 42 mol % AMS, at 100°C for 8 h. Figure 3(a)

Table IV. Bulk Polymerization of St at 100°C Initiated by PASs

Entry	Weight fraction of PAS (%)	Theoretical molar fraction of AMS in PASS (%)	Molar fraction of AMS in PASS ^a (%)	Mn ^b (g/mol)	PDI
PASS1-1	20	4.29	4.89	300,000	1.98
PASS1-2	30	6.46	6.74	287,000	1.99
PASS1-3	40	8.65	8.67	211,000	2.99
PASS2	40	12.09	11.96	132,000	2.45
PASS3	40	16.24	16.18	108,000	2.44

^a Values measured by ^1H NMR, referenced to TMS.

^b Values measured by GPC, calibrated with polystyrene standards.

Table III. The Values of R Obtained from eq. (4)

Reaction time (h)	2	6	12
R	0.68	0.62	0.93

showed the monomer conversions of the polymerization with reaction time initiated by PASs with different AMS content. The reaction rate increased when the molar fraction of AMS in PAS macroinitiators increased. In addition, as showed in Figure 3(b), the average molecular weights decreased with the increasing of AMS molar fraction in PASs. These behaviors were consistent with the conventional free radical polymerization mechanism, which supported that the AMS-containing weak bonds were initiating sites in the macroinitiator. Figure 3(c) showed that the concentration of radicals was almost constant during the polymerization. With the AMS content in macroinitiator increasing, the increase extents of the $\ln([M_0]/[M])$ increased while that of the molecular weight decreased. That was because that there were more AMS radicals in the polymerization when the AMS-containing weak bonds in the PAS macroinitiator increased. At the same time, given the degradation of AMS units became strong due to higher AMS radicals content, the propagation of the molecular chain got more difficult. The phenomena supported that the AMS-containing weak bonds in the macroinitiator acted as the active sites and the propagation sites in the polymerization. Moreover, the PDIs hardly changed with the evolution of the bulk polymerization. The compositions of the resulting PASS polymers determined by ^1H NMR spectra were listed in Table IV. The molecular weights and PDIs of the final products were also given in Table IV. It was showed that the large molecular weight products could be obtained by the process.

The Effects of Temperature on Bulk Polymerization of St Initiated by PAS

The bulk polymerizations of St at 90 and 100°C were performed for 6 h using PAS1 ($M_n = 6400$ g/mol, $\text{PDI} = 2.97$) as the macroinitiators. The weight fraction of PAS based on monomer St was 20 wt %. The monomer conversions of the polymerization with time at different temperatures were showed in Figure 4(a). The monomer conversion at 6 h went down from 60 to 30% with reducing temperature from 100 to 90°C . At the same time, the average molecular weight increased when the reaction temperature decreased, as shown in Figure 4(b). The behaviors were

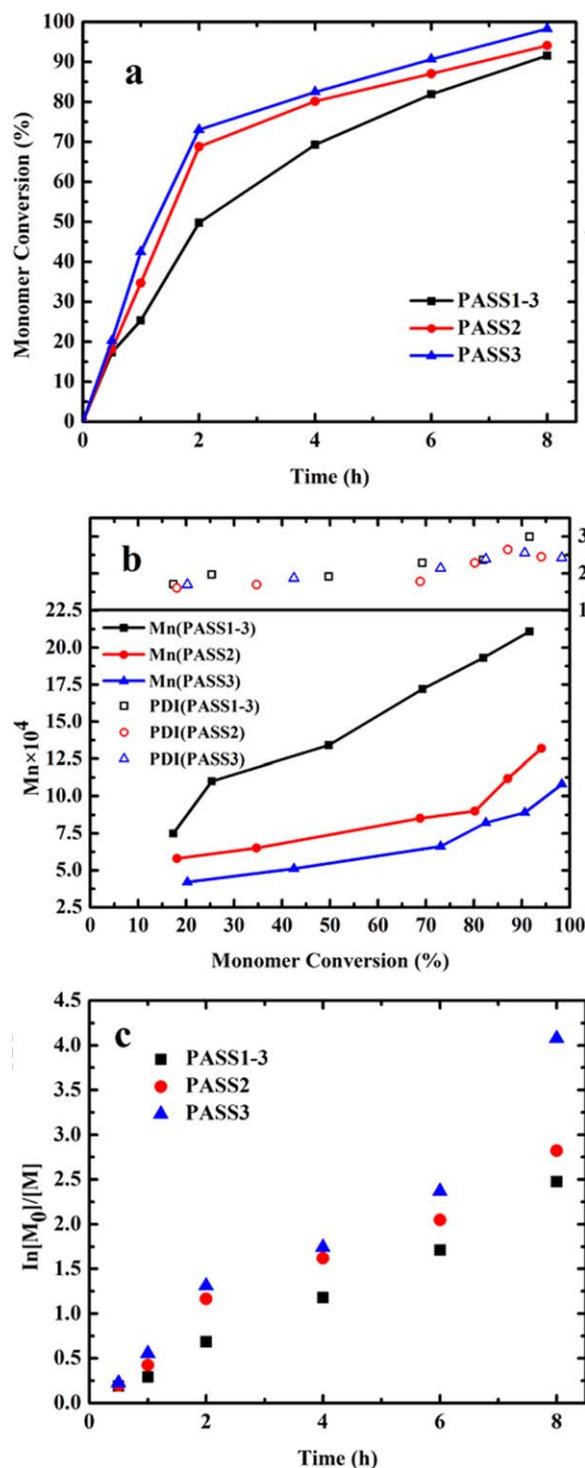


Figure 3. (a) Dependence of monomer conversions as function of time in the bulk polymerization initiated by PASs with different AMS content; (b) Dependence of average molecular weight (Mn) and polydispersity (PDI) as function of monomer conversion; and (c) Plots of $\ln([M_0]/[M])$ (where $[M_0]$ = concentration of the monomer at time $t=0$ h and $[M]$ = concentration of the monomer at the corresponding time) as function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

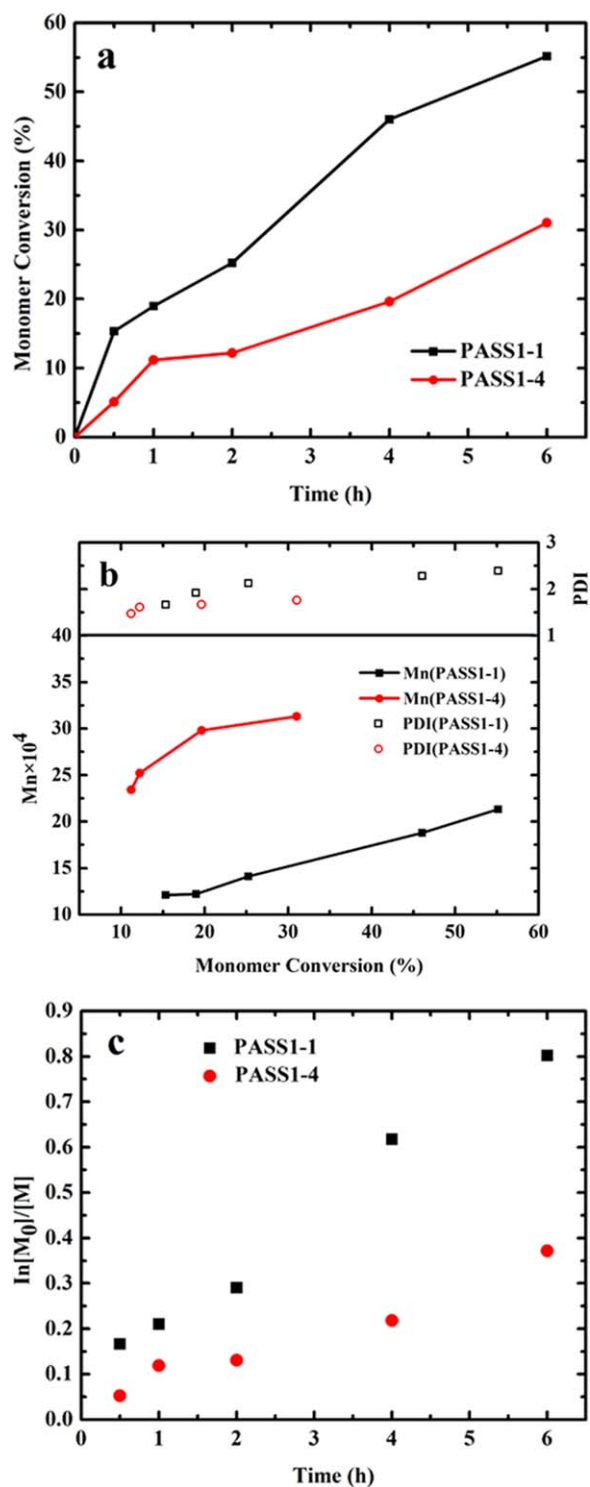


Figure 4. (a) Dependence of monomer conversions as function of time in the bulk polymerization initiated by PAS1 at 90 and 100°C; (b) dependence of average molecular weight (Mn) and polydispersity (PDI) as function of monomer conversion; and (c) plots of $\ln([M_0]/[M])$ (where $[M_0]$ = concentration of the monomer at time $t=0$ h and $[M]$ = concentration of the monomer at the corresponding time) as function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consistent with conventional free radical polymerization mechanism. However, with the decrease of reaction temperature, both slopes of the increases of molecular weight and the $\ln([M_0]/[M])$ decreased [as showed in Figure 4(c)]. As the degradation of AMS-containing polymer was strongly affected by the reaction temperature.^{16,17} The degradation rate of PAS macroinitiator at 90°C was lower than that at 100°C did. As a result, the concentration of radicals in the polymerization decreased with the temperature decreasing. Then the apparent chain growth in the St polymerization was slowed down. The phenomena further implied that the AMS-containing weak bonds acted as initiating group in PAS macroinitiator. In addition, the PDIs kept constant with the monomer conversions. However, due to the degradation in polymerization got stronger at 100°C, the PDIs went up with the temperature increasing.

CONCLUSIONS

The bulk polymerizations of St could be performed using the PASs as macroinitiators. It was found that the average molecular weights increased to high level with the evolution of the polymerization. This unique behavior was resulted from the reversible polymerization–depolymerization of AMS segments in the polymer chains at high temperature and the combination termination of St free radical polymerization. The multiple chain propagation sites were produced by multiple active sites in PAS macroinitiator in the AMS-mediated radical polymerization. As the PAS content, the AMS content in the PAS and reaction temperature increased, the effects of AMS-containing macroinitiator on the polymerization got stronger.

ACKNOWLEDGMENTS

The authors gratefully thank the Natural Science Fund of China (51033001 and 51221002) for financial support of this work.

REFERENCES

1. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
2. Wang, Y.; Soerensen, N.; Zhong, M.; Schroeder, H.; Buback, M.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 683.
3. Chiefari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. *Macromolecules* **1998**, *31*, 5559.
4. Patel, V. K.; Vishwakarma, N. K.; Mishra, A. K.; Biswas, C. S.; Maiti, P.; Ray, B. *J. Appl. Polym. Sci.* **2013**, *127*, 4305.
5. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.
6. Georges, M. K.; Veregin, R. P.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
7. Sciannamea, V.; Jérôme, R.; Detrembleur, C. *Chem. Rev.* **2008**, *108*, 1104.
8. Wieland, P. C.; Raether, B.; Nuyken, O. *Macromol. Rapid Commun.* **2001**, *22*, 700.
9. Kos, T.; Strissel, C.; Yagci, Y.; Nugay, T.; Nuyken, O. *Eur. Polym. J.* **2005**, *41*, 1265.
10. Luo, Y. D.; Chou, I.; Chiu, W. Y.; Lee, C. F. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4435.
11. Chen, D.; Shi, Y.; Fu, Z. F. *J. Appl. Polym. Sci.* **2009**, *111*, 1581.
12. Lowry, G. G. *J. Polym. Sci.* **1960**, *42*, 463.
13. Rudin, A.; Samanta, M. C. *J. Appl. Polym. Sci.* **1979**, *24*, 1665.
14. Rudin, A.; Chiang, S. S. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1974**, *12*, 2235.
15. Nogueira, R. F.; Tavares, M. I. B. *J. Appl. Polym. Sci.* **2003**, *88*, 1004.
16. Palmer, D. E.; McManus, N. T.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1981.
17. Martinet, F.; Guillot, J. *J. Appl. Polym. Sci.* **1999**, *72*, 1611.
18. Palmer, D. E.; McManus, N. T.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1753.
19. Rudin, A. M.; Samanta, C.; Van Der Hoff, B. *J. Polym. Sci.: Polym. Chem. Ed.* **1979**, *17*, 493.
20. Kukulj, D.; Davis, T. P.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 994.
21. Ueda, M.; Mano, M.; Mori, H.; Ito, H. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1779.
22. Martinet, F.; Guillot, J. *J. Appl. Polym. Sci.* **1999**, *72*, 1627.
23. Martinet, F.; Guillot, J. *J. Appl. Polym. Sci.* **1997**, *65*, 2297.
24. Ma, Y. H.; Zhang, B.; Zhao, C. W.; Liu, L. Y.; Jiang, S.; Liang, S. J.; Yang, W. T. *Acta Chim. Sin.* **2013**, *71*, 151.
25. Jiang, S.; Deng, J. P.; Yang, W. T. *Polym. J.* **2008**, *40*, 543.
26. Jiang, S.; Deng, J. P.; Yu, Q.; Yang, W. T. *J. Appl. Polym. Sci.* **2011**, *120*, 466.
27. Jiang, S.; Sun, A. P.; Deng, J. P.; Yang, W. T.; Yu, Q. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2011**, *48*, 846.
28. Jiang, S.; Fang, X. H.; Yu, Q.; Deng, J. P.; Yang, W. T. *J. Appl. Polym. Sci.* **2012**, *124*, 4121.
29. Cui, L. L.; Feng, S. G.; Liu, Y. F.; Wang, T.; Zhang, Q. W. US Pat. 20120101218A1, April 26, **2012**.
30. Deng, J. P.; Liang, S. J.; Zhang, C. R.; Yang, W. T. *Macromol. Rapid Commun.* **2007**, *28*, 2163.
31. Jiang, S.; Deng, J. P.; Yang, W. T. *Macromol. Rapid Commun.* **2008**, *29*, 1521.
32. Liu, Q.; Liu, L. Y.; Ma, Y. H.; Zhao, C. W.; Yang, W. T. *Chin. J. Polym. Sci.* **2014**, *32*, 986.
33. Guo, H.; Yu, J. X. *Polym. Mater. Sci. Eng.* **1990**, *15*, 172.
34. Nogueira, R. F.; Tavares, M. I. B. *J. Appl. Polym. Sci.* **2001**, *81*, 261.