Degradation and Initiation Polymerization Mechanism of α-Methylstyrene-Containing Macroinitiators

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ABSTRACT: Copolymers obtained from radical copolymerization of α-methylstyrene (AMS) and glycidyl methacrylate (GMA) behave as macroinitiators, when heated in the presence of a second monomer, giving rise to block copolymers. The relevant degradation and initiation polymerization mechanism of the macroinitiators were studied. Thermal depropagation of the macroinitiators generated monomers, identified by ^{1}H-NMR, photoionization mass spectroscopy and FT-IR. According to the results of structure analysis by GPC, ESR and NMR spectroscopy, the AMS-GMA (head-head) and AMS-AMS (head-head) bonds in the macroinitiators are easily scissored providing free radicals when the temperature is above 80°C. The radicals lead to subsequent polymerization of the second monomer, and thereby block copolymers are formed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 466–473, 2011

Key words: thermal degradation; α-methylstyrene; macroinitiator; radical polymerization; block copolymer

INTRODUCTION

It is known that AMS undergoes radical homopolymerization with much difficulty in general due to the steric hindrance and low enthalpy of polymerization.[1,2] However, AMS, as a comonomer, has been widely used in free radical co- and terpolymerizations. The polymerization processes and products have been extensively studied.[3–7] These polymerizations are found to exhibit slow polymerization rates and produce low molecular weights, which are consistent with thermally reversible polymerization,[8,9] steric hindrance to successive placements of AMS units in the polymer chain,[10] degradative chain transfer to AMS monomer,[11–13] and to kinetic factors.[10,14,15] The chain-transfer constants of styrene (St) and AMS were studied by Rudin and Samanta,[16] and it was found that the degradative chain transfer is not an important factor in the copolymerization of AMS and St.

Recently, we found a new exciting feature of AMS: AMS offers a novel and facile alternative for preparation of block copolymers.[17] Copolymerization of AMS and other vinyl monomers were carried out in solution via conventional radical polymerization, and the resulting AMS-containing copolymers were subsequently employed to prepare block copolymers. In the first step, a vinyl monomer is polymerized in tetrahydrofuran (THF) in the presence of AMS and using azobisisobutyronitrile (AIBN) as initiator. In the second step, with the presence of a new monomer, heating of the copolymers derived from AMS above leads to block copolymers. The formation of block copolymers starting from numerous monomers became possible by simply heating a preformed polymer containing AMS units in the presence of a second monomer, which is somewhat like the 1,1-diphenylethene method,[18–22] and the synthesis can be carried out in organic solvents, water or even without a solvent. However, the mechanism of the polymerization process, especially the formation of block copolymers, is still unclear although the block structures of the resulting copolymers were proved. Those AMS sequences of the AMS-containing macroinitiators were supposed to be responsible

for the second step polymerization. The aim of this contribution is to attest the AMS sequences in the macroinitiators and to clarify the thermal degradation process and the role of these preformed copolymers during the second step polymerization.

EXPERIMENTAL

Materials

α-Methylstyrene (AMS, 99%, Alfa Aesar) and glycidyl methacrylate (GMA, 99%, Aldrich) were distilled under vacuum. Methyl methacrylate (MMA, 99%), St(99%), and vinyl acetate (VAc, 99%) were purchased from Beijing Chemical Reagent and were distilled under reduced pressure before use; a,a'-AIBN was purchased from Beijing Chemical Reagent. It was recrystallized from absolute ethanol, dried under vacuum at room temperature, and stored in an amber bottle. 2,2-Diphenyl-1-picrylhydrazyl (DPPH, 99%, Alfa Aesar) was used as purchased. THF, toluene, methanol, and N,N-dimethylformamide (DMF) were obtained from Beijing Chemical Reagent and used as received.

Instruments

FT-IR spectra of gaseous products produced by the thermal degradation of polymers were recorded with Nicolet 6700 infrared spectrometer on gas samples. ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker AV600 spectrometer in CDCl$_3$ at room temperature. [1]H chemical shifts were referenced to tetramethylsilane with the residual nondeuterated solvent signal at $\delta = 7.23$ ppm. Molecular weight and molecular weight polydispersity (M_w/M_n) of the copolymers were determined by GPC (Waters 515-2410 system) calibrated by using polystyrenes (PSt) as standards and THF as an eluent. Electron spin resonance (ESR) spectrum was obtained on a Bruker ER 200D X-band spectrometer, operating at a frequency of 100 kHz. The field center was 3488 G, the sweep width was 60 G, and all spectra were recorded using a modulation amplitude of 1.02 G. The mass spectra were recorded by a photoionization mass spectrometer built by Yao et al.[23]

Preparation of poly(AMS-co-GMA) macroinitiators

Copolymerization of AMS and GMA was carried out at 65°C in THF using AIBN as initiator. The reactor was equipped with stirrer, reflux condenser, argon (Ar) inlet, and outlet. After 16-h copolymerization, the copolymer was recovered by precipitation from a large excess of methanol, purified by dissolution-precipitation cycles, dried in a vacuum oven at 50°C for 24 h, and stored in a desiccator. A series of poly(AMS-co-GMA) (PAG) samples with narrow molecular weight distributions (1.26–1.67) and molecular weights ranging from 3,000 to 10,000 g/mol were synthesized.

PGMA reference polymer synthesis

The synthesis and purification of poly(GMA) (PGMA) reference-polymer were carried out by the same method as above but without AMS.

Thermal degradation of PAG macroinitiators under air

A total of 0.1 g PAG powder was put into the reactor under air, sealed and heated. A series of experiments were carried out at 80 and 120°C. The products were analyzed by GPC and ^{1}H-NMR.

Thermal degradation of PAG macroinitiators under Ar

A total of 0.1 g PAG powder and 1 mL DMF were put into the sealed reactor. A series of experiments at 110 and 140°C were carried out under Ar atmosphere. The residual copolymer was recovered by precipitation from methanol and dried in a vacuum oven at 50°C for 24 h. To make the thermal degradation process clear, DPPH was used as radical scavenger. A total of 0.1 g PAG powder and 0.02 g DPPH were dissolved in 1 mL DMF. Experiments at 90 and 110°C were carried out by the same method as above.

Preparation of block copolymers with PAG macroinitiators

The synthesis of block copolymers were achieved by using PAG obtained above as macroinitiator. PAG and a second monomer were placed in the reactors and heated at 90°C in toluene under Ar atmosphere. Samples were taken by a syringe during the polymerization, precipitated from methanol and dried in a vacuum oven. Yields were determined gravimetrically. GPC measurements demonstrate the formation of a new polymer at higher molecular weight next to the dead polymers occurring at lower molecular weight.

RESULTS AND DISCUSSION

Thermal degradation of PAG macroinitiators under air

It has been shown by TGA under N$_2$ that the weight loss of PAG increases as the AMS moiety in PAG increases, demonstrating that weak bonds exist in the AMS sequences.[17] Polymer chain scission can
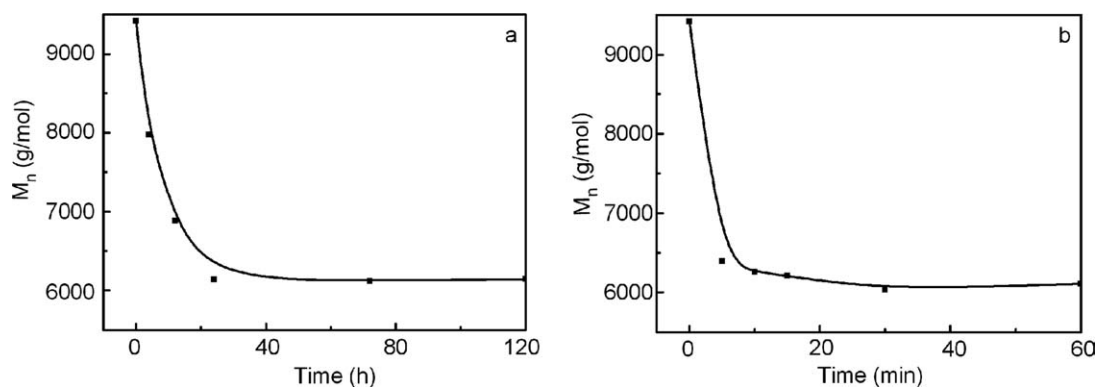
Figure 1 Comparision of the time dependence of molecular weights of PAG (F_{AMS} = 0.038, M_n = 9400 g/mol) at different temperatures (a) T = 80°C and (b) T = 120°C.

occur by three steps. The initiation step forms radicals, followed by a step of depropagation chain reactions (C—C bond cleavage by beta scission) to yield smaller molecular weight (M_w) products. The termination step (by recombination, disproportionation, or hydrogen abstraction) neutralizes radicals. Mechanistic modelings of polymer degradations have been studied by McCoy and Madras.[24]

Under air, the degradation of PAGs was first carried out at 80 and 120°C in bulk. As shown in Figure 1, the molecular weight of PAG (F_{AMS} = 0.038, M_n = 9400 g/mol) decreases so fast that at 120°C it turned from 9400 to 6500 g/mol in 5 min. The higher temperature improves the scission process a lot. At 120°C, the molecular weight of PAG turned to be constant in half an hour, whereas the same process took more than 20 h at 80°C.

The products obtained from the thermal degradation of PAG (F_{AMS} = 0.225, M_n = 3100 g/mol) at 120°C for 30min were detected by ^{1}H-NMR, as shown in Figure 2. The signals appearing at 5.1 and 5.3 ppm are assignable to the olefinic protons in AMS monomer, whereas the signals at 5.6 and 6.2 ppm are assignable to the olefinic protons at GMA monomer. The output of monomers is low, com-
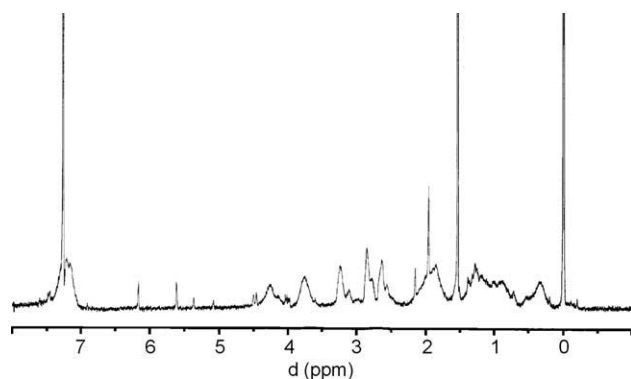
pared with the amount of remained polymer, and the mole ratio of AMS monomer to GMA monomer is about [1/3], which is consistent with the corresponding F_{AMS}. The F_{AMS} of remained polymer was calculated, and the value was ∼ 0.203. Considering the drastic decrease of molecular weight mentioned above, it can be concluded that in the degradation of PAG at 80 and 120°C, chain scission on some weak bonds should be the main reaction, along with some depropagation.

With inlet and outlet of oxygen, PAG with F_{AMS} = 0.225 (M_n = 3100 g/mol) was heated from room temperature to 300°C, and the products in the gaseous state produced at different temperatures were detected by FT-IR (Fig. 3). From Figure 3, when the temperature rose to 150°C, the double bond peaks at 1632 cm^{-1} and 1640 cm^{-1} could be observed clearly, and so did carbonyl band at 1740 cm^{-1}, phenyl band at 703 cm^{-1}, and glycidyl band at 901 cm^{-1}. Thus, it further confirmed the formation of both AMS and
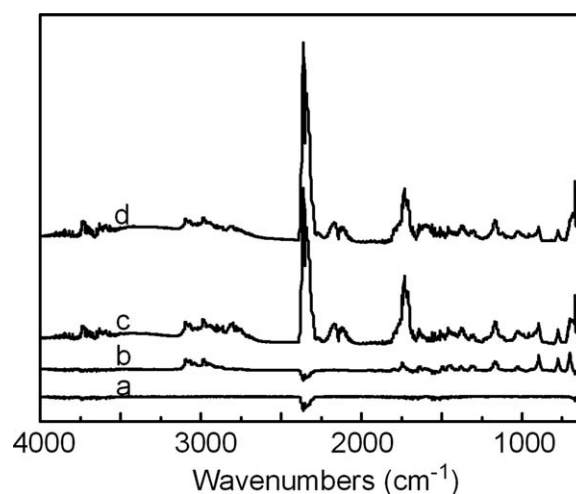

Figure 2 ^{1}H-NMR spectrum of PAG (F_{AMS} = 0.225, M_n = 3100 g/mol) after 30-min thermal degradation in air (T = 120°C).

Figure 3 FT-IR spectra of the gaseous products produced by thermal degradation of PAG under oxygen: (a) T = 100°C; (b) T = 150°C; (c) T = 200°C; and (d) T = 300°C (temperature range: 25-300°C and rate: 10°C/min; O$_2$ atmosphere).
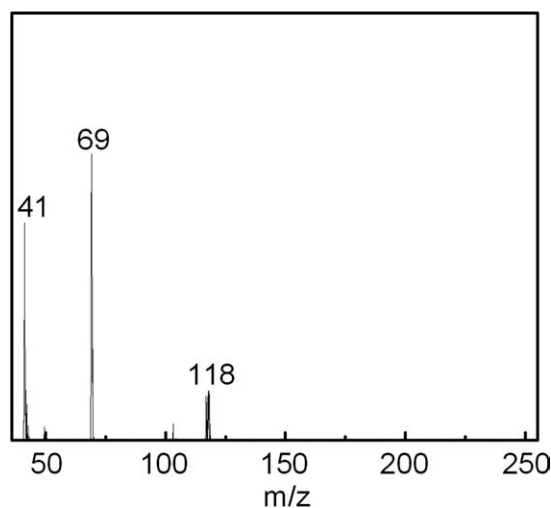
Figure 4 Photoionization mass spectrum of the gaseous products produced by thermal degradation of PAG under vacuum at 150°C (rate: 10°C/min; under vacuum).

Figure 5 FT-IR spectra of the gaseous products produced by thermal degradation of PAG under vacuum: (a) $T = 120$°C; (b) $T = 150$°C; (c) $T = 200$°C; and (d) $T = 300$°C (temperature range: 25-300°C and rate: 10°C/min; under vacuum).

GMA monomers during the thermal degradation of PAG. With temperature further rising above 200°C, all the monomer peaks observed above turned to be more remarkable. New peaks at 2365 and 2344 cm^{-1} were assigned to carbon dioxide, whereas those at 2175 and 2123 cm^{-1} belonged to carbon monoxide. The new peaks for $(CH_3)_2CHR$ at 1323, 1296, and 1170 cm^{-1} were observed and so were those for C—OH at 671 and 654 cm^{-1}.

Thermal degradation of PAG macroinitiators under Ar

Under vacuum, a series thermal degradation of PAG ($F_{AMS} = 0.225$, $M_n = 3100$ g/mol) were carried out from room temperature to 300°C. The gaseous products thus obtained were characterized by mass spectroscopy (Fig. 4) and FT-IR (Fig. 5). From Figure 4 and Figure 5, the signals for gaseous products could be observed clearly both from the mass spectra and the IR spectra when the temperature rose to 150°C. In Figure 4, the peak with $m/z = 41$ and 69 were consistent with the library spectra of GMA monomer, whereas that of $m/z = 118$ is assigned to AMS monomer. From Figure 5, when the temperature rose further above 150°C, the peaks indicating both AMS and GMA monomers also appeared. New peaks at 1323, 1296, and 1170 cm^{-1} were assigned to $(CH_3)_2CHR$.

To obtain deep insights into the thermal degradation of PAG, further detailed investigations were accomplished, and the results are as follows.

Initiation step

PAG was heated with DPPH in DMF at 110°C, and the solution color turned to be weak as time prolonged. It indicated that the radicals were formed in
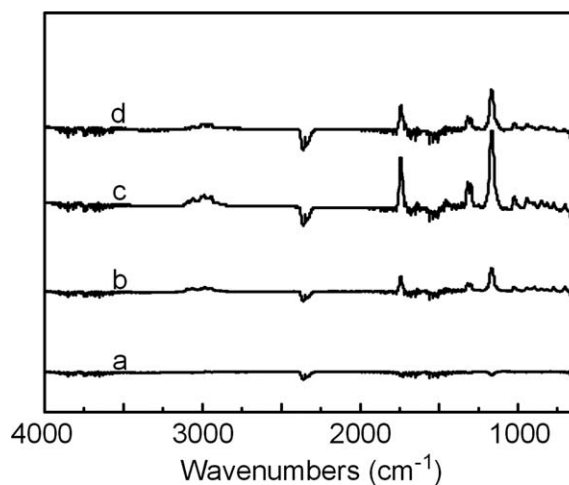
the degradation of PAG and then scavenged by DPPH. After PAG was heated with N-t-butyl-α-phenylnitrone (PBN) in toluene at 90°C for 30 min under Ar, the PBN adducts thus obtained were detected by ESR, providing direct evidence for free radical generation in the solution. The spectrum was characterized by hyperfine coupling constants of $a^H = 2.67$ and $a^N = 14.35$, demonstrating that carbon-centered radicals were generated (Fig. 6).

To make the structure of produced carbon-centered radicals clear, after PAG was heated with DPPH in toluene at 90°C for 24 h under Ar, both the original PAG and the products were characterized by ^{1}H-NMR spectra (Fig. 7).

As discussed before, radicals derived from the heating of PAG would react with DPPH immediately. From the ^{1}H-NMR spectrum of the products, no peak indicating monomers were found. It proved that all the radicals produced during the initiation

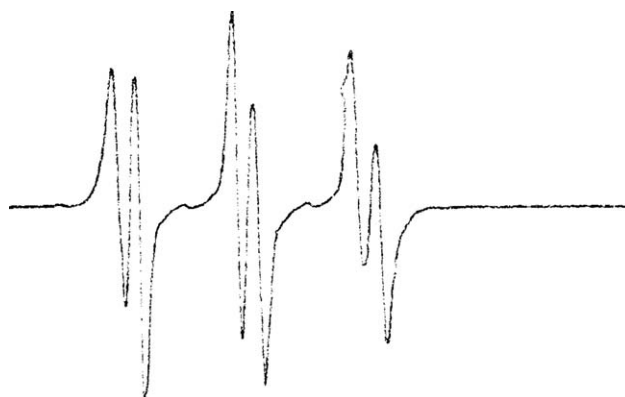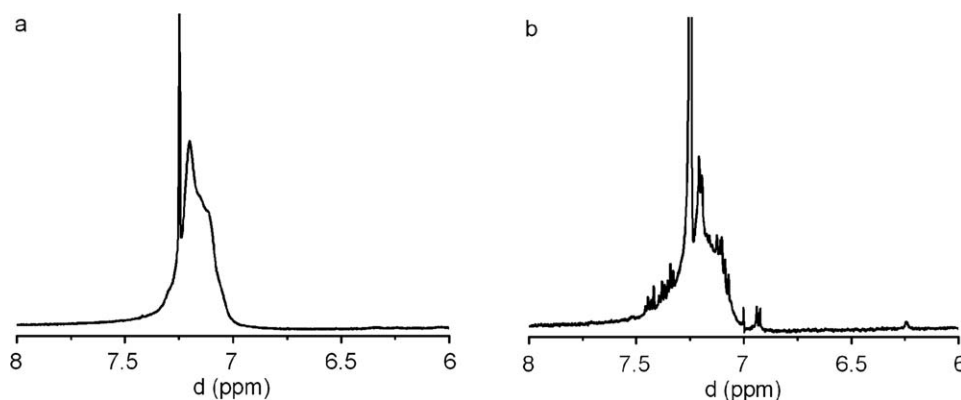**Figure 6** ESR spectrum of PAG ($F_{AMS} = 0.225$, $M_n = 3100$ g/mol) heated for 30 min under Ar with PBN ($T = 90$°C).

Figure 7 ^{1}H-NMR spectra of (a) PAG (F_{AMS} = 0.225, M_n = 3100 g/mol) and (b) the product produced by the reaction of PAG (F_{AMS} = 0.225, M_n = 3100 g/mol) and DPPH in toluene for 24 h (T = 90°C). The intense signals in the range of 7.1-7.5 ppm are due to 2,2-diphenyl-1-picrylhydrazine.[25]

step have been effectively scavenged by DPPH and no depropagation occurred. The signal of terminal methine proton from disproportionation termination between DPPH- and GMA-terminated polymeric radicals is observed at 7.0 ppm. The signal at 6.24 and 6.94 ppm are assigned to terminal methine protons from disproportionation termination between DPPH- and AMS-terminated polymeric radicals. Both polymeric radicals aforementioned could result from the scission of AMS-GMA (head-head), GMA-GMA (head-head), and/or AMS-AMS (head-head) bonds. Because no degradation of PGMA occurred until above 300°C,[17] it is obvious that the initiation step should have occurred by the scission of AMS-GMA (head-head) and AMS-AMS (head-head) bonds. Considering the preparation conditions of PAG macroinitiator, these bonds most probably come from the combination termination of the preparation step of PAG. The initiation reactions for polymeric radical generation and the reactions between them and DPPH are as follows (Fig. 8):

Further support for the initiation reactions was obtained from ^{13}C-NMR spectra (Fig. 9). In comparison with the original PAG macroinitiator, several signals between 35 and 55 ppm, which are attributed

to the quaternary carbons of the head-head structures proposed above, disappear after PAG reacting with DPPH radicals thoroughly.

Depropagation step

Once the GMA-terminated and AMS-terminated polymeric radicals were produced, they were supposed to undergo β-scission resulting in monomers and a slightly smaller end radical, which could be a 1° or 3° polymer radical because of the irregularity of the PAG synthesized by free radical copolymerization.[26]

Both of GMA and AMS units have a methyl group at α-position of vinyl group. These methyl groups can hinder the back biting reaction that would give birth to dimers and trimers.[27] Gravimetric measurements of PAG while heated at different temperatures in DMF are shown in Figure 10. Because the residual copolymer was recovered by precipitation from methanol, dried in a vacuum oven at 50°C for 24 h, by which the dimers and trimers cannot be removed, the weight losses of PAG were supposed to be equal to the yield of monomers. It was found that temperature had great influence on the PAG
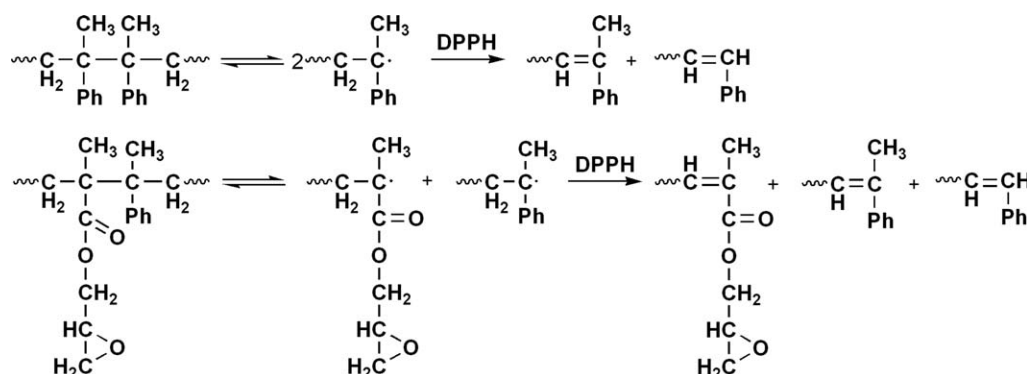

Figure 8 Schematic illustration of the initiation reactions and radicals-captured reactions with DPPH.
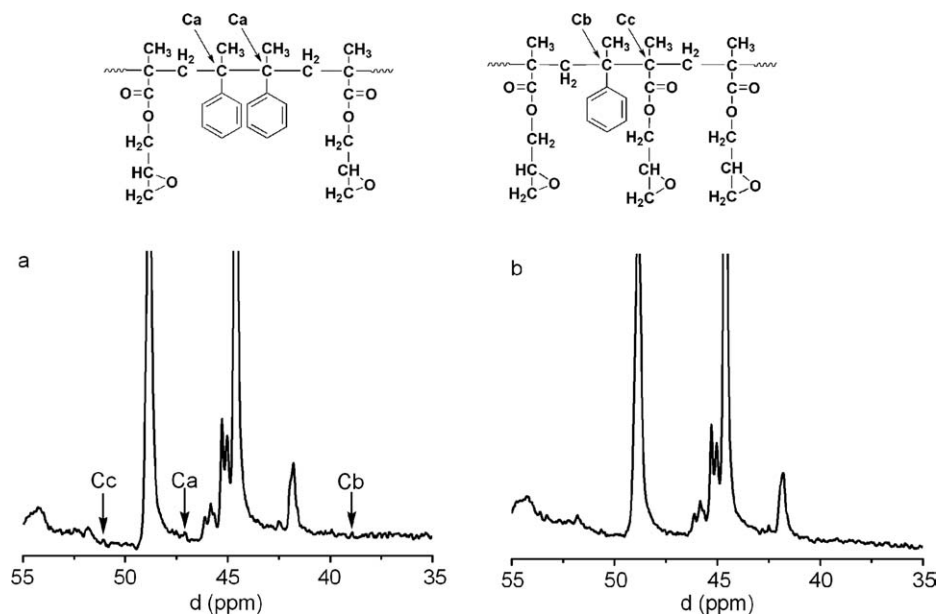
Figure 9 ^{13}C-NMR spectra of (a) PAG ($F_{AMS} = 0.225$, $M_n = 3100$ g/mol) and (b) the product produced by the reaction of PAG ($F_{AMS} = 0.225$, $M_n = 3100$ g/mol) and DPPH in toluene for 24 h ($T = 90°C$).

weight loss in solution degradation. At 110 and 140°C, which are above the PAMS ceiling temperature, an AMS chain end will irreversibly unzip to monomer only when the next unit is an AMS. Nevertheless, reactions could actually be much more complicated. The weight loss of PAG was found to be higher than the original AMS content, indicating that GMA monomers were also produced by the degradation, which agreed well with the thermal degradation under air and vacuum discussed earlier.

Termination step

Equilibrium would be finally achieved between copolymer chains and two monomers, as confirmed by the constant copolymer weight by the end of degradation. Radicals could be terminated by recombination, disproportionation, or hydrogen abstraction. During the thermal degradation in solution, the concentration of radicals is at such a low level that recombination and disproportionation are hardly to occur in comparison with hydrogen abstraction. The radicals can abstract hydrogen from a polymer molecule chain, when there are some accessible hydrogens in the polymer. Typical GPC curves of PAG ($F_{AMS} = 0.199$, $M_n = 6200$ g/mol) before degradation and PAG after 3 h degradation in DMF at 110°C are shown in Figure 11. As a result of chain scission, depropagation and hydrogen abstraction, the molecular weight decreased from 6200 to 5100 g/mol in 3 h.
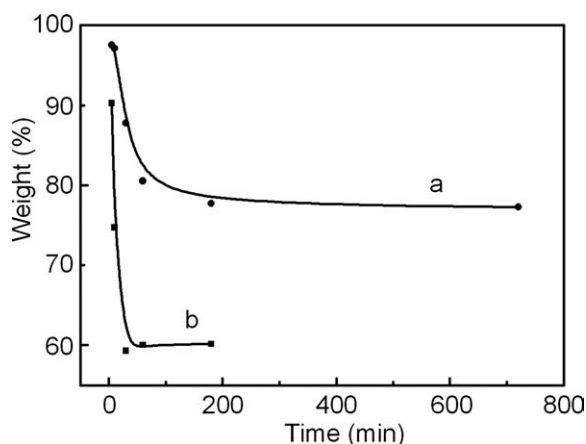

Figure 10 Time dependence of weight losses of PAG ($F_{AMS} = 0.199$, $M_n = 6200$ g/mol) at different temperatures (a) $T = 110°C$ and (b) $T = 140°C$.

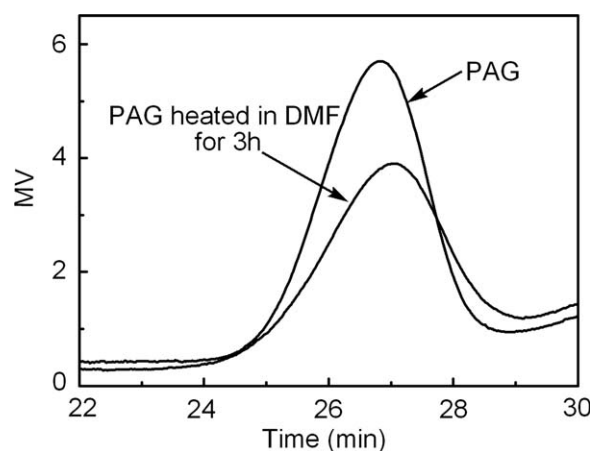**Figure 11** GPC curves of PAG ($F_{AMS} = 0.199$, $M_n = 6200$ g/mol) before and after thermal degradation in DMF for 3 h.

Monomer	Conversion of M (%)	$M_{n,PAG}$ (g/mol)[a]	N_{PAG} (mol)[b]	$M_{n,PAG-b-PM}$ (g/mol)[a]	$N_{PAG-b-PM}$ (mol)[b]	$N_{PAG-b-PM}/$ N_{PAG}
MMA	63.8	3200	7.81E–06	60,900	4.83E–06	0.62
St	22.3	3200	7.81E–06	44,700	2.62E–06	0.33

PAG/MMA (St)/toluene = 0.025 g/0.5 mL/2.5 mL and $T = 90°C$, time = 24 h.
[a] Values measured by GPC, calibrated with polystyrene standards.
[b] Values calculated by m/M_n. (m: mass).

Preparation of block copolymers with PAG macroinitiators

On the basis of the thermal degradation of the AMS-containing copolymers, a two-step method was developed to prepare block copolymers. In the first step, a vinyl monomer is polymerized in THF in the presence of AMS using AIBN as initiator. In the second step, in the presence of a new monomer, heating of copolymers derived from AMS leads to block copolymers. A series of block copolymers, PAG-block-PMMA, PAG-block-PSt, and PAG-block-poly (VAc) were thus prepared (Table I), and the conditions of reaction have been discussed before.[17]

During the second step polymerization, the monomer conversions increased as the reaction time prolonged at first. In 24 h, the percent conversion of MMA achieved 63.8%, whereas that of St was 22.3%. Since then, both of these data kept constant as reaction time further prolonged, indicating all the reinitiation units of PAG have been thoroughly consumed. It is well known that during the radical polymerization of MMA, chain radicals are mainly terminated by disproportionation, and when the monomer is St, the termination step is mainly carried out by combination. Because of the different termination ways, it is reasonable that the value of $N_{PAG-b-PMMA}/N_{PAG}$ (0.62) is higher than that of $N_{PAG-b-PSt}/N_{PAG}$ (0.33; here N represents the mole of the compounds (Table I). Since both the value of $N_{PAG-b-PSt}/N_{PAG}$ and $N_{PAG-b-PMMA}/N_{PAG}$ would be at least one if there were reinitiation units in every PAG chain (with the reinitiation efficiency supposed to be 100%), it can be concluded that only some PAG chains own the reinitiation units. As we have found from the GPC spectra before, the molecular weight of PAG-b-PSt did not increase as the polymerization processed.[17] Because the termination step is mainly realized by combination, the molecular weight should have been increasing if there were more than one reinitiation unit in one PAG chain. It can be inferred that only one reinitiation unit exist in most of these special PAG chains. Both of these speculations are consistent with the above idea that the reinitiation units come from the combination termination during the first step polymerization.

The way how the second monomer was added into the reaction system also had great influence on the polymerization. We compared experimentally two cases, adding MMA at the beginning and 3 h after heating of PAG at 110°C, respectively. Figure 12 showed that for the same polymerization time, the percent conversion of MMA in the first case was higher than that of the second, indicating the initiation step of degradation is irreversible. Once the macroradicals are produced, the depropagation and termination step will immediately occur and give birth to dead polymer chains and monomers. The polymerization initiated by PAG macroinitiator should follow the general rules in normal radical polymerizations.

VAc was also used as the new monomer for the second stage polymerization. As proved by GPC, the polymerization of VAc did occur. Nevertheless, the polymerization took place only at a temperature of 80°C and above, higher than the boiling temperature of VAc monomer. So this method is in deed not so perfect for VAc as for MMA and styrene. One reason is the severe monomer loss that explains partially why the percent conversion of VAc is much lower (only 3.1% in 3 h) than that of MMA and
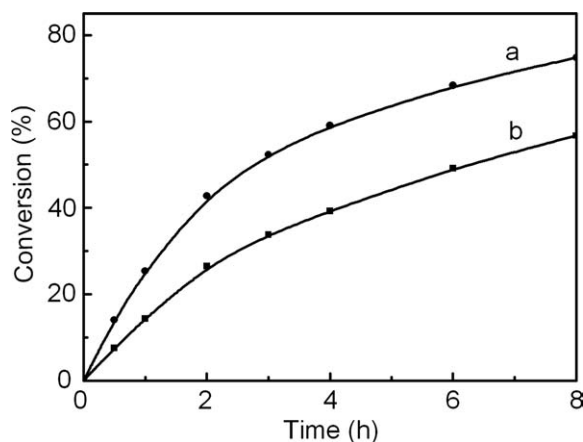

Figure 12 Time dependence of monomer conversion with MMA added at different time (a) adding MMA at the beginning of PAG degradation and (b) adding MMA after 3 h PAG degradation at 110°C (PAG/MMA/toluene = 1 g/10 mL/50 mL, reaction time = 8 h, $T = 110°C$).

styrene. Another reason is that VAc monomer is hard to react with the polymer chain ended with either an AMS radical or a GMA radical.

CONCLUSIONS

In the thermal degradation of PAG, the weak AMS-GMA (head-head) and AMS-AMS (head-head) bonds are first scissored into two macroradicals, which is followed by β-scission and hydrogen abstraction. Lots of evidence demonstrated that such kind of weak bonds are produced by the combination termination during the first step polymerization. These weak bonds open new routes for the synthesis of block copolymers. Such kind of AMS-containing macroinitiator method enables the free-radical synthesis of block copolymers from all common free-radical homopolymerizable or copolymerizable monomers in organic solvents, water, or without a solvent.

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