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ORIGINAL RESEARCH

Temperature resistance of AM/AMPS/NVP copolymer microspheres

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Abstract

Functional monomers, such as 2-acrylamide-2-methylpropionic sulfonic acid (AMPS), *N*-vinylpyrrolidone (NVP), and acrylamide (AM), were copolymerized into terpolymer microspheres by inverse suspension polymerization. The structure, morphology, swelling, and temperature resistance of the microspheres were comprehensively characterized through several means, including a ^{13}C nuclear magnetic resonance spectroscope, scanning electron microscope, optical microscope, and laser particle size analyzer (LPSA). The results showed that the AM, AMPS, and NVP monomers were initially polymerized to form smooth and uniformly dispersed terpolymer microspheres. The particle size distribution of the microspheres ranged from 60 to 90 µm at a stirring speed of 300 rpm. The microspheres fully absorbed water and swelled to 21.9 times at 120 °C compared with dry powder microspheres. The ternary copolymer microsphere/water dispersion system can only withstand a 120 °C temperature for 19 days. However, this temperature resistance of the microspheres can be effectively improved by adding the appropriate stabilizer solution. The microspheres can be stabilized for at least 42 days and 120 days in 0.1% thiourea--cobalt chloride composite stabilizer solution and 0.025% LY stabilizer solution, respectively, at 120 °C. It can be seen that the microspheres, water, and stabilizer systems have excellent long-term thermal stability. The AM/AMPS/NVP microspheres with temperature resistance will have broad application prospects in high-temperature reservoirs.

Keywords Ternary copolymer microspheres · Swelling property · Temperature resistance · Stabilizer concentration · Morphology

Introduction

An oilfield enters a stage of high heterogeneity and water cut during the later stage of its development. Deep profile control of injection wells in an old oilfield can effectively improve water injection, thus economically and effectively improving oil recovery from the oilfield despite the high water cut [1–3]. The conventional granular profile control agent has high strength and can effectively plug high permeability zones; however, its granular size is large, deep profile control effect is small, and the consequent enhancement of oil recovery is not ideal [4–6]. In contrast, cross-linked polymer microspheres have good water absorption, swelling, deformability, and controllability of particle size, which enable them to migrate deep through fractures and pore paths to conduct profile control along the formation which it would enhance oil recovery [7–9]. Generally, the preparation methods for cross-linked polymer microspheres include inverse suspension polymerization, inverse emulsion polymerization, and inverse microemulsion polymerization. A series of polymer microspheres with controllable sizes can be prepared through different polymerization methods to meet the needs of different reservoir conditions [10–12]. Because acrylamide has a wide range of sources, excellent water solubility, low activation energy, and low price, it has become a common main monomer in the preparation of polymer microspheres for deep profile control [13–15]. However, polyacrylamide microspheres can only be stable at 90 °C aqueous solutions for about 10 days [16]. The lactam group in the acrylamide molecule easily hydrolyzes at high temperatures, affecting the temperature resistance of the cross-linked polymer microspheres as a whole. This makes it particularly unsuitable for use in high temperature reservoirs

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(above 90 °C). Many researchers have attempted to solve this problem by introducing thermostable monomers into acrylamide (AM) to prepare copolymer microspheres. For example, Lou et al. also reported that microspheres could maintain thermal stability at temperatures below 105 °C when AMPS was added to the YG370-1 composition [17]. Zhu added two kinds of temperature resistant monomers, 2-acrylamide-2-methylpropionic sulfonic acid (AMPS) and *N*-vinylpyrrolidone (NVP) to AM to synthesize emulsion microspheres. The microspheres remained stable for 60 days in 20×10^4 mg/L formation water at 90 °C; then they slightly deformed but retained spherical structure for 120 days [18]. The microspheres prepared by copolymerization of AM, acrylic acid (AA), and temperature-resistant monomers AMPS and styrene by Fethi et al. and Roussennac et al. remained stable for more than 30 days at 99 °C [19, 20]. Yang et al. prepared a kind of DCA copolymer microspheres by adding a large amount of divinylbenzene to a small amount of AM. The microspheres were stable at 115 °C for 90 days but barely swelled in water, indicating poor deep migration abilities [21]. Zhu et al. used polyethylenimine (PEI) as an in situ surface decorating agent to improve the long-term thermal stability of the polymer microsphere [22]. The decorated microspheres remained stable at 150 °C for more than three months, and thermogravimetric analysis indicated that the in situ surface decorated polymer microspheres could remain stable at temperatures up to 310 °C. Unfortunately, the preparation method is cumbersome and the yield of microspheres is low.

From the point of view of molecular design, the introduction of rigid rings, large side groups or rigid groups can greatly improve the temperature resistance of polymers [23–25]. The monomer AMPS has large side groups: sulfonate ($–SO_3H$) and dimethyl [$–C(–CH_3)_2$]. Both of them can effectively enhance the steric resistance of the monomers, thereby enhancing the temperature resistance of the polymers. In addition, SO_3H is a strong polar group with excellent hydrophilic properties. Therefore, the addition of AMPS to AM cannot only improve the temperature resistance but also effectively improve the water absorption properties of the resultant microspheres [26, 27]. The monomer NVP has a rigid five-membered ring structure, which can inhibit the hydrolysis of amide groups in the AM chain and enhance the temperature resistance of the microspheres.

In this study, three-component copolymer microspheres were prepared using inverse suspension polymerization by reacting two kinds of thermostable monomers AMPS and NVP with the main agent AM. The structure, morphology, swelling, and thermostability of the microspheres prepared by the inverse suspension method were studied, particularly to determine the long-term thermal stability of microspheres in a microsphere/water dispersion system.

Experimental

Materials

The materials used were AM (Beijing Entrepreneur Science &Trading Co., Industrial grade, China); AMPS, industrial grade (Shandong Quanxin Chemical Co., China); NVP, analytical reagent (AR) (Tokyo Chemical Industry Limited Company, Japan); *N,N'*-methylenebisacrylamide (NMBA), CP (Tianjin Guangfu Fine Chemical Research Institute); potassium persulfate (KPS) (Tianjin Fuchen Chemicals, China), AR; cyclohexane, AR (Beijing Yili Fine Chemicals Co., China);Span80, AR(Beijing Yili Fine Chemicals Co., China); absolute ethanol, AR (Beijing Yili Fine Chemicals Co., China); methylene blue, AR(Beijing Yili Fine Chemicals Co., China); LY stabilizer (a series of different concentrations chromium acetate aqueous solution, 0.025–4.0 wt%); de-ionized water, self-made in laboratory.

Preparation of ternary copolymer microspheres

The AM/AMPS/NVP copolymer microspheres were prepared by inverse suspension polymerization. A certain amount (4 g) of Span80 was stirred in cyclohexane (80 g) to clarify the transparent oil phase. Certain amounts (16/2/2/0.1/0.2, g) of AM, AMPS, NVP, NMBA, and KPS were dissolved in a certain amount of water phase (20 g). The oil phase mixture was poured into a 250-mL flask in a constant temperature (30 °C) water bath. The device was connected, the stirring speed was adjusted, the water phase solution was added at constant pressure, and the oil–water mixture was stirred continuously for 30 min at 300 rpm; after several hours of reaction at 70 °C, the product was pumped out with anhydrous ethanol. The white copolymer microspheres were prepared by placing this product in a 50 °C oven for 24 h.

Structural characterization of the ternary copolymer microspheres

The structure and composition of the microspheres were characterized through 80 V vacuum Fourier transform infrared spectroscopy (VFTIR) and Advance III 500 nuclear magnetic resonance spectroscopy (NMR). The infrared spectrum of the AM/AMPS/NVP copolymer microspheres was determined with KBr pellet method. ^{13}C NMR spectroscopy was performed at 25 °C on a Bruker-500 ^{13}C NMR system operating at 9.4 T with corresponding ^{13}C resonance frequencies of 100.6 MHz using a 5 mm one NMR™ probe.

Characterization of morphology and size of ternary copolymer microspheres

The BX-41 optical electron microscope (produced by Olympus Company of Japan) was used to observe the morphology of the microspheres after swelling. The solid powder of the AM/AMPS/NVP copolymer microspheres was directly placed onto an electrically conductive film, the sample was sprayed with metal for 3 min, and the morphologies of the DCS and SCS microspheres were observed with a SEM SU8010 manufactured by the Hitachi Company of Japan.

Determination of swelling properties of ternary copolymer microspheres

The S3500 laser particle size analyzer manufactured by MACROTRAC was used to determine the particle size distribution of the microspheres after they were fully absorbed and swelled in de-ionized water.

Determination of temperature resistance of ternary copolymer microspheres

The ampoule bottle of a certain amount (40 mL) of microsphere/de-ionized water dispersion system was vacuum pumped, sintered, sealed using an alcohol blow torch, and placed in a high temperature oven. The ampoule bottles were carefully observed and photographed every 24 h, supplemented by optical microscopy and scanning electron microscopy. The initial time at which the ampoule bottle was placed in the 120 °C oven was taken as the starting time, and the number of days during which microsphere degradation in solution occurred was the number of days of temperature resistance.

Results and discussion

Structural characterization of the ternary copolymer microspheres.

FTIR characterization

Figure 1 shows the infrared spectra of ternary copolymer microspheres prepared by inverse suspension method, in which the ratio of monomer (AM:AMPS:NVP) is 7:1.5:1.5. In this figure, the strong and wide absorption peaks near 3420 cm^{-1} are primary amine in AM monomer and secondary amine in AMPS monomer. At 3180 cm^{-1}, they are one of the two peaks of primary amine N–H vibration. Because of overlapping with the strong absorption peaks of secondary amine N–H vibration, the peak type is concealed. The absorption peak of 2920 cm^{-1} is the characteristic absorption peak of C–H vibration. The strong absorption peak at 1670 cm^{-1} is C=O stretching vibration peak in amide group; the C–H vibration absorption peak at 1450 cm^{-1} is C–H vibration absorption peak of –CH$_2$ on AMPS molecule; the C–H vibration absorption peak at 1380 cm^{-1} is C–H vibration absorption peak in AMPS [–C(–CH$_3$)$_2$]; the C–N stretching vibration absorption peak at 1290 cm^{-1} is C–N stretching vibration absorption peak in NVP monomer; the strong absorption peak at 1090 cm^{-1} is C–N stretching vibration peak of AM and AMPS monomer; and the absorption peak at 1040 cm^{-1} is S=O. Vibration absorption peaks, 619 cm^{-1} and 530 cm^{-1}, are characteristic absorption peaks of -SO$_3$H. In FTIR spectra, the C=C stretching vibration absorption peak is near 1600 cm^{-1}, but in Fig. 1, there is no obvious absorption peak near 1600 cm^{-1}. It shows that the C=C double bonds in the three monomers are opened and the ternary copolymer microspheres are formed by initiation polymerization.

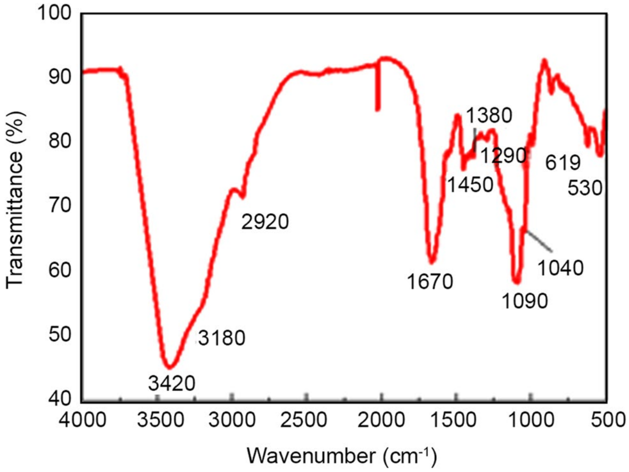

Fig. 1 FTIR spectrum of terpolymer microspheres by inverse suspension polymerization

^{13}CNMR characterization

Figure 2 shows the NMR spectra of three kinds of microspheres prepared by the reverse suspension method (AM:AMPS:NVP) with monomer ratios of 7:0:3, 7:1.5:1.5, and 7:3:0. The ^{13}C NMR spectra have absorption peaks corresponding to chemical shifts of 179 ppm, 58 ppm, 42 ppm, and 18 ppm. The spectra in Fig. 1a, b have absorption peaks near $\delta = 33$ ppm and those in Fig. 1b, c have absorption peaks near $\delta = 53$ and 29 ppm. Combining these data with the ^{13}C NMR data of the three monomers presented in Fig. 2, it can be seen that a $\delta = 33$ ppm peak in Fig. 3a, b corresponds to chemical shifts of the carbonyl-CH$_2$ in the quinary ring of the NVP monomer, while $\delta = 29$ ppm is attached. The near

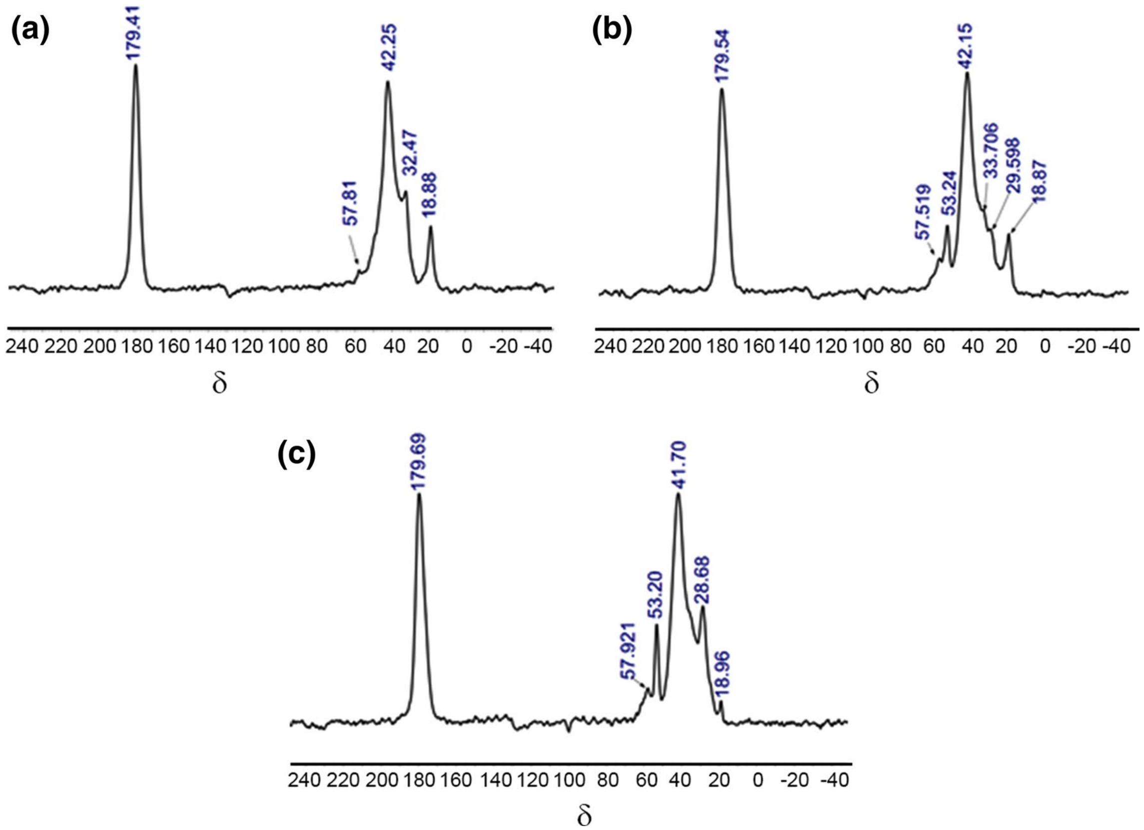

Fig. 2. ^{13}C NMR Spectra of the three kinds of terpolymeric microspheres at different monomer ratios:**a** AM:AMPS:NVP = 7:0:3, **b** AM:AMPS:NVP = 7:1.5:1.5, **c** AM:AMPS:NVP = 7:3:0

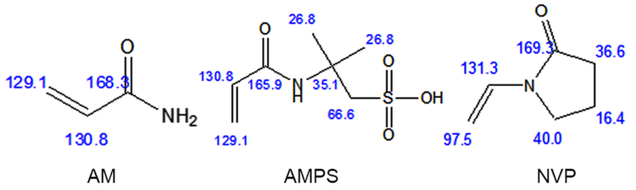

Fig. 3 Data on the ^{13}C NMR spectra of the three monomers

peak corresponds to a chemical shift of the CH_3 in the AMPS monomer. The ^{13}C NMR spectra of the three kinds of microspheres showed no chemical shift of the C=C double bond. The peak in Fig. 3b contains the characteristic absorption peaks of the three monomers. The above results show that two or three monomers of AM, AMPS, and NVP can be copolymerized.

SEM characterization

Figure 4 shows a SEM photograph of the microspheres (AM:AMPS:NVP = 7:1.5:1.5) prepared by inverse suspension polymerization at a stirring speed of 300 rpm. The surface of the microspheres is smooth and uniformly dispersed, and the size of the microspheres ranges from 60 to 90 µm.

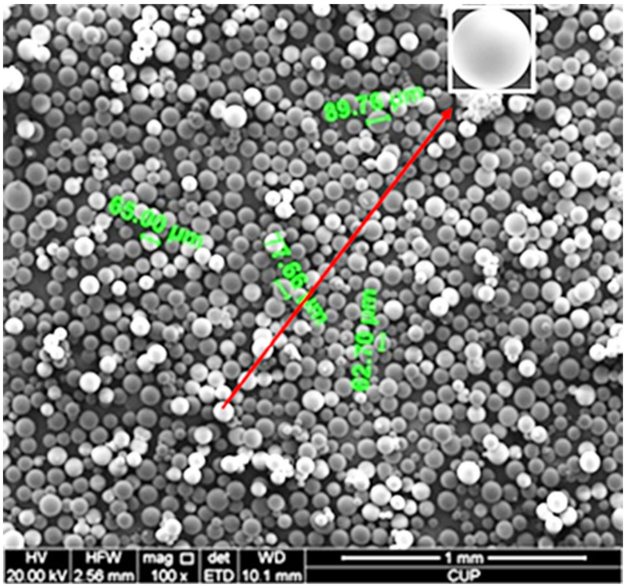

Fig. 4 SEM photo of terpolymeric microspheres

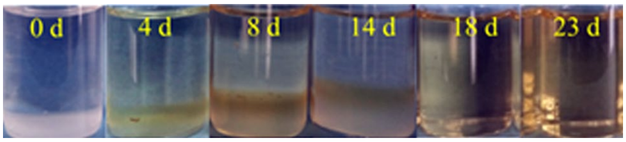

Fig. 5 Thermal stability of microspheres in water solution (temperature: 120 °C; concentration: 5000 mg/L; stirring speed: 300 rpm)

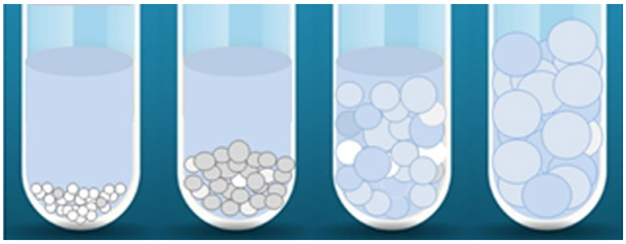

Fig. 6 Swelling process of microspheres in 120 °C water solution

Temperature resistance of the ternary copolymer microspheres

Temperature resistance of microsphere/water dispersion system

The microspheres (AM:AMPS:NVP = 7:1.5:1.5) prepared at a stirring speed of 300 rpm were placed in an oven, at a concentration of 5000 mg/L, at 120 °C. The state of the dispersion system was observed for days at different time points, as shown in Fig. 5. The volume of the microspheres increased significantly after swelling, and swelling increased with time. A clear solid–liquid interface was visible. The microspheres swelled almost completely by the 8th day and the solid–liquid interface disappeared. The microspheres could maintain this extremum state for approximately 14 days at 120 °C without obvious degradation. Then, the particle size of the microspheres began to decrease and gradually lost stereoscopic form. Subsequently, the microspheres prepared from low to high rotational speeds began to degrade successively. After 23 days, all the microspheres were completely degraded and the solution was clarified.

From the swelling and degradation processes observed with the microsphere/water dispersion system, it can be inferred that the swelling process of microspheres to the extremum value at high temperature increases with storage time, as shown in Fig. 6. At first, the microspheres settled at the bottom of the solution; the volume of the microspheres increased significantly after 4–7 days, and they remained at the bottom; at 7–9 days, the volume of microspheres increased further; however, after 9–11 days, the volume was at the limit. At this time, the water in the initial dispersion system disappeared and was absorbed by the microspheres. The water absorbed by the microspheres was at least 200 times their own weight.

The microspheres were placed in a 120 °C high temperature aqueous solution for 8 days, and microscopic photos were taken after natural air-drying with the methylene blue stain. These are shown in Fig. 7a; the particle size ranges from 100 to 200 µm. An appropriate amount of de-ionized water droplets was carefully added to the air-dried microspheres. After the microspheres were fully absorbed and swelled, microscopic photos were taken. These are shown in Fig. 7b; the diameter of the microspheres increased to 500–1000 µm. The results showed that the internal structure of the microspheres changed irreversibly at this time, which resulted in a significant difference between the water absorption and swelling properties of the microspheres at 25 °C and 120 °C. The volume increase of the microspheres at 25 °C was about 21 times, while that of the microspheres after temperature resistance was about 110 times the initial volume. Figure 8 presents a scanning electron microscopic photograph of the surface of microspheres when they reached their swelling extremum. On comparison with Fig. 7b, it is clear that the surface of the microspheres might have changed from smooth to rough under the action of high-temperature aqueous solution. There are many microholes and the surface has an overall groove-like texture, which is also the reason for their remarkable increase in water absorption at high temperatures.

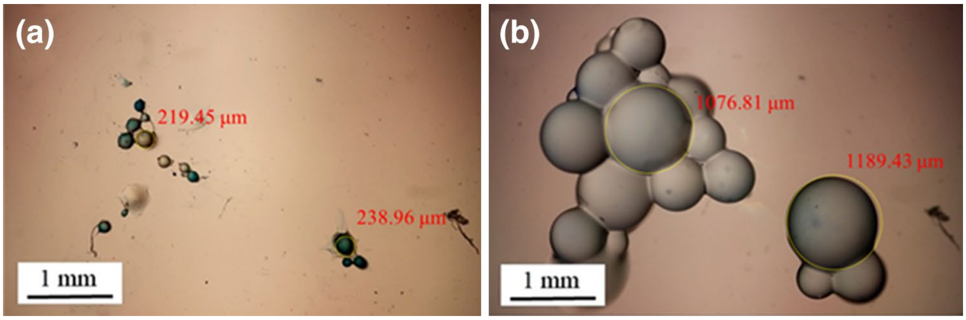

Fig. 7 Swelling of the microspheres in an aqueous solution at 120 °C for 8 days: **a** losing all the water and **b** full swelling (temperature: 30 °C)

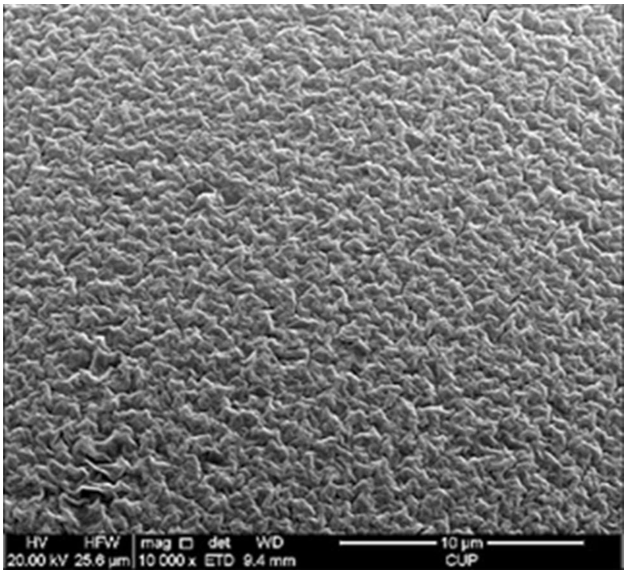

Fig. 8 SEM photo of the surface of a microsphere (120 °C)

Table 1 Thermal stability of microspheres with different concentrations of stabilizer solutions at 120 °C

Stabilizer solution concentration (%)	0	0.02	0.05	0.1
Temperature tolerance days (days)	19	30	35	42

Temperature: 120 °C; Concentration: 1000 mg/L

Effect of additives on the temperature resistance of the microsphere/water dispersion system

Microsphere solutions (AM:AMPS:NVP = 7:1.5:1.5) with a concentration of 1000 mg/L were dispersed by adding thiourea--cobalt chloride stabilizer solutions of different concentrations (thiourea:cobalt chloride = 3:1). Temperature resistance was measured at 120 °C. The results are shown in Table 1. From the data shown in Table 1, it is clear that with increase in thiourea--cobalt chloride stabilizer concentration, the number of days for which the microspheres remained temperature resistant in the dispersion system increased significantly. The microsphere dispersion system remained temperature resistant at 120 °C only for 19 days without the stabilizer, while with 0.1% stabilizer, it remained temperature resistant for 42 days. The thiourea--cobalt chloride stabilizer can stabilize microsphere water dispersion systems at high temperatures [28, 29]. Because thiourea and cobalt chloride react to form a new metal–organic crystal, the stabilizers improve the temperature resistance of AM/AMPS/NVP copolymer microspheres.

Microsphere dispersions containing 0.05% stabilizer for 35 days at high temperature were observed and microscopically photographed. The results are shown in Fig. 9. Figure 9a shows a dry powder microscopic photograph of microspheres with particle sizes below 100 μm. The microspheres stained with methylene blue after 15 days at high temperature are shown in Fig. 9b. The particle size in the latter case was larger than that of the microsphere powder, and the dyeing effect of methylene blue was good. After 30 days at high temperature, the microspheres were stained with methylene blue again and photographed. The results are

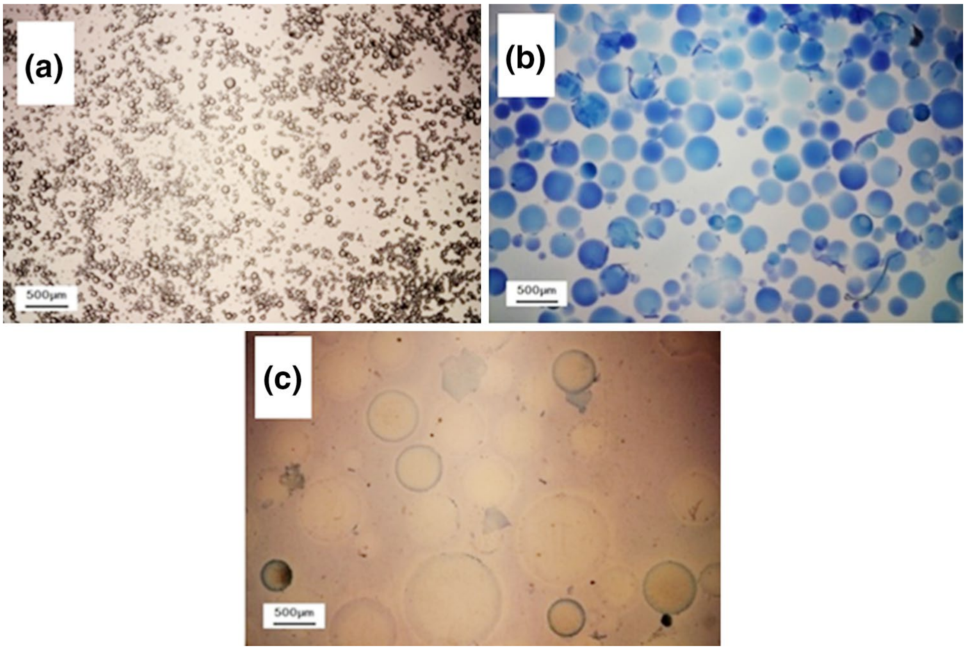

Fig. 9 Electron microscopic images of terpolymer microspheres in 0.05% stabilizer solution on different days of remaining at 120 °C: **a** the powder; **b** after 15 days; **c** after 30 days

shown in Fig. 9c. At this time, the particle sizes of the microspheres increased further than those of the microspheres photographed after 15 days, and the spheres were not dyed. It can be seen that high temperature conditions are conducive to water absorption and expansion for microspheres. Because the cationic group in methylene blue solution interacts with the anionic group (COO–) in the microsphere particles to form a dark blue component through electrostatic interaction, the microspheres are easier to observe under the staining microscope [8].

To further improve the temperature resistance of the microspheres, different concentrations of LY stabilizers were added into the 1000 mg/L dispersion system and the entirety was placed in a 120 °C oven to measure the temperature resistance. The state of the dispersion system on different days is shown in Fig. 10, and the results of the temperature resistance experiment are shown in Table 2.

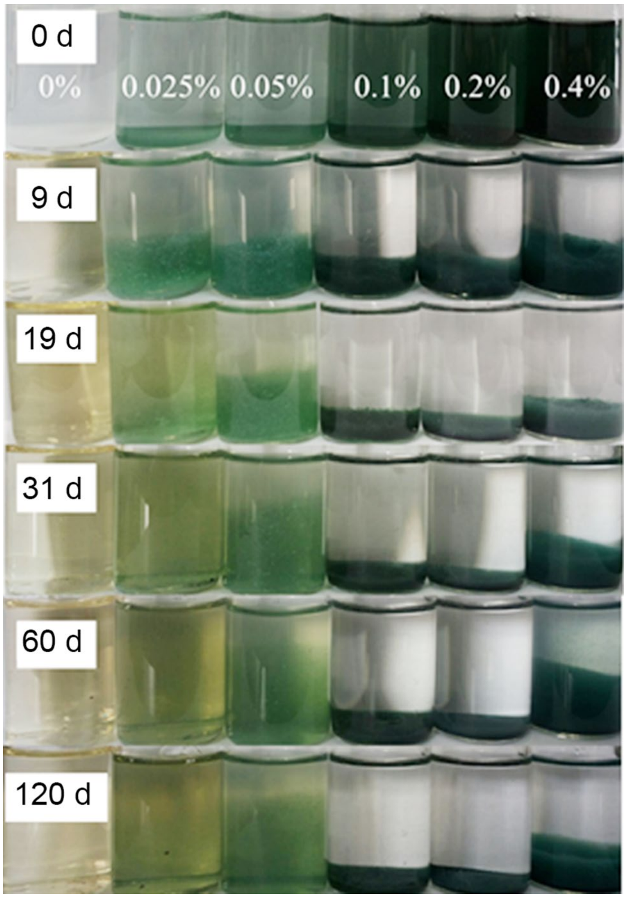

Fig. 10 Thermal stability performance of the microspheres with different concentrations of stabilizer solution at 120 °C

Figure 10 shows that the color of the microspheres in the bottle deepens from left to right with increase in LY stabilizer concentration. With increase in temperature resistance time and stabilizer concentration, microsphere swelling increases. After 9 days at high temperature, the microspheres without stabilizer reached the swelling extremum value. The swelling in the containers with 0.025% and 0.05% stabilizers was remarkable, while the microspheres in the containers with 0.1%, 0.2%, and 0.4% stabilizers settled at the bottom; in the latter case, the swelling was limited. After 19 days at high temperature, the volumes of microspheres in the containers with 0.025% stabilizer expanded to their limits, while the microspheres in the containers with 0.1%, 0.2%, and 0.4% stabilizers still settled at the bottom. The expansion in the volume of microspheres was very small in the latter cases, indicating that excessive concentration of stabilizer prevented the expansion microspheres. The macroscopic state of the microsphere dispersion system with 0.025% and 0.05% stabilizer solutions tended to remain stable, and the swelling ratio and morphology of the microspheres remained unchanged. Thus, LY stabilizer solutions with concentration greater than or equal to 0.025% stabilized the dispersions of ternary copolymer microspheres for at least 120 days.

Figure 11 presents the SEM photograph of the microsphere dispersion system containing 0.025% LY stabilizer at 120 °C before and after temperature resistance. Figure 11a shows the SEM photograph of the dry powder of microspheres before heat resistance and Fig. 11b shows the photograph of the microspheres after natural air-drying post 36 days of heat resistance. The particle sizes of the microspheres in the two pictures are similar. The photograph of one of the microspheres in Fig. 11b is gradually enlarged, and the results are shown in Fig. 11c. It is obvious that there are many irregular bulges on the surface of the sphere, and these bulges are separated by ravine-like depressions. These bulges seem to have formed by intertwining lines. There are many tiny holes on the surface, which assist in water absorption and expansion at high temperature.

Table 2 Thermal stability of microspheres with different concentrations of stabilizer solutions

Stabilizer concentration (%)	0	0.025	0.05	0.1	0.2	0.4
Temperature tolerance days (days)	19	> 120	> 120	> 120	> 120	> 120

Temperature: 120 °C; Concentration: 1000 mg/L

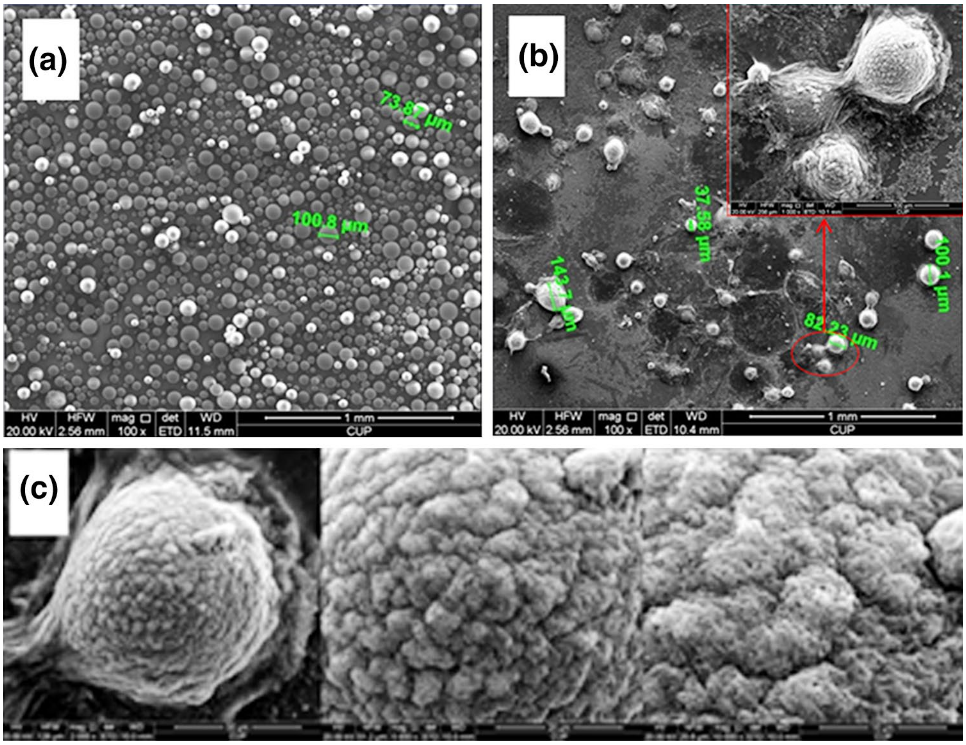

Fig. 11 SEM photographs of microspheres in stabilizer solutions at 120 °C: **a** powder of microspheres; **b** after 36 days; and **c** surface of the microspheres in b

Conclusion

(1) The ^{13}C NMR spectra showed that the AM/AMPS/NVP monomers were copolymerized by inverse suspension polymerization. The prepared microspheres had a smooth surface, and the particle size distribution of the microspheres ranged from 60 to 90 µm at a stirring speed of 300 rpm. The microspheres had certain swelling properties as well. (2) The addition of monomers AMPS and NVP effectively improved the temperature resistance of the microspheres. The ternary copolymer microspheres with a monomer ratio of 7:1.5:1.5 (AM:AMPS:NVP) had the best temperature resistance. With increase in swelling time, the particle size of the microsphere dispersions gradually increased to their extremum value and then began to degrade until the particles disappeared. The maximum volume swelling ratio of the microspheres was about 21.9 times. (3) The temperature resistance of the microspheres was effectively improved by adding an appropriate stabilizer solution. The thiourea--cobalt chloride composite stabilizer solution and LY stabilizer solution improved the temperature resistance of microspheres significantly. The microspheres were stabilized for at least 42 days and 120 days in 0.1% thiourea--cobalt chloride composite stabilizer solution and 0.025% LY stabilizer solution, respectively, at 120 °C. The AM/AMPS/NVP microspheres with temperature resistance may have broad application prospects for high-temperature reservoirs.

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Compliance with ethical standards

Conflicts of interest The authors declare no competing financial interests.

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