

A study of factors affecting properties of AM/AMPS/NVP terpolymeric microspheres prepared by inverse suspension polymerization

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Abstract. Terpolymeric microspheres were synthesized by the inverse suspension polymerization of functional monomers including AMPS, NVP, and AM. The morphology and size of the obtained microspheres were measured by scanning electron microscopy (SEM) and optical microscopy. Furthermore, the swelling performances of the obtained microspheres were measured with a laser particle analyzer (LPA), and the thermal stability of the microspheres obtained was measured by differential thermal analysis (DSC-TG) and high temperature experiments involving microsphere/water dispersion. The results revealed that the extreme value of the microsphere size distribution decreased from 280 μm to 20 μm as the stirring rate increased from 175 rpm to 500 rpm. At temperatures below 25°C, the maximum achieved swelling ratio of the microspheres was 21, and the thermal stability of the terpolymer microspheres was significantly higher than that of the dipolymer microspheres. The terpolymer/water dispersions were kept at 120°C for 19d before any damage was observed.

1. Introduction

In deep profile control of oil fields, polymer microspheres are able to travel through cracks and channels in high-pressure areas and get to deeper parts, thus achieving control along the profile. This capability can be attributed to ideal particle size, good swelling performance after absorbing water, deformation performance, thermal resistance, and shear resistance [1-3]. As profile control is such an important aspect of oil mining, studies on factors affecting the properties of polymer microspheres are of great significance [4-8].

Various lab experiments and practical applications performed in oil fields have indicated that polymer microspheres have a significant enhancement effect on oil recovery factors [9-10]. Deep profile control achieved by polymer microspheres can only be successful in cases where the particle size matches well with the size of the reservoir fractures and channels; polymer microspheres of various sizes can be synthesized using different polymerization methods [11-13]. Previous studies on the swelling performance, heat resistance, salt resistance, and strength of acrylamide-based polymer microspheres revealed that these microspheres showed reasonable swelling performance and stability in water at 90°C for more than 10 d [14-17]. Moreover, the particle size decreased as salt

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concentration and shear rate increase [18]. Although many studies have been carried out involving polymer microspheres, few reports on their thermal resistance have been published. In this article, copolymer microspheres were prepared by the inverse suspension polymerization of AM and two monomers (AMPS and NVP) with good thermal resistance [19]. Additionally, the effects of the AMPS:NVP ratio, stirring speed, concentrations of cross-linking agent and emulsifier on particle size, swelling performance, and thermal resistance were investigated.

2. Experimental

2.1. Materials

The materials used for the experiments of this research included the following items, which are listed with their grade and company of origin: AM (Acrylamide), analytically pure, Beijing Modern East Fine Chemical Co. Ltd.; AMPS (2-acrylamido-2-methyl propanesulfonic acid), industrial grade, Shandong Quanxin Chemical Industry Co. Ltd.; NVP (N-vinyl pyrrolidone), analytically pure, TCI-Tokyo Chemical Industry Co. Ltd.; NMBA (N, N-methylenebis acrylamide), chemically pure, Tianjin Guangfu Fine Chemical Industry Institute; KPS (potassium peroxydisulfate), chemically pure, Tianjin Guangfu Fine Chemical Industry Institute; Cyclohexane, analytically pure, Beijing Yili Fine Chemical Co. Ltd.; Span 80 (dehydrated sorbitan fatty acid ester), analytically pure, Beijing Yili Fine Chemical Co. Ltd.; absolute ethanol, analytically pure, Beijing Yili Fine Chemical Co. Ltd.; Methylene Blue, analytically pure, Beijing Yili Fine Chemical Co. Ltd.; D.I. water, made in lab.

2.2. Methods

2.2.1. Preparation of terpolymeric microspheres. A certain amount of span 80 was mixed with cyclohexane and stirred until clear and a transparent oil phase was observed; monomers, NMBA, and KPS were dissolved in water to obtain a water phase. Then, the oil phase was poured into a three-neck flask in a thermostatic waterbath. The stirring speed and waterbath temperature were adjusted accordingly and the water phase was added dropwise into the flask under a constant pressure. After several hours, the mixture was filtrated and the obtained products were washed with absolute ethanol and dried at 50°C for 24 h. Finally, pale yellow copolymer microspheres were obtained.

2.2.2. Measurement of microsphere size. The morphologies of the microsphere powder and microspheres after swelling were checked by microscope (Olympus BX-41). The size and surface morphology were checked by scanning electron microscopy (SEM, SIRION 200).

2.2.3. Measurement of swelling performance. The particle sizes before and after water absorption were measured by laser particle analyzer (MACROTRAC S3500).

2.2.4. Measurement of thermal resistance. The thermal resistances of the microspheres were measured by simultaneous thermal analyzer (SDT Q600) with a heating rate of 10°C/min (up to 600°C). The microspheres were dispersed in water and placed in a high-temperature oven. The samples were checked by microscope and SEM at 24 h intervals.

3. Experimental results

3.1. Effects of monomer ratio on the properties of microspheres

Seven kinds of microspheres were obtained by adjusting the monomer ratio (AM: AMPS: NVP), and the properties of these microspheres were evaluated.

3.1.1. Swelling behaviour. The initial average diameters, the average diameters after swelling in de-ionized water for 8 h, 24 h, and 72 h, and the swelling ratios of the seven kinds of spheres were measured, and are summarized in table 1. The microscopic images of the terpolymer microspheres

(monomer ratio AM: AMPS: NVP=7:1.5:1.5) before and after 24-hour swelling are shown in figure 1.

Table 1. Size distribution of microspheres with different ratios of monomers.

Monomer ratio AM: AMPS: NVP	Initial size (d) / μm	Size after swelling/ μm	8h	Size after 24 h swelling / μm	Size after 72 h swelling/ μm	Volumetric swelling (D^3/d^3)
7:0:3	76.46	99.61		124.26	126.17	4.29
7:0.5:2.5	67.04	97.15		120.67	119.35	5.83
7:1:2	60.45	91.52		116.75	115.96	7.21
7:1.5:1.5	55.69	100.24		139.23	139.85	15.63
7:2:1	51.83	103.74		139.49	141.14	19.49
7:2.5:0.5	49.28	132.58		206.98	206.26	74.09
7:3:0	46.62	165.46		209.78	210.52	91.11

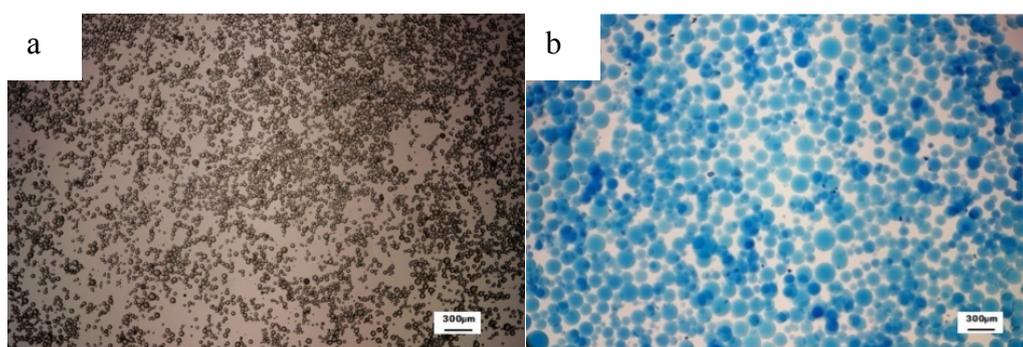


Figure 1. SEM images of terpolymer microspheres (a) before swelling; and (b) after swelling. The swelling temperature was 30°C and the microsphere concentration was 20 mg/L.

Figure 1(a) shows a SEM image of the dry-powdered terpolymer microspheres. As can be seen, the initial particle diameters were less than 90 μm . Figure 1(b) shows a SEM image of the microspheres after 24 h swelling and stained with methylene blue. As can be seen, the diameters of the spheres at this stage were in the range of 100-200 μm . After swelling, the microspheres maintained a spherical morphology and the diameters increased significantly.

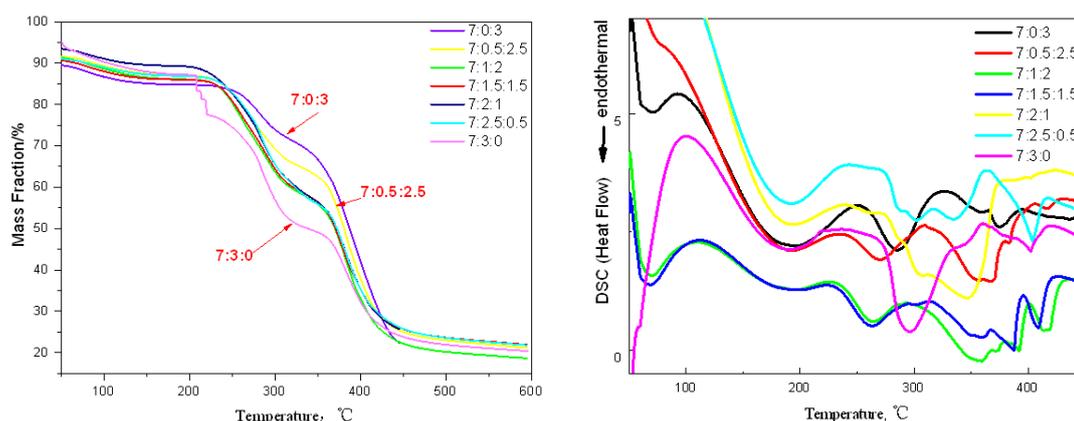
As shown in table 1, as the percentage of AMPS increased, the diameters of the microspheres decreased, while the swelling capability increased. After 8 h swelling, the diameters of the microspheres increased drastically. After 24 h swelling, the diameters of the microspheres increased further. However, after 72 h swelling, the diameter of the microspheres was similar to that of the microspheres after 24 h swelling, demonstrating that the spheres reached their swelling limit after 24h and the diameter of the microspheres did not increase further.

3.1.2. Thermal resistant properties in aqueous solution. Thermal stability durations of the microspheres in aqueous solution at 120°C were measured, and are shown in table 2. As can be seen, as the proportion of AMPS increased and the proportion of NVP decreased, the thermal stability durations of the microspheres in the aqueous solution first increased and then decreased. The thermal resistant duration was optimized (19 d) at AMPS: NVP = 1:1. The thermal resistances of the AM/NVP and AM/AMPS copolymer microspheres were relatively poor, with a thermal resistant duration of 8 d and 7 d, respectively. Therefore, it was indicated that optimum thermal resistance could only be achieved with the AM/AMPS/NVP terpolymer microspheres (with a proper monomer ratio).

Table 2. Thermal stability of microspheres with different ratios of monomers.

Monomer ratio (AM:AMPS:NVP)	7:0:3	7:0.5:2.5	7:1:2	7:1.5:1.5	7:2:1	7:2.5:0.5	7:3:0
Duration /d	8	11	16	19	15	10	7

3.1.3. Analysis of TG-DSC curves. The TG-DSC curves of the dry-powdered microspheres are shown in figure 2 and table 3. As shown in figure 2(a), the weight loss curves of the microspheres with monomer ratios (AM: AMPS: NVP) of 7:0:3, 7:0.5:2.5, and 7:3:0 were significantly different from the other curves, especially in the range of 200-400°C. At the same temperature, weight loss percentages of the microspheres with monomer ratios of 7:0:3 and 7:0.5:2.5 were lower than that of the other microspheres, while microspheres with a monomer ratio of 7:3:0 exhibited the lowest weight loss percentages. Figure 2(b) shows the DSC curves of different microspheres. As can be seen, the intensities and positions of all endothermic peaks of the microspheres with monomer ratios of 7:1:2 and 7:1.5:1.5 were similar to each other. The DSC curves of the microspheres with monomer ratios of 7:2:1 and 7:2.5:0.5 were similar at temperatures lower than 360°C. In the range of 150-230°C, all curves had similar endothermic peaks at the same temperature, indicating that all the microspheres decomposed in a similar way in this range.

**Figure 2.** TG and DSC curves of microspheres with different ratios of monomers.**Table 3.** Various temperatures of microspheres with different ratios of monomers.

Monomer ratio	GTT /°C	IDD /°C	Degradation temperatures corresponding to different weight loss					
			10	20	30	40	50	60
7:0:3	139	197.5	295.26	356.76	379.04	395.31	412.21	433.88
7:0.5:2.5	/	193.5	270.05	310.89	368.63	384.57	401.22	431.60
7:1:2	147.8	197.5	262.34	292.49	348.34	376.80	393.07	420.42
7:1.5:1.5	148.4	199.6	265.37	295.24	352.66	377.65	398.46	446.39
7:2:1	/	193.9	262.45	289.57	329.79	373.62	391.46	419.43
7:2.5:0.5	130	192.6	272.46	296.08	341.34	377.78	396.03	438.13
7:3:0	140	191.5	226.25	278.46	298.97	363.44	388.03	419.14

^a GTT: Glass transition temperature.

^b IDT: Initial degradation temperature.

As shown in table 3, the initial glass transition temperatures of the microspheres with monomer ratios (AM: AMPS: NVP) of 7:1:2 and 7:1.5:1.5 were significantly higher than that of the other microspheres, indicating these microspheres showed better thermal stability. The temperature corresponding to a weight loss of 60% for the microspheres with a monomer ratio of 7:1.5:1.5 was the highest (446.39°C), while that for the microspheres with a monomer ratio of 7:3:0 was the lowest

(419.14°C). Therefore, it was concluded that the microspheres with a monomer ratio of 7:1.5:1.5 demonstrated the optimized thermal resistance, while the microspheres with a monomer ratio of 7:0:3 had the worst thermal resistance in the practical temperature range of oil fields.

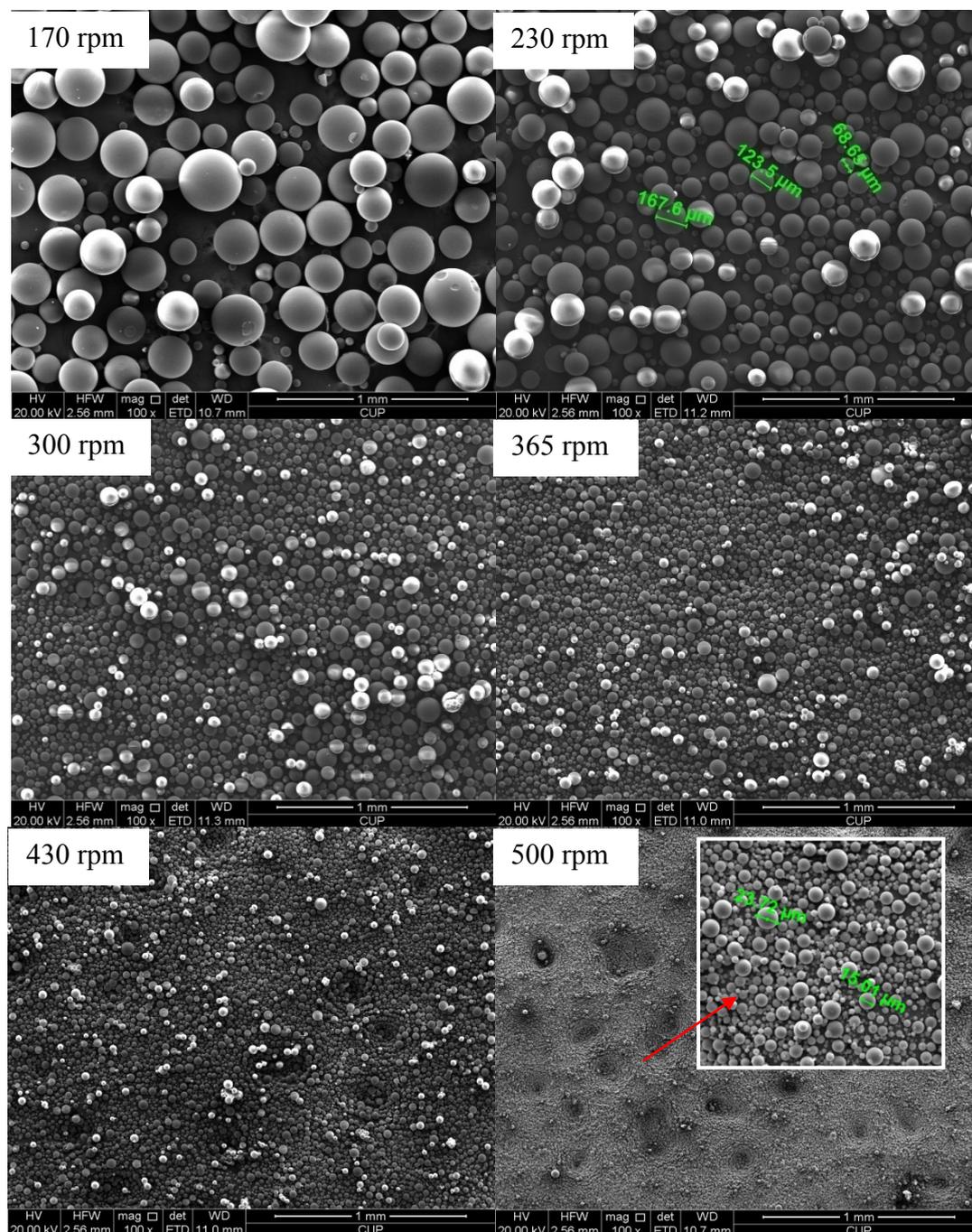


Figure 3. SEM images of microspheres prepared by different stirring rates.

3.2. Effects of stirring speed on the properties of microspheres

3.2.1. *Initial diameter.* With the other experimental conditions kept constant, six kinds of microspheres with different diameters were obtained by adjusting the stirring speed (170-500 r/min), and SEM images of these samples are shown in figure 3. As can be seen, the diameter of the

microspheres decreased as the mechanical stirring speed increased. As shown in table 4, the average initial diameter of the microspheres stirred at 175 rpm was 230.90 μm , while that of the microspheres stirred at 500 rpm was 11.14 μm , indicating that the stirring speed had a significant effect on the diameter of the microspheres. A possible reason is that in the inverse suspension system, external forces and the proper amount of emulsifier are needed to form stable water-in-oil droplets, and the stirring speed directly affects the size of the droplets containing monomers, initiators, and crosslinking agents, thus affecting the diameter of the polymer microspheres.

Table 4. Initial average size of microspheres with different stirring rates.

Stirring rate /rpm	175	230	300	365	430	500
Initial size / μm	230.90	136.00	69.81	41.71	30.68	11.14

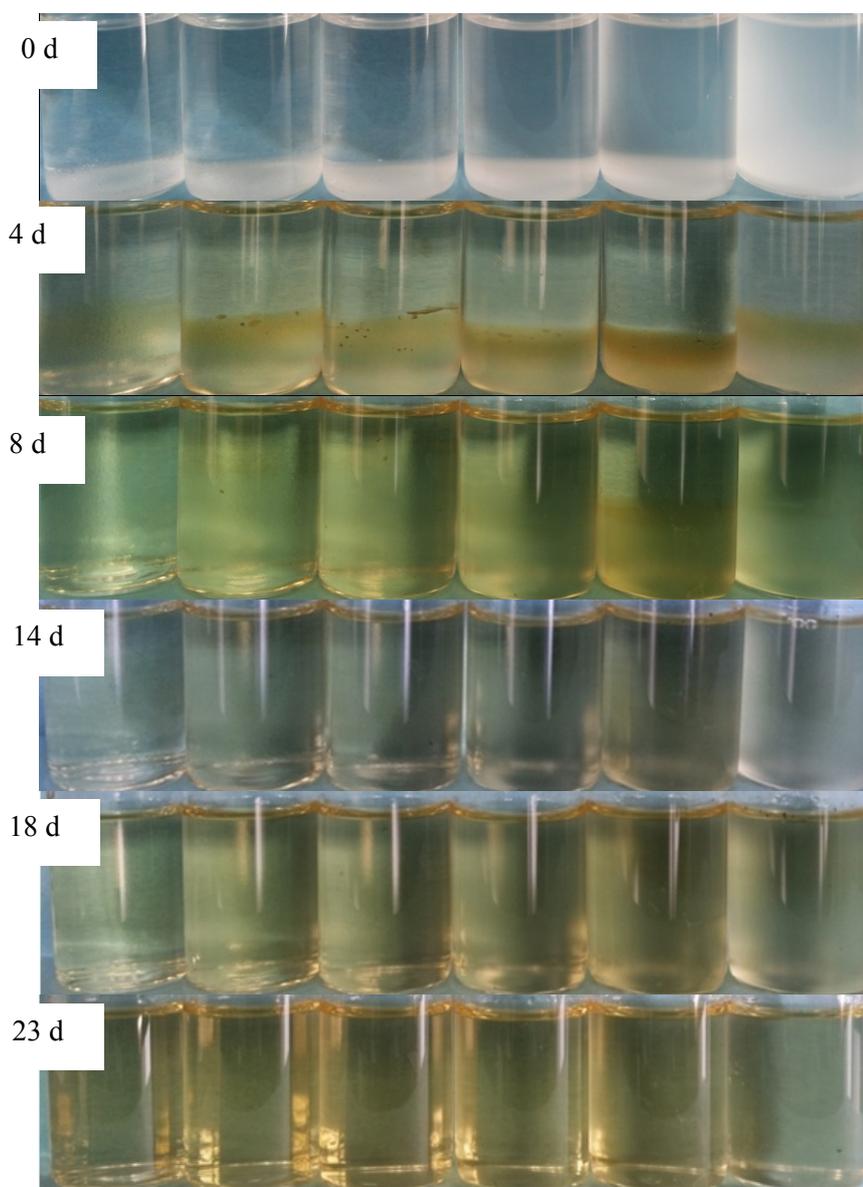


Figure 4. Thermal stability (in water solution) of microspheres prepared by different.

3.2.2. *Thermal stability in aqueous solution.* Microspheres obtained at different stirring speeds were transferred into 120°C water for different durations and monitored. As shown in figure 4 (stirring

speed increasing from left to right), the layered interfaces between the microspheres and water were obvious in the first four bottles, with the microspheres precipitated at the bottom. For the samples obtained at a stirring speed of 430 rpm, some suspended microspheres were observed, while most of the microspheres precipitated at the bottom. In the samples obtained at a stirring speed of 500 rpm, a turbid liquid different from the others was observed due to the small diameter of the microspheres. As the duration increased, microsphere swelling was observed due to water absorption. After 8 d, the microspheres obtained at 175 rpm occupied nearly all of the solution. In the next 48 h, the microspheres swelled further and filled the solution from left to right. This status was maintained for 5 d. After 14 d, decomposition of the microspheres obtained at 175 rpm was observed and the diameter of the microspheres started to decrease. Then, the decomposition continued from left to right. In the last 23 d of the experiment, the microspheres decomposed completely and the solutions were transparent.

The specific thermal resistant durations of the different samples are summarized in table 5. The number of days decreased as the microsphere diameters increased. This could be attributed to the increase in the amount of AMPS contained in a single microsphere and the amount of negative groups produced, which enhanced the interaction forces between polymer segments. Additionally, segments containing fewer negative groups were more fragile at elevated temperatures, resulting in accelerated decomposition of the microspheres.

Table 5. Thermal stability (in duration) of microspheres prepared by different stirring rates (water temperature = 120°C and microsphere concentration = 1 g/L).

Stirring rate /rpm	175	235	300	365	430	500
Stability duration/d	18	18	19	20	22	23

3.3. Effects of crosslinking agent amounts on the properties of microspheres

3.3.1. Initial diameter and swelling performance. A series of microspheres were prepared by adjusting the amount of crosslinking agents used (0.05%-2%). The average diameters of all the microspheres obtained before and after swelling are summarized in table 6. As the amount of crosslinking agent increased from 0.1% to 2%, the average diameter of the microspheres decreased from 63.63 μm to 47.95 μm . With the amount of crosslinking agents at 0.05%, the average diameter of the microspheres was 47.91 μm , indicating a negative correlation between the amount of crosslinking agent and the diameter of the microspheres. However, no obvious trends were observed for the average diameter of microspheres after swelling. With the amount of crosslinking agent in the range of 0.33%-1.5%, the swelling performance of the microspheres degraded.

Table 6. Initial size and swelling performance of microspheres with different amounts of cross-linker.

NMBA content/%	0.05	0.1	0.33	1	1.5	2
Initial size/ μm	47.91	63.63	60.06	56.3	54.26	47.95
Size after swelling/ μm	150.19	174.66	186.49	156.85	122.8	156.32
Swelling ratio	30.75	20.61	29.91	21.64	11.59	34.63

3.3.2. Thermal resistance

- TG-DSC curves

The TG curves of the microspheres obtained with different amounts of crosslinking agents are shown in figure 5. As can be seen, the different curves are highly similar to each other, and the decomposition and weight loss percentages at certain temperatures are almost identical, indicating that the amount of crosslinking agent had a negligible effect on the thermal resistance of the dry-powdered microspheres.

- Thermal resistance performance in high temperature aqueous solution

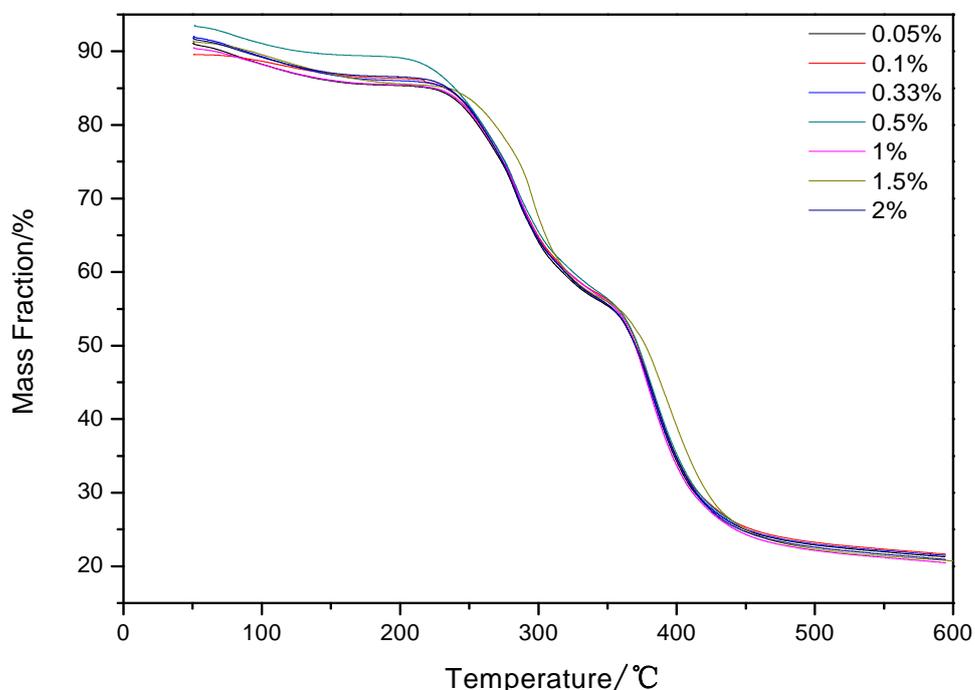


Figure 5. TG curves of microspheres prepared by different amounts of cross-linker.

Microspheres obtained with different crosslinking agent amounts (0.05%-2%) were dispersed in aqueous solution, and the thermal stability durations of these disperse systems were measured. As shown in table 7, the thermal stability durations of the microspheres dispersed in aqueous solution stayed constant at 18-19 das the amount of crosslinking agent was increased. This result was consistent with TG curves, thus verifying the conclusion that the effect of crosslinking agent amount on the thermal resistance of the microspheres was negligible.

Table 7. Thermal stability of microspheres prepared by different amounts of LX cross-linker.

NMBA content/%	0.05	0.1	0.33	0.5	1	1.5	2
Stability duration /d	18	19	18	19	19	18	18

3.4. Effects of emulsifier amount on the properties of microspheres

With the other experimental conditions kept constant, seven kinds of microspheres were obtained by adjusting the amount of emulsifier (1.6%-20%). The size distributions and thermal resistance durations in aqueous solution of all microspheres were obtained and are shown in table 8. It was observed that the average diameter of the dry-powdered microspheres decreased from 82.25 μm to 64.74 μm as the emulsifier amount increased from 1.6% to 20%; the emulsifier amount had a negligible effect on the thermal resistance duration. The results demonstrated that the diameter of the microspheres decreased when the emulsifier amount increased, while the thermal resistances of these microspheres were not affected.

Table 8. Initial size and thermal stability (in duration) of microspheres prepared by different amounts of emulsifier.

Emulsifier content /%	1.6	3.2	6.4	10.0	13.2	16.4	20
Initial size / μm	82.25	72.01	72.46	70.19	69.25	66.69	64.74
Stability duration /d	19	17	18	19	19	17	19

4. Conclusion

After performing the experiments described in this paper, the following conclusions could be drawn:

- The monomer ratio (AM: AMPS: MVP) had a significant effect on the properties of the microspheres obtained by inverse suspension polymerization. With the AM content fixed, the initial diameter of the microspheres decreased and the swelling performance was enhanced by increasing the amount of AMPS and decreasing the amount of NVP. After 24 h swelling, saturation was observed and the diameter of the microspheres remained constant thereafter. As the amount of AMPS increased and the amount of NVP decreased, the thermal resistance durations of the microspheres obtained in aqueous solution first increased and then decreased. With a monomer ratio of 7:1.5:1.5, the microspheres exhibited optimized thermal resistance (19 d). The TG curves suggested that the microspheres with a monomer ratio of 7:1.5:1.5 had an optimized thermal resistance, while those of the microspheres with a monomer ratio of 7:0:3 showed the lowest thermal resistance.
- The stirring speed significantly affected the initial diameter and the thermal resistance of the microspheres prepared by inverse suspension polymerization, as well as the thermal resistance of microspheres. With the formula fixed and stirring speed increased from 170 to 500 rpm, the initial average diameter of the microspheres decreased from 230.90 μm to 11.14 μm , while the thermal resistance durations increased from 18 d to 23 d.
- The effects of the crosslinking agent amount on the initial diameter, swelling performance, and thermal resistance of the microspheres were negligible. As the amount of crosslinking agents increased from 0.05% to 0.33%, the volumetric expansion ratio of the microspheres first decreased and then increased. As the amount of crosslinking agents increased from 0.33% to 1.5%, the swelling performance of the microspheres degraded initially and then improved. As the amount reached 2%, the swelling of the microspheres obviously increased until the maximum amount of crosslinking agents was added.
- The amount of emulsifier had a notable effect on the initial diameter of the microspheres, but not on the thermal resistance. As the amount of emulsifier increased, the initial diameter of the microspheres decreased from 82.25 μm to 64.74 μm , although no obvious trends were observed.

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