Preparation of P(MMA-co-EGDMA) Functional Composite Particles by Dispersion Microwave Polymerization

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ABSTRACT

Microwave dispersion polymerization of methyl methacrylate/glycidyl methacrylate (MMA-co-EGDMA). This phenomenon was ascribed to the acceleration of the initiator [2,2-Azobisisobutyronitrile (AIBN)] decomposition by microwave irradiation. Preparation of P(MMA-co-EGDMA) functional composite microsphere that the synthesis microsphere having various uniform size from 2 to 5 µm by dispersion microwave polymerization which the particle size was controled with initiator concentration, microwave power(400, 800, 1600W) and polymerization temperature. The microwave polymerization process was compared with that of the thermal method at $56(\pm1)\,°C$ under comparable reaction conditions. The structure of polymer spheres were characterized by TGA, FESEM and FTIR.

Keywords – dispersion polymerization. Microwave polymerization.

微波輻射分散聚合法製備共聚(甲基丙烯酸甲酯\二甲基丙烯酸乙二酯)功能性高分子微球

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摘　　要

　　微波輻射分散聚合法製備共聚甲基丙烯酸甲酯(MMA)和二甲基丙烯酸乙二酯(EGDMA)，研究是以微波聚合法製作共 MMA/EGDMA 功能性高分子微球，微波輻射反應加速了聚合反應，這是因為微波輻射加速了自由基起始劑(AIBN)的分解，快速形成自由基，研究微波輻射分散聚合法採用的微波功率分別為(400、800、1600W)，微波輻射分散聚合法所製備的功能性高分子微球具有單分散性及各種不同的粒徑(2~5µm)。微波輻射分散聚合反應，反應溫度控制在(56±1)℃，微球的鑑定採用熱重損失(TGA)、場發射掃描式電子顯微鏡(FESEM)、傅立葉紅外線(FTIR)。

關鍵詞：分散聚合法，微波聚合法

Ⅰ. INTRODUCTION

Industrial use of microwave radiation as an affordable alternative to thermal heating of the polymerization process has generated a lot of interest recently. Since the late 1960s, microwave irradiation has been used to synthesize and process polymeric materials as rapid heating and melting of neat and mineral-filled plastics for a number of purposes such as fast curing of thermosetting resins and composites, polymerization of vinyl monomers, rapid drying of aqueous solutions or dispersion of polymers and resins, and heat drawing of polymer rods and tubings (Parodi, 1998).Industrial use of microwave radiation as an affordable alternative to thermal heating of the polymerization process has generated a lot of intertest recently. The main advantages of microwave processing of materials are an increased rate of production, improved product characteristics, uniform processing, less floor space required, and convenience and controllability of the process. [1] Some of the applications of microwave dielectric heating include moisture analysis, [2] microwave catalysis, [3] wet ashing procedures of biological and geological materials, [4]and dissolution of ore samobples. [5] The number of applications of microwave-heating techniques in chemistry is growing rapidly. Many reactions thought to require lengthy heating periods in biochemical applications and polymer and organic chemistry are ideal for microwave promotion for rapid transformation and do not require extensive heating [6, 7].

There are four main types of liquid-phase heterogeneous free-radical polymerization; microemulsion polymerization, emulsion polymerization, miniemulsion polymerization and dispersion polymerization, all of which can produce nano- to micron-sized polymeric particles. It is well known that microemulsion, miniemulsion and dispersion polymerizations bare many similarities to emulsion polymerization in the kinetics of particle nucleation and growth and in polymer structure development. Therefore, for optimal design and operation of these heterophase free radical polymerizations, it is important to have detailed knowledge of the kinetics and mechanisms of emulsion polymerization. The microwave polymerization was conducted in a multimode cavity, which was designed with a rotating platform to prevent formation of "hot spots" due to non-uniform heating.

Anisotropic conductive adhesive (film) provides both electrical and mechanical interconnections between electronic components and the supporting substrate. These anisotropic conductive films (ACFs) offer numerous advantages in surface mount assembly, including flexible and simple process at low temperature, fluxless bonding which eliminates the need for cleaning, lead-free formulations and low cost [8,9]. The anisotropic nature of these materials makes them excellent candidates for very fine pitch component such as flip chip. These flip chip applications on flexible substrates such as smart cards, disk drives and driver chips for LCDs have attracted much interests and widespread use [10]. However, in flip chip technology, ACF dose not self align [11] that would allow misplaced chips to be pulled into correct position corresponding to substrate electrodes by surface tension forces of molten solder.

Poly(methyl methacrylate)-(ethyl glycol dimethacylate), poly(MMA-EGDMA) particles were prepared by microwave dispersion polymerization. This work examines the feasibility of adopting a novel microwave dispersion polymerization method , as seldom done previously to polymerization the copolymer microsphere. The size and structure of the beads were characterized using SEM and FT-IR spectroscopy, respectively.

Ⅱ. EXPERIMENTAL

2.1 Materials

Methyl methacrylate (MMA, ACROS Chemicals).Methanol(MeOH, ACROS Chemicals).Ethyl glycol dimethacylate (EGDMA; Kishida Chemical Industries, Tokyo, Japan)were of commercial grade.PVP (molecular weight 58,000, K-29~K32) was used without further purification, and 2,2-azobisisobutyronitrile (AIBN; ACROS Chemicals) was purified by recrystallization in Methanol.

2.2 Polymerization for microwave dispersion polymerization

Microwave dispersion polymerization was carried out in a 250 mL round flask with a mechanical stirring at 60 rpm under nitrogen atmosphere at 52~64°C. Pre-weighed Methanol and aqueous PVP solution were charged in the reactor and followed the addition of MMA, and EGDMA. Then, the AIBN dissolved in Methanol was added and the polymerization was initiated. The microwave polymerization was conducted in a multimode microwave cavity. The microwave source was from a 2.45 GHz frequency magnetron powered by a 1.26 KW variable power generator, which could be operated at different power levels. To prevent formation of hotspots due to non uniform heating, the cavity was designed with a rotating platform on which the sample could be placed. The microwave chamber temperature was measured by an optical fiber K-type probe (-50 to 250℃). The reaction apparatus is schematically presented in Fig.1.
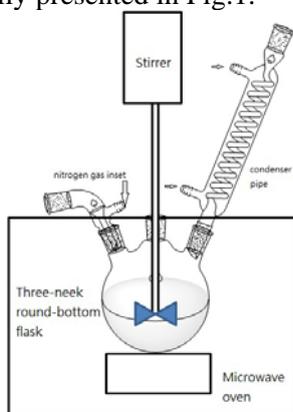

Fig.1 Sketch of the reaction apparatus for microwave irradiation

2.2 Characterization

After the polymerization, the final monomer conversion was measured gravimetrically. The size and size distribution of MMA-EGDMA copolymers were observed by scanning electron microscopy (SEM, S-3500N; HITACHI, Japan) for the dispersion polymerization. Thermal gravimetric analysis (TGA) of PMMA-EGDMA was carried out on a TA-STDQ600 (TA Instruments, New Castle, DE). The thermo grams were acquired between 25 and 500℃ at a heating rate of 10℃/min.

Nitrogen was used as the purge gas at a flow rate of 20 mL/min. Fourier transform infrared (FT-IR) spectra of the copolymer microsphere were recorded with a Nicolet (Madison, WI) 170SX FT-IR spectrometer in the attenuated total reflection mode, wavelength range 4000–650 cm⁻¹.

Ⅲ. RESULTS AND DISCUSSION

Dispersion polymerization is actually a precipitation polymerization in which the medium is miscible with the monomer but not the polymer. When the polymerization starts, free radicals formed by initiator decomposition grow in the continuous phase until their size reaches a critical chain length, at which point they precipitate by either a self or aggregative nucleation process [12], forming nuclei. When sufficient mature particles are formed which can capture all the radicals and nuclei in the continuous phase, no more particles will be formed, and the particle formation stage is completed [13].

3.1 Polymerization procedure

A graph of the fractional conversion of the monomer to the polymer as a function of time is shown in Fig2. The polymerization was accomplished with microwave and convection heating at 64°C with AIBN and MMA/EGDMA in a 195mL methanol solution. The polymerization based on MMA/EGDMA/AIBN/Methanol in the presence of microwaves had a higher rate of polymerization than that performed with convection heating. The induction period was 2min for microwave polymerization but 15 min for convection heating. After 20 minutes reaction, the monomer conversion for microwave polymerization was 60%,whereas the corresponding conversion for convection heating polymerization was only 5%.The increase of reaction rate was attributable to a dual effect: the activation of MMA polymerization and the acceleration of initiator decomposition, driven by the polar moieties in the radical oligomers or AIBN with dipolar relaxation under 2.45GHz electromagnetic wave. The second effect was systematically examined in our work. A solution with AIBN in methanol was used, and the

3

decomposition rates for AIBN undergoing convection heating, 400W microwave irradiation, and 800W microwave irradiation at 52, 56, 58, 60, and 64°C were measured.
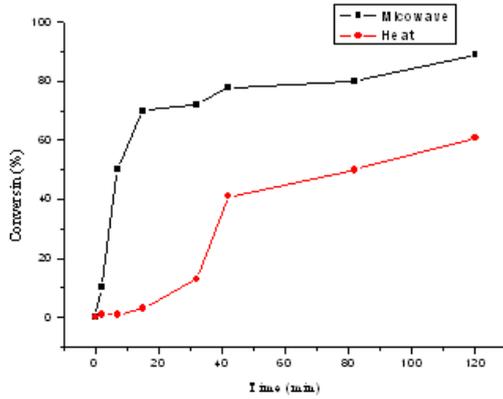
the different temperatures (52, 64°C) of SEM image.

Fig.2 Conversion curves of MMA during microwave irradiation polymerization and conventional thermal polymerization.

Fig.3 Effect of temperature on copolymer particle size

3.2 Particle size

The morphology, size, and size distribution of the PMMA microspheres were characterized with SEM (SEM, S-3500N; HITACHI, Japan). The diameters of more than 100 microspheres were measured from the SEM images. The number average diameter (Dn), weight-average diameter (Dw), and the poly dispersity index (PDI) were calculated as follows:

$$D_n = \sum_{i=1}^{k} N_i D_i / \sum_{i=1}^{k} N_i \qquad (1)$$

$$D_w = \sum_{i=1}^{k} N_i D_i^4 / \sum_{i=1}^{k} N_i D_i^3 \qquad (2)$$

$$\text{PDI} = D_w / D_n \qquad (3)$$

where N_i is the number of microspheres with diameter D_i.

3.3 Temperature

As illustrated in Fig.3 The copolymer prepared at temperatures of 52, 56, 58, 60 and 64°C had narrow size distributions with the particle diameter increasing from 3.13 um at 52°C to 4.15 um at 56°C to 4.64 um at 58°C to 4.96 um at 60°C to 5.13 um at 64°C. Fig.4a, 4b
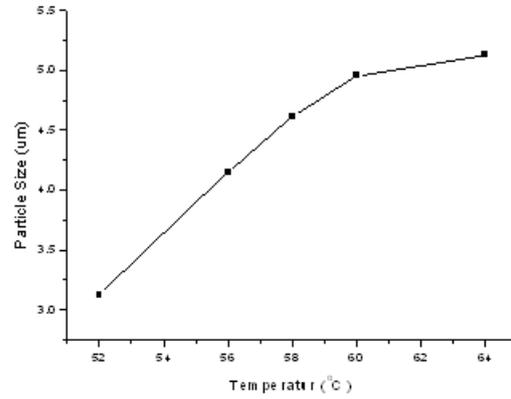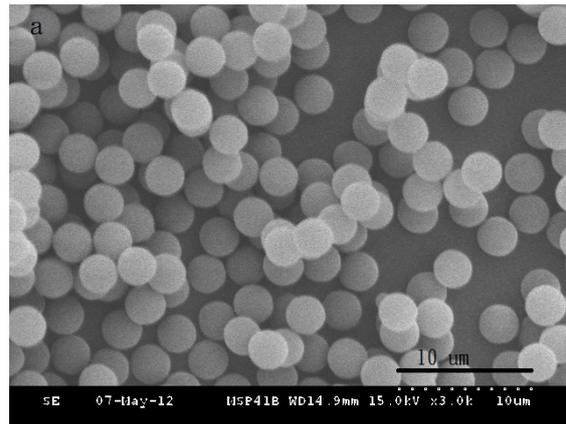

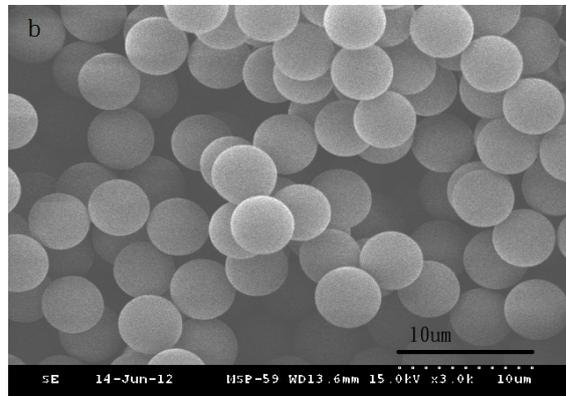Fig.4a The different temperatures (52°C) of SEM image.

Fig.4b The different temperatures (64°C) of SEM image

4

3.4 Effect of the Stabilizer Concentration on the Size and Size Distribution of the Microspheres

The effect of the PVP concentration on the size and size distribution of the Poly(MMA-co-EGDMA) microspheres is shown in Fig.5 As the concentration of PVP changed from 60 to 100 wt %, Dn of the microspheres decreased from 5.34 to 3.45 µm, and the size distribution of the Poly(MMA-co-EGDMA) microspheres decreased gradually. When the initial stabilizer PVP concentration was increased in the dispersion microwave polymerization, both the adsorption rate of the stabilizer and the viscosity of the continuous phase could be increased. On the other hand, the aggregation of nuclei was hindered at high PVP concentrations. This reduced the extent of aggregation and shortened the time of primary particle formation, thereby resulting in a smaller size and a narrow size distribution of the resulting particles and inhibiting the secondary nucleation. Fig.6a, 6b shows the effect of the PVP concentration (100 wt%, 60 wt%) of SEM image.
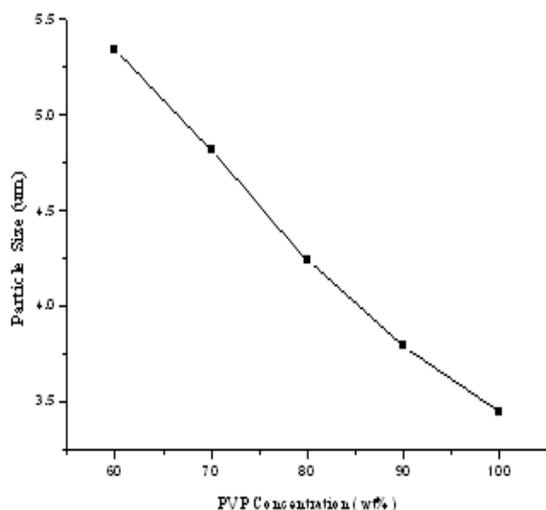

Fig.5 Effects of the PVP concentration on the size and size distribution of the microspheres prepared with 400-W microwave irradiation.
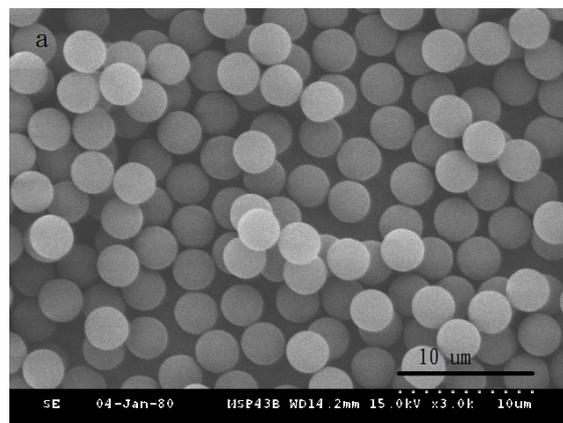

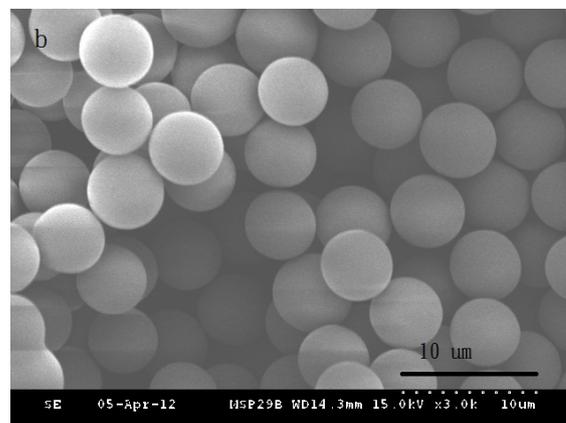Fig.6a Shows the effect of the PVP concentration (100 wt%) of SEM image

Fig.6b Shows the effect of the PVP concentration (60 wt%) of SEM image.

3.5 Effect of the Initiator Concentration on the Size and Size Distribution of the Microspheres

Fig.7 shows the effect of the initiator concentration on Dn and the size distribution of Poly(MMA-co-EGDMA) microspheres. Although the AIBN concentration was very low in the polymerization system, it could initiate MMA, EGDMA to polymerize in a polar medium with microwave irradiation. Moreover, the initial AIBN concentrations greatly affected the size and size distribution of the microspheres in the dispersion polymerization with microwave irradiation. With the AIBN concentration increasing from 0.1 to 0.5wt%, Dn of the microspheres increased from 3.43 to 5.82 µm. However, the size distribution of the Poly(MMA-co-EGDMA) microspheres decreased gradually as the AIBN concentration

increased in the dispersion polymerization with microwave irradiation. In the microwave field, the decomposition rate of AIBN could be accelerated, [14] and so the rate of the dispersion polymerization was increased. When the initial initiator concentration was increased, the number of free radicals increased, and the dispersion polymerization began with more radicals per unit of volume, which could form many oligomeric radicals. Fig.8 shows the effect of the initiator concentration (0.1, 0.5 wt%) of SEM image.
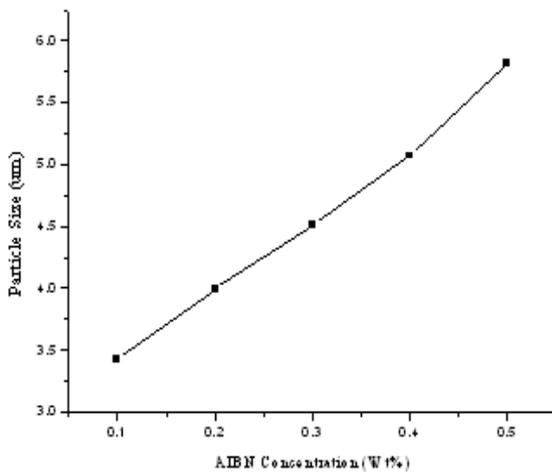

Fig.7 Effects of the initiator concentration onthe size and size distribution of the microspheres preparedwith 400-W microwave irradiation
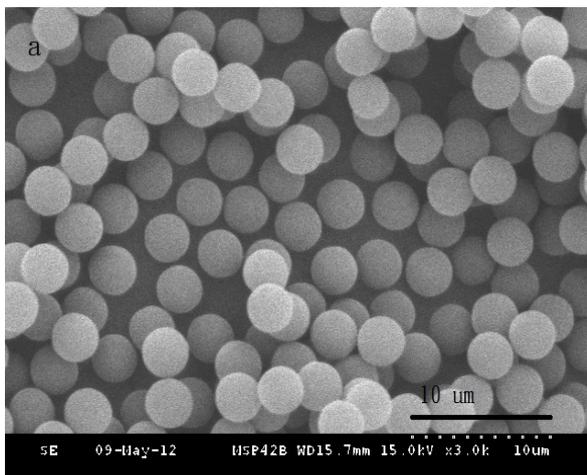

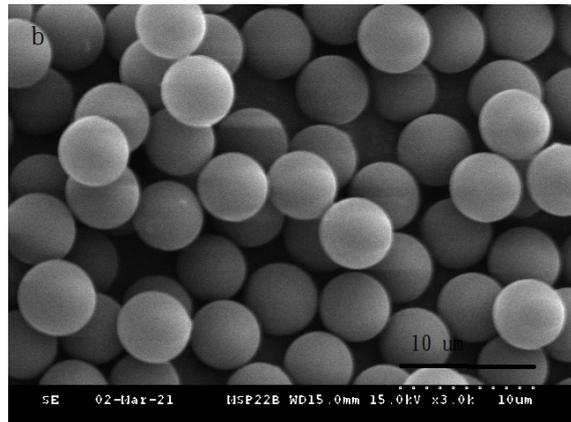Fig.8a shows the effect of the initiator concentration (0.1 wt%) of SEM image

Fig.8b shows the effect of the initiator concentration (0.5 wt%) of SEM image.

3.6 Microspheres thermal analysis

Fig.9 show the TGA thermographs of MMA-EGDMA copolymer microsphere. The TGA curves of MMA-EGDMA copolymer microsphere revealed there main weight loss regions. The first region at 80–150℃ was due to the removal of water; the second transition region at 200–400℃ was due to degradation of the polymer films; and the peak of the third stage, at 435℃, was due to cleavage of the polymeric backbone. The temperature of hot loss weight analysis is 234°C. We find hot loss weight analysis result, PMMA-EGDMA copolymer microsphere than one PMMA polymerization microsphere of hot loss weight analysis. The reason has adding micro EGDMA that the structure inner take shape crosslinking. The temperature increases of hot loss weight analysis.
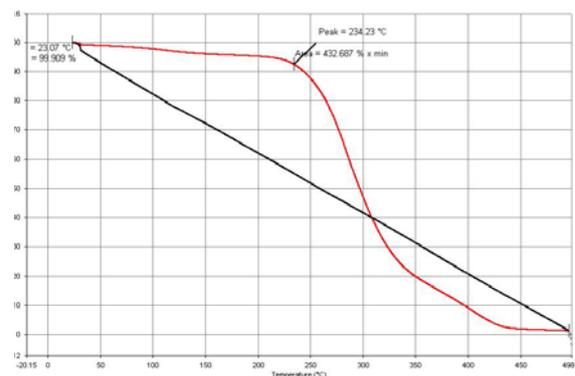

Fig.9 The PMMA-EGDMA copolymer microsphere of hot loss weight analysis.

6

3.7 FT-IR analysis

The FT-IR spectrum of Poly(MMA-GMA-EGDMA (shown in fig.10) indicates the details of functional groups present in the synthesized polymer beads. A sharp intense peak at 1721 cm^{-1}appeared due to the presence of ester carbonyl group stretching vibration. The broad peak ranging form 1260-1000cm^{-1}can be explained owing to the C-O (ester bond) stretching vibration. The broad band from 950-650 cm^{-1}is due to the bending of C-H. The broad peak ranging form 3100-2900 cm^{-1}is due to the presence of stretching vibration. There epoxy function groups in the structure of Glycidylmethacrylate actually. It's just due to other function groups are too strong to cover the signal of epoxy function group in the polymer.
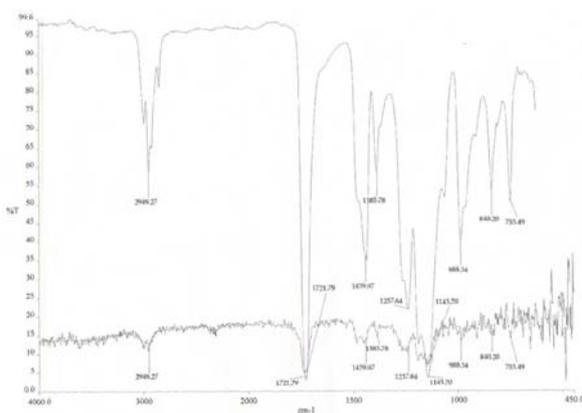

Fig.10 FT-IR spectra of MMA-GMA-EDGMA copolymer, MMA polymer

Ⅳ. CONCLUSIONS

Polymerization of a Poly(MMA-co-EGDMA) system was successfully performed using a microwave curing process. the preparation of uniform poly(MMA-co-EGDMA)microspheres was successfully accomplished by using the dispersion microwave polymerization technique. Monodisperse MMA-EGDMA copolymer microspheres with an average eparticle size from 2 to 5 mm. The effect of the cross linking agent showed the amount of EGDMA required to give cross linked networks in particles. The effects of St, AIBN, and PVP on the sizes and size distributions of the Poly(MMA-co-EGDMA) microspheres were studied. The size and size distribution of the Poly(MMA-co-EGDMA) microspheres prepared with dispersion polymerization with microwave irradiation increased as the initial MMA concentration increased. When the PVP concentration was high, small and narrow-distribution Poly(MMA-co-EGDMA) microspheres could be prepared, whereas large microspheres with narrow distributions could be obtained at high AIBN concentrations.

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