ELSEVIER

Polymer 43 (2002) 6653–6659

polymer

www.elsevier.com/locate/polymer

Preparation of cross-linked microparticles of poly(glycidyl methacrylate) by dispersion polymerization of glycidyl methacrylate using a PDMS macromonomer as stabilizer in supercritical carbon dioxide

Wenxin Wang[a], Rhiannon M.T. Griffiths[a], Andrew Naylor[a], Matthew R. Giles[a], Derek J. Irvine[b], Steven M. Howdle[a,*]

[a]School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK
[b]Uniqema R&D Department, The Wilton Research Centre, P.O. Box 90, Middlesbrough, Cleveland TS90 8JE, UK

Received 4 April 2002; received in revised form 29 July 2002; accepted 11 August 2002

Abstract

This paper describes the dispersion polymerization of glycidyl methacrylate (GMA) employing poly(dimethylsiloxane) monomethacrylate as the stabilizer in supercritical carbon dioxide. Under the optimized conditions fine free flowing powder of discrete and cross-linked micropolymer particles are produced with high monomer conversion during a very short reaction time (<4 h). The application of a power compensation calorimetry method to monitor the dispersion polymerization of GMA demonstrates a surprisingly short reaction time and clearly shows the progress of polymerization of GMA in supercritical carbon dioxide. The effects of reaction pressure and initial concentration of the initiator and stabilizer on the morphology of the final product were studied herein. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glycidyl methacrylate; Supercritical carbon dioxide; Dispersion polymerization

1. Introduction

Poly(glycidyl methacrylate) has been found to be effective for macromolecular drug carriers, immobilized enzymes and as a reagent for peptide synthesis [1]. These many applications require the poly(glycidyl methacrylate) material to be very pure and free from residual solvent. This purification stage for the polymers is often energy intensive and therefore expensive. One possible solution to this problem is to use supercritical carbon dioxide as the reaction medium. The carbon dioxide can be simply removed from the polymer at the end of the reaction by reducing the pressure.

The use of supercritical carbon dioxide as a reaction medium and in particular for polymerization has shown rapid growth in recent years [2,3]. DeSimone et al. [4] have demonstrated that methyl methacrylate (MMA) undergoes a dispersion polymerization in supercritical carbon dioxide utilizing homopolymeric stabilizers, e.g. poly(1,1 dihydroperfluorooctyl acrylate) [PFOA] or block co-polymer stabilizers where the soluble section is either poly(dimethylsiloxane) [PDMS] or [PFOA] [5,6]. By contrast, Lepilleur and Beckman [7] have synthesized a series of graft co-polymers, poly(methylmethacrylate-*co*-hydroxyethylmethacrylate)-*g*-poly(perfluoropropyloxide), which are also effective stabilizers for the dispersion polymerization of MMA in $scCO_2$. An alternative approach is the use of siloxane-based macromonomers [PDMS-Ma] for the dispersion polymerization in $scCO_2$ [8–12]. Macromonomers are oligomers or polymers with a polymerizable terminal functional group, which are commonly used for the formation of graft co-polymers in situ.

Recently, the dispersion polymerization of GMA in supercritical carbon dioxide has been reported by Otake et al. [13] using poly(heptadecafluorodecyl methacrylate) as the stabilizer. Shiho and DeSimone [14] also reported the dispersion polymerization of GMA employing PFOA and PS-*b*-PFOA as the stabilizer in supercritical carbon dioxide. However, the reaction time for the polymerization of GMA in both cases was very long (20 h). In this paper, we report

---

* Corresponding author. Tel.: +44-115-951-3486; fax: +44-115-951-3058.

E-mail address: steve.howdle@nottingham.ac.uk (S.M. Howdle).

PII: S0032-3861(02)00579-7

the successful dispersion polymerization of GMA in supercritical carbon dioxide using a simple commercially available poly(dimethylsiloxane) monomethacrylate [PDMS-Ma] as the stabilizer. Under the optimized conditions discrete polymer particles are produced with high monomer conversion during a very short reaction time (<4 h). The influence of reaction pressure and initial concentrations of the initiator, stabilizer and the reaction pressure have been investigated.

2. Experimental

2.1. Materials

The PDMS macromonomer, ($M_n \sim 10{,}000$) and glycidyl methacrylate supplied by Aldrich were used as received. Initiator 2,2′-azobis(isobutyronitrile) (Fluka) was purified through recrystallization with THF. High purity carbon dioxide (BOC Gases, SFC Grade) were used as received as well.

2.2. Polymerization

Polymerizations were performed in a 60 ml stainless steel autoclave fitted with a magnetically coupled overhead stirrer with a simple 'paddle' blade (NWA GmbH) and motorized driver (RW20, Janke and Kunkel) controlled at 300 rpm. The cell was modified with an internal heater and a thermocouple was inserted directly into the fluid through a ferrule sealed inlet, which provided an accurate temperature measurement of the reaction fluid. The temperature and heater power level was controlled using the HEL automate™ electronics and software. In a typical polymerization, the autoclave was charged with reactants and then pressurized to ca. 3000 psi with high grade N_2. This procedure was designed to leak test the equipment and to degas the reaction system. Following careful release of the N_2, the autoclave was filled with CO_2, stirred and heated to the preset temperature using a preheated thermocouple controlled oil bath. The internal heater was then turned on. Once the desired reaction temperature was reached, the desired working pressure was attained with additional CO_2 as required and the reaction was allowed to proceed with stirring for a certain time. All experimental data such as reaction pressure, reaction temperature, power and stirrer current were automatically recorded by the computer. To quantify the reaction yield, the reaction cell was rinsed with dichloromethane to remove any residual polymer product and stabilizer. The monomer conversion was measured gravimetrically.

2.3. Polymer characterization

Molecular weight data were obtained by gel permeation chromatography with chloroform as the solvent at 30 °C using Plgel 5 μm Mixed-D columns (Polymer Laboratories) and fitted with an evaporative light scattering detector. Calibration was accomplished with PMMA narrow standards (Polymer Laboratories). Both the sample analysis and the calibration were conducted at a flow rate of 1 ml min^{-1}. Scanning electron microscopy (SEM) data were collected using a JEOL 6400 SEM. Samples were mounted on an aluminium stub using an adhesive carbon tab and were gold coated.

3. Results and discussion

3.1. The polymerization of glycidyl methacrylate in $scCO_2$

Previously we have demonstrated that power compensation calorimetry can be used to monitor the dispersion polymerization of MMA in $scCO_2$ [15]. The experimental results have proved that the calorimetric method leads to a good understanding of the polymerization process. The polymerizations of glycidyl methacrylate in $scCO_2$ were also analysed using this method. The polymerizations were performed in $scCO_2$ at 65 °C. The heater jacket was set to 55 °C, and the remaining 10 °C required to obtain the reaction temperature was supplied by the internal heater cartridge. The calorimetric power trace (Fig. 1) clearly shows the progress of the reaction at a monomer content of 10 g glycidyl methacrylate in the presence of initiator (1% AIBN) and PDMS macromonomer stabilizer (5% (w/w w.r.t. monomer)).

When the reaction mixture reached the desired reaction temperature at 65 °C, the polymerization reaction started and the polymerization rate accelerated as shown by the decrease in heating power. At this point, the power to the heater is automatically reduced to compensate for the temperature rise caused by the exotherm of reaction. As the reaction proceeds more heat is generated by the exothermic nature of the reaction, and the heater power is correspondingly reduced to maintain the reaction temperature at 65 °C for approximately 40 min. It is thought that the polymerization rate is very fast and the gel effect occurs during this period. After this process most of the monomer is consumed and the reaction slows corresponding to a gradual diminution in the residual monomer. The reaction temperature starts to fall as the polymerization reaction is no longer generating so much heat, and the power to the internal compensating heater now begins to increase to maintain the fluid at 65 °C (arrow 1). After another approximately 40 min, monomer in the reaction system is almost consumed and the reaction stops (arrow 2). The heat losses for the system are now equal to the power input and the power to the heater remains constant. This polymerization process in $scCO_2$, which can be drawn from the profile of the calorimetry data, is similar to that observed in the dispersion polymerization of MMA in $scCO_2$ [15]. Furthermore, this calorimetric profile demonstrates a rapid

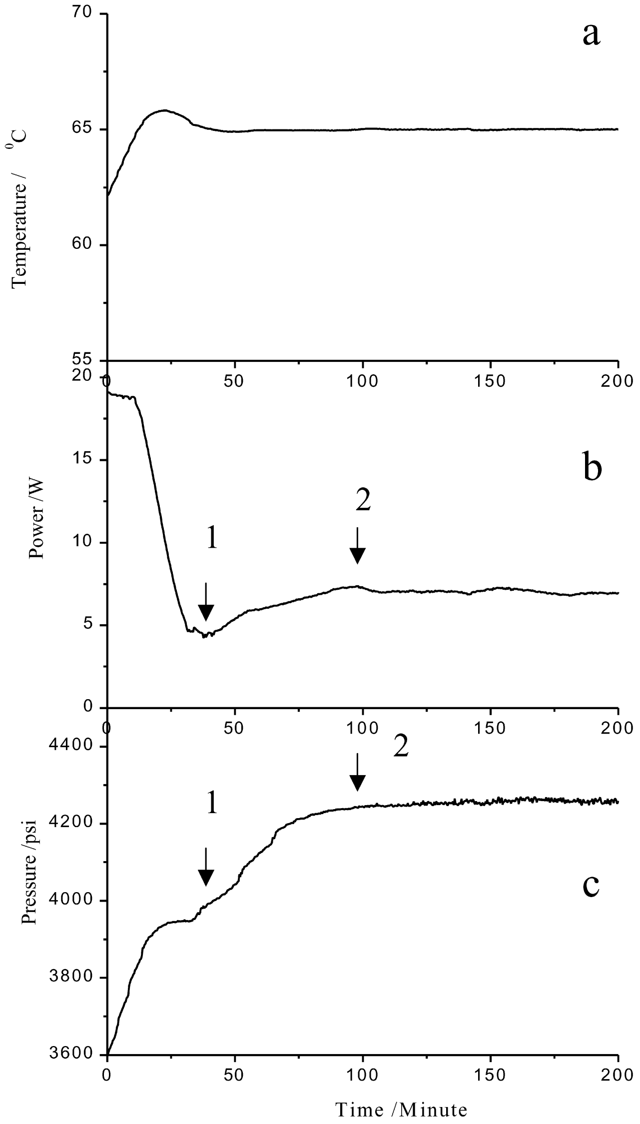


Fig. 1. Power compensation calorimetry traces for polymerization of glycidyl methacrylate in $scCO_2$ (reaction conditions: 10 g of GMA, 65 °C, 0.5 g of stabilizer, 0.1 g of initiator). The temperature curve (a) demonstrates the attainment of thermal equilibrium in the system after an initial equilibration period. The heater power trace (b) shows clearly the onset of polymerization, the point at which the exotherm begins to 'tail off' and the end of reaction at which the internal heater provides a constant power. These points are mirrored by the changes in the system pressure (c).

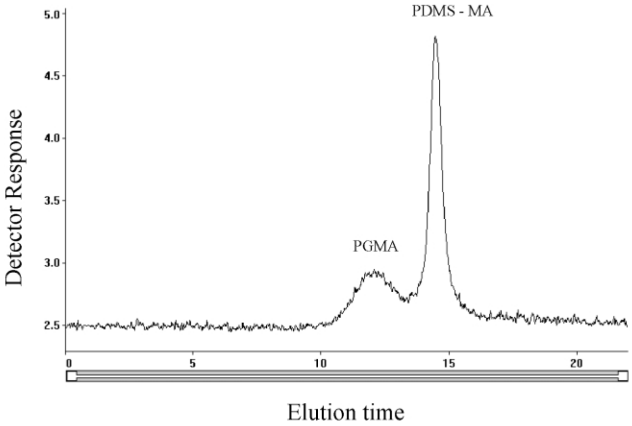


Fig. 2. GPC spectrum of the small quantity of linear PGMA. The gel fraction of the product is ca. 97% reflecting significant cross-linking.

polymerization rate of glycidyl methacrylate in $scCO_2$. This is quite different from the previously reported results [13,14, 16] for the dispersion polymerization both in $scCO_2$ and common organic solvents. The polymerization of glycidyl methacrylate at 65 °C in $scCO_2$ was reported by Shiho and DeSimone [14] to require 20 h to achieve a high monomer conversion. Similarly, the dispersion polymerization of glycidyl methacrylate at 70 °C in the mixture solution of toluene and ethanol reported by Zhao et al. [16] required 24 h to achieve a high monomer conversion. In our case both the calorimetry profile and the final monomer conversion calculated by the gravimetric method prove that using PDMS-Ma as stabilizer a much fast polymerization rate is obtained for the glycidyl methacrylate in $scCO_2$.

Through monitoring the reaction pressure during the polymerization, it can also be seen that the trend in heater power conforms to the changing trend of reaction pressure. When the heater power starts to decrease, the reaction pressure correspondingly increases. At the point when the heater power changes from decreasing to an increasing trend, the reaction pressure also suddenly changes (arrow 1). Both curves begin to become constant at the same time. This result further demonstrates the calorimetry studies. From the profiles of power and reaction pressure, useful information about polymerization can be obtained.

In addition, we have found that cross-linked microparticles are produced in our experiments. GPC results clearly show that most of polymer synthesized by this method is cross-linked and only a small proportion of polymer remains in a linear state. Under normal reaction conditions (10 g of GMA, 65 °C, 0.5 g of stabilizer, 0.1 g of initiator) we find that ca. 97% of product is cross-linked (Fig. 2). According to previous research [16] cross-linked poly(GMA) particles normally require addition of coupling agent during the polymerization. In our synthesis, no such reagent is necessary and we propose that the ring opening reaction of the epoxide might be initiated through a cationic mechanism in the side chain of glycidyl methacrylate. This could be caused by the in situ formation of carbonic acid, formed by CO_2 reacting with the trace water in the reaction system. Further research to control this reaction in order to adjust the degree of cross-linking inside the particles is in progress.

3.2. *Effect of initiator concentration*

The dispersion polymerizations were conducted at three different concentrations of initiator (Table 1). In all cases, the contents of PDMS-Ma stabilizer and monomer added to the system were kept constant at 10% (w/w w.r.t. monomer) and 10 g, respectively. Fig. 3 shows the scanning electron

Table 1
Effect of the initiator concentration on the dispersion polymerization of GMA in CO_2

Entry	Initiator concentration (%w/w w.r.t. monomer)	Yield[a] (%)	Dn[b] (μm)	Morphology of the final product
1	0.33	91	2.0	Partially aggregated particles
2	1	93	2.0	Partially aggregated particles
3	1.5	90	1.8	Highly aggregated particles

Reaction conditions: 10 g of GMA, 4000 psi, 65 °C, 4 h; 1.0 g of stabilizer.
[a] Yields were determined gravimetrically.
[b] Dn, mean diameter of the primary particles.

micrograph of the poly(GMA) obtained from these reactions. The diameter of the primary particles is effectively constant when the initiator concentration decreased from 1.5 to 0.33%. Others have reported that a change in the initiator concentration can influence the particle size and particle size distribution in various ways. Sudol [17] reported that in a typical dispersion polymerization using an organic solvent as the continuous phase, increasing the initiator concentration increases the particle size.

3.3. Effect of stabilizer concentration

As shown in Table 2, the primary particle size was affected significantly by the concentration of the stabilizer. The primary particles, though retaining narrow particle size distributions, showed an increase in diameter from 2.0 to 5.5 μm when the concentration of PDMS-Ma stabilizer decreased from 10 to 2% (w/w w.r.t. monomer) (Fig. 4). At very high concentrations, i.e. 15% stabilizer concentration, a highly aggregated final product is obtained.

In the presence of PDMS-Ma, the oligomeric poly(GMA) radicals will rapidly adsorb the stabilizer prior to aggregation with other particles. As the stabilizer concentration increases, there will be an increase in the number of stable nuclei, so correspondingly smaller particles are produced. However, at high stabilizer concentration the smaller particles are unstable and more liable to aggregate. The trend is apparent in Fig. 4, where high concentration of stabilizer leads to flocculation (Fig. 4(a)), whereas at low concentration of stabilizer (Fig. 4(c)) discrete particle formation is observed. We have ascribed this to the weak stabilizing effect of PDMS-Ma that is apparent when most monomer is consumed and the co-solvent effect disappears. Additionally, the PDMS-Ma might act as a chain transfer agent. This leads to formation of lower molecular weight oligomers through chain transfer of the growing poly(GMA) to the acrylate terminus of the stabilizer. This does not favour the formation of nuclei and decreases the stability of particles [8,9]. The combination of these two factors results in the more flocculated final product under the higher stabilizer concentration.

It is known that cross-linking can have a strong effect on particle agglomeration and colloidal stability. Cooper et al. [18] have previously reported that microspheres of poly(divinylbenzene) can be formed in the absence of added stabilizer by polymerization in $scCO_2$. Our experiments have demonstrated formation of cross-linked microparticles of poly(GMA). So we attempted the polymerization of GMA in $scCO_2$ in the absence of stabilizer. However, the polymerization rate was found to be very slow and only a very highly aggregated final product was formed. We speculate that although the cross-linking is present, the degree of cross-linking of the polymer is not high enough to prevent the particles from flocculating together.

3.4. Effect of reaction pressure

When the reaction pressure was varied from 2000 to 4200 psi (at 65 °C) there was a dramatic change in the final product morphology (Table 3). This demonstrates the very important effect of varying the density of the continuous phase; a unique property of supercritical fluids (at 65 °C, 2000 psi: 0.49 g/ml versus 4200 psi: 0.80 g/ml). By observing the reaction system in a view cell autoclave, we noted that a heterogeneous reaction system was initially present at the lower pressure 2000 psi, and with vigorous stirring this formed an unstable emulsion. At the higher density, the monomer

Table 2
Effect of the stabilizer concentration on the dispersion polymerization of GMA in CO_2

Entry	Stabilizer concentration (%w/w w.r.t. monomer)	Yield[a] (%)	Dn[b] (μm)	Morphology of the final product
1	15	91	–	Highly aggregated particles
2	10	93	2.0	Partially aggregated particles
3	5	92	4.0	Partially aggregated particles
4	2	90	5.5	Slightly aggregated particles

Reaction conditions: 10 g of GMA, 4000 psi, 65 °C, 4 h; 0.1 g of initiator.
[a] Yields were determined gravimetrically.
[b] Dn, mean diameter of the primary particles.

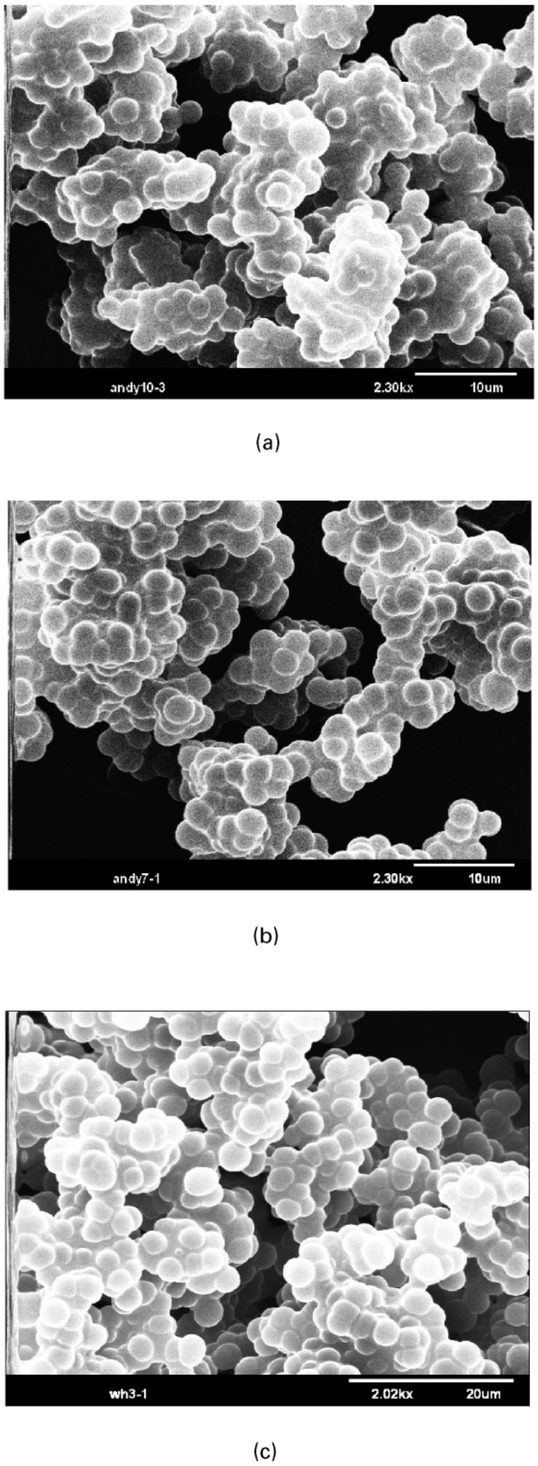


Fig. 3. SEM micrographs of PGMA produced from reactions with various initiator concentrations. (a) 1.5%, partially aggregated particles; (b) 1%, partially aggregated particles; (c) 0.33%, partially aggregated particles. (Reaction conditions: 10 g of GMA, 4000 psi, 65 °C, 4 h; 1.0 g of stabilizer.)

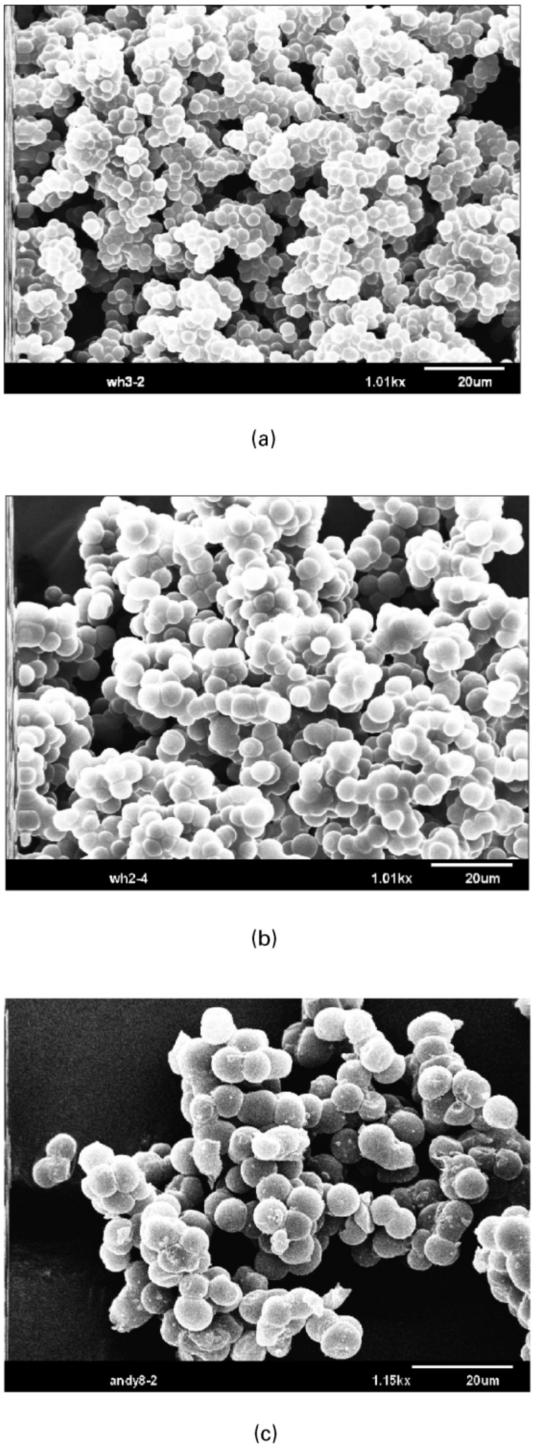


Fig. 4. SEM micrographs of PGMA produced from reactions at different stabilizer concentrations. (a) 10%, partially aggregated particles; (b) 5%, partially aggregated particles; (c) 2%, slightly aggregated particles. (Reaction conditions: 10 g of GMA, 4000 psi, 65 °C, 4 h; 0.1 g of initiator.)

and stabilizer were completely dissolved and a homogeneous solution formed. The primary particles obtained from the polymerization reaction reflect these differences. At the higher density they are slightly aggregated, but are highly coagulated at low pressure (Fig. 5). The coagulation also indicates that although the PDMS-Ma initially is a good stabilizer it was not able to effectively sterically stabilize the latex at low pressures after the monomer co-solvent effect disappeared.

Table 3
Effect of reaction pressure on the dispersion polymerization of GMA in CO_2

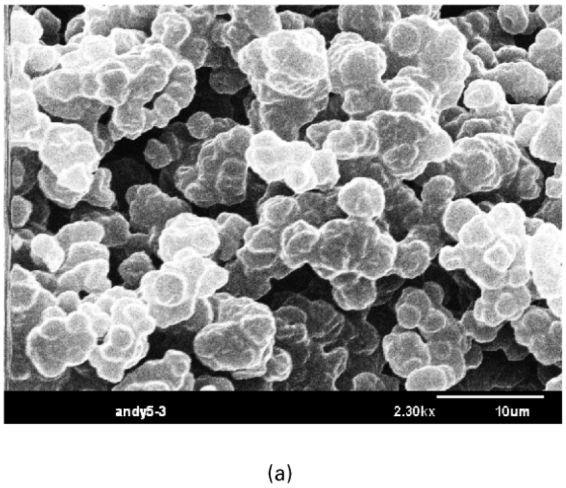
Entry	Reaction pressure (psi)	Yield[a] (%)	Dn[b] (μm)	Morphology of the final product
1	2000	89	–	Highly aggregated particles
2	4200	92	1.5	Partially aggregated particles

Reaction conditions: 10 g of GMA, 65 °C, 4 h; 1.0 g of stabilizer, 0.1 g of initiator.

[a] Yields were determined gravimetrically.

[b] Dn, mean diameter of the primary particles.

Johnston et al. [9] reported a similar experimental result for the dispersion polymerization of MMA using PDMS-Ma as the stabilizer. They found that at low pressure the inability of the poorly solvated PDMS-Ma stabilizer to impart stability to the polymerization results in precipitation polymerization. As the pressure increased, the solvency of the medium for PDMS stabilizer chains increased, and results in the more stable dispersion system in $scCO_2$.



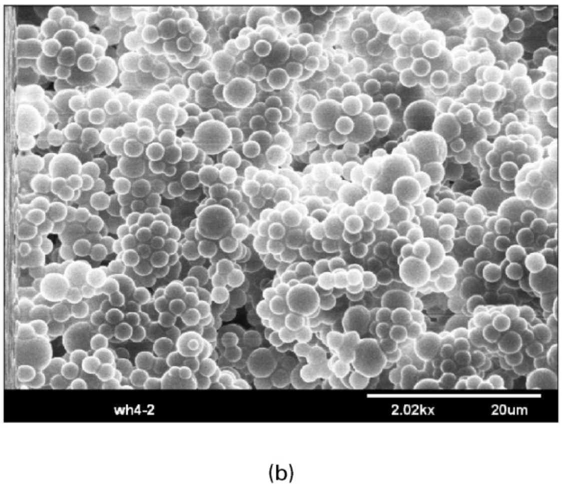


Fig. 5. SEM micrographs of PGMA produced from reactions at two different initial pressures. (a) 2000 psi, highly aggregated particles and (b) 4200 psi, partially aggregated particles. (Reaction conditions: 10 g of GMA, 65 °C, 4 h; 1.0 g of stabilizer, 0.1 g of initiator.)

4. Conclusions

This work has shown that the dispersion polymerization of GMA employing poly(dimethylsiloxane) monomethacrylate [PDMS-Ma] as the stabilizer in supercritical carbon dioxide can be achieved. Under optimized conditions discrete cross-linked polymer particles are produced with high monomer conversion during a very short reaction time (<4 h). The application of the power compensation calorimetry method to monitor the dispersion polymerization of GMA further demonstrates this result and clearly shows the polymerization process of GMA in supercritical carbon dioxide. The reaction pressure and stabilizer concentration have important effects on the final product morphology. Most importantly, nearly all the samples reported here are obtained in high yields as dry, fine, free flowing powdered material directly from the reaction vessel.

Acknowledgements

We gratefully acknowledge The University of Nottingham Institute of Materials (Unimat) the EPSRC, and Uniqema for their support. We thank also Mr A.J. Busby, Mr D. Litchfield, Mr R. Wilson, Mr K. Hind, Mr P. Fields and Mr J. Whalley for their advice and technical assistance.

References

[1] Soykan C, Ahmedzade M, CosKun M. Eur Polym J 2000;36:1667.
[2] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999;99:543.
[3] Cooper AI. J Mater Chem 2000;10:207.
[4] DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ, Combes JR. Science 1994;265:356.
[5] Canelas DA, DeSimone JM. Macromolecules 1997;30:5673.
[6] Yong TM, Hems WP, Van Nunen JLM, Holmes AB, Steinke JHG, Taylor PL, Segal JA, Griffin DA. Chem Commun 1997;1811.
[7] Lepilleur C, Beckman EJ. Macromolecules 1997;30:745.
[8] O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. Macromolecules 1998;31:2838.
[9] O'Neill ML, Yates MZ, Johnston KP, Smith CD, Wilkinson SP. Macromolecules 1998;31:2848.
[10] Shaffer KA, Jones TA, Canelas DA, DeSimone JM, Wilkinson SP. Macromolecules 1996;29:2704.
[11] Christian P, Giles MR, Howdle SM, Major RC, Hay JN. Polymer 2000;41:1251.
[12] Giles MR, Hay JN, Howdle SM, Winder RJ. Polymer 2000;41:6715.

[13] Otake K, Sako T, Sugeta T, Yoda S, Takebayashi Y, Nakazawa N, Kamizawa C. ISSAF 5, Atlanta; 2000.

[14] Shiho H, DeSimone JM. Macromolecules 2001;34:1198.

[15] Wang W, Griffiths RMT, Giles MR, Williams P, Howdle SM. European Polymer Journal. In press.

[16] Zhao Z, Yang S, Yang Y, Tian X, Su T. Acta Polym Sinica 1999;1:31.

[17] Sudol ED. In: Asua JM, editor. Polymeric dispersions: principles and applications. The Netherlands: Kluwer; 1997. p. 141–54.

[18] Cooper AI, Hems WP, Holmes AB. Macromolecules 1999;32:2156.