

Thermally Robust Highly Crosslinked Poly(methyl methacrylate-co-divinyl benzene) Microspheres by Precipitation Polymerization

Sang Eun Shim, Sunhye Yang, Hyejeon Jung, and Soonja Choe*

Department of Chemical Engineering, Inha University, 253 Yonghyun, Namgu, Incheon 402-751, Korea

Received March 3, 2004; Revised March 30, 2004

Abstract: We prepared thermally robust fully crosslinked poly(methyl methacrylate-co-divinyl benzene) [poly(MMA-co-DVB)] microspheres successfully by precipitation polymerization in the absence of a stabilizing agent. The DVB concentration plays a pivotal role not only in the formation of the individually stable microspheres but also in the polymerization characteristics, including the particle size, the uniformity of size, the polymerization yield, and the thermal properties. The number-average diameter of the microspheres increased linearly, from 0.72 to 2.15 μm , and the particle size distribution became narrower, by elevating the uniformity from 1.35 to 1.12, as the DVB concentration increased from 20 to 75 mol%. In addition, the yield of the polymerization increased, from 73.4 to 98.6%, as the DVB concentration increased. Since the prepared particles possess fully crosslinked microstructures, no glass transition temperatures were observed, but all the samples prepared with DVB concentrations ranging from 20 to 75 mol% possess enhanced thermal properties. Based on the DSC and TGA data, the thermal stability of the microspheres prepared by the precipitation polymerization is significantly improved as a result of crosslinking with DVB.

Keywords: microspheres, poly(MMA-co-DVB), precipitation polymerization, thermal properties.

Introduction

Polymer colloids have been extensively used in vast traditional areas including coatings, adhesives, inks, leather finishing, and construction and so on.¹ Nowadays, such polymer particles have broadened their applications to more advanced fields such as information technology, electric and electronic science, and biotechnology including biochemicals and biomedical.²⁻⁶ In accord with the explosive expansion of their applications, precise control of the properties of the polymer colloids has become more important. Their size, uniformity of size, functionality of the base polymer, morphology of the polymer beads, and the degree of crosslinking are the main concerns in controlling properties.

Fully crosslinked micron-sized spherical polymer particles have received much attention since they possess unique applications due to their superior strength, thermal and solvent resistance, and anti-slip properties.⁷ Such polymer microspheres are used in high-end products such as packing materials in column chromatography or spacers in liquid crystal display. Since the synthesis of such microspheres is not easy, its production cost is quite high. Therefore, extensive research on the development of an inexpensive process to prepare fully

crosslinked polymer microspheres is always in interest.

Two-step swelling method has been firstly introduced by Ugelstad, in which relatively small seed polymer particles are prepared by either emulsion or dispersion polymerization. Then these are used for swelling process and a subsequent polymerization of monomer-swollen seed particles.⁸⁻¹¹ Obviously, a long and complicated procedure is a drawback of the swelling process. Shirasu porous glass (SPG) membrane emulsification with a subsequent polymerization, which is a modified suspension polymerization technique, can also produce crosslinked polymer microspheres in the range of 1 -60 μm in a single step with an additional emulsification apparatus.^{12,13} In addition, dispersion polymerization method produces stable micron-sized spherical particles ranging from 1 to 10 μm in organic media.¹⁴ However, high degree of crosslinking is not achieved in the dispersion polymerization since the concentration of crosslinking agent is generally limited below 0.5 wt% based on main monomer. The addition of high amount of crosslinking agent (more than 0.5 wt%) in dispersion polymerization introduces a coarse surface of the final polymer particles or even popcorn-shaped particles.¹⁵⁻¹⁷

Most recently, the precipitation polymerization of crosslinkable monomer has been found that fully crosslinked microspheres can be prepared even without any stabilizers in the polymerization system.¹⁸ Several monomers includ-

*e-mail: sjchoe@inha.ac.kr

1598-5032/04/233-07 © 2004 Polymer Society of Korea

ing methacrylate,¹⁹ maleic anhydride,²⁰ and chloromethyl styrene²¹ have been copolymerized to form microspheres with DVB as the crosslinkable monomer using the precipitation polymerization. The precipitation polymerization is quite similar to dispersion polymerization beside the absence of steric stabilizer. The formation of individually stable microsphere is achieved with crosslinkable monomer by high degree of crosslinking in the precipitation polymerization.

In our previous study, polystyrene microspheres containing various concentrations of DVB from 5 to 75 mol% were synthesized by the precipitation polymerization and their unexpectedly superior thermal properties to those of polystyrene prepared by emulsion and suspension polymerization were found due to fully crosslinked microstructure.²² In this article, poly(MMA-*co*-DVB) microspheres with various concentrations of DVB are prepared by the precipitation polymerization and the characteristics and thermal properties of the microspheres are investigated.

Experimental

Materials. Methyl methacrylate (MMA; Samchun Chemicals, Korea) and divinylbenzene (DVB; 55% mixture of isomers, Aldrich Chemical Co., USA) were purified using an inhibitor removal column (Aldrich) and stored at -5°C prior to use. As an initiator, analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei Chemicals, Japan) was used without further purification. Acetonitrile (Junsei, Japan) as the polymerization medium was in analytical grade. For a comparison of the thermal properties of PMMA prepared by the dispersion polymerization, poly(*N*-vinyl pyrrolidone) (PVP; weight-average molecular weight = 40,000; Aldrich), was used as a steric stabilizer. In dispersion polymerization, ethanol and methanol (Samchun Chemicals) were used as a reaction medium and for the purification of the resulting microspheres, respectively.

Polymerization. The polymerization ingredients simply consist of medium, various compositions of MMA and DVB comonomer mixtures, and AIBN. The total amount of monomers was set at 2 vol% for the medium and 2 wt% of AIBN with respect to the total amount of the monomers was used. After charging 18 mL of polymerizing mixture in glass vial, nitrogen was purged for 15 min and then the vial was sealed. Polymerization was carried out in a shaking water bath with an agitation speed of 30 rpm at 70°C for 24 hrs. After completion of the polymerization, the resultant particles were obtained by centrifugation and washed with methanol, repeatedly.

Dispersion polymerization was carried out in a 50 mL capped vial with magnetic stirring under nitrogen atmosphere. 25 g of ethanol was first introduced and 10 wt% MMA (2.5 g) relative to the medium was charged in the vial. 12 wt% PVP (0.3 g) relative to MMA was used as a stabilizer. The amount of AIBN (0.025 g) was fixed at 1

wt% relative to the monomer and the dispersion polymerization was conducted at 70°C under nitrogen atmosphere for 24 hrs and the resultant was rinsed off with methanol repeatedly.

Characterization. Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to study the morphology of poly(MMA-*co*-DVB) particles. Number-average diameter (D_n) and uniformity (D_w/D_n , where D_w denotes weight-average diameter.) were achieved using Scion Image[®] Analyzer software by counting individual 100 particle from SEM microphotographs. The circularity of the microspheres as a function of the DVB concentration was measured by Flow Particle Image Analyzer, FPIA-2100[®] (Sysmex Co., Japan). The glass transition temperature of the beads (gel) and sol was measured using the differential scanning calorimeter (DSC; Perkin-Elmer DSC-7, USA). The thermal degradation of the crosslinked microspheres was studied using a thermogravimetric analyzer (TGA; Perkin-Elmer TGA-7, USA) under atmospheric environment. The yield of the polymerization was determined gravimetrically.

Results and Discussion

Synthesis of Fully Crosslinked Poly(MMA-*co*-DVB). Figure 1(a)-(e) show the SEM microphotographs of poly(MMA-*co*-DVB) particles prepared by the precipitation polymerization in neat acetonitrile with 2 wt% AIBN at 70°C for 24 hrs, where a monomer composition consists of increasing amount of DVB from 10 to 75 mol% relative to MMA. It is noted that the formation of the particles is not obtained in the absence of DVB in the precipitation polymerization of MMA. After the 24 hrs of the polymerization period, the final resultant remains in transparent solution since no particles are generated. At 10 mol% of DVB as seen in Figure 1(a), only coagulum is achieved due to the lack of DVB. The final resultant is jelly-like cream instead of particle-suspended solution. However, the coagulum was not soluble in THF for a molecular weight analysis. Above 20 mol% of DVB relative to MMA, individually stable spherical microspheres are obtained without discernable coagulation. In our previous study of precipitation copolymerization of styrene and DVB, the microspheres were achieved from 5 mol% of DVB relative to styrene.²² This would be related to the difference in chemical affinity of DVB with styrene and MMA since DVB has a quite similar structure to that of styrene.

Table I represents the circularity of the microspheres as a function of the DVB concentration measured by FPIA-2100[®]. The circularity of the particles²² is defined as the ratio between the circumference of circle of the equivalent area to the particle and the perimeter of the particle itself as follows:

$$\text{Circularity} = \frac{\text{Circle circumference}}{\text{Perimeter of projected particle image}} \quad (1)$$

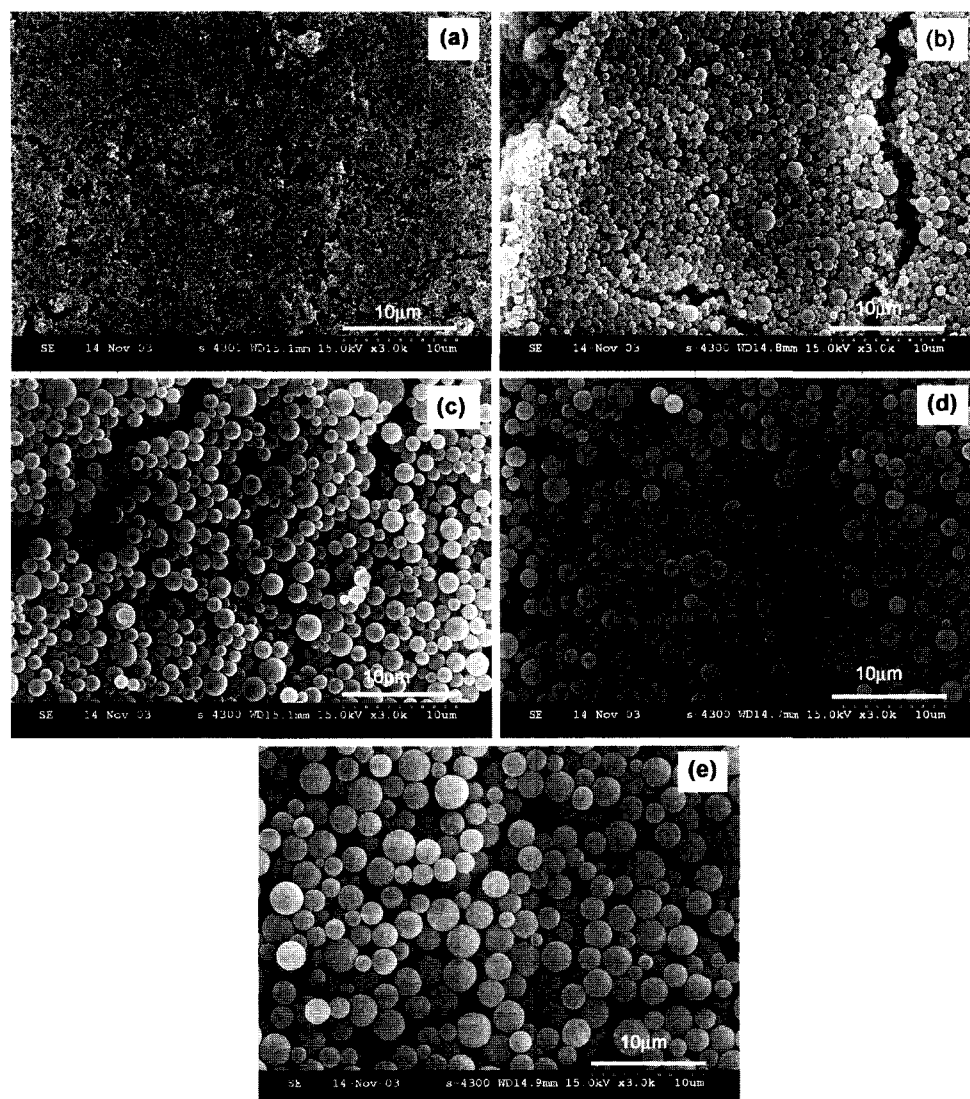


Figure 1. SEM micrographs of poly(MMA-co-DVB) particles prepared with varying concentrations of DVB in acetonitrile at 70°C. (a) 10 mol%, (b) 20 mol%, (c) 40 mol%, (d) 50 mol%, and (e) 75 mol%.

Table I. Circularity of the Poly(MMA-co-DVB) Microspheres Prepared by Precipitation Polymerization with Varying Concentration of DVB in Neat Acetonitrile at 70°C

DVB mol%	Circularity	Particle Shape
10	N/A	Coagulum
20	0.993	Spherical
40	0.991	Spherical
50	0.993	Spherical
75	0.995	Spherical

The circularity is a measure to specify the shape of particles; the more spherical particle, the closer its circularity to unity, and the more elongated particle, the lower its circularity is

observed. As seen in Table I, the circularity values in the range of DVB concentration of 20–75 mol% are close to unity. This means that the poly(MMA-co-DVB) microspheres in this range of DVB concentration are individually stable as a spherical shape without a formation of doublets or multiplets. This observation confirms the SEM micrographs as seen in Figure 1.

The particle size and its uniformity of the microspheres are depicted in Figure 2. At 20 mol% of DVB, the poly(MMA-co-DVB) microspheres have the number-average diameter of 0.72 μm and the uniformity of 1.35. As the DVB concentration increases up to 75 mol%, the particle size linearly increases to 2.15 μm , whereas the particle size distribution becomes narrower by decreasing the uniformity of 1.12. Although the dispersion polymerization is quite

similar to the precipitation polymerization except the existence of stabilizer in the polymerization system, the effect of a crosslinking agent on the particle size and uniformity can not be studied since the concentration of a crosslinking agent above 5 mol% relative to a main monomer causes a significant coagulation or deterioration of the final particle shape.¹⁵⁻¹⁷

Figure 3 represents the effect of DVB on the yield of the polymerization. The use of "yield" term is more reasonable

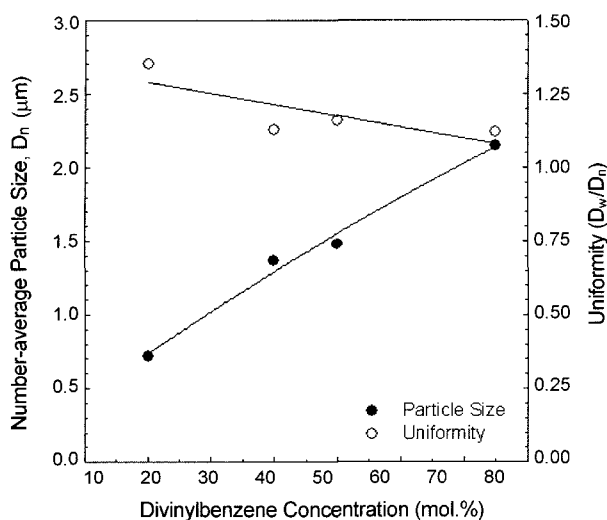


Figure 2. Number-average particle diameter and its uniformity of the poly(MMA-*co*-DVB) microspheres prepared with varying concentrations of DVB in acetonitrile at 70°C.

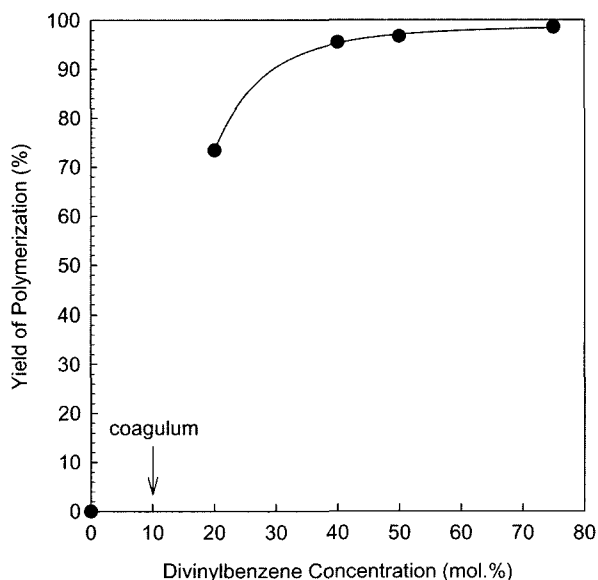


Figure 3. Yield of the precipitation copolymerization of MMA and DVB upon varying concentrations of DVB in acetonitrile at 70°C. Yield indicates the percent of the resultant obtained as microspheres.

than "conversion" because the monomer is converted to polymer during the precipitation polymerization and the polymerized substances are classified into two different species; gel and sol. Although polymeric molecules are formed in the precipitation polymerization, significant portion of the polymer having a low degree of crosslinking is dissolved in the medium as sol. Only insoluble portion of the polymer due to high degree of crosslinking is precipitated into the spherical particles to be obtained as gel form. Therefore, the term of "yield" means the portion of the monomer converted to spherical particles.

Interestingly, neither coagulated resultants nor microspheres are obtained in the absence of DVB. Therefore, the polymerization system remains transparent after completion of the polymerization for 24 hrs. The presence of crosslinkable monomer such as DVB is an essential feature in the precipitation polymerization. The formation of stable spherical particles by precipitation polymerization is strongly dependent on the degree of crosslinking of the particles.

As shown in Figure 1(a), a porous resin-like coagulum instead of particles is achieved due to insufficient stability arisen from the low concentration of DVB at 10 mol%, thus the yield of the polymerization falls zero. The yield of the polymerization is therefore meaningful above 20 mol% of DVB: it increases from 73.4% for 20 mol% DVB to 98.6% for 75 mol% DVB. For the system with 20 mol% DVB, the rest of 26.6% is still dissolved in acetonitrile in a sol portion. The dependence of the yield on the DVB concentration may be explained in terms of the reactivity ratios²⁸ of MMA and DVB as listed in Table II. The DVB used in this study consists of 55% (*meta* + *para*) isomers and the remnant is mainly ethylvinylbenzene. It is seen that the *m*-DVB has the similar reactivity ratios as MMA, but the *p*-DVB has a 7.7 times higher reactivity ratio of r_2 than r_1 . This indicates that DVB is depleted much faster than MMA during the copolymerization. When the concentration of DVB is low, the formation of particles is suppressed since small amount of DVB is much quickly consumed than MMA. Therefore, the polymerized resultant exists completely in sol in the case of 0 mol% of DVB and only 73.4% of yield is achieved with 20 mol% DVB.

Thermal Properties of Poly(MMA-*co*-DVB) Microspheres. Figure 4 shows the DSC thermograms of poly(MMA-*co*-DVB) prepared by the precipitation polymerization with varying concentration of DVB. The thermogram for the PMMA with 10 mol% DVB represents the coagulum. It was initially expected that the glass transition temperature

Table II. Reactivity Ratios in Copolymerization of MMA (1) and DVB (2)²⁸

Monomer (2)	r_1	r_2
<i>m</i> -divinylbenzene	0.43	0.62
<i>p</i> -divinylbenzene	0.11	0.85

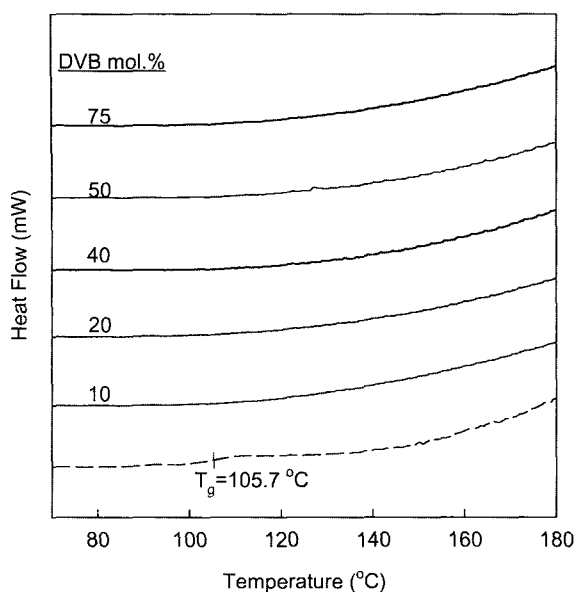


Figure 4. DSC thermograms of the poly(MMA-co-DVB) prepared with varying concentrations of DVB in acetonitrile at 70°C. Dashed line denotes the thermogram of neat PMMA prepared by dispersion polymerization in the absence of crosslinking agent.

would be observed at low concentration of DVB. Contrary to our expectation, the glass transition region was not observed for the all samples involved with DVB from 10 to 75 mol%. Disappearance of the glass transition temperature was reported to observe above 40 mol% of DVB with styrene in emulsion polymerization.²³ In Figure 4, the glass transition temperature of PMMA prepared by the dispersion polymerization in the absence of DVB is drawn in dashed line; the glass transition temperature is clearly observed at 105.7°C. No observation of the glass transition temperature would be sought from the different mechanism between the precipitation and dispersion polymerization. In the precipitation polymerization, only crosslinked intermediate species having higher molecular weight than the critical limit, i.e. insoluble in medium, precipitate into primary particles. Therefore, the formed particles possess a fully crosslinked microstructure which causes no glass transition temperature. In addition, it is noted that disappearance of the glass transition temperature was not caused by the low conversion of monomer since the higher yield above 70% was generally achieved as shown in Figure 3.

In Figure 5, the TGA thermograms of the poly(MMA-co-DVB) microspheres prepared with DVB concentrations are portrayed. As a reference, the TGA trace of the PMMA particles prepared in the absence of DVB by the dispersion polymerization shows higher weight loss, implying that the thermal degradation starts much earlier and that no residual char is formed due to the absence of crosslinks. In the TGA thermograms, three distinct degradation regions are observed

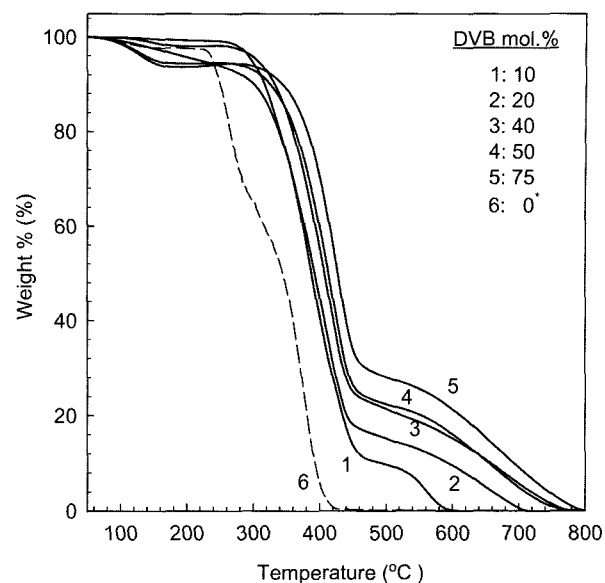


Figure 5. TGA thermograms of the poly(MMA-co-DVB) prepared with varying concentrations of DVB in acetonitrile at 70°C. *Dashed line denotes the thermogram of neat PMMA prepared by dispersion polymerization in the absence of DVB.

for the crosslinked microspheres. In the range of 100–300°C, 5–10% of weight loss was first observed. This is due to the degradation of relatively small molecular weight species. In the precipitation polymerization, it has been known that the spherical particle achieved at the end of the polymerization contains approximately 5–10% of sol.²¹ Thus the sol portion causes the initial thermal degradation at this temperature range. Next, the ordinary weight loss in the range of 300–450°C occurs due to a random chain scission as the second degradation, resulting the thermal properties of the poly(MMA-co-DVB) with DVB concentration is enhanced. Above 450°C, the similar trend was observed representing the less weight loss and increased amount of the residual char with DVB content.

Figure 6 depicts the degradation onset temperature and the amount of char at 500°C from the TGA thermogram curves in Figure 5. For the case of uncrosslinked PMMA microspheres prepared by the dispersion polymerization (open symbols in Figure 6), the thermal degradation onset temperature is 300.6°C and the amount of residual char at 500°C is only 0.22%. It is seen that both the thermal degradation temperature and residual char increase with DVB concentration. Up to date, a clear relationship between the thermal stability and the degree of crosslinking is not yet established. For example, the thermal stability was not increased for PMMA or PS (polystyrene) crosslinked with up to 40 mol% diacrylate relative to MMA or styrene.²⁴ The enhanced thermal stability of PMMA or PS was achieved using DVB as a crosslinker;²⁵ the aromatic character of DVB was rationalized to be responsible for the improved

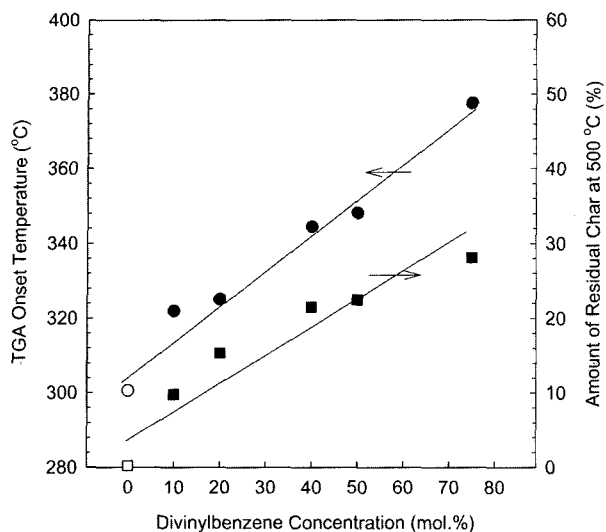


Figure 6. Thermal degradation onset temperature of the poly(MMA-*co*-DVB) prepared with varying concentrations of DVB in acetonitrile at 70 °C. Open symbols denote the data for the neat PMMA prepared by dispersion polymerization in the absence of crosslinking agent.

thermal stability.

In Figure 7, the mechanism²⁴ explaining the improvement of the thermal stability due to DVB is illustrated. The thermal degradation of PMMA is known to take place by an unzipping radical chain reaction without chain transfer to give monomer.^{26,27} The onset of the degradation for cross-linked poly(MMA-*co*-DVB) microspheres begins at the sol part consisting of neat PMMA or at a gel part having a low degree of crosslinking, producing a tertiary radical which is

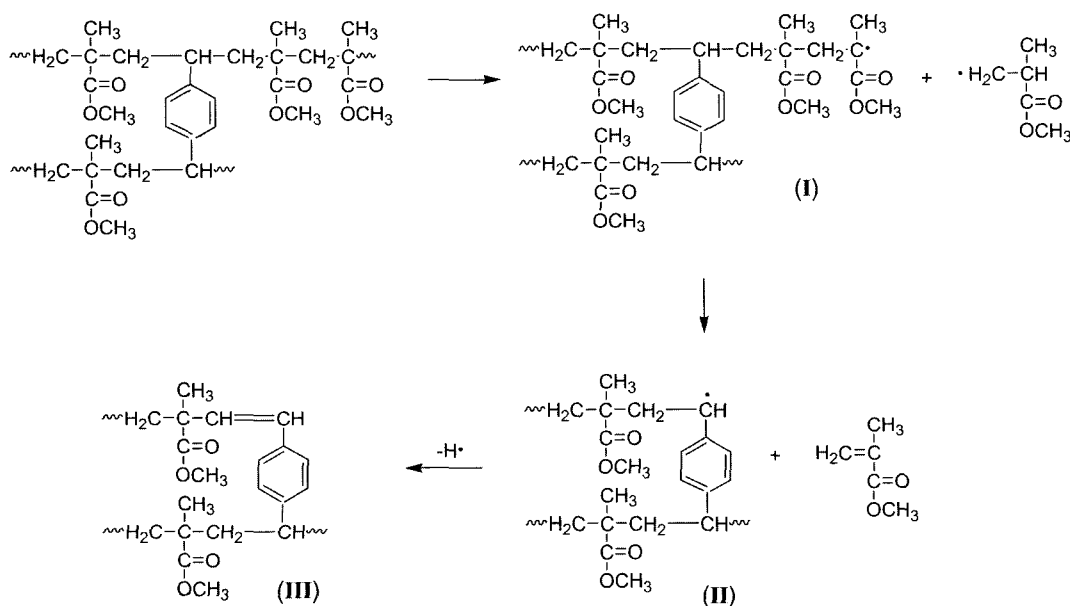


Figure 7. Thermal degradation mechanism for poly(MMA-*co*-DVB) copolymer.²⁴

capable of depropagation to form monomer. This step occurs in the relatively low temperature range of 100~300 °C. Once the crosslinked points are reached, the degradation is stopped since the benzene ring deactivates radical (II) and further stabilization is achieved by hydrogen abstraction from methylene groups. This step takes place in the temperature range of 300~450 °C. The new double bond (III) could participate in new crosslinking reactions at higher temperatures, increasing the fraction of non-volatile residue. This step occurs at the temperature above 450 °C. The formation of the char residue correspondingly increases with the DVB concentration as shown in Figure 6. Apparently, the residual char for the uncrosslinked PMMA microspheres prepared by the dispersion polymerization in the absence of DVB exists no longer, which supports the mechanism of the thermal degradation of the PMMA crosslinked with DVB. Therefore, the enhancement of the thermal stability is attributed by crosslinking of DVB.

Based on the DSC and TGA data, it is obviously seen that the thermal stability of the microspheres prepared by the precipitation polymerization is significantly improved.

Conclusions

The thermally robust crosslinked poly(MMA-*co*-DVB) microspheres, which are difficult to synthesize by other methods, are prepared by the precipitation polymerization in the absence of a stabilizing agent. It is found that the DVB concentration plays a pivotal role in the not only formation of individually stable microspheres but also polymerization characteristics including the final size, uniformity of the size, yield of the polymerization, and the thermal properties. The

stable microspheres without discernable coagulation are achieved above 20 mol% of DVB relative to MMA. In the absence of DVB, neither coagulum nor particle is obtained and the resultant remains a transparent solution. At 10 mol% of DVB, only jelly-like coagulum is achieved due to the lack of DVB. The circularity values in the DVB concentration ranging 20 to 75 mol% are close to unity, indicating the poly(MMA-co-DVB) microspheres are individually stable without coagulated doublets or multiplets. The number-average diameter of the microspheres linearly increases from 0.72 to 2.15 μm and the particle size distribution becomes narrower by decreasing the uniformity from 1.35 to 1.12 with the DVB concentration from 20 to 75 mol%. In addition, the yield of the polymerization increased from 73.4 to 98.6% with the DVB concentration as well. The dependence of the yield is ascribed to the much faster reactivity ratio of DVB than that of MMA. No glass transition temperatures and the enhancement of the thermal properties for the all poly(MMA-co-DVB) particles are observed and attributed by crosslinking of DVB. Based on the DSC and TGA data, it is obviously seen that the thermal stability of the microspheres prepared by the precipitation polymerization is significantly improved.

Acknowledgements. It is acknowledged that this work was supported by NRL (National Research Laboratory of Ministry of Science and Technology in Korea) project by a grant number of M10203000026-02J0000-01410 in the year of 2002-2007 and partially supported by Korea Research Foundation Grant number KRF-2001-041-E00500. The authors also appreciate Hongin Tech Co. Ltd., for their partial financial support.

References

- (1) D. Urban and K. Takamura, Eds., *Polymer Dispersions and Their Industrial Applications*, Wiley-VCH, Weinheim, 2002.
- (2) H. Fudouzi and Y. Xia, *Adv. Mater.*, **15**, 892 (2003).
- (3) J. Ugelstad, P. Stenstad, L. Kilaas, W. S. Prestvik, A. Rian, K. Nustad, R. Herje, and A. Berge, *Macromol. Symp.*, **101**, 491 (1996).
- (4) V. L. Covolani, L. H. I. Mei, and C. L. Rossi, *Polym. Adv. Technol.*, **8**, 44 (1997).
- (5) S. H. Im, O. O. Park, and M. H. Kwon, *Macromol. Res.*, **11**, 110 (2003).
- (6) G. Khang, S. A. Seo, H. S. Choi, J. M. Rhee, and H. B. Lee, *Macromol. Res.*, **10**, 246 (2002).
- (7) M. Hattori, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 2027 (1993).
- (8) J. Ugelstad, P. C. Mork, K. Herder Kaggerud, T. Ellingsen, and A. Berg, *Adv. Colloid Interf.*, **13**, 101 (1980).
- (9) J.-W. Kim and K.-D. Suh, *Macromol. Chem. Phys.*, **202**, 621 (2001).
- (10) M. Okubo and T. Nakagawa, *Colloid Polym. Sci.*, **270**, 853 (1992).
- (11) K. Ogino, H. Sato, K. Tsuchiya, H. Suzuki, and S. Moriguchi, *J. Chromatogr. A*, **699**, 59 (1995).
- (12) S. Omi, K. Katami, A. Yamamoto, and M. Iso, *J. Appl. Polym. Sci.*, **51**, 1 (1994).
- (13) S. Omi, *Colloids Surface A*, **109**, 97 (1996).
- (14) K. E. J. Barrett, Ed., *Dispersion Polymerization in Organic Media*, Wiley, London, 2002.
- (15) K. Li and H. D. H. Stöver, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 473 (1993).
- (16) M. Hattori, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, **50**, 2027 (1993).
- (17) J. Choi, S.-Y. Kwak, S. Kang, S.-S. Lee, M. Park, S. Lim, J. Kim, C. R. Choe, and S. I. Hong, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 4368 (2002).
- (18) K. Li and H. D. H. Stöver, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 3257 (1993).
- (19) W.-H. Li and H. D. H. Stöver, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2899 (1998).
- (20) R. S. Frank, J. S. Downey, and H. D. H. Stöver, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2223 (1998).
- (21) W.-H. Li and H. D. H. Stöver, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2295 (1998).
- (22) S. E. Shim, S. Yang, H. H. Choi, and S. Choe, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 835 (2004).
- (23) Y.-J. Cha, Dissertation. Synthesis of Crosslinked Polystyrene Beads and Characterization as a Filler in SBR Matrix, Department of Chemical Engineering, Inha University, Korea, 1995.
- (24) G. F. Levchik, K. Si, S. V. Levchik, G. Camino, and C. A. Wilkie, *Polym. Degrad. Stab.*, **63**, 395 (1999).
- (25) F. M. Uhl, G. F. Levchik, S. V. Levchik, C. Dick, J. J. Liggat, C. E. Snape, and C. A. Wilkie, *Polym. Degrad. Stab.*, **71**, 317 (2001).
- (26) A. Meisters, G. Moad, E. Rizzardo, and D. H. Solomon, *Polym. Bull.*, **20**, 499 (1988).
- (27) S. M. Lomankin, R. M. Aseeva, and G. E. Zaikov, *Polym. Degrad. Stab.*, **36**, 187 (1992).
- (28) D. F. Christopher and A. J. Rudin, *Macromol. Sci. Chem.*, **A16**, 1275 (1981).