

Stability Study of Inverse Suspension Copolymerization of 1,1,3,3-Tetramethylguanidium Acrylate and *N,N'*-Methylenebisacrylamide

Jie Dong,¹ Linbo Wu,¹ Dong An,¹ Bo-Geng Li,¹ Shiping Zhu²

¹Department of Chemical and Biological Engineering, State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

²Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

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ABSTRACT: In a previous study, we synthesized crosslinked P(TMGA-*co*-MBA) via an inverse suspension copolymerization of 1,1,3,3-tetramethylguanidium acrylate (TMGA) and *N,N'*-methylenebisacrylamide (MBA) and found that the product is a good SO₂ sorbent. However, the polymerization stability appeared to be poor under some reaction conditions and is far from being elucidated. In this study, the inverse suspension copolymerization was carried out using cyclohexane as solvent, Span60 as dispersant, and ammonium persulfate (APS) as initiator. The effects of the reaction conditions such as stirring speed, dispersant concentration,

and temperature on the polymerization stability and particle size were systematically examined. It is found that the polymerization stability is a strong function of these parameters. Stable crosslinked poly(TMGA-*co*-MBA) particles from micrometer to millimeter diameters were synthesized under optimized conditions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1450–1454, 2010

Key words: radical polymerization; inverse suspension polymerization; crosslinked polymer particles; ionic liquid polymer; 1,1,3,3-tetramethylguanidium acrylate

INTRODUCTION

Ionic liquids (ILs) emerged in the last decades as nonvolatile organic melt salts and have been now widely used or explored as designable green solvents or catalysts in organic synthesis and separation. Some ILs have been reported to be able to dissolve or absorb acidic gasses such as CO₂^{1–9} and SO₂.^{9,10} This makes ILs promising materials for CO₂ and SO₂ separation in gasses emission from fossil-fuel combustion. However, direct applications of ILs to gas absorption may suffer from their high viscosity and relatively small gas–liquid interface. Compared to ILs, polymerized ILs^{11–14} and immobilized ILs,^{15–17} as solid particles or powders, possess large specific surfaces and thus exhibit higher sorption capacities and faster sorption rates. From an industrial viewpoint, these IL-derived solid sorbents are more attractive in applications.

In our previous studies,^{11,12,15} we reported the synthesis and SO₂ sorption properties of linear

poly(1,1,3,3-tetramethylguanidium acrylate) (PTMGA) powder and crosslinked poly(1,1,3,3-tetramethylguanidium acrylate-*co*-*N,N'*-methylene bisacrylamide) P(TMGA-*co*-MBA) particles. These polymers have good SO₂ sorption capacity and high sorption rate, and can be reused in many cycles. Compared to PTMGA, the crosslinked P(TMGA-*co*-MBA) gives acceptable mechanical stability attributed to its crosslinked structure and is, therefore, more practical SO₂ sorbent. However, our previous study showed that the stability has been an issue in the inverse suspension polymerization of TMGA and MBA. The particles were prone to coagulate and foul the agitator and reactor wall under certain conditions, and only small particles (10² μm) were obtained.¹¹ For application in a filled bed for gas separation, adsorbent particles with high porosity and large size are more desired. So, in this article, we report on the effects of reaction conditions on the polymerization stability and the particle size in this system. P(TMGA-*co*-MBA) particles with various sizes were successfully prepared under optimized conditions.

Correspondence to: L. Wu (wulinbo@zju.edu.cn).

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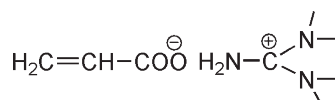
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EXPERIMENTAL PART

Materials

Acrylic acid (AA, C.P., Sinopharm Chemical Reagent, China) was distilled under vacuum at about 35°C prior to use. 1,1,3,3-Tetramethylguanidine (TMG) (≥99.2%, Zibo Senjie Chemical Auxiliary,



Scheme 1 Chemical structure of TMGA.

China), *N,N'*-methylenebisacrylamide (MBA, J&K Chemical, China), cyclohexane, Span60 (trade name of sorbitan monostearate), and ammonium persulfate (APS) were used as received. 1,1,3,3-Tetramethylguanidine acrylate (TMGA) (see Scheme 1) was synthesized via direct neutralization of TMG and AA as previously described.¹¹

Inverse suspension copolymerization of TMGA and MBA

Inverse suspension copolymerization of TMGA and MBA was carried out using cyclohexane as oil phase, Span60 as dispersant, and APS as initiator. In brief, cyclohexane and Span60 were added to a four-neck flask (500 mL), heated to 65°C, and stirred (with E350 PTEF blade paddle, ϕ 70 mm) under N₂ for half an hour. An aqueous solution of TMGA, MBA, and APS was then added in 10 min through a dropping funnel. An inverse suspension mixture was formed and the polymerization was run under stirring for 6 h. At the end of the reaction, the stirring was stopped and the supernatant solvent was removed. The polymer particles were collected and then vacuum-dried at 80°C until constant weight. The dry particles of P(TMGA-co-MBA) were stored in a desiccator. The detailed polymerization conditions are discussed in the section of Results and Discussion.

Characterization

The pictures of the particles were taken by a digital camera. Hundred to three hundred particles (more

particles for smaller particle size) were randomly selected and treated with AutoCAD 2004 to estimate the particle size distribution (PSD). The measurement of d_n and d_v/d_n showed good reproducibility, with relative errors <5%.

RESULTS AND DISCUSSION

In the inverse suspension copolymerization of TMGA and MBA, cyclohexane made up a continuous phase (oil phase) and the aqueous solution of TMGA and MBA constituted a dispersed phase (aqueous droplets) that was stabilized by a surfactant, Span60. In a previous study,¹¹ we found that it was difficult to achieve stable polymerization. The polymerization stability strongly depended on the reaction conditions. In general, inverse suspension polymerization is a thermodynamically unstable system in nature, but the droplets or particles can be dynamically stabilized, depending on the balances between stirring shear and interfacial tension.¹⁸ Therefore, the effects of stirring speed and surfactant concentration on the stability and particle size were investigated in this study.

The effects of stirring speed on the stability, number-average particle size (d_n), ratio of volume-average particle size (d_v) to d_n , and particle size distribution (PSD) are shown in Table I and Figure 1. The polymerization system was not stable and was agglomerated to form irregular agglomerates at <200 rpm. However, the stability was enhanced and the particles of millimeter diameters (0.5–3 mm) were successfully prepared at 235–270 rpm. The average particle size was strongly reduced as the stirring speed increased. The PSD was relatively narrow and almost constant (d_v/d_n : 1.2–1.3) at 235–270 rpm. Fine powdery particles with average particle size of about 100 μ m and much broader PSD (d_v/d_n : 3.2) were obtained at 300 rpm, which is very typical of inverse suspension polymerization. At higher speed,

TABLE I
Effect of Stirring Speed on Inverse Suspension Copolymerization of TMGA and MBA^a

Run	M_a^b (%)	N (rpm)	Span60 ^c (%)	MBA ^c (%)	APS ^c (%)	T (°C)	Stability	d_n (mm)	d_v/d_n^d
1	60	200	0.25	2	0.15	65	Agglomerate	–	–
2	60	235	0.25	2	0.15	65	Stable	2.7	1.2
3	60	250	0.25	2	0.15	65	Stable	2.2	1.2
4	60	270	0.25	2	0.15	65	Stable	0.46	1.3
5	60	300	0.25	2	0.15	65	Stable	0.10	3.2

^a The O/W ratio was 4/1 (v/v), and the polymerization time was 6 h.

^b The weight percent of monomer mixture (TMGA and MBA) in the aqueous phase.

^c The weight percent based on the monomer mixture.

^d The d_v and d_n are the volume and number-average particle size, respectively, before vacuum drying.

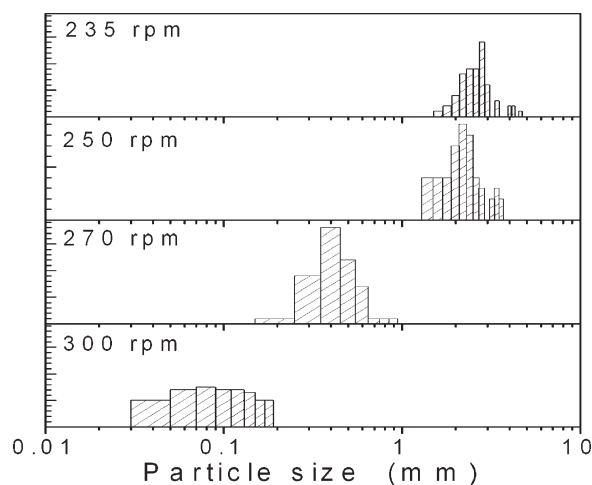


Figure 1 Number distribution of P(TMGA-co-MBA)s particles prepared at various stirring speeds (235–300 rpm, other conditions are shown in Table I).

the polymerization kept stable but the effect of stirring speed on particle size decreased.

The effect of surfactant concentration is shown in Table II and Figure 2. At a given stirring speed of 250 rpm, the polymerization was unstable when the Span60 amount was lower than 0.1 wt % based on

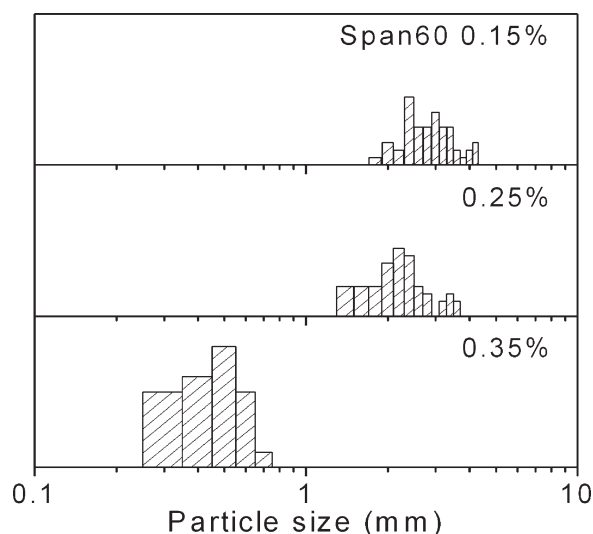


Figure 2 Number distribution of P(TMGA-co-MBA)s particles prepared at various surfactant concentrations (Span60 0.15–0.35 wt %, other conditions are shown in Table II).

the monomer mixture (Run 6). As the amount increased from 0.15 to 0.35%, the particles became stabilized, the particle size decreased from 2.9 mm to 0.5 mm, but the particle size distribution (PSD)

TABLE II
Effect of Surfactant Concentration on Copolymerization of TMGA and MBA^a

Run	M_a^b (%)	N (rpm)	Span60 ^c (%)	MBA ^c (%)	APS ^c (%)	T (°C)	Stability	d_n^d (mm)	d_v/d_n^d
6	60	250	0.10	2	0.15	65	Agglomerate	–	–
7	60	250	0.15	2	0.15	65	Stable	2.9	1.1
3	60	250	0.25	2	0.15	65	Stable	2.2	1.2
8	60	250	0.35	2	0.15	65	Stable	0.46	1.4
9	60	250	0.50	2	0.15	65	Stable	Powdery	–

^a The O/W ratio was 4/1 (v/v), and the polymerization time was 6 h.

^b The weight percent of monomer mixture (TMGA and MBA) in the aqueous phase.

^c The weight percent based on the monomer mixture.

^d The d_v and d_n are the volume and number-average particle size, respectively, before vacuum drying.

TABLE III
Effect of Temperature on Copolymerization of TMGA and MBA^a

Run	M_a^b (%)	N (rpm)	Span60 ^c (%)	MBA ^c (%)	APS ^c (%)	T (°C)	Stability	d_n (mm)	d_v/d_n^d
10	60	250	0.25	2	0.15	70	Wall adhesion	–	–
11	60	250	0.25	2	0.15	65	Stable	2.2	1.2
12	60	250	0.25	2	0.15	60	Stable	2.3	1.3
13	60	250	0.25	2	0.15	55	Stable	2.2	1.3
14	60	250	0.25	2	0.15	50	Incomplete polymn.	–	–

^a The O/W ratio was 4/1 (v/v), and the polymerization time was 6 h.

^b The weight percent of monomer mixture (TMGA and MBA) in the aqueous phase.

^c The weight percent based on the monomer mixture.

^d The d_v and d_n are the volume and number-average particle size, respectively, measured before vacuum drying.

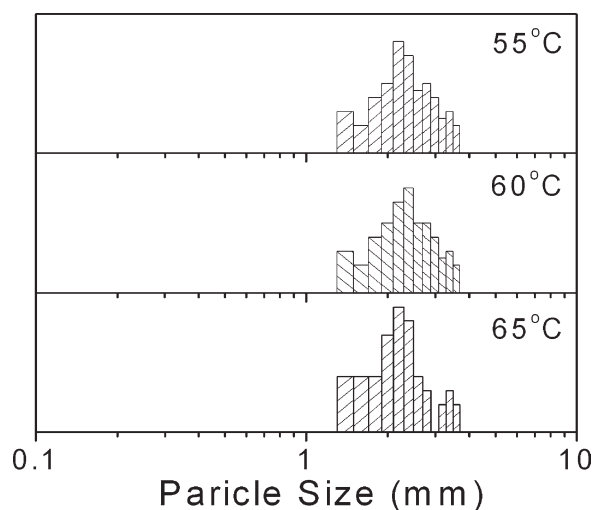


Figure 3 Number distribution of P(TMGA-co-MBA)s particles prepared at various temperatures (other conditions are shown in Table III).

was broad. When more Span60 was used, powdery particles in micrometer diameter were obtained.

The surfactant, Span60, is often used in W/O suspension system. It enriches at the W/O interface and decreases the interfacial tension. The balance between the interfacial tension and shear force determines the polymerization stability and particle size. Therefore, an adequate level of Span60 was essential to cover the surface of the aqueous droplets and to ensure the polymerization stability. Increasing Span60 amount decreased the particle size at a given stirring speed. Similar results are also reported for the inverse suspension polymerization of sodium acrylate¹⁹ and acrylic acid and acrylamide.^{20,21} At a slow stirring speed, the shear force was too weak to balance the interfacial tension so that the particles were prone to agglomerate and lost their stability. At a higher stirring speed, the shear force became adequate to balance the interfacial tension and as a result, the particles were dynamically stabilized. The higher stirring speed led to smaller particle with broader PSD.

The reaction temperature also had a significant influence on the polymerization stability. At the given conditions shown in Table III, the crosslinking copolymerization was successfully carried out only at a narrow temperature window of 55–65°C. The temperature has no clear effect on particle size and PSD in this range. When the temperature was lower than 55°C, viscous polymers were produced, suggesting an incomplete crosslinking, possibly due to a low reactivity of the crosslinkable comonomer MBA. When the temperature was over 70°C, polymer was rapidly formed, but readily adhered to the reactor wall before it was stabilized as well-dispersed particles. The poor stability at high temperature may be resulted from the low glass transition temperature of the water-swelled particles. The stable temperature region may be changed or extended by changing the concentrations of the initiator and comonomer (Fig. 3).

In addition, adequate amounts of initiator APS and comonomer MBA seemed necessary to ensure the successful crosslinking copolymerization. At <0.15% APS, the polymerization was too slow to produce stable particles. When another initiator, potassium persulfate, was used, the stability was poorer. At <2% MBA, the polymer was not fully crosslinked so that the particles were not stable and prone to wall adhesion. When the amount of APS was >0.15% and that of MBA >2%, the polymerization system was stable, and these amounts had no much effect on the particle size, as shown in Tables IV and V.

On the basis of the above study, it can be seen that all the reaction conditions examined have significant effects on the polymerization stability and that the particle size was mainly determined by the stirring speed and the concentration of the surfactant. Crosslinked P(TMGA-co-MBA) particles with particle sizes from 100 μm to 3 mm can be successfully synthesized under certain conditions. The gelatinous particles thus prepared are transparent or semitransparent. When they were vacuum-dried at 80°C for

TABLE IV
Effect of Initiator Concentration on Copolymerization of TMGA and MBA^a

Run	M_a^b (%)	N (rpm)	Span60 ^c (%)	MBA ^c (%)	APS ^c (%)	T (°C)	Stability	d_n (mm)	d_w/d_n^d
15	60	250	0.25	2	0.05	65	Incomplete polymn.	–	–
16	60	250	0.25	2	0.15	65	Stable	2.2	1.2
17	60	250	0.25	2	0.25	65	Stable	2.1	1.3

^a The O/W ratio was 4/1 (v/v), and the polymerization time was 6 h.

^b The weight percent of monomer mixture (TMGA and MBA) in the aqueous phase.

^c The weight percent based on the monomer mixture.

^d The d_v and d_n are the volume and number-average particle size, respectively, measured before vacuum drying.

TABLE V
Effect of Crosslinker Concentration on Copolymerization of TMGA and MBA^a

Run	M_a^b (%)	N (rpm)	Span60 ^c (%)	MBA ^c (%)	APS ^c (%)	T (°C)	Stability	d_n (mm)	d_w/d_n^d
18	60	250	0.25	1	0.15	65	Wall adhesion	–	–
19	60	250	0.25	2	0.15	65	Stable	2.2	1.2
20	60	250	0.25	4	0.15	65	Stable	2.0	1.4

^a The O/W ratio was 4/1 (v/v), and the polymerization time was 6 h.

^b The weight percent of monomer mixture (TMGA and MBA) in the aqueous phase.

^c The weight percent based on the monomer mixture.

^d The d_w and d_n are the volume and number-average particle size, respectively, measured before vacuum drying.

about 12 h, opaque porous particles were obtained and could be used in SO_2 sorption.¹¹

CONCLUSION

The inverse suspension copolymerization of TMGA and MBA was carried out using cyclohexane as solvent, Span60 as dispersant, and APS as initiator. It was found that the polymerization stability was very sensitive to reaction conditions. Sufficient stirring speed, adequate levels of dispersant, initiator and crosslinker concentrations, and proper temperature range are essential for good polymerization stability. The particle size reduced with increased stirring speed and dispersant concentration, but appeared to be independent of temperature and the initiator and crosslinker concentrations. Crosslinked poly(TMGA-co-MBA) particles with average particle sizes from 100 μm to 3 mm were successfully synthesized in stable and repeatable manner.

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