Crosslinked Microparticle Preparation in Supercritical Carbon Dioxide with Photopolymerization

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ABSTRACT: An antisolvent processing technique by simultaneous compressed antisolvent precipitation and photopolymerization for cross-linked polymer microparticles formation was presented in this paper. In this process, photopolymerization of the homogeneous solution composed of methylene chloride, poly(ethylene glycol)600 diacrylate (PEG600DA) as monomer and diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) or 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator resulted to microparticle when it was sprayed into supercritical carbon dioxide ($scCO_2$) and simultaneously exposed to initiating light. High miscibility of the solvent in $scCO_2$ made methylene chloride quickly extracted from the dispersion phase, leaving very high concentrations of monomer (PEG600DA) dispersed in $scCO_2$. The high monomer concentration combined with photo initiating polymerization facilitates rapid reaction rates and ultimately lead to polymer precipitation. Particle size and morphology were adjustable by changing the processing conditions, such as temperature and pressure. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1460–1466, 2012

Key words: supercritical carbon dioxide ($scCO_2$); photopolymerization; microparticle; precipitation

INTRODUCTION

Polymer microparticles have been attracted considerable attention for their diverse and potential applications in the fields of optics, electronics, colloidal chemistry, biochemistry, and biomedicine. In the past decades, more and more studies have been focused on the synthesis of particles with different sizes and with various morphologies by special polymerization techniques.[1]

One common conventional method for forming polymer microparticle is solvent emulsion evaporation (SEE), which uses double emulsion–solvent evaporation method.[2] But the process is difficult to scale up because of large quantities of environmentally unfriendly solvents and requirement of dissolving the polymer in solvent, which is unsuitable for processing insoluble or cross-linked polymers.[2]

Another conventional method is emulsion polymerization,[1,3] in which droplets of monomer were dispersed in a continuous solvent phase composed of solvents, emulsifiers and surfactants. Emulsion polymerization can be used to produce microparticle of highly cross-linked polymer, but sometimes it had to involve high temperatures in order to complete the thermal polymerization, and large quantity of solvents and additives, which limits its use for medical and food purposes.[4–7]

Photopolymerization of aerosols also can lead to mono dispersed and smooth particles, but it suffers from poor yield due to sluggish solvent evaporation and insufficient polymerization.[1,8–11]

Polymer particles can also be formed from polymerizations of monomer, thermal initiators, and surfactants by introduced them into supercritical fluid.[12–15] In fact, supercritical fluid processing (SFP) can overcome some of the disadvantages of conventional methods, because carbon dioxide has easily accessible critical conditions [critical temperature (T_c) 31.1°C; critical pressure (p_c) 7.38 MPa)]. $ScCO_2$ is an environmentally friendly alternate to volatile organic compounds and chlorofluorocarbons,[16–19] which could reduce undesirable effluents. The direct manufacture of polymer in a dry form could also eliminate separation steps and reduce the extensive energy consumption to dry the product. It could be adopted in polymerizing monomers which are difficult or even impossible to solute in ordinary solvent. Otherwise, this method would enable the researcher to design polymer with distinct physical or structural properties, which may facilitate

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processing or open new applications for such polymers.[20,21]

In this work, scCO$_2$ was obtained by adding carbon dioxide into the chamber and adjusting the temperature and pressure befittingly. Then carbon dioxide, solution of reactive monomer and photo initiator were sprayed simultaneously into the high pressure chamber to form mist of the reactants interacting with carbon dioxide and the further uniform dispersion system of reactant in supercritical carbon dioxide could be got by anti solvent effect. The photopolymerization of active monomer in supercritical carbon dioxide performed under irradiation of UV light resource and crosslinked polymer microparticle was produced. The effects of changing process, such as temperature and pressure, on the morphology and particle size of the resulting cross-linked micro particles were investigated.[22]

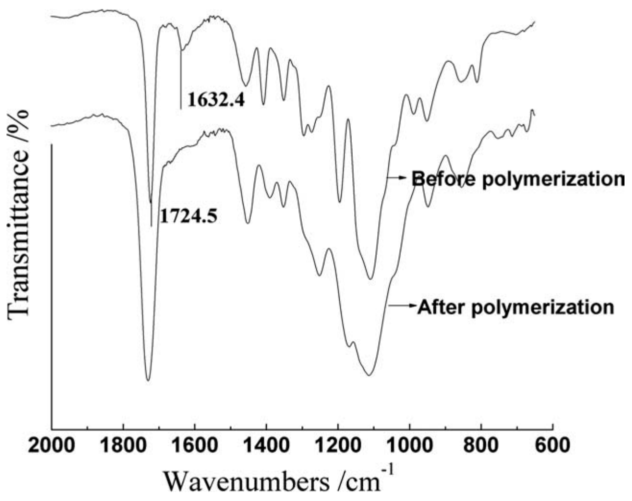

Figure 1 FTIR of PEG600DA and poly-(PEG600DA) particles processed at 45°C, 10.0 MPa.

EXPERIMENTAL

Materials

Photopolymerizable monomer poly(ethylene glycol)600 diacrylate (PEG600DA, Eternal, China), photoinitiators 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Ciba) and diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO, Ciba) and carbon dioxide (SFC Grade, Ruilong, China) were used as received. Methylene chloride (Beijing Chemical Works, Beijing, China) was used after distilling.

Photopolymerization

CO$_2$ was deoxygenated with O$_2$ scrubber and transferred into compressed gas pumps at temperature of −5°C. The high-pressure chamber was pressurized with deoxygenated CO$_2$ and allowed to equilibrate to 7.0–10.0 MPa at 25–55°C. Reactant solution for the photopolymerization process was prepared by dissolving 25 wt % PEG600DA in methylene chloride with 3 wt % (relative to monomer) photoinitiator, DMPA, or TPO, which was then pressurized to 7.0–10.0 MPa by another pump. The solution was sprayed into the chamber at constant flow rate (1 mL/min) through a 100 μm capillary nozzle. Concurrently, the CO$_2$ was flowed at constant rate of 15mL/min into the high-pressure chamber. A spot light source (EFOS Series 1000, with 200–500 nm filter and 5-mm crystal optical fiber, Canada) with light intensity of 200 mW/cm^2 (Ultraviolet Light Radiometer, 365 nm, Beijing Normal University, China) supplied the light through the borosilicate window to initiate the photopolymerization in the chamber. After spraying and photopolymerization, the chamber was slowly depressurized (30min) at the operating temperature. The produced particle was collected and purified by swelling and washing the solvent and residual monomers with methylene chloride and then dried at 40°C for 24 h.

Instruments

Fourier transform infrared spectra (FTIR) were recorded on Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Samples were prepared on KBr pellet and scanned against a blank KBr pellet background at range of 4000–650cm^{-1} with resolution of 4.0cm^{-1}. UV–vis spectra were recorded on Hitachi U-3010 UV–vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Scanning Electron Microscope (SEM) was observed by Hitachi S-4700 (Hitachi Company, Japan). The particles were attached to aluminum stubs by using conductive tape and sputter-coated with a thin layer of gold before examination. Optical Microscope was observed by optical microscope (Chongqing Optical and Electrical Instrument Corporation, XSZ-HS3 Optical Microscope, China) at 240 times magnification. Particle size distribution was measured by a laser scattering particle size distribution analyzer (Horiba, LA-300, Japan). The resulting particles of roughly 0.05 g were dispersed in 30 mL methylene chloride and the particle size distribution range is 0.1–600 μm.

RESULTS AND DISCUSSION

With UV irradiation, the photoinitiator produced two kinds of free radicals by photocleavage reaction, which induces photopolymerization of PEG600DA. FTIR spectra of PEG600DA and poly-(PEG600DA) were shown in Figure 1. PEG600DA have two characteristic absorption bands at 1730 cm^{-1} (stretching vibration of C=O) and 1630 cm^{-1} (stretching

TABLE I
Effect of the Photoinitiator (45°C, 8.5MPa)

	1 wt %	3 wt %	5 wt %
DMPA	No polymer received	No polymer received	No polymer received
TPO	No polymer received	Particle polymer	Particle polymer

vibration of C=C). After UV irradiation, the character absorption band of the carboxyl group (C=O) were unchanged, while the carbon–carbon double bond absorption peak at 1632.4 cm^{-1} disappeared, indicating the occurrence of photocrosslinking.

The decrease of the C=C absorption peak area from 1631 to 1633 cm^{-1}accurately reflects the extent of the polymerization. After baseline correction, conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as the following: each sample was repeated three times:

$$\text{DC}(\%) = (A_0 - A_t)/A_0 \times 100$$

Where DC is the degree of methacrylate double bond conversion at t time, A_0 the initial peak area before irradiation and A_t is the peak area of the double bonds at t time. The rate of photopolymerization is calculated by the differential of conversion of double bond versus irradiation time. The results obtained from Figure 1 showed that final DC was about 80%.

The initiating results of DMPA and TPO were listed in Table I, which showed that DMPA was not as effective as TPO. It can be attributed to the strong absorption at 200–350 nm of the borosilicate window used in scCO_2 apparatus, which covered the absorption wavelength range of DMPA. But the absorption range of TPO allocated about 380–420 nm, it could be adopted as suitable initiator.

It also could be seen that photopolymerization was not proceeded effect when TPO concentration was 1 wt % relative to PEG600DA, but when TPO was 3 or 5 wt %, the photopolymerization proceeded effectively. The morphology of the productions were shown in Figure 2, it could be seen that there is no obvious difference among them, then 3 wt % TPO was selected in further experiments.

Photopolymerization at different conditions lead to different morphology of productions. Table II showed the morphology, size, and size distribution of the product through photopolymerized in gaseous CO_2 (7.0 MPa, 45°C), scCO_2 (8.5 MPa, 45°C), and liquid CO_2 (8.5 MPa, 25°C) respectively. There was no notable production observed in gaseous CO_2. In scCO_2, consistent spherical particles with a bimodal size distribution range of 0.1–100 μm were produced, while productions obtained in liquid CO_2 have widely shape and size range. This difference was caused by different solubility of each CO_2 state to monomer and polymer. Polymer solubility in gas carbon dioxide was typically very low. Process variables such as temperature and pressure could be manipulated to alter the solubility of SCCO_2, which was impossible in liquid carbon dioxide. Morphology of production in liquid CO_2 and scCO_2 also exhibited difference character as shown in Figure 3.

It is well known that the density of CO_2 decreased with increasing of temperature when pressure kept constant around critical pressure (p_c) and increased with increasing of pressure under stated

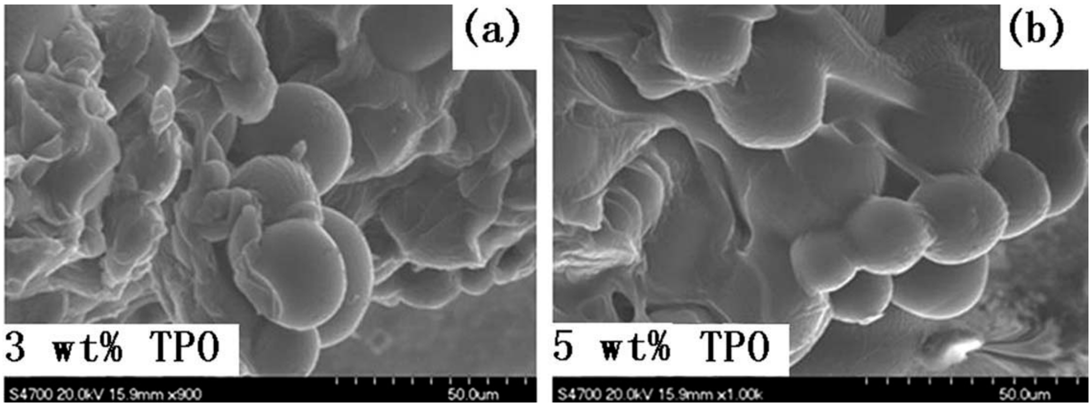

Figure 2 SEM photographs of poly-(PEG600DA) particles photopolymerized with: (a) 3 wt % TPO, (b) 5 wt % TPO, related to PEG600DA at 45°C, 8.5 MPa.

TABLE II
Morphology, Size, and Size Distribution of the Production Photopolymerized in Gaseous CO_2, $scCO_2$ and Liquid CO_2

	Gaseous CO_2	$ScCO_2$	Liquid CO_2
Morphology	No polymer received	Consistent spherical	Unequal
Size	No polymer received	0.1–100 μm	Uneven
Size distribution	No polymer received	Bimodal particles	Wide distribution

temperature.[23] Some literatures had derived equations correlating the solubility of solid solute in SCF with the density of the pure SCF and the absolute temperature.

One model advanced by Chrastil[24] based on the supposition that one molecule of solute, A, associates with k molecules of the SCF solvent, B, to form a solvate-complex AB_k, in equilibrium with the system. The definition of the equilibrium constant, which is obtained throughout several thermodynamic considerations, leads to the following expression for the solid solubility:

$$\ln S = k \ln \rho + \frac{\alpha}{T} \beta$$

In this expression, S (kg/m^3) is the solubility of the solid in the supercritical phase, ρ (kg/m^3) is the density of the pure supercritical fluid, k is the association number, α is a constant, defined as $\Delta H/R$ (where ΔH is the sum of the enthalpies of vaporization and solubility of the solute, and R is the gas constant) and β is another constant somehow related to the molecular weight of the solute and solvent. The parameters, k, α, β are obtained performing a multiple linear regression on the experimental solubility data.

According to this expression, particle size and morphology were adjustable by changing the processing conditions (temperature and pressure). Because changes of temperature and pressure could change the solubility of $scCO_2$, which caused the particles precipitated to the bottom of the chamber with different diameters.

Micrographs in Figures 4 and 5 showed the effect of operating conditions on the morphology of the particles obtained. With temperature increasing from 40 to 55°C, particles size was decreasing gradually. But in contrary, the particle size inclined by increasing the pressure of chamber. Figures 4 and 5 also showed that at supercritical conditions, some spherical particles could be obtained, but the samples looked like agglomerated particles.

Figure 6 showed the effect of temperature on particle size distribution of poly-(PEG600DA) through photopolymerization process. It was found that all the polymer particles exhibited bimodal size distribution and 45°C could be believed the best condition due to the narrowest size distribution.

This phenomenon is attributed to the effect of combination of some different reasons, because the process of forming particle is very complex, when monomer and CO_2 were sprayed into chamber. First, there are some liquid droplets with different diameter formed by those undissolved monomer; second, there are different polymerization kinetic in different phase resulted from phase separation process; third, even in the same phase or droplet, there would exist versatile agglomeration and concomitant process.[25] All of above mentioned heterogeneity would lead to

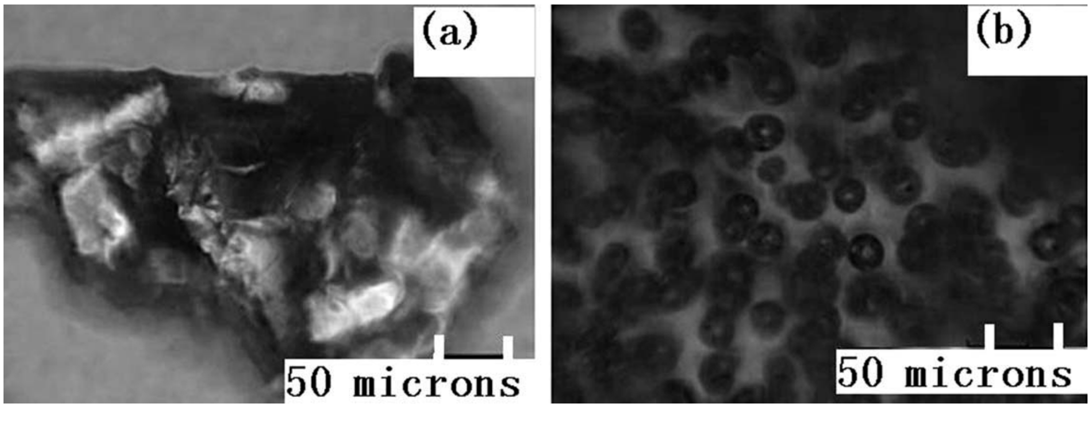

Figure 3 Morphology of the production photopolymerized: (a) in liquid CO2; (b) in scCO2.

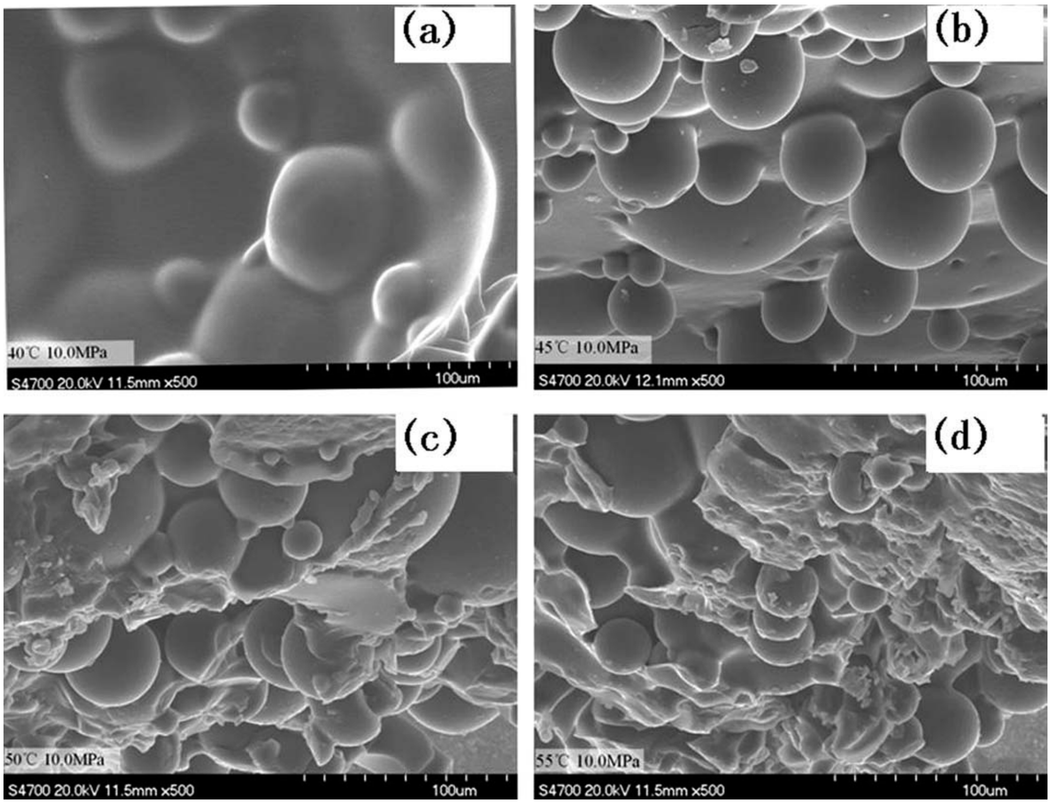

Figure 4 SEM photographs of poly-(PEG600DA) particles photopolymerized with various temperature: (a) 40°C, (b) 45°C, (c) 50°C, (d) 55°C.

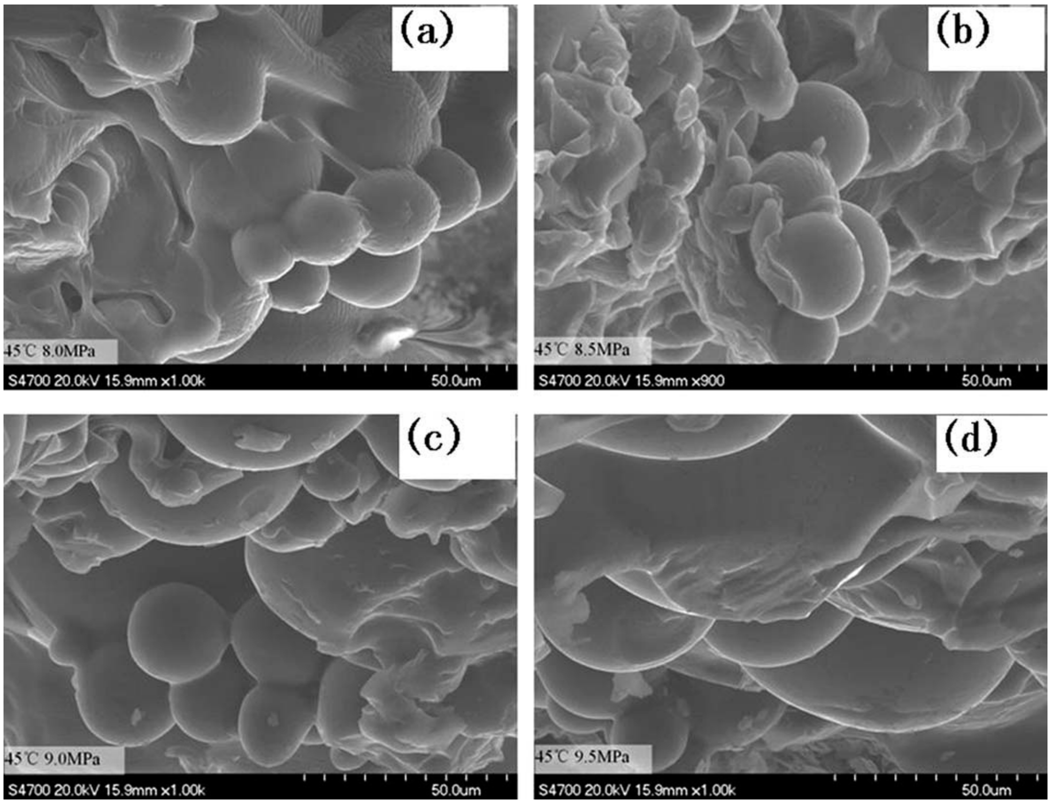

Figure 5 SEM photographs of poly-(PEG600DA) particles photopolymerized with various pressure: (a) 8.0 MPa, (b) 8.5 MPa, (c) 9.0 MPa, (d) 9.5 MPa.

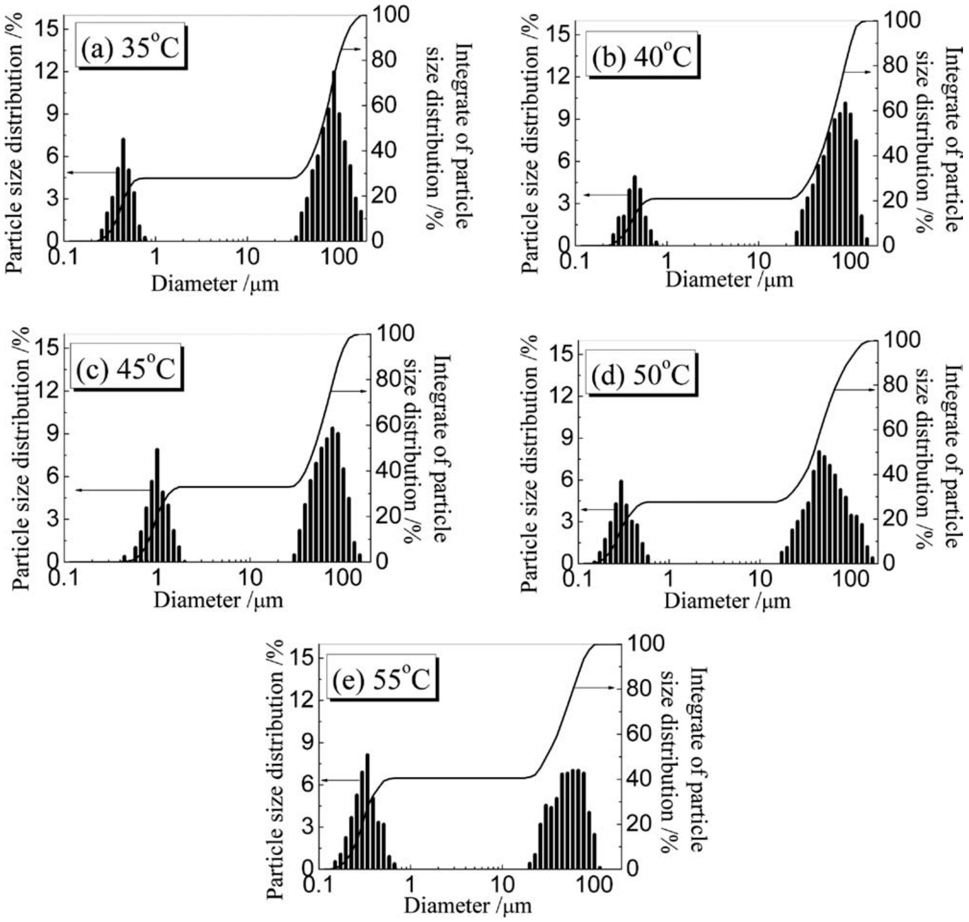

Figure 6 Particle size distribution for poly-(PEG600DA) particles photopolymerized at 10.0MPa and (a) 35°C, (b) 40°C, (c) 45°C, (d) 50°C, (e) 55°C. The bars represent particle size distribution. The line represents the integration of particle size distribution.

the forming of different diameter particle. But the relationship between the particle diameter and these reasons would worth of further exploration.

To discern the effect of the operating conditions, the relationship between the average diameters of poly-(PEG600DA) particles and temperature as well as pressure was studied. The particles size decreased by both increasing temperature and decreasing pressure, which decreased the density of scCO$_2$ and then led to poorer solubility of scCO$_2$.

CONCLUSIONS

Photopolymerization proceeded effectively in homogeneous mist when solutions of methylene chloride, PEG600DA, and TPO or DMPA simultaneously sprayed into scCO$_2$ and exposed to UV light at the same time. Using multifunctional monomer PEG600DA, the highly cross-linked microparticle with a consistent spherical morphology and a bimodal size distribution could be acquired. Depending upon the temperature and pressure, various particle morphologies could be achievable.

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