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ORIGINAL PAPER

Preparation of water soluble Am–AA–SSS copolymers by inverse microemulsion polymerization

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Abstract Inverse microemulsion copolymerization of acrylamide (Am), acrylic acid (AA), and sodium 4-styrenesulfonate (SSS) initiated by redox initiators composed of ammonium peroxodisulphate (APS) and sodium bisulfite, and stabilized by the mixed emulsifier system sorbitan monooleate (Span-80) and polyoxyethylene sorbitan monooleate (Tween 80) were examined as a function of the combination of hydrophilic (Tween 80) and hydrophobic (Span 80) emulsifiers, reaction temperature, AM/AA mass ratio, SSS concentration, and initiator concentration. The physicochemical and thermal properties and the structure of this copolymer were also determined and discussed. The reaction rates for all runs of the experiments exhibited two intervals, which were typical of microemulsion polymerization. The copolymer had only one glass transition temperature of 115.5 °C, indicating a random structure.

Keywords Inverse microemulsion · Copolymerization · Emulsifier ·
Water-soluble polymers · Redox initiators

Introduction

Water-soluble polymers have presently received much attention not only for academic researchers but also for technology-focused industrial scientists because

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of their important applications such as stabilizers, flocculants, absorbents, and aqueous viscosity modifiers in tertiary oil recovery, latex paint systems, and pigment printing for textiles and coatings.

Microemulsions are isotropic, transparent or translucent, and thermodynamically stable multicomponent fluids, normally composed of an aqueous component, an oily component, an amphiphile as surfactant, and frequently a co-surfactant (usually an alcohol of intermediate chain length). Unique properties of microemulsions such as lower viscosity, greater stability and transparency due to uniformly dispersed smaller droplets have made them attractive media for polymerization [1–5]. Since 1980s, a new polymerization method was developed: inverse microemulsion polymerization and it has become an attractive way to produce high molecular-weight water-soluble polymers. Therefore, inverse microemulsion polymerization has recently attracted considerable attention and become an increasingly growing field of research in water-soluble polymer synthesis.

Up to now many water-soluble polymers have been prepared by inverse microemulsion polymerizations, most of them are AM-based ones. Renteria [6] investigated the inverse microemulsion polymerization of acrylamide in a paraffinic solvent stabilized by a mixture of nonionic surfactants and studied the influence of factors such as the initiator composition, HLB, percentage of the aqueous phase, and addition of the monomer by steps on the final conversion and polyacrylamide molar masses. Candau [7] prepared two types of water-soluble polymers through an inverse microemulsion polymerization route: (i) copolymers of acrylamide with sodium-2-acrylamido- 2-methylpropanesulfonate and (ii) copolymers of acrylamide and sodium acrylate hydrophobically modified with an amphiphilic monomer, and obtained stable, clear microlatexes of moderate particle size containing up to 25% high molecular weight polymer in the medium. Barton [8, 9] studied the kinetics of free-radical homopolymerization and copolymerization of acrylamide (Am) and styrene (S) initiated by water-soluble ammonium peroxodisulfate, (APS) or by toluene soluble dibenzoyl peroxide (DBP) in inverse microemulsion toluene/S/AOT (sodium bis(2-ethylhexyl) sulfosuccinate)/water/AAm, and the inverse microemulsion polymerization leads to the formation of partly hydrophobized crosslinked polymer particles of tailored chemical composition, degree of crosslinking, and polymer particle size. Sanz [10, 11] investigated flocculants by the inverse microemulsion copolymerization of acrylamide with 60% 2-acryloxyethyltrimethyl ammonium chloride in the monomer feed initiated by ammonium persulfate/sodium disulfite redox system and studied the influence of the formulation composition, HLB, starting polymerization temperature, and reaction time on the polymerization and final product properties as flocculants. Kaneda [12] investigated a series of poly(dimethylacrylamide-co-2- acrylamido- 2-methyl-1-propanesulfonic acid) microgels polymerized in single-phase reversed micelles of about 50 nm in diameter.

In our previous studies [13], we have prepared a series of copolymer superabsorbents based on acrylamide (AM), acrylic acid(AA) by inverse microemulsion copolymerization using ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as the crosslinking agent and OP-10 and SDS as complex surfactants. The synthetic variables (amount of crosslinking agent and initiator, water/oil ratio, monomer/surfactant ratio, and AA/Am ratio) and their effects on the absorbencies of the synthesized superabsorbents were investigated.

However, the kinetics of inverse microemulsion copolymerization of acrylamide, acrylic acid, and sodium 4-styrenesulfonate using sorbitan monooleate (Span-80) and polyoxyethylene sorbitan monooleate (Tween-80) as mixed emulsifiers, has not yet been studied. In this article, we investigate the kinetic behaviors of inverse microemulsion copolymerization of acrylamide (Am), acrylic acid (AA), and sodium 4-styrenesulfonate (SSS) initiated by redox initiators composed of ammonium peroxodisulfate (APS) and sodium bisulfite, and stabilized by the mixed emulsifiers Span-80/Tween-80. The aim of this study was to elucidate the copolymerization mechanism in these four-component microemulsion media. Thus, the influences of the inverse microemulsion copolymerization conditions, such as the emulsifiers, temperature, SSS content, and initiator content on the conversion of the inverse microemulsion copolymerization using gravimetric method were examined and evaluated. The physicochemical properties and the structure of this copolymer were also determined and discussed.

Experimental

Materials

Acrylic acid(AA), analytical grade was purified by distillation under vacuum; Acrylamide(Am), chemical grade, was purified by recrystallization; Sodium 4-styrenesulfonate (SSS),chemical grade, was purified by recrystallization from 9:1 (v/v) mixture of methanol and water at 60 °C and dried under vacuum. Sorbitan monooleate (Span-80) and polyoxyethylene sorbitan monooleate (Tween 80), chemical grade, ammonium persulfate (APS) and sodium bisulfite, analytical grade, were used without further purification.

Preparation of Am–AA–SSS copolymers by inverse microemulsion polymerization

A series of the Am–AA–SSS copolymers with different amounts of SSS, redox initiators, emulsifiers, and different temperature were prepared by the following procedure: Typically, acrylic acid (4 g) was dissolved in 10 mL distilled water and then acrylamide (2 g) and sodium 4-styrenesulfonate (1 g) were added to the above monomer solution and the mixed solution was stirred at room temperature for 30 min. Then, the solution was added dropwise to the inverse microemulsions formed by 100 g cyclohexane, 4 g Span80, and 2 g Tween 80. The water bath was heated slowly to 50 °C with mild stirring after redox initiator APS (55 mg) and sodium bisulfite (15 mg) was introduced to the above inverse microemulsions. After 3 h of the reaction, the resulting product was washed several times with ethanol, dried at 70 °C to a constant weight, then milled and screened.

Conversion measurement

Conversion was followed by gravimetry: samples were withdrawn from the reacting system at given times and were cleaned by washing with ethanol several times to remove the surfactant. Samples were then weighed and oven-dried.

The conversion C% of the inverse microemulsion polymerization was determined by weight method and calculated as follows:

$$C\% = (W_1/W_2) \times (1/W) \times 100\%$$

where the W_1 and W_2 were weights of the dry polymer and the polymer latex, respectively. The W was weight percent of the monomer in the feed.

Characterizations

UV–visible absorption spectra were recorded on a Thermo Spectronic Genesys TM 10 series spectrophotometer with a quart cuvette possessing an optical path length of 1 cm. Infrared spectra were taken with a 510 Nicolet FTIR spectrometer. TGA of the copolymer was measured on a Dupont 2100 instrument. The temperature program was 10.0 K/min from 50 to 500 °C under N_2 atmosphere. DSC of the copolymer was measured on Perkin-Elmer DSC-7 instrument. The temperature program was 10.0 K/min from 50 to 150 °C under N_2 atmosphere.

Results and discussions

Effects of initiator concentration on the inverse microemulsion polymerization rate

Figure 1 depicted conversion as a function of time for the copolymerization of AA, AM, and SSS in a microemulsion stabilized with mixed emulsifiers of Span80/

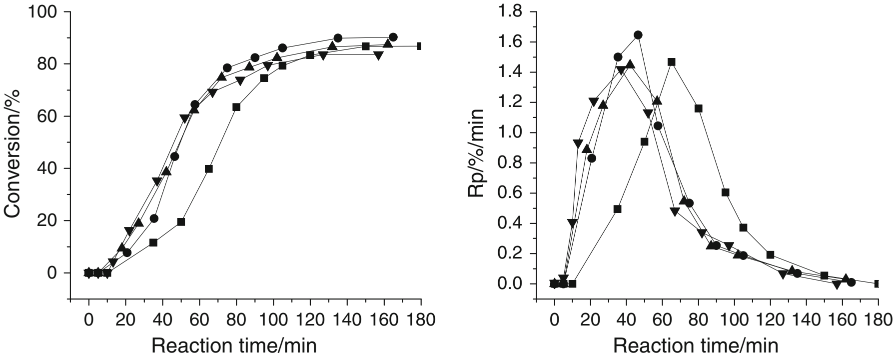

Fig. 1 Conversion (*left*) and polymerization rate (*right*) as a function of time and initiator concentration at 50 °C with different APS concentration:(*filled square*) 0.5 wt%; (*filled circle*) 1.0 wt%; (*filled triangle*) 1.5 wt%; (*filled inverse triangle*) 2.0 wt%

Tween80 of different initiator concentrations. It could be seen that the process was initially very rapid, reaching a maximum value of Rp at about 30–45% conversion. Later, the polymerization rate decreased until the process stopped. Notice that increasing initiator concentration yields faster polymerization rates and higher conversions up to 1%. However, further increase to above 1% caused a decrease of reaction rate. This finding strongly deviated from the classical emulsion polymerization where the rate of polymerization was proportional to the initiator concentration.

The increasing polymerization rate when the initiator concentration increased, was mainly due to the increasing flux of the free radicals, giving a higher probability of being trapped by droplets (heterogeneous nucleation) or by monomer in the aqueous phase to induce formation of oligomers (homogeneous nucleation) to produce active particles.

Before polymerization, APS was mainly distributed in the reverse micelles or the microdroplets of the monomer. APS radicals generated in the aqueous phase were less likely to be autoterminated (low radical concentration, electrostatic repulsion between negatively charged radicals, depressed reaction of primary radicals with oligomeric radicals due to the gradient in the water-solubility, etc.,). However, the two decomposed radicals in the same reverse micelle or microdroplet tended to couple rapidly if further increase of KPS content above 1%, and there might exist high rate of autotermination of primary radicals due to the reverse micelles or the microdroplet cage effect. Therefore, the polymerization rate decreased.

Effects of SSS concentration on the inverse microemulsion polymerization rate

The conversion and polymerization rate versus time curves at variable SSS content were shown in Fig. 2. An increase of the polymerization rate was seen with increasing SSS concentration. For water-soluble monomer such as SSS, most of the monomer was solubilized in the monomer-swollen micelles which should be the main field for initiation, nucleation, and then propagation of the latex particles. The

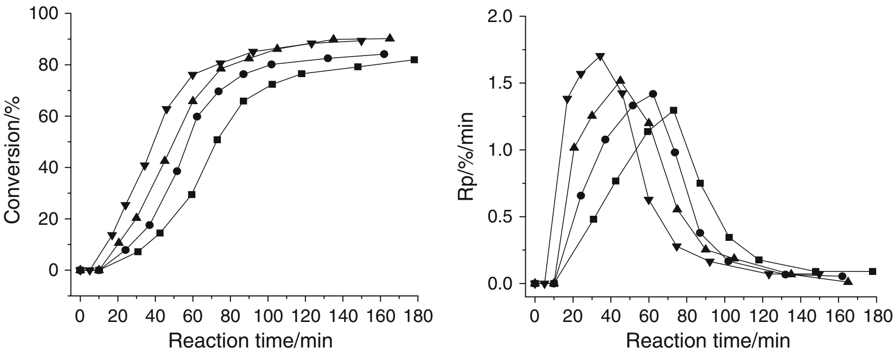

Fig. 2 Conversion (*left*) and polymerization rate (*right*) as a function of time and SSS concentration at 50 °C with different SSS concentration: (*filled square*) 5 wt%; (*filled diamond*) 10 wt%; (*filled triangle*) 15 wt%; (*filled inverse triangle*) 20 wt%

larger the monomer content in the parent microemulsion was, the larger the number and size of monomer-swollen micelles were, and the larger the polymerization rate was [14]. The increase in polymerization rate with increasing monomer content should be the result of the increase in the size and number of the monomer-swollen micelles, which enhanced the probability of radical capture by the micelles.

Effects of Span80/Tween80 ratio on the microemulsion polymerization rate

The influences of HLB on the conversion and polymerization rate were indicated in Fig. 3 and HLB value can be calculated as follows:

$$\mathrm{HLB} = \mu_{\mathrm{Span}}\mathrm{HLB}_{\mathrm{Span}} + \mu_{\mathrm{Tween}}\mathrm{HLB}_{\mathrm{Tween}} \qquad (1)$$

where μ_{Span} is the mass ratio of Span 80, μ_{Tween} is the mass ratio of Tween 80, $\mathrm{HLB}_{\mathrm{Span}}$ is the HLB value of Span 80, $\mathrm{HLB}_{\mathrm{Tween}}$ is the HLB value of Tween 80.

According to our experimental results, working at a lower HLB value (7.1) leads to higher conversion and polymerization rate. The presence of mixed emulsifiers with different alkyl chain lengths offered some possibilities to regulate the polymerization process with respect to a certain structure of interface. A lower HLB value implied a change in the composition of the surfactant in the microemulsion where more hydrophobic Span 80 and less hydrophilic Tween 80 were used. This favored the formation of inverse microemulsions and formed more monomer-solubilized reverse micelles. Therefore, the system formed relatively larger inverse microemulsion area which was suitable for microemulsion polymerization, and conversion, and polymerization rate increased in lower HLB value. However, further increase in Span/Tween mass ratio to 4/1 with HLB value of 6.5, the system became unstable and turbid and no inverse microemulsions were formed. Therefore, under Span/Tween mass ratio to 3/1 with HLB value of 7.1, the system was suitable for microemulsion polymerization.

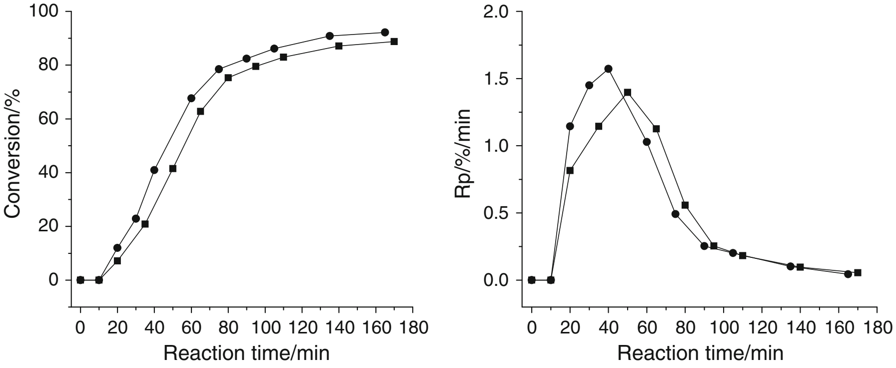

Fig. 3 Conversion (*left*) and polymerization rate (*right*) as a function of time and Span/Tween mass ratio at 50 °C with different Span/Tween mass ratio: (*filled circle*) 3/1; (*filled square*) 2/1 and different HLB: (*filled circle*) 7.1; (*filled square*) 8.0

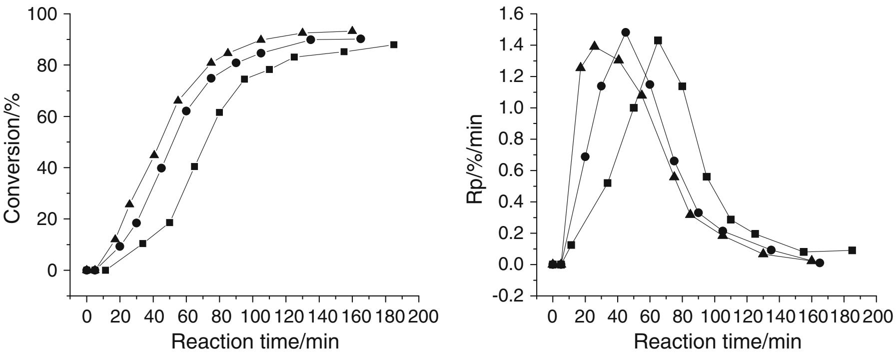

Fig. 4 Conversion (*left*) and polymerization rate (*right*) as a function of time and different AA/Am mass ratio: (*filled square*) 7/3; (*filled circle*) 4/6 and (*filled triangle*) 3/7

Effects of AA:AM ratio on the microemulsion polymerization rate

Figure 4 reported the conversion and polymerization rate as a function of time for the copolymerization of Am–AA–SSS with different mass ratio of AA/Am. The plot showed that the polymerization process was influenced by the mass ratio of AA/Am. In our reaction system, pH was near 5 so the acid units of AA were partially screened by the Nat ions, which were added to the system by SSS. On the other hand, Am was not protonated and neutral at pH 5. Therefore, Am showed higher reactivity than AA at pH = 5 in the reaction systems. Similar results were reported earlier by Paril and Rintoul [15, 16]. Therefore, the polymerization rate increased with decreasing AA content and increasing Am content.

Effects of temperature on the microemulsion polymerization rate

The effects of temperature on conversion and rate of polymerization were examined at 50, 60, and 65 °C and the results were shown in Fig. 5. As could be seen,

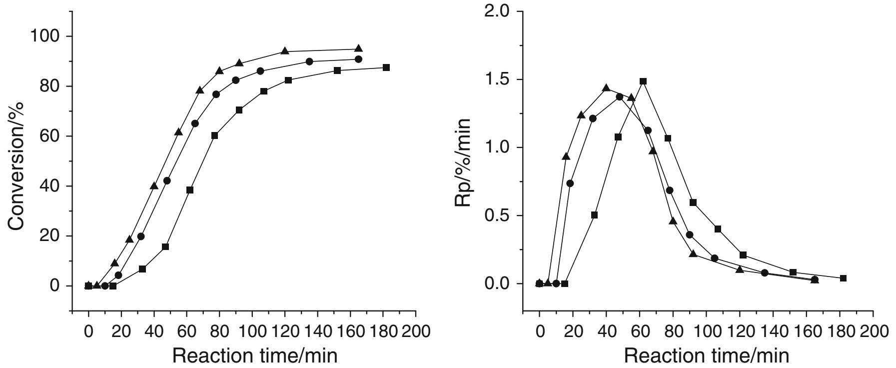

Fig. 5 Conversion (*left*) and polymerization rate (*right*) as a function of time and different temperature: (*filled square*) 50 °C; (*filled circle*) 60 °C, (*filled triangle*) 65 °C

temperature had a strong effect on reaction rate and conversion. Both the rate of polymerization and final conversion increased with the increasing temperature. This was due to the rapid increase of initiator decomposition rate as well as an increase of the propagation rate constant with temperature. Both effects resulted in an increase in reaction rate and overall conversion. As a result, the maximum rate was shifted to lower conversion with increasing temperature.

As can be seen in Figs. 1, 2, 3, 4, and 5, inverse microemulsion approach was successfully applied to copolymerize AA, AM, and SSS in the presence of mixed emulsifiers of Span80/Tween80. The copolymerization in three-component microemulsions was fast and conversion close to 90% was achieved in 2 h. The initially transparent w/o microemulsions became increasingly turbid as the polymerization proceeded due to the particle growth and the increase in the refractive index difference between the particles and the oil phase as the water-soluble monomers gradually changed into polymers.

Regardless of initiator and SSS concentration, mixed emulsifiers, monomer feed composition and reaction temperature, two distinct rate intervals were observed as the rate of polymerization increased rapidly and reached to the maximum, followed by a steady decreasing rate of polymerization, which was a characteristic of microemulsion polymerization.

UV–Vis spectrum study

UV/vis spectrum of Am–AA–SSS copolymer was shown in Fig. 6. As indicated in Fig. 6, UV/Vis spectrum of Am–AA–SSS copolymer in aqueous solution showed high absorbency in the range of 200–300 nm, and contained characteristic phenyl group band ($\lambda = 254$ nm) which belonged to SSS segment in the polymer chain [17]. This observation proved that SSS units were incorporated into the copolymer molecules.

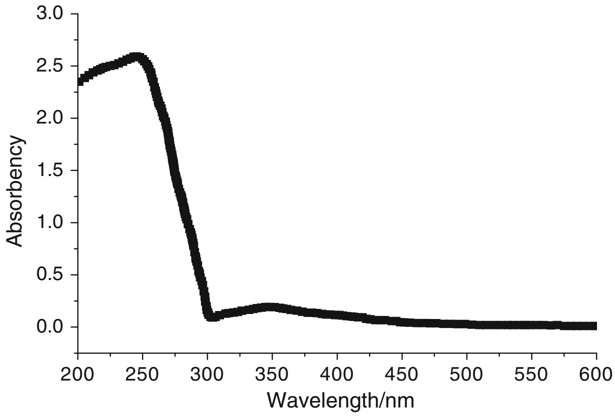

Fig. 6 UV/Vis spectrum of Am–AA–SSS copolymer

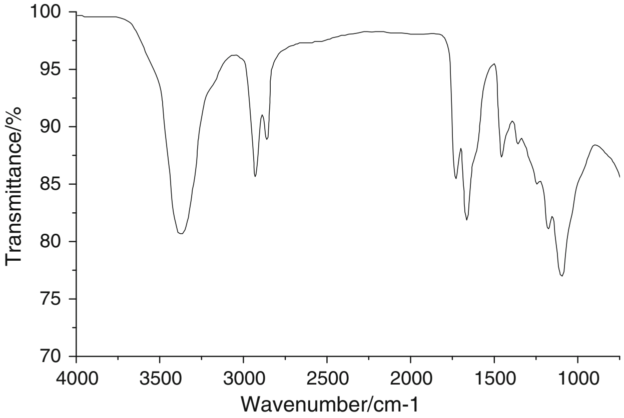

Fig. 7 FTIR spectrum of Am–AA–SSS copolymer

FTIR spectrum study

The typical FTIR spectrum of the Am–AA–SSS copolymer was shown in Fig. 7. The C–H asymmetric and symmetric stretching peaks, appeared at about 2,925 and 2,854 cm^{-1}, respectively. Stronger absorption peaks at 3,385 cm^{-1} was attributed to NH_2 groups. Absorptions at 1,664 cm^{-1} resulted from the overlap of C=O stretching ($CONH_2$) and phenyl stretching, and the absorbency at 1,727 cm^{-1} was characteristic peaks for C=O stretching of AA unit. 1,448 cm^{-1} was attributed to asymmetric stretching of the SO_2 group. This indicated that sulfonate, amide, and carboxyl groups were incorporated in the copolymer molecules.

Differential scanning calorimetry

The glass transition temperature (T_g) of the Am–AA–SSS copolymer was determined by DSC and the DSC curve of Am–AA–SSS copolymer in the temperature range of 80 to 150 °C was shown in Fig. 8. As exhibited in this curve, only one glass transition temperature appeared on the curve, at 115.5 °C, indicating the absence of formation of a mixture of homopolymer or the formation of a block or a graft copolymer. Therefore, a random Am–AA–SSS copolymer was obtained.

TGA study

The thermogravimetric curve (TG) and the differential thermogravimetric curve (DTG) of the Am–AA–SSS copolymer was shown in Fig. 9. As shown in Fig. 9, the DTG curve exhibited two different peaks, indicating that the copolymer was degraded under two stages. The first stage at 180–230 °C might be assigned to the water release of the non-cyclic anhydrides formation in the acrylic acid repeat unit [18]. Moreover, the copolymer also showed the degradation starting from 230 to 380 °C. This might be due to the degradation of carboxylic acid pendant group

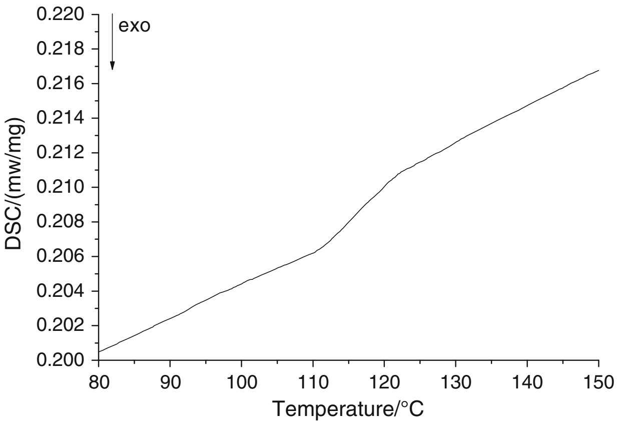

Fig. 8 DSC curve of Am–AA–SSS copolymer

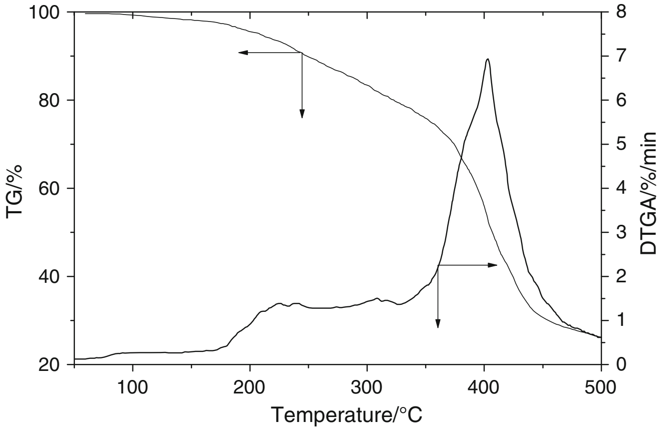

Fig. 9 TGA and DTAG curves of Am–AA–SSS copolymer

[19–22]. The second stage at 380–500 °C might be owing to the thermal decomposition of AM and SSS segments [23].

Conclusions

An inverse microemulsion polymerization technique was used to prepare copolymers of acrylamide (AM), acrylic acid (AA), and sodium 4-styrenesulfonate (SSS). The influence of factors such as emulsifiers, reaction temperature, AM/AA mass ratio, SSS concentration, and initiator concentration on the final conversion were discussed. The conversion curves for all runs of the experiments exhibited two intervals and confirmed the character of microemulsion polymerization. FTIR spectrum indicated that AM, AA, and SSS segments were incorporated in the copolymer molecules. DSC curve indicated the glass transition temperature of the copolymer was 115.5 °C.

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