J Mater Sci (2008) 43:2300–2306
DOI 10.1007/s10853-007-2042-7

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Stabilizer architectures based on fluorinated random and block copolymers for the dispersion polymerization of 2-hydroxyethyl methacrylate in supercritical carbon dioxide

**Hullathy Subban Ganapathy · Ha Soo Hwang ·
Min Young Lee · Yeon Tae Jeong · Yeong-Soon Gal ·
Kwon Taek Lim**

Received: 15 November 2006 / Accepted: 20 July 2007 / Published online: 4 October 2007

Abstract Different types of stabilizers architectures based on copolymers composed of hydrophilic components and CO_2-philic fluorinated acrylate groups were investigated for the free radical dispersion polymerization of 2-hydroxyethyl methacrylate (HEMA) at 65 °C in supercritical carbon dioxide ($scCO_2$). Four categories of random and block copolymeric stabilizers consisting of 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (FOMA), oligo(ethylene glycol) methacrylate (OEGMA), dimethyl amino ethyl methacrylate (DMAEMA), and ethylene oxide (EO) were selected as stabilizers for HEMA. The effect of the stabilizer architecture on the polymerization results was investigated in terms of stabilizer concentration, the nature of the hydrophilic anchor groups, and block versus random copolymers. White free-flowing poly(HEMA) powders in high yield were obtained with all stabilizers. While the monomer conversion was independent, the morphology of particles was found to be considerably affected by the nature of the stabilizers.

Introduction

Polymers based on 2-hydroxyethyl methacrylate (HEMA) are important materials used extensively in wide range of both industrial and biomedical applications. Because of their excellent biocompatibility, molecularly engineered hydrogels based on poly(HEMA) homopolymer have been potential carriers in drug delivery, dental, ophthalmic, and neural tissue engineering applications [1–3]. Additionally, microspheres prepared from copolymers of poly(HEMA) could be useful in the immobilization of several enzymes, and also in the isolation of genomic DNA [4, 5]. In many of these applications, however, extremely pure materials are required, particularly in the case of biomedical applications. Traditionally, these materials have been synthesized in water or water/organic solvent mixtures. Thus, the final product requires a considerable purification which is time consuming and needs multistage processing, involving the evaporation of a large volume of liquid. It is, in other words, often energy intensive process and therefore becomes expensive. An intense research activity concentrated in the last decade has demonstrated that supercritical carbon dioxide ($scCO_2$) could be used as an attractive alternative replacement for the aqueous and organic solvents because it is inexpensive, nontoxic, nonflammable, and environmentally benign [6–8]. Moreover, CO_2 separates products from polymerization by the simple depressurization of system, leading to a clean and dry product and thus could reduce a large amount of cost for the product recovery at industrial scale. Due to the solubility of wide range of monomers and insolubility of most polymers in $scCO_2$, a majority of work in heterogeneous radical polymerizations have been focused on dispersion polymerizations. Desimone et al. reported the first dispersion polymerization of methyl methacrylate (MMA) in $scCO_2$ using a highly soluble amorphous fluorinated polymer [poly (dihydroperfluorooctyl acrylate)] as a stabilizer [9]. Since then, a number of other stabilizers based on block, graft, and random copolymers have been developed and extensively studied mostly for

H. S. Ganapathy · H. S. Hwang · M. Y. Lee ·
Y. T. Jeong · K. T. Lim (✉)
Pukyong National University, Busan 608-739, Korea
e-mail: ktlim@pknu.ac.kr

Y.-S. Gal
Kyung Il University, Gyeongsang buk-do 712-701, Korea

the dispersion polymerization of MMA [8]. On the other hand, only very few articles have appeared for the dispersion polymerization of HEMA in $scCO_2$ media [10–12]. Prior to this report, two different diblock copolymers, polystyrene-*b*-poly(1,1-dihydroperfluorooctyl acrylate) and poly(ethylene oxide)-*b*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (poly(EO-*b*-THFDA)) have been used as stabilizers for the dispersion polymerization of HEMA in $scCO_2$ [10, 11]. A random copolymer composed of 1,1-dihydroperfluorooctyl acrylate and 3-*O*-methacryloyl-D-glucopyranose was also investigated, recently [12]. The objective of this work is to design several other stabilizer architectures based on fluorinated copolymers containing hydrophilic components and investigate them as potential stabilizers in the dispersion polymerization of HEMA in $scCO_2$. Four categories of random and block copolymer composed of 1*H*,1*H*,2*H*,2*H*–perfluorooctyl methacrylate(FOMA) (as CO_2-philic) and hydrophilic groups such as oligoethylene glycol methacrylate (OEGMA), dimethyl amino ethyl methacrylate (DMAEMA), ethylene oxide (EO) [poly(OEGMA-*co*-FOMA), poly(DMAEMA-*co*-FOMA), poly(DMAEMA-*b*-FOMA), and poly(EO-*b*-FOMA)] were expected to be appropriate stabilizers for the polar vinyl monomer, HEMA. The effect of stabilizer structures such as block versus random, the concentration of the stabilizers, and the nature of the hydrophilic anchor groups on the polymerization results was investigated in terms of the yield and morphology of poly(HEMA).

Experimental part

Materials

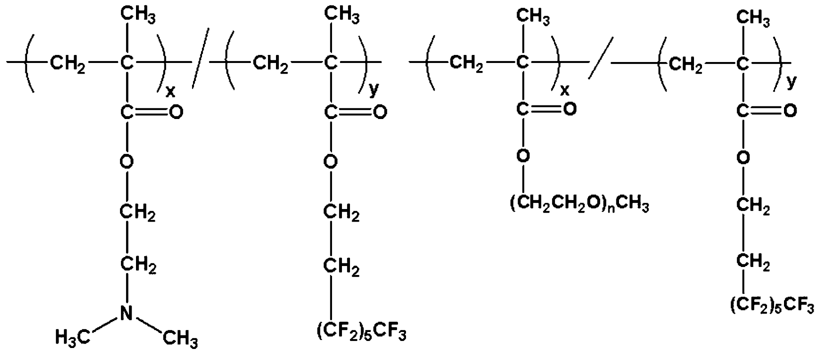
2-Hydroxyethyl methacrylate (HEMA, Aldrich), DMAEMA (Aldrich), OEGMA ($M_n = 300$; Aldrich), FOMA (SynQuest), ethyl 2-bromoisobutyrate (Aldrich) were stored over CaH_2 and then vacuum distilled before use. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) was purified by recrystallization from methanol. Trifluorotoluene (TFT) and benzene were distilled over CaH_2. Copper (I) bromide (Aldrich), 2,2′-bipyridine (bipy) (Aldrich), trichlorofluoromethane ($CFCl_3$) (Aldrich), and research grade CO_2 (Daeyoung Co., Korea, 99.99%) was used as received.

Preparation of copolymeric stabilizers

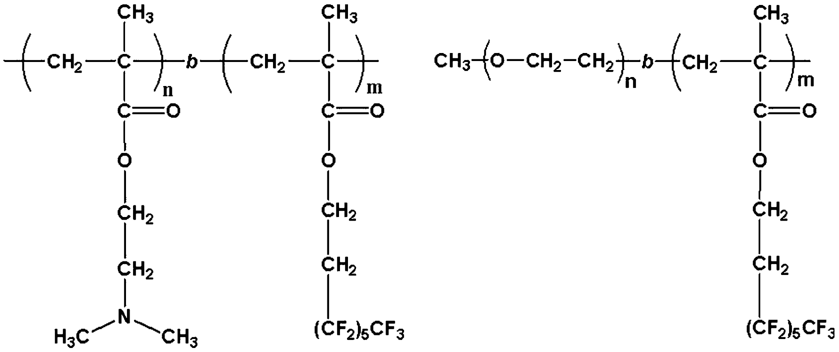
The copolymeric stabilizers selected for the investigation of dispersion polymerization of HEMA in $scCO_2$ are shown in Fig. 1. The random copolymers, poly(OEGMA(300)-*co*-FOMA) (1.8K/6.0K by ^1H NMR) and poly(DMAEMA-*co*-FOMA) (0.8K/4.2K by GPC) were synthesized via atom transfer radical polymerization (ATRP) using ethyl-2-bromoisobutyrate as the initiator and bipy/CuCl as the catalytic system [13]. For poly(OEGMA-*co*-FOMA) (1.8K/6.0K), 0.72 g (2.39 mmol) of OEGMA and 2.36 g (5.46 mmol) of FOMA were copolymerized in the presence of 0.14 g (0.70 mmol) of ethyl 2-bromoisobutyrate, 0.10 g (0.70 mmol) of CuBr, and 0.48 g (2.10 mmol) of bipy in the mixed solvent of TFT (1.5 g) and benzene (1.5 g). The reaction proceeded for 8 h at 110 °C under argon atmosphere. In the case of poly(DMAEMA-*co*-FOMA) (0.8K/4.2K), 0.27 g (1.72 mmol) of DMAEMA and 1.63 g (3.77 mmol) of FOMA were used in the same reaction condition as poly(OEGMA-*co*-FOMA). The ratio of monomers incorporated in copolymeric stabilizers was determined by ^1H NMR spectra (JEOL-400). The polydispersity of poly(DMAEMA-*co*-FOMA) and poly(OEGMA-*co*-FOMA) were determined to be 1.26 and 1.19, respectively, by GPC. The block copolymer poly(EO-*b*-FOMA) (2K/20K by ^1H NMR) was prepared by ATRP of FOMA with PEO macroinitiator and characterized according to our earlier reports [14]. The synthesis of poly(DMAEMA-*b*-FOMA) (4.3K/5.3K by ^1H NMR) by group transfer polymerization has been reported previously [15].

Dispersion polymerization of HEMA in $scCO_2$

The experimental set up and apparatus used for the dispersion polymerizations in $scCO_2$ consists of a high-pressure stainless steel reactor equipped with a sapphire quartz window and a high-pressure syringe pump (ISCO model 260D) for pressurizing the carbon dioxide. Heating was provided by a water bath and the temperature was measured with a thermocouple (Doric Trendicator 400A). The water bath was controlled with a temperature controller (Jisico model J-IVW8, Korea). Polymerizations were conducted in a 10 mL high-pressure cell. In a typical experiment, 0.4 g of HEMA (15 w/v % in CO_2), a desired amount of copolymeric stabilizer (2–20 w/w % of monomer), 0.004 g of AIBN (1 w/w % of monomer), and a Teflon-coated stir bar were put into the view cell reactor. The reactor was then pressurized by ISCO syringe pump containing compressed CO_2 at a pressure of 70 bar and the cell was immersed in a water bath. As the reactor was heated to 65 °C, the remaining CO_2 was added into the reaction mixture until the desired pressure of 345 bar (5000 psi) was reached. Then, the reactor was sealed and the polymerization was allowed to continue with stirring for 20 h. After polymerization, the reactor was cooled in an ice water bath and residual HEMA was extracted with ~20 mL of liquid CO_2 at 138 bar and at ambient temperature. At the end of extraction, the remaining CO_2 was slowly vented out and the polymer product was collected



poly(DMAEMA-*co*-FOMA) poly(OEGMA-*co*-FOMA)



poly(DMAEMA-*b*-FOMA) poly(EO-*b*-FOMA)

Fig. 1 Stabilizer architectures based on fluorinated random and block copolymers investigated for the dispersion polymerization of HEMA in $scCO_2$

and weighed. The monomer conversion was measured gravimetrically and the morphology of the poly(HEMA) particles were analyzed by a Hitachi S-2400 scanning electron microscope. The mean particle diameter D_n and polydispersity index D_w/D_n were determined by measuring 100–150 particles in pictures obtained by SEM.

Results and discussion

Dispersion polymerization of HEMA in $scCO_2$ in the presence of random copolymers

The random copolymers, poly(DMAEMA-*co*-FOMA) and poly(OEGMA(300)-*co*-FOMA) were selected for this study based on their efficient performance as successful stabilizers demonstrated previously for the dispersion polymerization of MMA in $scCO_2$ [16, 17]. Thus, it was hypothesized that the hydrophilic components of the copolymers, OEGMA and DMAEMA, could act as effective anchoring groups and were expected to stabilize the dispersions of polar vinyl monomer, HEMA in CO_2. Because of the high FOMA content, both of the copolymers were highly soluble in $scCO_2$. Under the initial experimental conditions (15 w/v % HEMA, $T = 65$ °C, $P = 345$ bar), the starting reaction medium was clear and homogeneous for all stabilizers. Then, the polymerization solution became slightly dull and opalescent within 5–10 min after reaching the reaction conditions, indicating the nucleation of small particles. Observation made through the view cell confirmed that white latexes formed after 15–20 min of reaction which remained stable all along the particle growth regime. At the end of the reaction white powders were finally obtained after venting CO_2 from the reactor.

The results from dispersion polymerizations with the random copolymeric stabilizers are summarized in Table 1. Polymerizations were carried out in the presence of poly(DMAEMA-*co*-FOMA) (0.8K/4.2K) with the stabilizer concentrations varying from 20 w/w % to 2 w/w % (with respect to the monomer) and the HEMA concentration of 10 and 20% (w/v to CO_2). The polymer products retrieved from the cell were in the form of a free-flowing powder in high yield for all cases independent of the stabilizer concentration (see entry 2–6 in Table 1). Representative SEM pictures for the morphology of poly(HEMA) particles are shown in Fig. 2. Though, all the particles are not in spherical shape, almost discrete polymer particles in the size range of 0.7–1.8 μm were obtained even at 2 wt.% stabilizer concentrations without severe aggregation (see Fig. 2a). However, with reducing HEMA concentration to 10 wt.%, the polymerization resulted in

Table 1 Data for the dispersion polymerizations of HEMA in $scCO_2$ with random copolymeric stabilizers[a]

Entry	Stabilizer[a]	Stab. conc.[b] (wt.%)	HEMA conc. (w/v % of CO_2)	Yield[c] (%)	D_n^d (μm)	Morphology
1	None	0	15	85	–	Aggregated
2	A	2	15	91	1.8	Fine powder
3	A	5	15	93	1.0	Fine powder
4	A	5	10	92	1.6	Fine powder
5	A	10	10	93	0.9	Fine Powder
6	A	20	10	94	0.7	Fine powder
7	B	2.5	15	92	1.2	Fine powder
8	B	5	10	94	Granular	Fine powder
9	B	10	10	95	Granular	Fine powder
10	B	20	10	96	0.8	Fine powder

[a] A: poly(DMAEMA-*co*-FOMA) (0.8K/4.2K), B: poly(OEGMA(300)-*co*-PFOMA) (1.8K/6.0K)

[b] Reaction conditions: 1 wt.% of AIBN (w/w % to HEMA), 345 bar, 65 °C, and 20 h

[c] Yields were determined gravimetrically

[d] D_n = Mean particle diameter

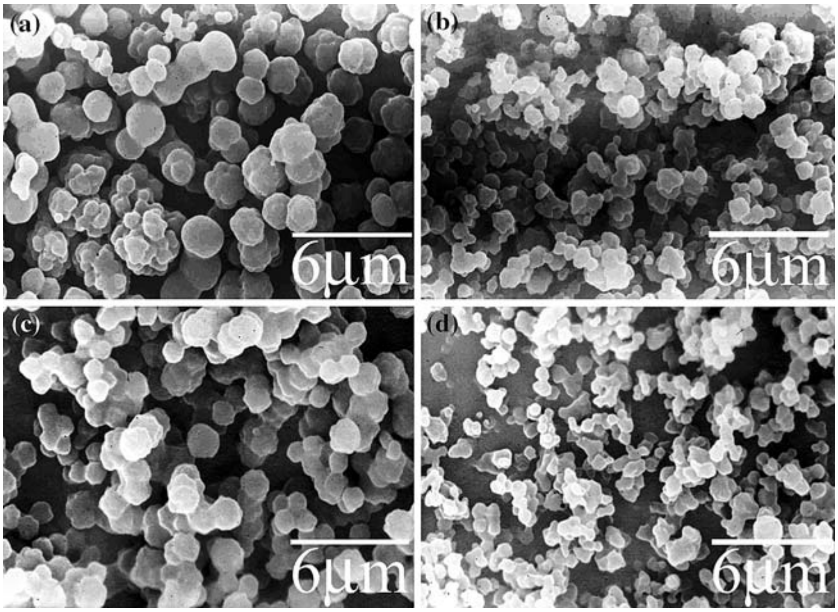


Fig. 2 Scanning electron micrographs of poly(HEMA) particles prepared with various concentrations (w/w to monomer) of the random copolymeric stabilizers, poly(DMAEMA-*co*-FOMA) (0.8K/4.2K): (**a**) 2% and (b) 5% (with 15 w/v % HEMA in CO_2); (**c**) 10% and (d) 20% (with 10 w/v % of HEMA in CO_2)

the aggregation of particles. As a common phenomenon in dispersion polymerizations, the particle size was found to decrease with an increase in the stabilizer concentration. On the other hand, the precipitation polymerization of HEMA that was conducted in the absence of copolymeric stabilizer produced a highly aggregated solid in high yield (see entry 1 in Table 1, SEM picture was not shown). The molecular weight of poly(HEMA) has not been determined because the polymer turned out to be insoluble in common organic solvents used in the size exclusion chromatography. It was suggested that the insolubility of poly(HEMA) could be possibly due to ethylene glycol dimethacrylate (EGDMA) which is known to be a common impurity of HEMA and also an efficient cross-linker even at a low concentration [18]. The slight cross-linking of the particles is most likely the reason for the poly(HEMA) obtained in high yield without the presence of any stabilizer [11]. The molecular weight data of previous studies on poly(HEMA) products obtained from the dispersion polymerization in $scCO_2$ were also not reported, presumably because of the same reason [10–12]. We have recently demonstrated that the same random copolymer, poly(DMAEMA-*co*-FOMA), with as low as 34 wt.% FOMA content is a successful dispersant which provided an abnormally large stabilization for the dispersion polymerization of MMA, leading to the formation of micron-sized spherical particles [16]. The successful stabilization effect was mainly attributed to the structural architecture and the physiochemical properties of the poly(DMAEMA-*co*-FOMA). The N-methylated branches of DMEAMA, electron rich carbonyl group with basic nitrogen, and low T_g of the polymer provided by DMAEMA combined with the low cohesive energy of FOMA were believed to be the main factors which allowed favorable interaction between the copolymer and $scCO_2$ [16]. Despite of the fact that a much higher wt.% FOMA was used in this study, the results suggest that DMAEMA in poly(DMAEMA-*co*-FOMA) (0.8K/4.2K) as an anchor-group functionality has good compatibility with HEMA, though they all are dissimilar functional groups.

The polymerizations of HEMA conducted with the another random copolymer poly(OEGMA(300)-*co*-FOMA) (1.8K/6.0K) with the stabilizer concentrations varying from 20 w/w % to 2.5 w/w % were also found to be efficient in producing free-flowing powders in high yield (see entry 7–10, Table 1). The SEM images of poly(HEMA) obtained from these polymerizations are shown in Fig. 3. Two different morphologies were observed with varying stabilizer concentration. While a low stabilizer concentration (2.5 wt.%) resulted in the formation of slightly distorted spherical particles in the size range of 0.8–1.2 μm (see Fig. 3a), at higher concentrations the particle surface became granular. Such type of particle formations with the surface granularity has been recently observed for the dispersion polymerization of HEMA and MMA in organic media [19, 20]. It was suggested that the phase separation between poly(HEMA) and the polymeric stabilizer chains could be the possible reason for the granular type of particle formation.

The effect of block copolymeric stabilizers

To elucidate further the effect of stabilizer architecture on the polymerization of HEMA in $scCO_2$, fluorinated block copolymers containing PDMAEMA and PEO as anchoring blocks were utilized in the polymerization. The results from polymerizations carried out in the presence of poly(DMAEMA-*b*-FOMA) (4.3K/5.3K) with varying stabilizer concentration (2–10 w/w % with respect to HEMA) are shown in Table 2. The polymerization conducted with 2 wt.% of the stabilizer did not provide sufficient stabilization and subsequently resulted in the formation of a foamy powder with highly flocculated morphologies (see Fig. 4a and entry 1 in Table 2). In contrast, higher stabilizer concentration (>5 wt.%) resulted in the formation of free-flowing poly(HEMA) powders with slight agglomeration which were obtained directly from the reactor at the end of the reaction. SEM images showed that spherical particles in the size range of 140–165 nm were formed (Fig. 4b).

Finally, the block copolymer containing nonacrylate anchor group functionality, poly(EO_{2K}-*b*-$FOMA_{20K}$), was investigated for the polymerization of HEMA in CO_2. Surprisingly, poly(EO-*b*-FOMA) (2K/20K) turned out to be most successful among all the stabilizers investigated in this study. Fine white polymeric powder in high yield was obtained with a stabilizer concentration of 10 wt.% (HEMA at 10 wt.%). SEM images showed that the morphology of the poly(HEMA) was in the form of spherical particles with an average diameter of 500 nm. This result was comparable to the previous study carried out by Ma et al. in which poly(EO-*b*-THFDA) (2K/21K) with same EO anchor group functionality was used for the polymerization of HEMA in CO_2 [11].

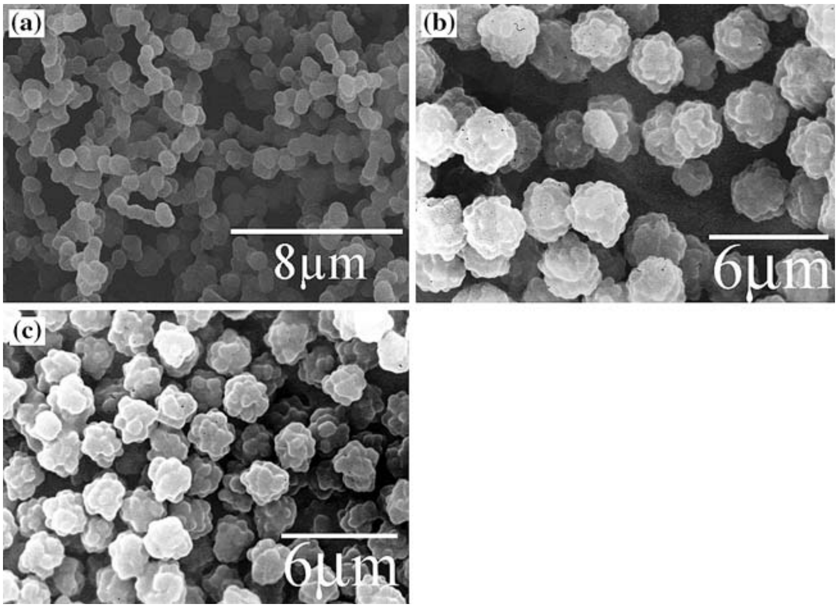


Fig. 3 Scanning electron micrographs of poly(HEMA) particles prepared with various concentrations (w/w to monomer) of the random copolymeric stabilizer, poly(OEGMA-*co*-FOMA) (1.8K/6.0K): (**a**) 2.5% (with 15 w/v % HEMA in CO_2); (**b**) 5% and (**c**) 10% (with 10 w/v % of HEMA in CO_2)

Table 2 Data for the dispersion polymerizations of HEMA in $scCO_2$ with block copolymeric stabilizers

Entry	Stabilizer[a]	Stab. conc.[b] (wt.%)	HEMA conc. (w/v % of CO_2)	Yield[c] (%)	D_n^d (nm)	Morphology
1	C	2	15	92	–	Foamy powder
2	C	5	15	90	145	Fine powder
3	C	5	10	94	160	Fine powder
4	C	10	10	92	155	Fine powder
5	D	10	10	91	500	Fine powder

[a] C: poly(DMAEMA-*b*-FOMA) (4.3K/5.3K), D: poly(EO-*b*-PFOMA) (2K/20K)

[b] Reaction conditions: 1 wt.% of AIBN (w/w % to HEMA), 345 bar, 65 °C, and 20 h

[c] Yields were determined gravimetrically

[d] D_n = Mean particle diameter

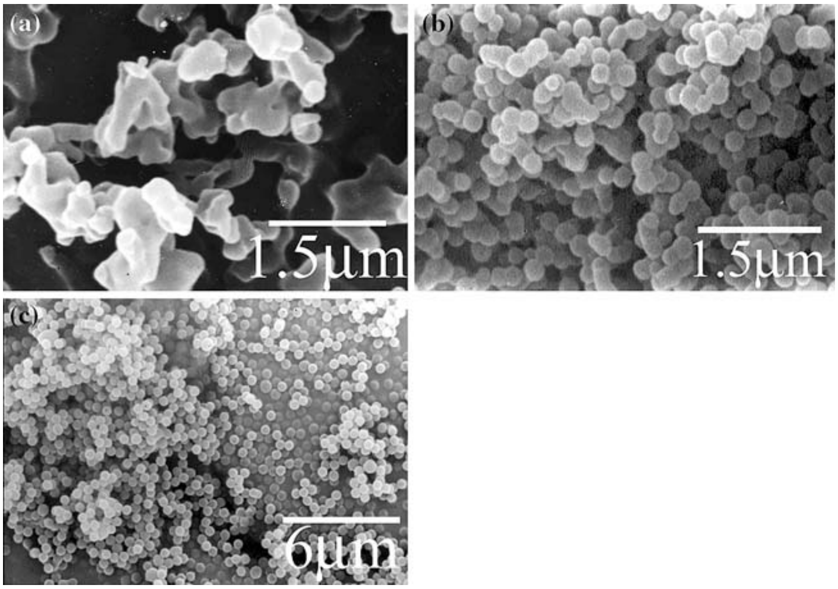


Fig. 4 Scanning electron micrographs of poly(HEMA) particles prepared with various concentrations (w/w to monomer) of the block copolymeric stabilizers: (**a**) 2.5% and (**b**) 5% of poly(DMAEMA-*b*-FOMA) (4.3K/5.3K) (with 15 w/v % HEMA in CO_2); (**c**) 10% of poly(EO-*b*-FOMA) (2K/20K) (with 10 w/v % of HEMA in CO_2)

It is notable that the random copolymeric stabilizers mostly produced micron-sized particles, whereas the block copolymeric stabilizers resulted in particles with less than 500 nm. As expected, the block copolymers might adsorb more strongly and produce smaller particle sizes than the random copolymers. Additionally, the successful stabilization of poly(EO-*b*-FOMA) (2K/20K) over poly(DMAEMA-*b*-FOMA) (4.3K/5.3K) copolymer could be attributed to the better anchor-soluble balance of former than the later.

Conclusions

Four different stabilizers architectures based on copolymers composed of hydrophilic components and CO_2-philic fluorinated acrylate groups were investigated for the dispersion polymerization of HEMA in $scCO_2$. Random copolymers poly(DMAEMA-*co*-FOMA) (0.8K/4.2K) and poly(OEGMA-*co*-FOMA) (1.8K/6.0K) and block copolymers poly(DMAEMA-*b*-FOMA) (4.3K/5.3K) and poly(EO-*b*-FOMA) (2K/20K) were utilized in this study with varying stabilizer concentrations. Free-flowing powders of poly(HEMA) were obtained in all the cases. While the random copolymeric stabilizers produced micron-sized particles, the block copolymeric stabilizers resulted in the formation of particles with less than 500 nm. In the presence of poly(EO-*b*-FOMA) (2K/20K) stabilizer, monodisperse, discrete, spherical particles were obtained, whereas particles were produced as an aggregated form with poly(DMAEMA-*b*-FOMA) (4.3K/5.3K) stabilizer.

Acknowledgement This research was supported by Ministry of Environment as “The Eco-technopia 21 project” and the second stage of BK21 Program.

References

1. Carbonetto ST, Gruver MM, Turner DC (1982) Science 216:897
2. Cadotte AJ, Demarse TB (2005) J Neural Eng 2:114
3. Abraham S, Brahim S, Ishihara K, Guiseppi-Elie A (2005) Biomaterials 26:4767

4. Yavuz H, Bayramoglu G, Kacar Y, Denizli A, Arica MY (2002) Biochem Eng J 10:1
5. Krizova J, Spanova A, Rittich B, Horak D (2005) J Chromatogr A 1064:247
6. Jessop PG, Leitner W (ed) (1999) Chemical synthesis using supercritical fluids. Wiley-VCH, Weinheim
7. Licence P, Ke J, Sokolova M, Ross SK, Poliakoff M (2003) Green Chem 5:99
8. Kendall JL, Canelas DA, Young JL, Desimone JM (1999) Chem Rev 99:543
9. Desimone JM, Maury EE, Menceloglu YZ, Mcclain JB, Romack TR, Combes JR (1994) Science 265:356
10. Shiho H, Desimone JM (2000) J Polym Sci Part A Polym Chem 38:3783
11. (a) Ma Z, Lacroix-Desmazes P (2004) Polymer 45:6789; (b) Lacroix-Desmazes P, Boutevin B (2006) Preparation of dispersed systems in liquid or supercritical carbon dioxide, 4th world emulsion congress, proceedings, 3–6 Oct 2006, Lyon (France)
12. Ye W, Desimone JM (2000) Ind Eng Chem Res 39:4564
13. Matyjaszewski K, Wang JL, Grimaud T, Shipp DA (1998) Macromolecules 31:1527
14. Lim KT, Lee MY, Moon MJ, Lee GD, Hong SS, Dickson JL, Johnston KP (2002) Polymer 43:7043
15. Hwang HS, Heo JY, Jeong YT, Jin SH, Cho D, Chang T, Lim KT (2003) Polymer 44:5153
16. Hwang HS, Gal YS, Johnston KP, Lim KT (2006) Macromol Rapid Commun 27:121
17. Hwang HS, Lee WK, Hong SS, Jin SH, Lim KT (2007) J Supercrit Fluids 39:409
18. Mikos AG, Peppas NA (1987) J Control Rel 5:53
19. Takahashi K, Miyamori S, Uyama H, Kobayashi S (1996) J Polym Sci Part A Polym Chem 34:175
20. Kobayashi S, Uyama H, Choi JH, Matsumoto Y (1993) Polym Int 30:265