

Copolymerization of α -Methylstyrene and Styrene*

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Abstract In this paper, the effects of temperature from 60 °C to 80 °C and the molar ratios in monomer feed on the copolymerization of α -methylstyrene (AMS) and styrene (St) were studied. The resulting copolymers, designated as PAS, were characterized by FTIR, GPC, NMR and TGA. When the reaction temperature was below 75 °C, the molecular weights increased almost linearly as the evolution of the copolymerization. The phenomenon revealed that AMS could mediate the conventional free radical polymerization having some features of a controlled system. As the AMS/St = 50/50 (molar) in feed, the overall fraction of the AMS unit incorporated into the copolymer was as high as 42 mol%, the monomer conversion could be more than 90 wt% and the molecular weights could reach as high as 4400. However, since the styrene is more reactive than AMS, the AMS fraction in copolymer increased with the overall monomer conversion. The ¹³C-NMR revealed the products were random copolymers which had triads, such as -AMS-AMS-AMS-, -St-AMS-AMS- (-AMS-AMS-St-) and -St-AMS-St-. TGA curves demonstrated that the degradation temperature of the resulting copolymers went down from about 356.9 °C (0 mol% AMS) to 250.2 °C (42 mol% AMS). This behavior demonstrated that there exist weak bonds in the AMS-containing sequences which could be used as potential free radical generators.

Keywords: α -Methylstyrene; Styrene; Bulk polymerization; Thermal decomposition.

INTRODUCTION

Due to the steric hindrance of methyl group at α -position of α -methylstyrene (AMS) monomer, PAMS has higher thermal resistance ($T_g = 168$ °C), better mechanical property and radiation stability than polystyrene does. Thus, the polymerizations (copolymerizations) of AMS monomer and properties of AMS copolymers have been intensively investigated. For example, the low molecular weight AMS-containing copolymers were used as the additives for plastics and rubbers^[1–3]. In addition, AMS was also exploited to replace, at least partially, styrene monomer to improve the heat resistance of styrene and acrylonitrile copolymer (SAN) and acrylonitrile-butadiene-styrene (ABS)^[4, 5]. However, the mass production of SAN and ABS resins with AMS as comonomer has not come into industrial mass production yet. Thus, application of AMS in mass production of polymer materials is still very limited. So it is necessary to develop new technologies to consume AMS in synthetic polymers. It is well-known that AMS is hardly to get high molecular weight homopolymer by free radical polymerization due to its steric hindrance and the low enthalpy of polymerization^[6]. High molecular weight PAMS was usually prepared by cationic or anion polymerization processes^[7–10].

Although free radical homopolymerization of AMS is not practical to get high molecular weight products, the copolymerization with other vinyl monomers is feasible. The effects of degradation on the copolymerization

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51033001 and 21074006).

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Received November 7, 2013; Revised December 22, 2013; Accepted December 31, 2013

doi: 10.1007/s10118-014-1469-y

were an attractive topic in these studies. Wittmer *et al.*^[11] studied the copolymerization of AMS and methyl methacrylate (MMA) at low monomer conversion at the reaction temperature from 60 °C to 150 °C. The result showed that the reactivity ratios satisfied much well with the robust Wittmer's model than that of the Mayo-Lewis model. Martinet and Guillot^[12, 13] also studied the reactivity ratios at low monomer conversions of bulk and solution polymerization and improved the model for the copolymerization. In solution copolymerization of AMS with MMA, the experimental result indicates that the equilibrium of polymerization-depolymerization could not be neglected when the polymerization temperatures are higher than 60 °C. The monomeric reactivity ratios of bulk copolymerization of AMS with MMA at three different temperatures are $r_{\text{AMS}} = 0.47$, $r_{\text{MMA}} = 0.47$, at 50 °C; $r_{\text{AMS}} = 0.53$, $r_{\text{MMA}} = 0.51$, at 60 °C; and $r_{\text{AMS}} = 0.49$, $r_{\text{MMA}} = 0.47$, at 80 °C respectively. Palmer *et al.*^[14, 15] studied the bulk and solution polymerizations of AMS and MMA from the low to high monomer ratios during full conversions at elevated temperatures. In the presence of AMS, both bulk and solution polymerizations showed low polymerization reaction rates and yielded low molecular weight products (at about 60 °C, $M_n = 1600$ –5900 for bulk polymerization and $M_n = 1500$ –7000 for solution polymerization, respectively). Martinet and Guillot^[16] also investigated the emulsion polymerizations of AMS and MMA. Even with the high AMS fraction in monomer feed (50 mol%, 70 °C), the results showed that the monomer conversions could be near to 90 % and the molecular weight of the products were up to $M_n = 50000$ –400000 at 70 °C.

In past decades, the living free radical polymerization technologies, such as ATRP, RAFT, NMP and *etc.*, have offered many robust tools for tailoring polymer architectures and properties. Their industrial applications for mass products are still with great challenges. Thus it is necessary to develop novel controlled free radical polymerization technologies to balance the controllability and the cost of the operation. Nuyken *et al.*^[17] reported that nonpolymerizable vinyl compound 1,1-diphenylethylene (DPE) could mediate the conventional free radical polymerization to a controlled system. In the presence of DPE, the molecular weight increased with the monomer conversion almost linearly and the molecular weight distribution was much narrower than that of the control run. The semiquinone structure formed in the presence of DPE in the copolymerization would be scissored into macroradicals when heated^[18]. This technology has been successfully applied to prepare block copolymers, for example, PMMA-*b*-PS^[17], PMMA-*b*-PBA^[19] and PMMA-*b*-PVAc^[20]. However, when the propagation chain added a DPE molecule the chain could not add a monomer any more. The chain free radical (active chain) ended with DPE unit could only be terminated by free radical coupling or disproportionation reaction. Each oligomer chain with DPE unit likely had only one initiating group. With the similar structure to DPE, Yang *et al.*^[21] developed AMS controlled free radical polymerization. The research showed the similar polymerization behavior to the DPE system. However, there has also some difference. AMS is a polymerizable monomer and could form -AMA-AMS- segment in the copolymer chain which could have multiple potential initiating groups. Again, the copolymers of AMS and glycidyl methacrylate (GMA) could perform as macromolecular initiator to initiate the polymerization of MMA or St to prepare block polymers^[22]. Because the steric hindrance of AMS is weaker than that of DPE, it was believed that AMS-containing polymer might have more “living” points (potential initiating sites) in the polymer chain. The degradation mechanism of the AMS/GMA copolymer was demonstrated by the ESR with *N*-*t*-butyl- α -phenylnitrone as radical scavenger^[23]. It demonstrated that the weak bonds in AMS-containing polymer chains could generate radicals to initiate new polymerization. AMS/butyl acrylate (BA)/acrylic acid (AA) copolymers and AMS/AA/MMA copolymers were also prepared by emulsion-free process^[24]. In addition, the AMS/BA/AA copolymer was used to initiate the emulsion-free polymerization of styrene (St) to produce the core-shell nanoparticle, of which the core was PS and the shell was AMS/BA/AA copolymer^[25]. The size of the core-shell nanoparticle was range from 126 nm to 282 nm. The oligomers of AMS and GMA could be also grafted onto polypropylene in molten blending^[26]. When the oligomer was added to a blend of PP/Nylon 66, the crystallinity degree of Nylon 66 decreased due to the *in situ* compatibilization. Moreover, the AMS/GMA oligomers and AMS/St oligomers have been successfully grafted onto multi-walled carbon nanotubes (MWCNTs) when heated^[27]. Recently, a series block polymers with good performance as dispersant has been developed based on AMS copolymer macroinitiator technology^[28].

However, the molar ratios of AMS unit incorporated into copolymers of AMS with (meth)acrylates are always much lower than its molar ratios in monomer feeds. It was difficult to raise the AMS contents in the copolymer by simply changing the monomer ratio in feed. Considering the structural similarity of St and AMS, it is possible to prepare AMS/St copolymers with high AMS contents. Rudin and Samanta^[29–31] studied copolymerizations of AMS and St during different processes. The solution copolymerization showed slow reaction rate and produced low molecular weight copolymers due to the chain transfer to AMS monomer. On the contrary, the effect of chain transfer to AMS monomer in emulsion copolymerization was not as significant as in solution copolymerization.

To our best knowledge, the bulk polymerization of St with AMS, especially at high AMS molar ratio in monomer feed and high monomer conversion, has not been investigated thoroughly yet. Recently, we launched a project to exploit the bulk copolymerization of AMS and St with high AMS monomer ratios in feed and application of resulting copolymer as macroinitiator in preparing novel polymers. In this report, the bulk copolymerization of AMS and St was investigated in details. The effects of reaction temperature and AMS molar ratio in the monomer feed on the monomer conversions, molecular weights and compositions of the products were revealed. It was found that the molecular weights increased significantly with the monomer conversion. This behavior was not consistent with the conventional free radical polymerization mechanism. In addition, the thermal degradation of the copolymers with different AMS contents was also investigated. These results are of importance for AMS/St copolymer as a macromolecular initiator.

EXPERIMENTAL

Materials and Reagents

α -Methylstyrene (AMS, Alfa Aesar) and styrene (St, Beijing Chemical Reagent Co.) were distilled under reduced pressure before use. *N,N'*-azobisisobutyronitrile (AIBN, Beijing Chemical Reagent Co.) was recrystallized from absolute ethanol and dried under vacuum at room temperature.

Instruments

NMR spectra were obtained in CDCl_3 at room temperature with a Bruker AV600 spectrometer. FTIR spectra were recorded with a Thermo Nicolet Nexus 670 infrared spectrometer with pellets pressed with KBr. Molecular weights and polydispersities (PDIs, M_w/M_n) of the products were determined by GPC (Waters 515–2410 system). The GPC was calibrated with polystyrene standards and with THF as an eluent.

Bulk Polymerization of AMS with St

Bulk copolymerization of AMS and St was carried out at 60–80 °C using 5 wt% AIBN as initiator under nitrogen atmosphere in a tube reactor. When the polymerization time was ended, the crude product was dissolved in THF and precipitated in excess methanol to remove the residual monomers. This solve/precipitation process was repeated thrice. The final product was dried under vacuum at room temperature for 48 h and stored in a desiccator. The conversion of the monomers was determined gravimetrically. The products were characterized by FTIR, GPC and ^1H - and ^{13}C -NMR spectroscopy.

Bulk Polymerization of St as a Control Run

The control bulk polymerization of St was carried out at 70 °C with 5 wt% AIBN as initiator. The others were similar as bulk copolymerization of AMS with St and summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and Characterization of PAS Obtained at Different Temperatures

Bulk copolymerization of AMS and St was carried out at 60–80 °C using 5 wt% (based on total monomers) AIBN as initiator under nitrogen atmosphere for 24 h until the conversion near to 100%. The molar fraction of AMS in the monomer mixture was about 30 mol%. The resulting copolymer was designated as PAS. FTIR spectra of PAS and PS are given in Fig. 1. There is an absorption peak appeared at 1380 cm^{-1} in FTIR spectrum

of PAS which is related to the methyl group at α -position of AMS monomer. Moreover, the asymmetric stretching vibration band of methyl group of AMS appears at 2960 cm^{-1} in FTIR spectrum of PAS. The result demonstrated that the AMS was incorporated into the copolymer.

Table 1. The summary of the bulk polymerization of AMS and St^a

Run	Reaction temperature ($^{\circ}\text{C}$)	AMS:St (mole:mole)
PAS1-1	60	3:7
PAS1-2	65	3:7
PAS1-3	70	3:7
PAS1-4	75	3:7
PAS1-5	80	3:7
PAS2	70	4:6
PAS3	70	5:5

^a AIBN as initiator, the amount was about 5 wt% to monomers.

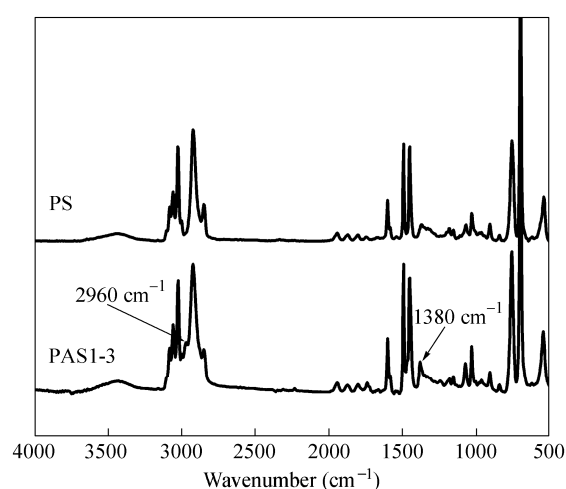


Fig. 1 FTIR spectra of PS and PAS1-3

The dependence of monomer conversions on the reaction times of copolymerization is shown in Fig. 2(a). The results showed that the conversions increased quickly at the early stage of the polymerization and then leveled off. The overall reaction rates went up with the raise of temperature from $60\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$. This behavior is consistent with conventional free radical polymerization. However, when the reaction temperature went up to $80\text{ }^{\circ}\text{C}$, the conversions of monomers were lower than those of $70\text{ }^{\circ}\text{C}$ and $75\text{ }^{\circ}\text{C}$ at the later stage of polymerization. This difference is related to the reversible equilibrium of polymerization and depolymerization of AMS which is affected strongly by the reaction temperature^[13, 15]. At higher temperatures, the apparent chain propagation rate of copolymerization was decreased.

Figure 2(b) shows the dependence of molecular weights of copolymers with 30 mol% AMS as function of time at different reaction temperatures. The overall molecular weights decreased when the reaction temperature went up. However, both molecular weight and PDI increased significantly during the reaction in all experiments. These observations were quite different from the conventional free radical polymerization. The phenomena revealed that there were some chains keeping “living” during the copolymerization, which was similar to the polymerization in the presence of nonpolymerizable monomer DPE^[17]. The effect of depolymerization becomes significant in the copolymerization of AMS and other monomers when the reaction temperature is above the ceiling temperature of AMS. As discussed in the literature^[22], with the similar structure of DPE, the AMS containing weak bonds in molecular chain would generate new radicals to initiate new polymerization. In the copolymerization of AMS and St, the AMS radical would form liable bonds by the coupling termination in molecular chain. These liable bonds could be thermolysis to give the birth of the new chain radicals when the

reaction temperature is higher than the ceiling temperature of AMS. The new chain free radicals could initiate St molecules to form new polymer chains. The polymerization-depolymerization of AMS in the reaction could keep the growth of polymer chains (shown in Scheme 1). When the reaction temperature was below 70 °C, the molecular weight increased almost linearly as the evolution of the copolymerization. It is well-known that when the temperature is higher than 61 °C, there exist the competitive reactions between the polymerization and depolymerization which are strongly affected by the temperature. Generally, the propagation rate was much greater than the degradation rate when the copolymerization was carried out below 70 °C. When the temperature was higher than 70 °C, the increase of molecular weight slowed down at the later stage of the copolymerization. The propagation of molecular chains got difficult because degradation rate increased significantly. As a result, the impact of degradation is likely over that of chain propagation, especially at the later stage of the copolymerization when the monomer concentration was greatly dropped.

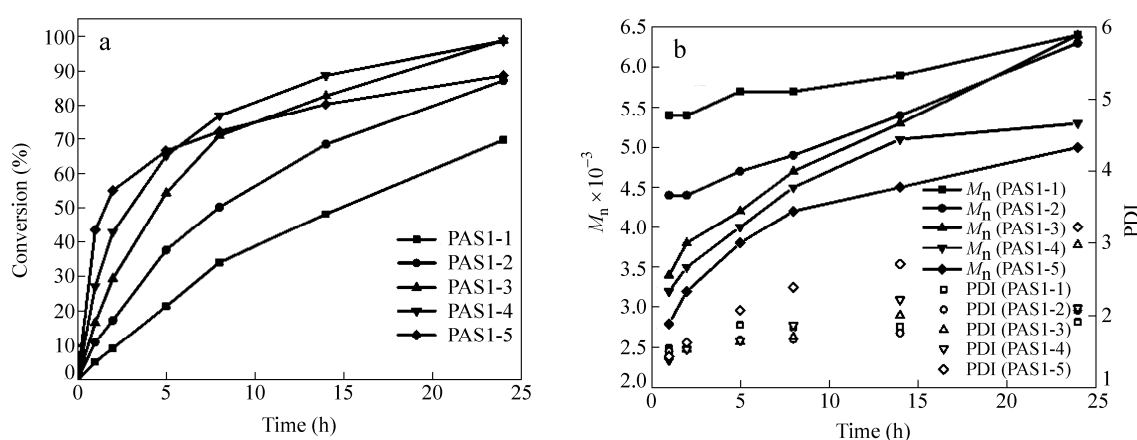
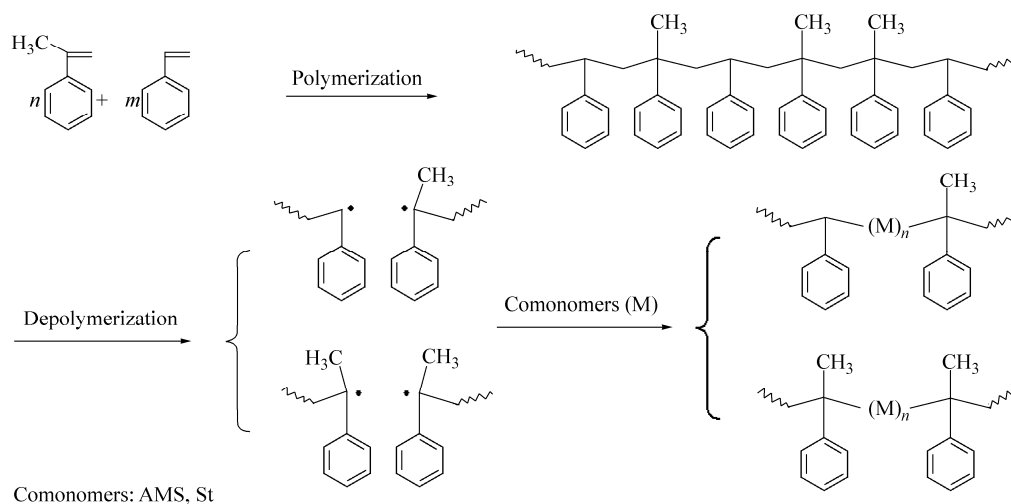


Fig. 2 Dependence of monomer conversion (a) and molecular weights (b) as function of time in the copolymerization of AMS and St at different temperatures initiated by 5 wt% AIBN



Scheme 1 The proposed copolymerization mechanism of AMS and St

To understand the mechanism of the molecular weight change with the temperature, the typical GPC curves of copolymers of AMS and St are shown in Fig. 3. The peaks of molecular weight moved toward high molecular weight end with the extension of the polymerization time at all three different reaction temperatures. Especially at 60 °C and 70 °C (Figs. 3a and 3b), the GPC traces are nearly symmetrical and the molecular weights increased

steadily. However, at 80 °C, the GPC trace was also nearly symmetrical only at the early stage (about 1 h, the total monomer conversion about 45 wt%). With extending the reaction time to 5 h, the overall monomer conversion up to about 65 wt%, there was clearly a shoulder at high molecular weight end and the shoulder became stronger at 14 h. The changes of PDI with reaction time were similar to those of molecular weight. These observations implied that there might be different mechanisms at different polymerization stages. As AMS molar fraction was as high as 30 mol% in monomer feed, more and more -AMS-AMS- chain segments which would exist in dynamic equilibrium of active free radicals and dormant chains would likely be formed when the monomer conversion went up. When the monomer concentration was high, the more chain free radicals were most likely to add to a new monomer to continue chain propagation. However, with the significant decreasing of the monomer concentration at the later stage of the polymerization, the chance of the coupling reaction between chain free radicals increased significantly leading to the formation of high molecular weight copolymers which was account for the appearance of the shoulder at high molecular end on the GPC trace. In this regard, 70 °C is an optimal reaction temperature for the copolymerization of AMS and St.

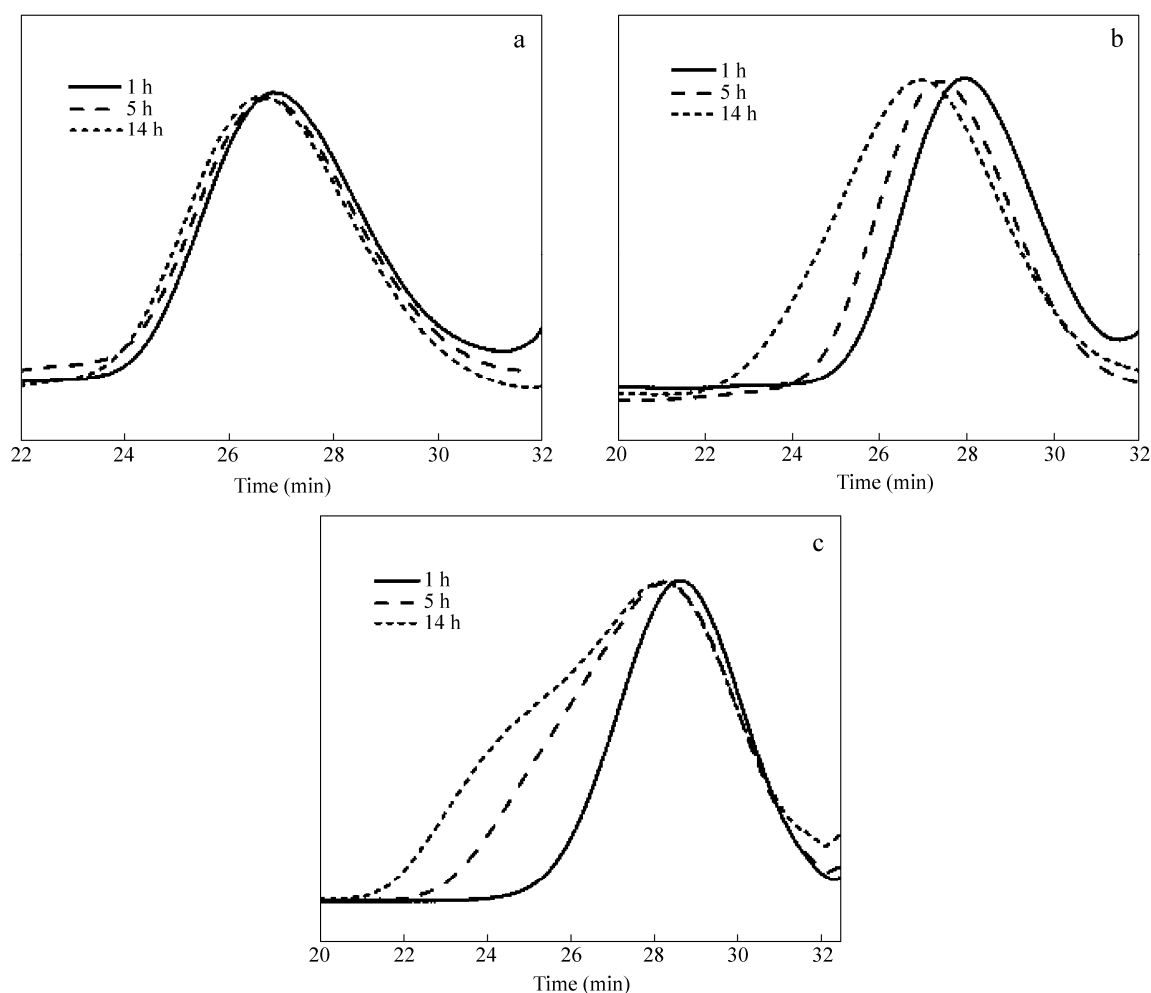


Fig. 3 GPC curves for samples obtained during bulk copolymerization of AMS and St at different temperatures: (a) 60 °C, (b) 70 °C and (c) 80 °C

The Effects of AMS/St Ratios in Monomer Feed

The effect of AMS/St ratios on the bulk copolymerization was investigated at three different values, 30 mol%, 40 mol% and 50 mol% (AMS molar fraction) respectively with AIBN at 70 °C. The reaction time varied from

about 24 h to 144 h until the monomer conversion close to 100%. ^1H -NMR spectrum of the resulting AMS/St copolymer is shown in Fig. 4(a). The molar fraction of AMS in the copolymer could be calculated by comparing the integral areas of the chemical shifts assigned to the $-\text{CH}_3$ of AMS to the integral areas of aromatic protons in the copolymers^[29]. The results of AMS content in the PAS copolymers are summarized in Table 2. The fraction of AMS structural units in the resulting PAS copolymers was relatively higher than that in the copolymerization of AMS with (meth)acrylates though there were still a gap compared to the mole ratio of the AMS in monomer feed. When the AMS content of AMS/GMA copolymer could get 22.5 mol% with the monomer conversion up to 40 %, at least 33.3 mol% AMS monomer should added in the monomer mixture before the reaction^[22]. This difference might be caused by the lower reactivity of AMS to GMA. With the increasing of the AMS molar ratio in the monomer feed the molecular weight and PDI of the products decreased. The AMS could be incorporated into the copolymers of AMS with St as high as 42 mol%.

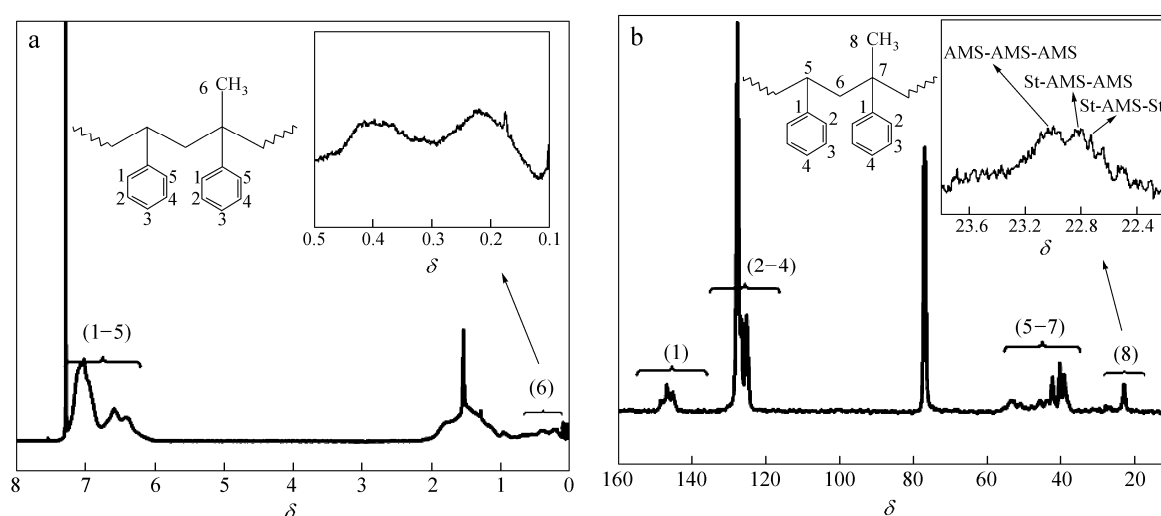


Fig. 4 (a) ^1H - and (b) ^{13}C -NMR spectra of PAS1-3

Table 2. Polymerization data of AMS and St in bulk at 70 °C initiated by 5 wt% AIBN

Run	AMS in monomer (mol%)	AMS fraction in the copolymer ^a (mol%)	M_n^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 Determined by ^1H -NMR; ^b Measured by GPC, calibrated with polystyrene standards

^{13}C -NMR spectrum of the resulting AMS/St copolymer is shown in Fig. 4(b). According to literature, the CH_3 of the AMS (C8, Fig. 4b) is the most sensitive carbon of the copolymer and its chemical shift is within the δ range of ca. 22.8^[32]. The three triads of -AMS-AMS-AMS-, -St-AMS-AMS- (-AMS-AMS-St-) and -St-AMS-St- can be differentiated from the chemical shift of C8: chemical shift of -AMS-AMS-AMS- is at 22.9; chemical shift of -St-AMS-AMS- (-AMS-AMS-St-) is at 22.8; and chemical shift of -St-AMS-St- is at 22.7. The spectrum supports the comonomer units are randomly distributed in molecular chains.

The relationship of the monomer conversion with the polymerization time at different AMS/St molar ratios is shown in Fig. 5(a). The result showed that the conversions increased quickly at the early stage of the polymerization and then slowed down. Moreover, both the apparent polymerization rate and the molecular weight decreased with the increasing of the AMS molar fraction in monomer feed. The dependence of molecular weights and PDIs of the copolymers on the copolymerization times is presented in Fig. 5(b). As a whole, the average molecular weights of the copolymers were increased with the polymerization times at different AMS

molar ratios in the feeds. The AMS containing liable bonds formed by the coupling termination of AMS radical could give the birth of the new chain radicals above the ceiling temperature of AMS. The new chain free radicals could add to the new monomer molecules to keep the growth of polymer chains (Scheme 1). However, when the AMS fraction in monomer feed went up, the extent of the molecular weight increase was narrowed. At high AMS ratio in feed, the actual AMS monomer ratio in reactant increased with the evolution of the polymerization due to the lower reactivity of AMS compared to styrene. On the other hand, the effect of depolymerization on the copolymerization became stronger with increasing the AMS fraction in chains when the AMS content in monomer feed increased. In this case, the propagation of the molecular chain got more difficult especially at the later stage of the copolymerization above the ceiling temperature.

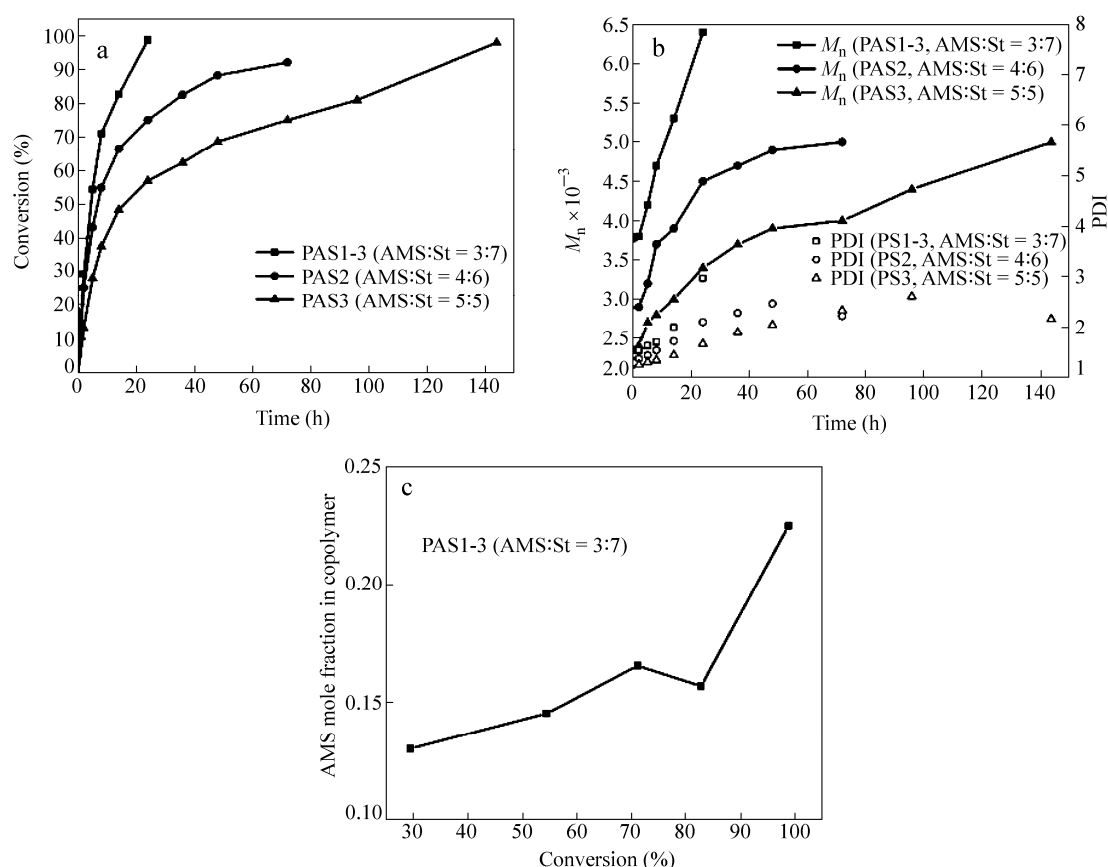


Fig. 5 Change of monomer conversion (a), molecular weight (b) and composition (c) in the copolymerization of AMS and St with different AMS contents initiated by 5 wt% AIBN

The compositions of the copolymers at different reaction times (PAS1-3, AMS mole fraction in monomer feed was 30 mol%) were determined by $^1\text{H-NMR}$. The results are shown in Fig. 5(c). As expected, the fractions of AMS units incorporated in the copolymers increased with the on-going of the copolymerization. At the early stage of the polymerization, the fraction of AMS incorporated into the polymer chain was much lower than that in the instant monomer mixture. With the extension of copolymerization time, the relative concentration of AMS in monomer increased obviously. In this case, the possibility of the propagation chain radicals added with AMS molecules was also increased significantly. As a result, the reduction of the copolymerization rate and the increase of the fraction of AMS units in copolymers depended on the copolymerization time.

Thermal Degradation of AMS/St Copolymers

The thermal degradation behaviors of PASs with different AMS contents were studied by TGA at a heating rate of 10 K/min under nitrogen atmosphere from 25 °C to 600 °C. The TGA curves of PASs and PS are shown in Fig. 6. The TGA curve of homopolymer PS has only one step with an inflection point at 356.9 °C, corresponding to the degradation by random scission of the molecular chain. However, the PASs subjected a two-step degradation in the TGA measurement. There are two inflection points at 284.2 °C and 358.1 °C, respectively, in the TGA curve of PAS1. The liable bonds, which were possibly due to the presence of AMS sequences, would be scissored first at lower temperatures^[33].

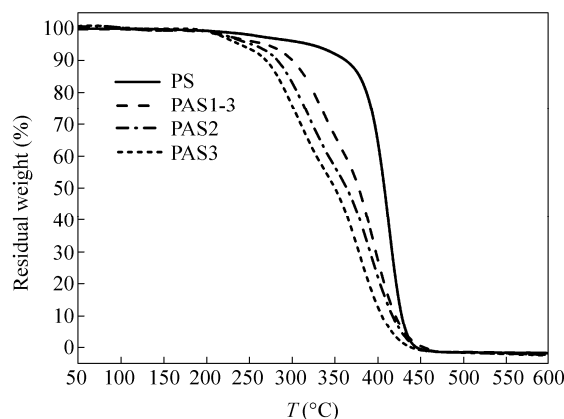


Fig. 6 TGA curves for PS and PAS with different AMS contents

As the AMS content in copolymer increased, the onset degradation temperature shifted from 284.2 °C (as shown in the curve for PAS1) to 250.2 °C (as shown in the curve for PAS3). It was suggested that the weak bonds, which caused the degradation, were increased with the amounts of AMS unit in the copolymer. The thermal cleaving reaction of the weakest bonds would generate new radical species, and then initiate the decomposition of the PASs. Moreover, the thermal cleaving reaction was carried out more easily with the increasing of the weak bond concentration, which related to the increase of the AMS content. The molar fractions of AMS unit in the copolymers are listed in Table 2.

CONCLUSIONS

The bulk copolymerization of AMS and St was investigated in detail. With the extension of the polymerization, the monomer conversion could be close to 100% with AMS up to 50 mol% in monomer feed. The average molecular weights of the AMS and St copolymers increased with the monomer conversions, which showed some features of controlled free radical polymerization. This unique polymerization behavior was likely resulted from the polymerization-depolymerization of AMS when the temperature was higher than the ceiling polymerization temperature of AMS. When the reaction temperature raises, the degradation or the thermolysis of the liable bonds in copolymer chains would be greatly enhanced. Above observations demonstrated that it was feasible to prepare copolymers of AMS and styrene with very high AMS contents. Thermal decomposition of AMS/St copolymers with different AMS contents was possibly initiated by the AMS containing weak bonds in the copolymer chains. Furthermore, due to lots of AMS containing liable bonds in the resulting copolymer, the AMS/St copolymer could generate chain free radicals when was heated. The following work of this series would focus on the evaluation of the performance of the AMS/St copolymer as a macromolecular initiator and its application in synthesis of novel copolymers.

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