

## Verification of Core/Shell Structure of Poly(glycidyl methacrylate-*co*-divinyl benzene) Microspheres

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**Abstract:** The core/shell type structure of the highly crosslinked poly(glycidylmethacrylate-*co*-divinylbenzene) microspheres prepared in the precipitation polymerization in acetonitrile was thoroughly verified by means of swelling, <sup>1</sup>H NMR, XPS, TEM and TGA measurements. In the XPS measurement, the higher the GMA content, the higher the oxygen content was observed, implying that the higher content of GMA is observed in the particle surface. The further verification of the core/shell structure of the poly(GMA-*co*-DVB) particles was carried out using <sup>1</sup>H NMR and TEM techniques, resulting in the poly(GMA-*co*-DVB) particles with the GMA rich-phase and DVB rich-phase. In overall, the poly(GMA-*co*-DVB) microspheres consist of a highly crosslinked DVB rich-phase in the core and slightly or non-crosslinked GMA rich-phase in the shell part due to the different reaction ratios between two monomers and self-crosslinking density of DVB.

**Keywords:** precipitation polymerization, poly(GMA-*co*-DVB), core/shell particle.

### Introduction

Recently, polymer microspheres that consist of both organic or inorganic cores and shells have attracted much interest. Generally, in the core/shell structures, the core controls the type and size of the polymeric particles, whereas the shell provides numerous applications through surface properties.

Poly(methyl methacrylate)/polystyrene (PMMA/PS) core/shell latex particles were prepared using the two-stage seeded growth-emulsion polymerizations.<sup>1</sup> Búcsi and Forcada<sup>2</sup> reported monodisperse core/shell particles prepared by a two-step emulsion polymerization using macromonomers in a batch reactor. Core/shell poly(styrene/sulfonated *n*-hydroxyethyl aniline) latex particles were prepared by chemical oxidative polymerization in emulsion polymerization.<sup>3</sup> Core/double shell microspheres consisting of polystyrene in the core and methacrylic acid/ethyl acrylate 1:1 statistical copolymer in the shell were prepared in alcoholic media by dispersion polymerization.<sup>4</sup>

Precipitation polymerization is a unique technique to prepare crosslinked monodisperse polymer particles without any added surfactant or stabilizer. Monodisperse crosslinked core-shell polymer microspheres were prepared by two-step precipitation polymerization in the absence of any stabilizer.<sup>5</sup> Divinylbenzene (DVB) was used for the core and several functional monomers including chloromethylstyrene,

monovinyl, or divinyl methacrylic monomers were incorporated into the shell in acetonitrile and toluene/acetonitrile mixtures as reaction media. Precipitation polymerization goes on through the effective precipitation of nucleated oligomers or particles onto the surface of primary particles due to the nonswellability of crosslinked primary particles.<sup>6,7</sup> Crosslinked polymer particles<sup>8</sup> in the range from 0.5 to 8  $\mu\text{m}$  were prepared by precipitation polymerization from a variety of monomer, such as alkyl methacrylates,<sup>9</sup> chloromethylstyrene,<sup>10</sup> maleic anhydride,<sup>11</sup> methacrylic acid and poly(ethylene glycol) methacrylate.<sup>6,10</sup>

Since glycidyl methacrylate (GMA) contains dual functionalities of methacrylate and epoxy group, polymers derived from GMA are attractive as a reactive starting material with various functional groups. Poly(GMA) spherical particles ranging in diameter from 0.5 to 4  $\mu\text{m}$  was synthesized in the presence of alcoholic media and stabilizers in the dispersion polymerization.<sup>12,13</sup> Both the particle size and size distribution reduced with increasing stabilizer concentration, and no evidence of crosslinking in poly(GMA) particles was observed due to the solvation in  $\text{CDCl}_3$ .<sup>12</sup> Monodisperse-sized poly(styrene-*co*-GMA) spherical particles were synthesized in the dispersion polymerization and the effects of various polymerization parameters on the particle size and distribution were systematically investigated.<sup>14</sup> The preparation of narrow- and mono-disperse crosslinked micron-sized core/shell polymer particles containing different functional groups such as methyl methacrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, methyl

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acrylate, acrylamide, acrylonitrile, styrene, and *p*-chloromethyl styrene, etc. in the shell layers were prepared by a two-stage precipitation polymerization. DVB was used for the core and was precipitation polymerized in acetonitrile without any stabilizer as the first-stage polymerization.<sup>15</sup>

Recently, we have reported the preparation of stable microspheres of poly(GMA-*co*-DVB) having various concentrations of DVB in acetonitrile in the precipitation polymerization.<sup>16</sup> The number-average diameter of the copolymer was linearly increased from 2.92 to 3.34  $\mu\text{m}$ , the uniformity improved from 1.09 to 1.02, the yield of the polymerization increased from 30.6 to 79.7%, and the particle size distribution became narrower with the DVB concentration, respectively. No observation of the glass transition temperature and higher thermal degradation temperature suggested that the poly(GMA-*co*-DVB) would be core-shell type structure.

In this article, the core/shell type structure of the crosslinked poly(GMA-*co*-DVB) microspheres composed of various concentrations of DVB from 25 to 100 mol% through the precipitation polymerization was verified by means of swelling test, <sup>1</sup>H-NMR, XPS, TEM and TGA measurements.

## Experimental

**Materials.** Monomer, glycidylmethacrylate (GMA; Aldrich Chemical Co., USA) and comonomer, divinylbenzene (55% divinylbenzene isomers, 45% ethylstyrene isomers, Aldrich Chemical Co., USA) as a crosslinking agent were purified using an inhibitor removal column (Aldrich, USA) and stored at -5 °C prior to use. Analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei, Japan) was used as an initiator without further purification. Acetonitrile (Aldrich Chemical Co., USA) in analytical grade was used as the polymerization medium. Solvents, tetrahydrofuran (THF) and CDCl<sub>3</sub>, were purchased from Aldrich Chemical Co., USA, and used as received for swelling test and NMR measurement, respectively.

**Polymerization.** The precipitation polymerization was carried out using glycidyl methacrylate (GMA) and DVB mixtures in the presence of AIBN in acetonitrile using a shaking water bath with an agitation speed of 20 rpm at 70 °C for 24 h. The total monomer content was set at 6 wt% of the medium and AIBN was 4 wt% relative to the monomer content. The DVB concentration increased from 25 to 100 mol% with respect to monomer. After charging 30 mL of the polymerizing mixtures in a scintillation vial, dry nitrogen was purged for 15 min and then sealed. After the completion of the polymerization, the resultant particles were obtained by centrifugation and repeatedly washed with methanol. The powders were then dried in vacuum oven at 80 °C for 48 h. For comparison, dispersion polymerization of GMA was carried out using 1 wt% of GMA relative to solvent, methanol, and 10 and 0.1 wt% of PVP and AIBN relative to monomer at 70 °C for 12 h, respectively. In the

precipitation polymerization, since the molecular weight of the product is not sufficiently small, which is necessary for the measurement of reactivity ratio, due to crosslinking, it was not possible to measure the reactivity ratio. Thus, the reactivity ratios measured in the free radical polymerization are referenced;  $r_{st}=0.26$ ,  $r_{DVB}=1.18$  for  $r_{st}$ =styrene,  $r_{DVB}$ =*p*-divinylbenzene<sup>17</sup> and  $r_{st}=0.48$ ,  $r_{GMA}=0.6$  for  $r_{st}$ =styrene,  $r_{GMA}$ =GMA,<sup>18</sup> respectively. From these two results, the reactivity ratios of GMA and DVB can be induced to  $r_{DVB}=2.18$ ,  $r_{GMA}=0.6$ . This means that DVB has a much higher reactivity than GMA. Therefore, poly(DVB-*co*-GMA) formed at initial stage of the polymerization contains more DVB units than GMA.

**Characterization.** The swelling experiment was carried out by immersing 1 wt% of the sample in 250 g of THF at 50 °C for 12 h. The particles were collected by centrifugation and repeatedly washed with water and methanol, followed by drying under a vacuum oven at ambient temperature.

A Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to investigate the morphology and size of the poly(GMA-*co*-DVB) particles. The coefficient of variation (CV) was achieved using Scion Image<sup>®</sup> Analyzer software by counting individual 100 particles from the SEM microphotographs.

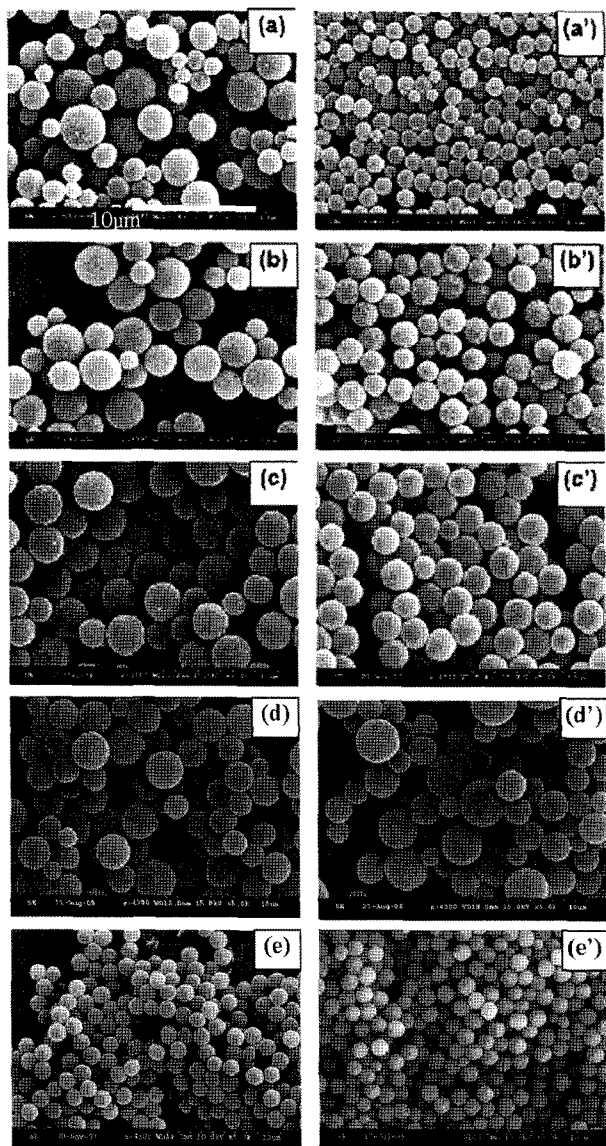
A Varian 400 MHz <sup>1</sup>H NMR using CDCl<sub>3</sub> containing TMS (tetramethylsilane) as the solvent was utilized to determine the structure of the GMA, DVB and the synthesized poly(GMA-*co*-DVB).

The surface analysis was carried out using an X-ray photoelectron spectroscope (XPS) in a VG MultiLab2000 MK Spectrometer with a Mg K $\alpha$  X-ray source (1253.6 eV) and an energy analyzer set at a constant retardation ratio of 20. The X-ray source was run at a power of 300 W (15 kV and 20 mA) and the chamber pressure was maintained lower than 10<sup>-9</sup> mbar.

The transmission electron microscopy (TEM) experiment was performed on a Hitachi-600 at an accelerating voltage of 100 kV. Thin sections were cut serially (50 nm) by ultra microtome (MTX, RMC) and mounted on 100 mesh grids.

## Results and Discussion

Figure 1 represents the scanning electron microscopy (SEM) photographs of the DVB content dependent poly(GMA-*co*-DVB) microspheres prepared by precipitation polymerization in acetonitrile with 4 wt% AIBN at 70 °C for 24 h. It is noticed that no precipitation polymerization of GMA was taking place for forming spheres.<sup>16</sup> As seen in Figure 1(a), 25 mol% of DVB is sufficient to form spherical particles due to the self-stabilization of crosslinking agent, DVB. In addition, a slightly increased diameter of spherical particles were obtained upon the increased DVB contents from 25 to 90 mol% in Figures 1(a)–(d), respectively. Then,



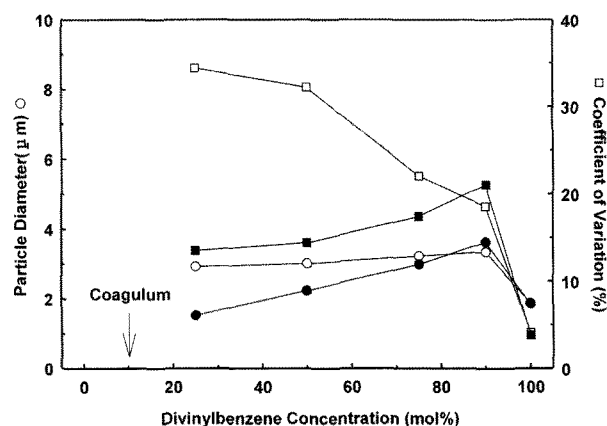
**Figure 1.** SEM photograph of the poly(GMA-*co*-DVB) particles prepared in acetonitrile at 70 °C for 24 h [(a)~(e)] and immersed in 50 °C THF for 12 h for swelling test [(a')~(e')]. DVB concentrations; (a) 25, (b) 50, (c) 75, (d) 90, and (e) 100 mol%.

the particle diameter abruptly decreased at 100 mol% of DVB in Figure 1(e). This indicates that the incorporation of DVB affects the enlargement of the poly(GMA-*co*-DVB) particles.

Since the reaction rate of DVB was much higher than that of GMA (reactivity ratio of GMA to DVB is  $r_{DVB}=2.18$ ,  $r_{GMA}=0.6$ , respectively), it is suggested that the copolymer form the core/shell type structure, where the core part would be DVB rich-phase and the shell part would consist of GMA rich phase.<sup>16</sup> Thus, we designed the following as the polymerization process; the core part would be highly crosslinked with DVB in the initial stage, the intermediate would be partially crosslinked between DVB and GMA,

and the shell part would be polymerized with GMA rich-phase in the final stage. In order to verify the core/shell structure of poly(GMA-*co*-DVB), the swelling test was carried out and the results were shown in Figures 1(a')~(e'). The SEM photographs in Figures 1(a)~(e) and Figures 1(a')~(e') are the representative samples before and after swelling test, respectively. The particle sizes with 25, 50, and 75 wt% of DVB between before and after swelling test reduced in a fairly monodisperse form as seen in Figures 1(a')~(c'), respectively. This behavior suggested that the reduced particle size would be the result of the dissolution of poly(GMA) mostly consisting of the shell part. If poly(GMA) is dissolved out from the core part, the particle surface would be partially sunken or pored. However, this was not occurred. On the other hand, a slight increase in the particle size is observed with 90 mol% of DVB as seen in Figure 1(d'), indication of swelling due to a slight crosslinking between GMA and DVB in the shell part. Whereas, no particle size difference of the 100 mol% poly(DVB) between before and after swelling test was observed in Figures 1(e) and 1(e'), respectively. Thus, the poly(GMA-*co*-DVB) microspheres are heterogeneously crosslinked due to the difference in the self-crosslinking density between DVB and GMA (actually, there is no self-crosslinking density in GMA). These results imply that the core part of poly(GMA-*co*-DVB) consists of heavily crosslinked DVB rich-phase and that of the shell part is formed with non- or slightly crosslinked GMA rich-phase depending on the compositions. Recently, core/shell polymer particles were prepared by two-stage precipitation polymerization containing poly(DVB) in a core part and different functional groups in the shell part.<sup>15</sup>

Figure 2 shows the analyzed data of the number-average particle size and coefficient of variation of poly(GMA-*co*-DVB) obtained before and after swelling test as seen in Fig-

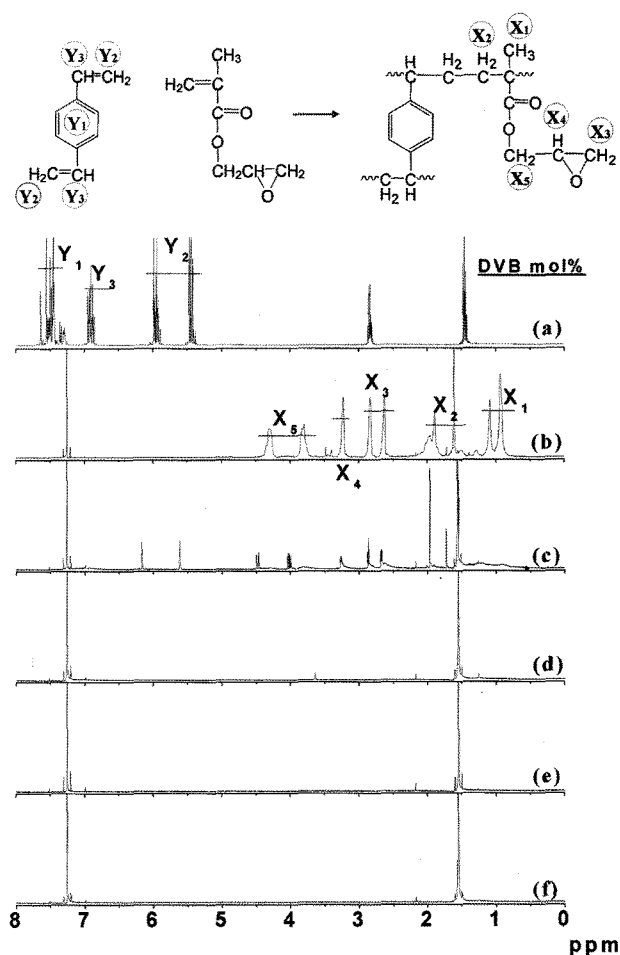


**Figure 2.** Number-average particle diameter and coefficient of variation of the poly(GMA-*co*-DVB) microspheres prepared in 50 °C THF for 12 h. The open symbol represents the results before swelling (circle represents the particle diameter and square means the coefficient of variation) and the solid symbol indicates the results after swelling test.

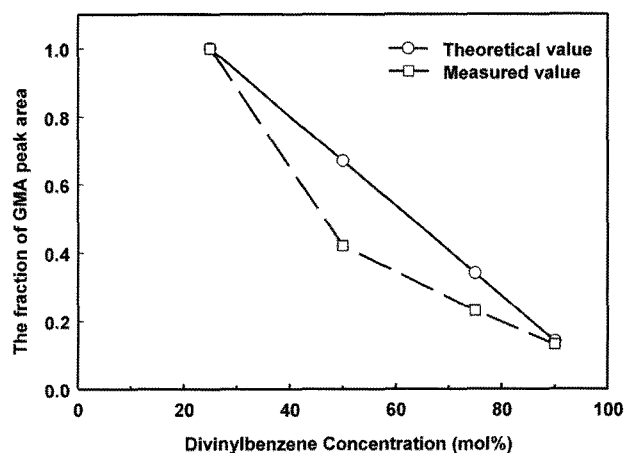
ures 1(a)–(e) and Figures 1(a')–(e'), respectively. The particle sizes of poly(GMA-*co*-DVB) with 25, 50, 75, 90, and 100 mol% DVB before swelling were 2.91, 2.98, 3.12, 3.29, and 1.97  $\mu\text{m}$ , respectively. After swelling, those varied to 1.62, 2.35, 2.98, 3.62, and 1.97  $\mu\text{m}$  as well. The difference in the particle size before and after swelling test varied depending on the composition of GMA; the higher the GMA content, the higher the swelling was observed during the polymerization and as a result, the higher reduction was obtained after swelling test. This indicates that the highly crosslinked poly(DVB) is tightly packed in the core, but that the non-crosslinked poly(GMA) is loosely packed with amorphous phase in the shell. In addition, the CV of the poly(GMA-*co*-DVB) particles is slightly improved after swelling. This is the evidence that the higher content of DVB makes highly crosslinked spheres in the core resulting in the less swollen particles upon dissolution. However, when 90 mol% DVB evolved, the spherical particles were swollen from 3.29 to 3.62  $\mu\text{m}$ , suggesting that 10 mol% GMA with 90 mol% DVB would be slightly crosslinked at the particle surface. On the other hand for pure poly(DVB), no variation in the particle size was obtained due to fairly high crosslinking between DVBS. For comparison, the swelling test of the pure poly(GMA) prepared in the dispersion polymerization was carried out, but the particles were completely dissolved in THF, indicating that GMA is not self crosslinkable material.

Since the decreased particle size of the copolymer was believed to occur upon dissolution of poly(GMA), the chemical component and content of the resultant solution of poly(GMA-*co*-DVB) in THF were verified using the  $^1\text{H}$  NMR spectroscopy. The chemical structures of poly(GMA) and DVB, and the peak assignment of each group are drawn in Figure 3. The peak assignments of DVB at the region of 6.5–8.0 ppm and two extra peaks at 5.5 and 6 ppm,<sup>19</sup> and those of GMA are given in Figures 3(a) and 3(b), respectively. In Figure 3(a) exhibits two peaks at 1.2 and 2.6 ppm, which originated from ethyl styrene because the divinylbenzene used in this study consists of ethyl styrene. In addition, the  $^1\text{H}$  NMR of the dissolution of poly(GMA-*co*-DVB) with various contents of GMA from 75 to 10 mol% is drawn in Figures 3(c)–(f), respectively. The peak area of the GMA characteristic peak decreased with the DVB content implying that the non-crosslinked GMA rich-phase in the particle surface of poly(GMA-*co*-DVB) was dissolved in THF.

The measured GMA peak area obtained from Figure 3 was normalized and plotted with the theoretical value in Figure 4. It is noticed that the theoretical data is entirely based on the monomer composition without any chemical reaction. The reference composition is 75:25 in poly(GMA-*co*-DVB), respectively. Under this condition, the measured GMA peak area is lower than that of the theoretical one for 50:50 and 25:75, but similar to 10:90 (GMA:DVB) of poly(GMA-*co*-DVB), respectively. As a consequence, the shell

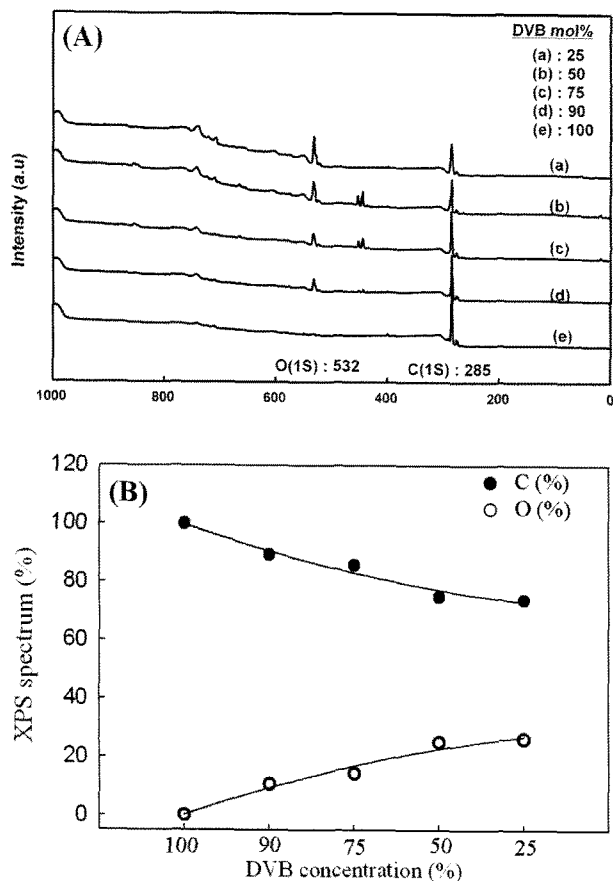


**Figure 3.**  $^1\text{H}$  NMR spectra of (a) poly(GMA), (b) DVB, and poly(GMA-*co*-DVB) in various DVB mol%; (c) 25, (d) 50, (e) 75, (f) 90 in the resultant solution after immersion in THF.



**Figure 4.** The fraction of GMA in the resultant solution of the poly(GMA-*co*-DVB) particles in THF; theoretical vs. measured value.

part comprised with GMA-rich phase (for more than 50 mol% GMA) is dissolved upon immersion in THF. This is

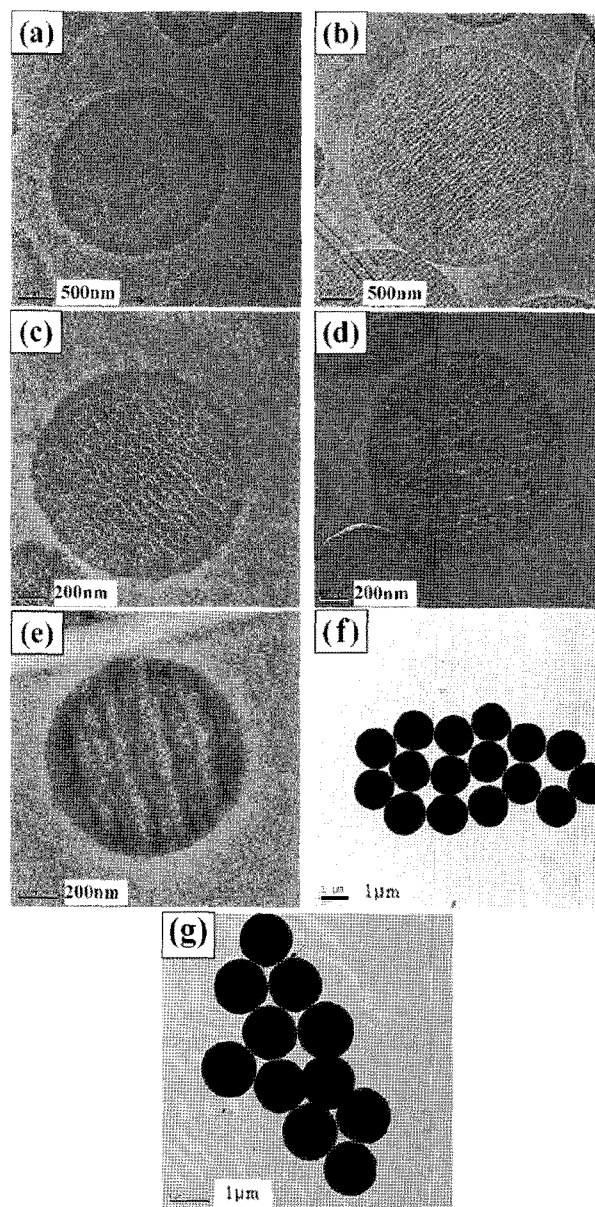


**Figure 5.** (A) XPS spectrum of the poly(GMA-*co*-DVB) prepared with various concentrations of DVB in acetonitrile at 70 °C. (a) 25, (b) 50, (c) 75, (d) 90, and (e) 100 mol% DVB. (B) The portion of carbon and oxygen as a function of DVB concentration.

due to the different crosslinking level upon different monomer ratios.

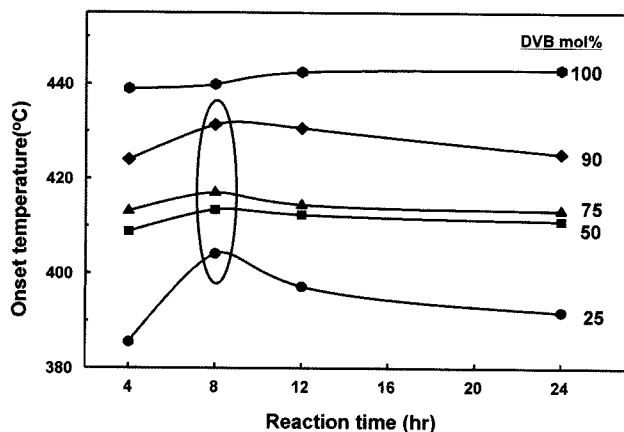
The further verification of the core/shell structure of poly(GMA-*co*-DVB) is carried out using the XPS spectrum as seen in Figure 5. Since GMA only consists of oxygen, the content ratio of C1s at 285 eV and O1s at 532 eV of binding energy for the surface (10 nm) of poly(GMA-*co*-DVB) is calculated and the result is the following. As the GMA content decreased from 75 to 10 mol%, the ratio of the carbon to oxygen varied to 71.9:28.1, 75.0:25.0, 85.7:14.3, and 89.2:10.6, respectively. This implies that the higher the GMA content, the higher the oxygen content was observed, which means that the surface of the poly(GMA-*co*-DVB) particle consists of GMA rich-phase.

Figure 6 represents the TEM photography of the poly(GMA-*co*-DVB) particles prepared at 70 °C for 24 h as a function of the DVB content. The microtomed face morphology of the particles shows different phenomenon depending on the different compositions of DVB. Since microtoming is carried out under same force and speed, the roughness of the cross section in the TEM image indicates the degree of



**Figure 6.** TEM photography of the microtomed poly(GMA-*co*-DVB) surface in various DVB concentrations in mol%; (a)25, (b)50, (c)75, (d)90, (e)100, and unmicrotomed particles of (f) 100 mol% GMA, and (g) 100 mol% DVB.

hardness or difficulty during microtoming. In Figure 6(a) with 75 mol% GMA and 25 mol% DVB, no particular difference between the DVB-core and GMA-shell is observed. However, in Figures between 6(b) and 6(d), the wave-like cross section in the core was observed indicating that the degree of hardness and roughness of the microtomed surface due to the relative density difference between the DVB rich-phase and GMA rich-phase. In addition, the higher the DVB content, the thinner the GMA rich-phase of the shell part was observed. Furthermore, in Figure 6(e), the phase morphology of poly(DVB) is completely different from the



**Figure 7.** The maximum TGA onset point of the poly(GMA-co-DVB) particles upon reaction time.

rest of the samples, indicating that the highly rough cross-section represents high crosslinked poly(DVB). This result strongly supports that the poly(GMA-co-DVB) particle consists of the DVB rich-phase in the core and GMA rich-phase in the shell part. For reference, TEM images of unmicrotomed particles of 100 mol% GMA and 100 mol% DVB are shown in Figures 6(f) and 6(g), respectively. The unmicrotomed photos are just black particles as usual.

The core/shell structure of the poly(GMA-co-DVB) particles was verified by the analysis of the TGA thermograms. The maximum TGA onset point of the thermal degradation temperature of poly(GMA-co-DVB) is plotted as a function of reaction time in Figure 7. For poly(GMA-co-DVB) particles with increased DVB contents from 25, 50, 75 to 90 mol%, the TGA onset temperature increased from 404, 412, 417 to 431 °C until the reaction time of 8 h, respectively. After then, the TGA onset temperature decreased and saturated. On the other hand for 100 mol% DVB, the TGA onset temperature increased from 438, 440 to 443 °C for the reaction time from 4, 8 to 12 h, respectively, and then saturated up to 24 h. For 100 mol% GMA, the TGA onset temperature varied from 183 to 205 °C during the reaction time between 4 and 12 h, respectively, and then leveled off. From the above results, the following can be suggested; (a) The increased maximum TGA onset point with the increased DVB content implies that the thermal stability improves due to the crosslinked DVB-rich phase in the core. (b) The increased maximum TGA onset point up to 8 h and then decreased phenomenon indicate that the core consists of the highly self-crosslinked DVB-rich phase and that the shell part consists of the slightly crosslinked DVB with GMA or poly (GMA). This may come from the different reactivity ratios between GMA and DVB.

## Conclusions

The crosslinked poly(GMA-co-DVB) microspheres com-

posed of various contents of DVB were synthesized in the precipitation polymerization and the core/shell structure of the particles was investigated using various techniques such as swelling test,  $^1\text{H}$  NMR, XPS, TEM and TGA measurements. The swelling test verified that the shell part of the GMA-rich phase dissolved upon immersing the particles in THF. The poly(GMA-co-DVB) microspheres were found to be heterogeneously crosslinked due to the different self-crosslinking density of DVB and reactivity ratios between GMA and DVB. In the XPS measurement the higher the GMA content, the higher the oxygen content was observed implying that the higher content of GMA is observed in the particle surface. The further verification of the core/shell structure of the poly(GMA-co-DVB) particles by NMR and TEM techniques showed that the poly(GMA-co-DVB) particles composed of the GMA rich-phase in the shell part and the DVB rich-phase in the core part. The maximum TGA onset point increased with the increased DVB content implying that the thermal stability of the particle improved due to the crosslinked DVB-rich phase in the core. The increase of the maximum TGA onset point up to 8 h of reaction time also suggested that core of the particle consist of the highly crosslinked DVB-rich phase and that shell part be slightly crosslinked DVB with GMA. In overall, the poly (GMA-co-DVB) microspheres consist of a highly crosslinked DVB rich-phase in the core and slightly or non-crosslinked GMA rich-phase in the shell part due to the different reaction rates between two monomers and self-crosslinking density of DVB.

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