

Stable Poly(Glycidyl Methacrylate-co-Ethylene Glycol Dimethacrylate) Microspheres via Precipitation Polymerization

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ABSTRACT: Narrow-dispersion or monodisperse with stable and smooth surface polymer microspheres were prepared without a significant coagulum by precipitation polymerization in the absence of any stabilizer. The monomer glycidyl methacrylate (GMA) was copolymerized with ethyleneglycol dimethacrylate (EGDMA) as crosslinker by precipitation polymerization technique with 2,2'-azobisisobutyronitrile as initiator in neat acetonitrile. The effects of the content of EGDMA on the polymerization character-

istics and size/uniformity of the microspheres were investigated. The onset of the thermal degradation temperature at higher temperature and the swelling test suggest that the prepared particles were highly crosslinked. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 963–968, 2010

Key words: precipitation polymerization; Poly(GMA-co-EGDMA); crosslinking; swelling; copolymerization

INTRODUCTION

The synthesis and application of polymeric microspheres have received increasing attention in many fields of scientific research as well as for industrial importance, because such polymer microspheres have been used in advanced fields such as information technology, electronics, and biotechnology.^{1–4} Fully crosslinked polymer microspheres have been receiving considerable attention because of their improved thermal, chemical, and physical properties. Control of polymer particle size and its uniformity, especially for particles in micron size has been the important research topic in the past years.^{5,6} However, synthesis of such polymer colloids microspheres is technically difficult in a way.

As we know, emulsion, suspension, and dispersion polymerization are usual methods for the preparation of polymer particles. However, the emulsion processes usually lead to monodisperse submicrometer particles, while the suspension polymerizations give micrometer range particles, but often with broad size distributions. Moreover, all the above mentioned preparation processes require the use of

suitable ionic or steric stabilizers, such as [poly(*N*-vinyl pyrrolidone)] or [poly(vinyl alcohol)].^{7,8} Precipitation polymerization, which was developed by Stover's group, provides a simple pathway to synthesize fully crosslinked spherical polymer particles.⁹ The uniqueness of the precipitation polymerization lies in the absence of any stabilizing agent such as surfactants or steric stabilizers for obtaining spherical particles. These microspheres are formed by aggregation of oligomers in poor solvents, followed by desolvation of the resulting microgels and continuous capture of oligomers from solution to ultimately yield monodisperse microspheres.

Polymers derived from glycidyl methacrylate (GMA) are attractive as a reactive starting material for the design of a whole range of compounds with various functional groups, because GMA monomer can offer both epoxy and acrylic functional groups, and give the user maximum freedom and flexibility in designing the polymer. Shapoval and Horak¹⁰ prepared 0.5 ~ 4 μm of poly (GMA) particles by dispersion polymerization, but it seemed not to be crosslinked. Smigol and Svec¹¹ reported the use of seeded suspension polymerizations to prepare monodisperse crosslinked copolymer microspheres incorporating GMA and ethylene glycol dimethacrylate (EGDMA), but the method is rather complex because at least two steps were needed in the swelling process. Uniform poly(glycidyl methacrylate-co-divinylbenzene) and poly(glycidyl methacrylate-co-ethylene dimethacrylate) porous microspheres were

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TABLE I
The Reaction Recipe of Poly(GMA-co-EGDMA) Microspheres in the Precipitation Polymerization

Medium, CH ₃ CN	Initiator, AIBN	Monomer 3.0 wt % (to medium)				Yield (%)
		GMA	EGDMA	Dn	Uniformity	
	2 wt % (to monomer)	90	10	soluble polymer with coagulum		
		80	20			5.5
		70	30	2.9	1.09	34.5
		60	40	3.2	1.04	51.0
		50	50	3.0	1.03	61.0
		40	60	2.5	1.01	58.4
		30	70	2.3	1.01	74.6
		20	80	2.2	1.08	79.9
		10	90	1.1	1.15	81.3

successfully prepared by Su and Wang¹² using membrane emulsification-polymerization technology, but this method needs special apparatus kit. Choe and Jin¹³ prepared highly crosslinked poly(glycidyl methacrylate-co-divinylbenzene) particles by precipitation polymerization.

Upto now, precipitation polymer microspheres are usually styrenic in nature, there are many monomers including methacrylate, maleicanhydride, chloromethyl styrene, and acrylamide have been copolymerized with divinylbenzene (DVB) as the crosslinkable monomer to form microspheres with precipitation polymerization. Styrenic monomers are strongly hydrophobic substances, but for many applications, it is desirable to have access to monodisperse microspheres having wider ranges of polarity and functionality than those achievable with styrenic monomers. For many applications the polarity of the polymer microspheres is an important variable. To extend the application, we have now explored the possibility of forming highly crosslinked polymer particles with the more hydrophilic crosslinkers EGDMA replacing the DVB crosslinker. In this study, the more hydrophilic and crosslinked poly(GMA-co-EGDMA) microspheres were synthesized using a simple precipitation polymerization in neat acetonitrile. The effects of EGDMA on the polymerization characteristics and size/uniformity of the microspheres, and the reactivity of epoxy groups were investigated.

EXPERIMENTAL

Materials

GMA and EGDMA were purchased from Yantai Yunkai Chemical Reagent, Shandong, China, and used as received. Analytical grade of 2,2-azobisisobutyronitrile (AIBN; Shanghai Chemical Reagent, China) was used as an initiator without further purification. 4,4'-azobis(4-cyanopentanoic acid) (ACPA) was purchased from Fluka. Acetonitrile (Shanghai

LinFeng Chemical Reagent, China) in analytical grade was used as the polymerization medium.

Preparation of poly(GMA-co-EGDMA) microspheres

The polymerization ingredients consist of medium, which is acetonitrile, various compositions of GMA and EGDMA comonomer mixtures, and AIBN. No stabilizer was employed. The total amount of monomers was set at 3.0 wt % for the medium and 2 wt % of AIBN with respect to the total amount of the monomers used. The concentration of the crosslinking agent, EGDMA, increased from 10 to 90 mol % with respect to the amount of GMA. After charging the polymerizing mixture in an evaporating flask, the solutions were sonicated for 5 min, deoxygenated with nitrogen for 15 min, and then sealed. Polymerization was carried out in a rotary evaporator with an agitation speed of 20 rpm at 70°C (water bath) for 24 h. After the completion of polymerization, the resultant particles were obtained by centrifugation and washed with methanol, repeatedly. Then, the samples (powder type) were dried in vacuum drier at room temperature for 2 days. The reaction recipe is listed in Table I. For comparison, the poly(GMA-co-DVB) microspheres was prepared by the same way.

Hydrolysis and aminolysis of poly(GMA-co-EGDMA) microspheres

A gram of poly(GMA-co-EGDMA) microspheres was mixed with 10 mL of 0.2-M sulfuric acid under stirring for 8 h at 80°C. Supernatant liquid was removed by centrifugation, the product washed with methanol repeatedly and dried in vacuum drier at room temperature for 2 days. IR spectrum was measured on the content of epoxy groups. In aminolysis, the same amount of poly(GMA-co-EGDMA) microspheres was mixed with 10 mL of 25% aqueous ammonia under stirring for 9 h at 50°C. After

the same purification procedure, the content of nitrogen was determined by CHN analysis.

Azoinitiator modification of poly(GMA-*co*-EGDMA) microspheres

Poly(GMA-*co*-EGDMA) (0.6 g) microspheres were dispersed in 10 mL dimethyl sulfoxide, then 0.1 g ACPA and 2.5 mL pyridine were added. The mixtures were sonicated for 5 min and deoxygenated with nitrogen for 15 min, then sealed. The reaction was carried out in a rotary evaporator with an agitation speed of 60 rpm at 50°C (water bath) for 5 h. The Modified particles were obtained by centrifugation and washed with methanol repeatedly. Then, the samples (powder type) were dried in vacuum drier at room temperature for 12 h, and preserved at -10°C. IR spectrum was measured on the content of epoxy groups. The content of ACPA grafted on the surface of poly(GMA-*co*-EGDMA) microspheres was determined by CHN analysis.

Characterization

Particle size and size distribution were determined by scanning electron microscopy (SEM) using a Hitachi S-4300 scanning electron microscope. All of the SEM size data reflect an average of about 100 particles each, which were calculated according to the following formula (1):

$$U = D_w/D_n, \quad D_n = \sum_{i=1}^k n_i D_i / \sum_{i=1}^k n_i, \\ D_w = \sum_{i=1}^k n_i D_i^4 / \sum_{i=1}^k n_i D_i^3 \quad (1)$$

where, U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number of measured particles, and D_i is the particle diameter of the determined microspheres.

Fourier-transform infrared analysis (FTIR) was performed with a VECTOR-33 FTIR spectrometer. All samples were mixed and ground with spectroscopic grade potassium bromide and the diffuse reflectance spectra were scanned over the range 400 ~ 4000 cm^{-1} .

Thermogravimetric analysis (TGA) was carried out with a STA-449C integrative thermogravimetric analyzer, at a heating rate of 10°C/min, upto 600°C in N_2 atmosphere.

The swelling experiment was carried out by immersing 1.0 mL powder of the sample in 5.0 mL solvent with different solubility parameters in a centrifugation tube for 24 h at room temperature.

The yield of polymerization was determined gravimetrically.

RESULTS AND DISCUSSION

Figure 1 represents the SEM photographs of the EGDMA content dependent poly(GMA-*co*-EGDMA) microspheres prepared by precipitation polymerization in acetonitrile with 2 wt % AIBN at 70°C for 24 h. Figure 1(a,f) shows different compositions between 30, 40, 50, 60, 70, and 90 mol % of EGDMA based on GMA, respectively. No formation of particles was observed when the mol % of EGDMA is 10, which means that 10 mol % of EGDMA is insufficient to form poly(GMA-*co*-EGDMA) particles by self-crosslinking in the precipitation polymerization. However, spherical particles were obtained with 20 mol % of EGDMA, but with some coagulum. Dissolution of the coagulated resin in THF may explain the partially coagulated resin represents uncrosslinked PGMA, but the spheres are crosslinked poly(GMA-*co*-EGDMA). Thus, the concentration of EGDMA is an important factor to form spherical particles with GMA. In precipitation polymerization, the formation of stable particles is achieved by means of the crosslinking reaction in the absence of any stabilizer, so in order to avoid coagulation, a high degree of crosslinking is essential.

Table I summarizes the size, size distribution, and yield of poly(GMA-*co*-EGDMA) microsphere by precipitation polymerization at 70°C for 24 h. As the EGDMA content increased from 20 to 90 mol %, the diameter had a tendency to decrease with the EGDMA content, which was same as the poly(Styrene-*co*-DVB) microsphere¹⁴ prepared by precipitation polymerization, but opposite with poly(GMA-*co*-DVB) microsphere that its size increased with the DVB content. Because the solubility parameters of polymerization ingredients play a significant role in determining the successful formation of a stable spherical shape in precipitation polymerization,⁹ a solubility parameter was considered for explaining the variation of the sizes. The final particle size was determined by the number of primal nuclei that grow to become individual particles at the end of polymerization, whereas the number of nuclei strongly depends on the solubility of the polymerization medium. If the medium acts as a good solvent for the nuclei, oligomeric species with a relatively high molecular weight is dissolved in the medium, resulting in a reduction of number of nuclei. When the nuclei are formed, the monomers are adsorbed onto the surface of the nuclei and polymerized to form microspheres. A small number of nuclei in the initial stage of polymerization would lead to a larger particle size after completion of the polymerization. The solubility parameters for GMA,

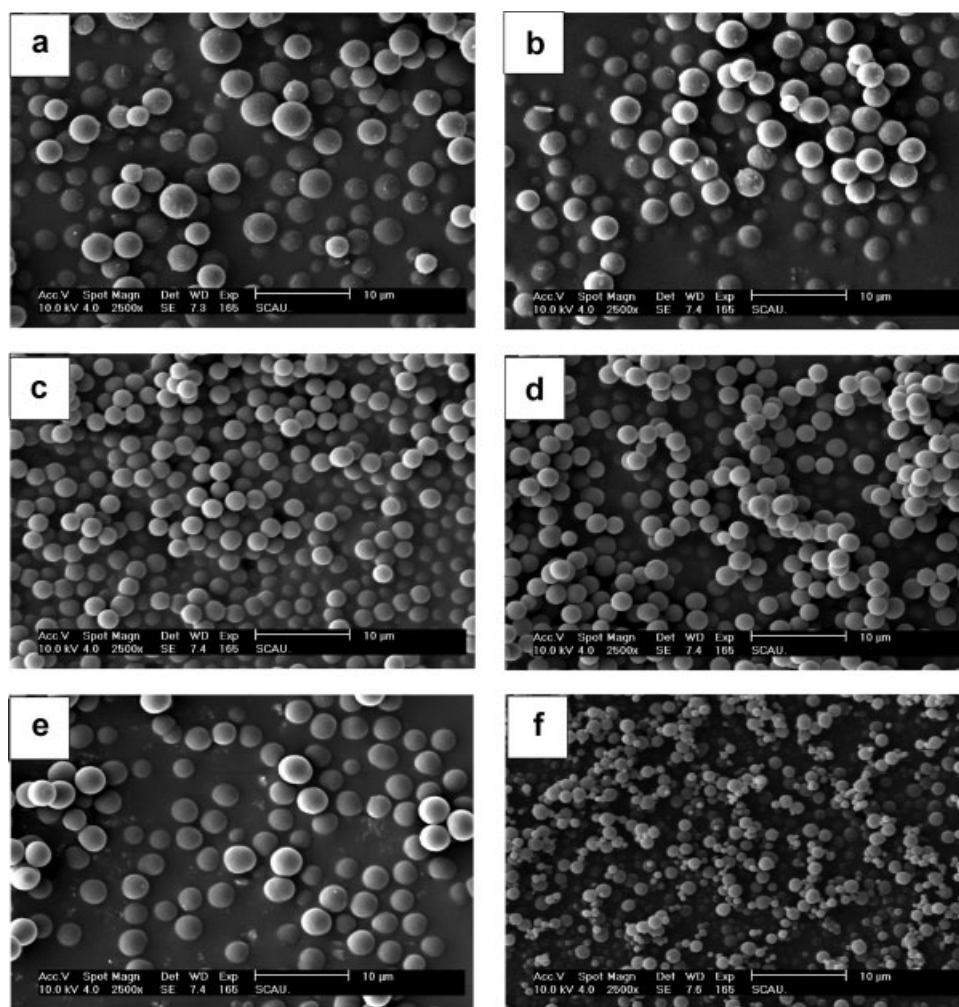


Figure 1 SEM micrographs of poly(GMA-*co*-EGDMA) microspheres prepared with various concentrations of EGDMA in acetonitrile at 70°C for 24 h: (a) 30, (b) 40, (c) 50, (d) 60, (e) 70, and (f) 90 mol %.

EGDMA, and acetonitrile are 19.4, 18.2, and 24.6 (MPa)^{1/2}, respectively. According to the “Like dissolves like” principle, acetonitrile used as the medium in this precipitation polymerization seems to be a better solvent for GMA rather than EGDMA because its solubility parameter is close to GMA. As the concentration of EGDMA in monomer composition increased, the solubility of the nuclei in acetonitrile would become poor, and a large number of nuclei were formed in the initial stage, which led to the smaller final particle size.

Monodisperse microspheres were obtained with the EGDMA content from 40 to 70%. The others with higher or lower EGDMA loadings afforded the particles with broader distribution, indicating that the second particle was formed during the precipitation polymerization.

As the EGDMA content increased from 20 to 90 mol %, the yield increased from 5.5 to 81.3%, respectively. The more the EGDMA content, the higher the yield was obtained because of high degree of crosslinking leading to the increase of the number of pri-

mary particles formed by precipitation of the oligomeric species. Therefore, the desirable high yield could be obtained by increasing the crosslinker concentrations in the precipitation polymerization. In addition, the surface smoothness was also improved with the EGDMA content possibly by the high degree of crosslinking. The similar trend was also observed for poly(GMA-*co*-DVB) microspheres in the precipitation polymerization.

Figure 2 shows the TGA thermograms of the poly(GMA-*co*-EGDMA) particles prepared with various concentrations of EGDMA. The numbers from 1 to 4 represent the various concentrations of EGDMA from 90 to 20 mol %, respectively. For the poly(GMA-*co*-EGDMA) particles between 20 and 90 mol % EGDMA, the abrupt weight loss of the samples is at about 300°C, the onset of the thermal degradation temperature at high temperature indicate that the poly(GMA-*co*-EGDMA) is crosslinked. However, for the sample with 80 mol % of GMA, the weight loss between 150 and 250°C is relatively high due to high content of GMA, which is not able to form self-crosslinking.

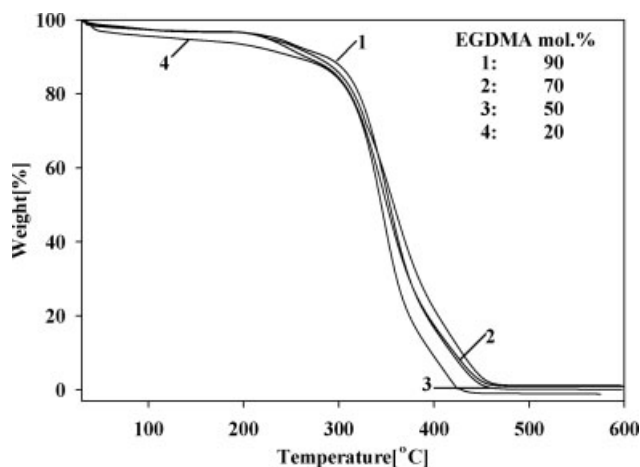


Figure 2 TGA thermograms of the poly(GMA-*co*-EGDMA) prepared with various concentrations of EGDMA in acetonitrile at 70°C for 24 h.

To confirm the reaction between GMA and EGDMA, the FTIR spectra were further studied (shown in Figure 3). The FTIR spectra had strong peaks between 1725–1728 cm^{-1} and weak peaks 1635–1637 cm^{-1} corresponding to the C=O and C=C stretching vibration adsorption and very broad hydroxyl (–OH) band of the ring opening reaction of the epoxy group in GMA near 3550 cm^{-1} . The peak at 908 cm^{-1} was the stretching vibration adsorption of epoxy group. As seen in Figure 3, the adsorption peaks at 3550 cm^{-1} and 908 cm^{-1} changed with the monomers loading. The relative intensity of the characteristic bands is qualitatively in agreement with the ratio between the two components used (Fig. 3, spectra 1–4).

For supporting that the copolymer particles were crosslinked, the swelling ratio measurement was carried out by storing 1.0 mL poly(GMA-*co*-EGDMA) powder in 5.0 mL solvent with different solubility parameters in a centrifugation tube for 24 h at room temperature. Then the swelling ratio q_v was calculated by the following eq. (2):

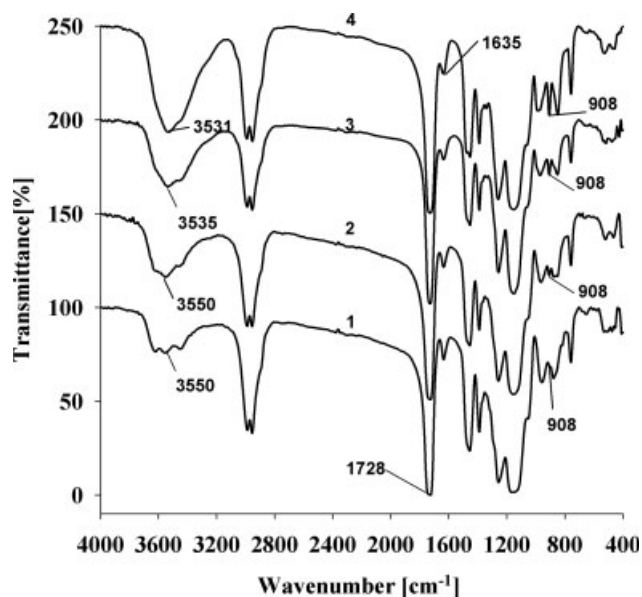


Figure 3 FTIR spectra of poly(GMA-*co*-EGDMA) microspheres. (1) GMA: 10 mol %, (2) GMA: 30 mol %, (3) GMA: 50 mol %, and (4) GMA: 70 mol %.

$$q_v = (V_{\text{dry polymer}} + V_{\text{solvent}}) / V_{\text{dry polymer}} = V_{\text{swollen polymer}} / V_{\text{dry polymer}} \quad (2)$$

where $V_{\text{dry polymer}}$ is the volume of the dry polymer and V_{solvent} is the volume of absorbed solvent at equilibrium swelling. The swelling ratios of poly(GMA-*co*-EGDMA) microspheres with various compositions between 90 and 20 mol % of EGDMA based on GMA were given in Table II. The experimental results show that these microspheres have good antiswelling capabilities. The abrupt increase in the swelling ratio at EGDMA (20 mol %) would be the result of uncrosslinked PGMA. The decrease in the swelling ratio with the content of EGDMA increase would be the result of the higher crosslinking between GMA and EGDMA.

The reactivity of epoxy groups in poly(GMA-*co*-EGDMA) microspheres were tested using three reactions: hydrolysis, aminolysis, and modified with

TABLE II
Swelling Ratios of Poly(GMA-*co*-EGDMA) Microspheres in Different Solvents

Solvent (δ)	Swelling ratios (q_v)				
	P (80 mol % GMA)	P (50 mol % GMA)	P (30 mol % GMA)	P (20 mol % GMA)	P (10 mol % GMA)
Water (23.4)	1.10	1.04	1.04	1.02	1.00
Methyl alcohol (14.5)	1.25	1.15	1.11	1.05	1.02
Tetrahydrofuran (9.9)	1.30	1.18	1.15	1.08	1.04
Toluene (8.9)	1.60	1.27	1.20	1.12	1.07

δ is solubility parameter

azoinitiator ACPA. No epoxy groups were found in the IR spectrum of poly(GMA-co-EGDMA) after the reactions of hydrolysis (Fig. 4, spectrum 4), the characteristic band of epoxy at 908 cm^{-1} disappeared and the epoxy groups were transformed to hydroxyl groups completely. Ammonium-modified microspheres (with 70 mol % of GMA) contained 1.35 mmol of amine groups per gram of polymer and the weak peak appeared at 1577 cm^{-1} was the N—H bend vibration adsorption (Fig. 4, spectrum 3). The remaining oxirane groups were transformed to hydroxyl groups because the reactions were proceeded in an aqueous medium. After the modification of azoinitiator ACPA, the relative intensity of the characteristic peak of epoxy at 908 cm^{-1} decreased and the characteristic band of N=N appeared at 1585 cm^{-1} (Fig. 4, spectrum-2), which shows that the azoinitiator ACPA was immobilized on the surface of poly(GMA-co-EGDMA) microspheres by the reaction of ACPA with epoxy groups. The content of ACPA on the surface of poly(GMA-co-EGDMA) microspheres with various compositions between 40, 50, 60, and 70 mol % of GMA based on EGDMA are given in Table III. The experimental results show that the content of ACPA increased from 0.09 to 0.28 mmol/g with the increase of the GMA loading.

To compare the hydrophilic of poly(GMA-co-EGDMA) microspheres with poly(GMA-co-DVB), the wettability of the surface of these microspheres by water was investigated. A qualitative technique was to investigate the degree of microspheres agglomeration when they were immersed in the water. These microspheres were thus immersed in the water studied by optical microscopy. Whereas the pronounced poly(GMA-co-EGDMA) microspheres seemed to be better dispersed in the water, which indicated that the surface of these microspheres is more hydrophilic.

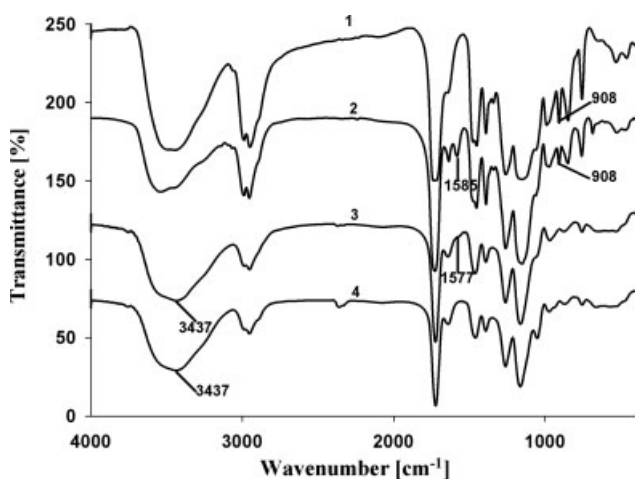


Figure 4 (1) FTIR spectra of poly(GMA-co-EGDMA) microspheres, (2) modified with azoinitiator ACPA, (3) aminolysis, and (4) hydrolysis.

TABLE III
The Content of ACPA Introduced onto the Poly(GMA-co-EGDMA) Microspheres

P _{GMA-EDMA} (GMA mol %)	Content of Nitrigon/%	Content of ACPA/(mmol/g)
P _{GMA-EGDMA} (70%)	1.54	0.28
P _{GMA-EGDMA} (60%)	1.22	0.22
P _{GMA-EGDMA} (50%)	0.74	0.13
P _{GMA-EGDMA} (40%)	0.48	0.09

CONCLUSIONS

In conclusion, the precipitation polymerization of poly(GMA-co-EGDMA) was investigated with increasing concentrations of EGDMA in acetonitrile. Stable poly(GMA-co-EGDMA) microspheres were first obtained above 20 mol % EGDMA via precipitation polymerization. The resultant copolymer particles had a spherical shape with a clean surface and narrow-dispersion or monodisperse diameters in the range of $1.1 \sim 3.2\ \mu\text{m}$. As the concentration of EGDMA increased from 20 to 90 mol %, the number-average particle diameter decreased. The yield of polymerization was also dependent on the concentration of EGDMA: the higher the EGDMA content was, the greater the polymerization yield resulted. The lack of swelling in organic solvent and water, along with the onset of the thermal degradation temperature at higher temperature serves as evidence that the prepared particles were highly crosslinked poly(GMA-co-EGDMA) microspheres. These microspheres are of significant interest, as the epoxy groups may be chemically modified postpolymerization.

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