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The homo and copolymerisation of 2-(dimethylamino)ethyl methacrylate in supercritical carbon dioxide

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Abstract

This paper describes the free radical dispersion homopolymerisation of 2-(dimethylamino) ethyl methacrylate (DMA) and copolymerisation of DMA with methyl methacrylate (MMA) in supercritical carbon dioxide ($scCO_2$). The polymerisations are performed in the presence of two commercially available stabilisers, poly(dimethylsiloxane) monomethacrylate macromonomer (PDMS-mma) and the carboxylic acid terminated perfluoropolyether (Krytox 157FSL). Dry, fine powdered polymer product was produced for the copolymer under optimised conditions, but only aggregated solid is formed for homo poly(DMA). The effect of reaction time, stabiliser, copolymer composition and reaction pressure on the yield, molecular weight and morphology of the copolymers has been investigated.

Keywords: 2-(Dimethylamino)ethyl methacrylate; Supercritical carbon dioxide; Dispersion polymerization

1. Introduction

The homopolymer and copolymers of 2-(dimethylamino) ethyl methacrylate (DMA) are used extensively as stabilisers for latex formation, as potential carriers for drug delivery systems and for a wide range of cosmetics applications [1–4]. However, in many of these applications extremely pure materials are required, particularly in the case of biomedical applications. Traditionally, these materials have been synthesized in water or water/acetone mixtures. Thus, the final product requires considerable purification and processing, this is often an energy intensive process and therefore expensive. An ideal solution would be to synthesize such polymers in the absence of contaminating organic solvents. One possible solution to this problem is to use supercritical carbon dioxide ($scCO_2$) as the reaction medium. The carbon dioxide can be easily removed by depressurisation at the end of the polymerisation leading to a clean, dry product.

In recent years, there has been a significant increase in the use of $scCO_2$ as a reaction medium for free radical dispersion polymerisation. $ScCO_2$ is environmentally friendly, relatively inexpensive, has tuneable properties and leaves no toxic solvent residues [5,6]. DeSimone et al. reported the first dispersion polymerisation of methyl methacrylate in $scCO_2$ using a highly soluble amorphous fluorinated polymer (poly(dihydroperfluorooctylacrylate) pFOA) as a stabiliser [7]. Since then, the successful dispersion polymerisation of a very wide range of vinyl monomers has been reported, including methyl methacrylate [8–14], 2-hydroxyethyl methacrylate [15], styrene [16–19], vinyl acetate [20], acrylonitrile [21], *N*-vinyl pyrrolidinone [22,23], glycidyl methacrylate [24,25], and copolymerisation of methyl methacrylate and ethyl methacrylate [26].

In this paper, we report the homopolymerisation of DMA and the copolymerisation of DMA with MMA in supercritical carbon dioxide. The effect of reaction time, composition and two different stabiliser systems are investigated.

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2. Experimental part

2.1. Materials

The commercially available methacrylate terminated poly(dimethylsiloxane) (PDMS-mma, $M_n \sim 10,000$, Aldrich), DMA (Aldrich), Krytox-157FSL (carboxylic acid terminated perfluoropolyether, Dupont) and methyl methacrylate (ICI, inhibited with 2 ppm of Topanol) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Fisher Chemicals) was purified via recrystallisation from THF.

2.2. Polymerisation

Polymerisations were performed in a 60 ml stainless steel autoclave equipped with a magnetically coupled overhead stirrer. The autoclave was charged with reactants, then pressurised to ca. 3000 psi with high grade N_2. This procedure was designed to leak test the equipment and to degas the reaction system. After venting, the autoclave was then filled with CO_2 to ca. 800 psi, then stirred and heated to the desired reaction temperature using a preheated thermocouple controlled aluminium block. Once the reaction temperature was reached, the desired reaction pressure was attained with the addition of CO_2 and the reaction was allowed to proceed with stirring (300 rpm). At the end of the reaction, the autoclave was cooled to room temperature, and then CO_2 was slowly vented. Finally, the autoclave was opened and the product retrieved. To quantify the reaction yields, the autoclave was rinsed with THF to collect any residual polymer product and stabiliser. The collected sample was dried under vacuum. The monomer conversion was measured gravimetrically.

2.3. Polymer characterisation

Polymer molecular weight and distribution were obtained by gel permeation chromatography using THF as the eluent with 2% triethylamine and BHT stabiliser at 20 °C, using two Plgel 5 μm Mixed-D columns (Polymer Laboratories) and a RI 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. Infrared data were collected on a Nicolet 730 using OMNIC software. The samples were prepared as thin liquid films on calcium fluoride discs and mounted in transmission mode in the FTIR spectrometer. Scanning Electron Microscopy (SEM) data were collected using a JEOL 6400. Samples were mounted on an aluminium stub using an adhesive carbon tab and were sputter-coated with gold prior to examination. The number-average particle size and particle size distribution were determined by measuring the diameter of least 100 particles. ^{1}H NMR spectra were obtained with a Bruker 300 MHz spectrometer in $CDCl_3$ or acetone-D_6 as solvent. T_g data were collected on a Perkin–Elmer DSC-7, using a heating and cooling rate of 10 °C/min.

3. Results and discussion

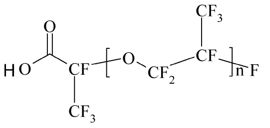
3.1. Homopolymerisation of DMA

Homopolymerisation of DMA was carried out in the presence of 10% of PDMS-mma (w/w with respect to monomer) as the stabiliser, 1% AIBN (w/w with respect to the monomer) as initiator at 65 °C, 300 rpm stirring and 3200 psi for 48 h. On venting, polymer was produced in 92% yield as white, sticky, porous solid. The molecular weight of the polymer was found to be low ($M_n = 6700$, PDI $= 3.1$) and the glass transition temperature (T_g) of the polymer is just 16 °C. SEM analysis of this polymer shows that an aggregated morphology is formed. Compared to the result obtained in the absence of stabiliser ($M_n = 8100$, PDI $= 3.7$), the addition of stabiliser does not improve the molecular weight and morphology of final product. Such aggregates have been encountered previously with other polymers exhibiting a low T_g, for example poly(ethyl methacrylate) [26]. We believe that the morphology of final product is largely dependent on the T_g of the polymer formed. Polymers formed that exhibit a low T_g tend to agglomerate, a phenomenon exacerbated by the plasticising effect of $scCO_2$.

Previous work using Krytox-157FSL as a stabiliser has employed IR spectroscopy to investigate its mode of action [27,28]. Fig. 1 shows the thin film IR spectra of the ν(C=O) region for Krytox, DMA monomer and the mixture. Krytox shows a single peak at 1775 cm^{-1} and pure DMA a single peak at 1721 cm^{-1}. On mixing, the peak for Krytox shifts to 1758 cm^{-1} and the DMA peak to 1715 cm^{-1}. This indicates that there is a hydrogen bonding interaction between the carbonyl group in DMA and the carboxylic acid headgroup in Krytox. Thus, polymerisation experiments were conducted using 1% Krytox as the stabiliser. However, the molecular weight of the polymer was still low ($M_n = 10,000$, PDI $= 2.8$, 90% monomer conversion), the appearance of DMA homopolymer product in the autoclave was similar to that obtained using PDMS-mma as stabilizer, after venting no particles were formed. This result again demonstrates that polymers with a low T_g tend to agglomerate, and stabilisers are not able to significantly influence the morphology of final product.

3.2. The copolymerisation of DMA with methyl methacrylate

For copolymerisation it is important to determine the compositional drift of the copolymer during the reaction. This factor will determine whether a block, alternating or statistical copolymer is formed, and has implications for the material properties of the final product. One method to do this is to monitor polymerisation by terminating the reaction



Krytox acid

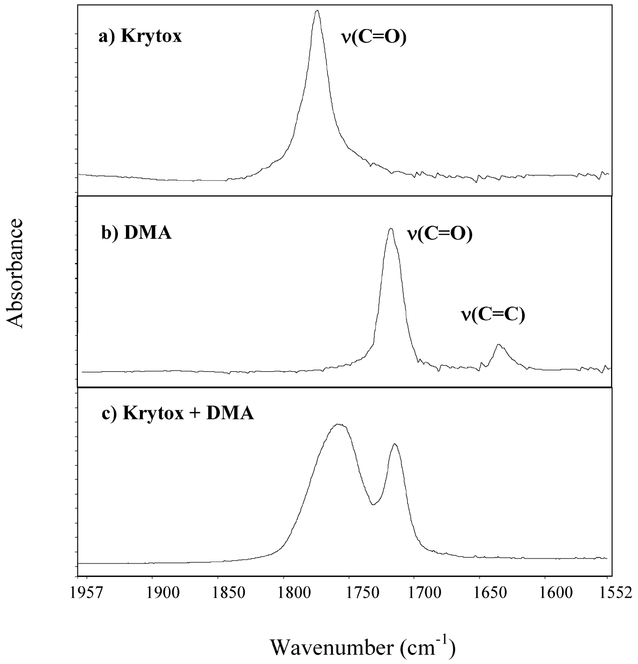


Fig. 1. Thin film IR spectra for (a) Krytox 157FSL, (b) DMA and (c) Krytox and DMA mixture. The spectra demonstrate that on mixing the carbonyl peaks of carboxylic acid moiety of the Krytox stabiliser and the DMA monomer shift, indicating an anchoring interaction.

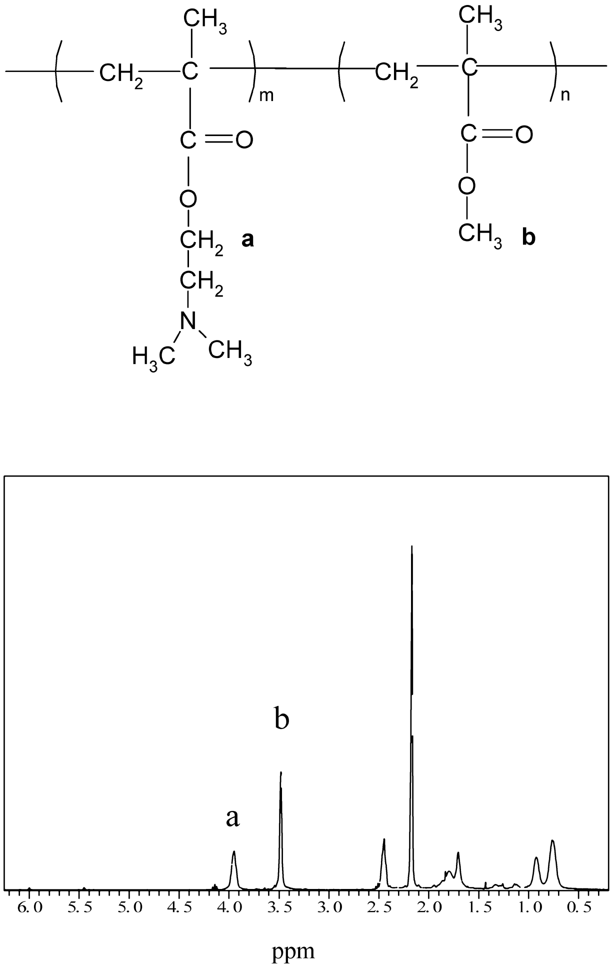


Fig. 2. ^{1}H NMR spectrum of the copolymer of DMA and MMA-composition was determined by comparison of the OCH_3 resonance (3.5 ppm) in MMA with the OCH_2 resonance in DMA (3.95 ppm), entry 5 in Table 1.

at different degrees of conversion, and measuring the composition of the copolymer.

For this reason, a number of copolymerisations of DMA and MMA in equimolar mixture were carried out in 4000 psi CO_2 at 65 °C, using Krytox 157 FSL as the stabiliser. The reactions were allowed to proceed for set periods of time, from 2.5 h up to a maximum of 48 h. The copolymer composition was determined via ^{1}H NMR in $CDCl_3$, by comparison of the OCH_3 resonance (3.5 ppm) in MMA with the OCH_2 resonance in DMA (3.95 ppm), see Fig. 2. The results obtained are shown in Table 1.

After 2.5 h, poly(MMA-*co*-DMA) was produced in 20% yield, and ^{1}H NMR analysis indicated that the copolymer comprised approximately 60 mol% DMA (entry 1 in

Table 1
The effect of reaction time on the copolymer of 50:50 molar mixture of MMA and DMA using 1% Krytox 157FSL as stabiliser

Entry	Reaction time (h)	MMA in the polymer[a] (%)	DMA in the polymer[a] (%)	Yield (%)	M_n[b]	M_w[b]	PDI[b]	Polymer appearance[c]
1	2.5	40	60	20	20,600	67,200	3.2	Oil
2	5	45	55	35	17,100	82,800	4.8	Oil
4	10	44	56	65	19,900	62,700	3.1	Oil and white solid
5	18	45	55	67	16,400	73,200	4.4	White solid
6	24	47	53	86	12,300	43,100	3.5	White solid
7	48	47	53	94	13,600	44,900	3.3	White solid

Polymerisations were carried out at 65 °C at 4000 psi.

[a] As determined by ^{1}H NMR.

[b] As determined by GPC.

[c] Appearance of polymer in cell directly after venting.

Table 2
The copolymerisation of MMA and DMA with different molar feedstock compositions

Entry	Ratio of MMA/DMA[a]	MMA in the polymer[b] (%)	DMA in the polymer[b] (%)	Yield (%)	M_n[c]	M_w[c]	PDI[c]	T_g[d] (°C)	Polymer appearance[e]
1	50:50	45	55	77	10,000	26,800	2.7	54	Viscous liquid and white solid
2	75:25	74	26	89	11,800	31,200	2.6	59	White solid
3	90:10	89	11	92	25,500	95,300	3.7	83	White fine powder
4	95:5	96	4	93	41,700	162,100	3.9	103	White fine powder

Polymerisations were carried out at 65 °C at 4000 psi, 20 h, using 10% PDMS-mma as stabiliser.

[a] The molar ratio of monomers at the beginning of the reaction.

[b] As determined by ^{1}H NMR.

[c] As determined by GPC.

[d] As determined by DSC.

[e] Appearance of polymer in cell directly after venting.

Table 1). This indicates a preferential reaction rate of the active chain end with DMA monomer. An increase in reaction time to 5 h resulted in a copolymer containing 55 mol% DMA (entry 2 in Table 1).

At longer reaction times, the MMA content in the copolymer increased until the composition approached the 50 mol% comonomer feed ratio. The reacting probability of a DMA or MMA monomer unit is indicating that a statistical/slightly tapered copolymer is formed. This is reflected in the glass transition temperature of the polymer, which shows a single T_g at 54 °C (entry 1 in Table 2) (T_g of PMMA: 117 °C, T_g of PDMA: 16 °C). These results are consistent with those observed in conventional solvents where the reactivity ratio for MMA/DMA is 0.42 and 1.01, respectively, [29], i.e. the chance of a DMA monomer unit becoming incorporated is higher.

3.2.1. Effect of varying the comonomer feed ratio

Varying the comonomer compositions in the initial reaction mixture allows adjustment of the copolymer composition and leads in turn to control over physical properties. Ideally, one would prefer to do this by varying the feed of one of the monomers to the reaction, but in a high pressure reaction system this is technically very challenging. In these experiments, a number of DMA–MMA copolymers were synthesised from monomer mixtures varying from 50 to 95 mol% MMA. The polymerisations were carried out at 4000 psi, 65 °C for a period of 20 h in presence of 10% (w/w) PDMS-mma as the stabiliser.

The compositions of the copolymer products are shown in Table 2. In all cases, the copolymers were produced in high yields. The M_w was found to increase as the MMA content of the copolymer was increased. In addition, as one would predict, the T_g of the polymer increases with the percentage of MMA. This change in T_g is reflected in the morphology of the polymers. The SEM images show that the morphology of the final product ranged from an aggregated material (at 50 mol% MMA) to spherical particles (at 95 mol% MMA) as shown in Fig. 3(a)–(c). These data suggest that at a high DMA content it is difficult to stabilise the microparticles of the copolymer. Thus the T_g must be a contributing factor to the aggregation of copolymers within the dispersion polymerisation. Similar observations were reported for copolymerisation of MMA with ethyl methacrylate [26].

3.2.2. Effect of reaction time

When comparing Fig. 4 (6 h, entry 1 in Table 3) with Fig. 3(a) (20 h, entry 2 in Table 3), it is interesting to note that, spherical particles are clearly formed at low monomer conversion. As the monomer conversion increases, the morphology of the final product changes from spherical particles to agglomerated. It is clear that there is an effect of the monomer conversion upon the morphology of the copolymer produced. Johnston et al. [30] reported that particle size increased with reaction time during the dispersion polymerisation of MMA in $scCO_2$. This is ascribed to the initial high concentration of monomer in the reaction system acting as a cosolvent for the growing polymer chain, increasing stabiliser efficiency. This is

Table 3
Copolymers of MMA and DMA with different reaction time

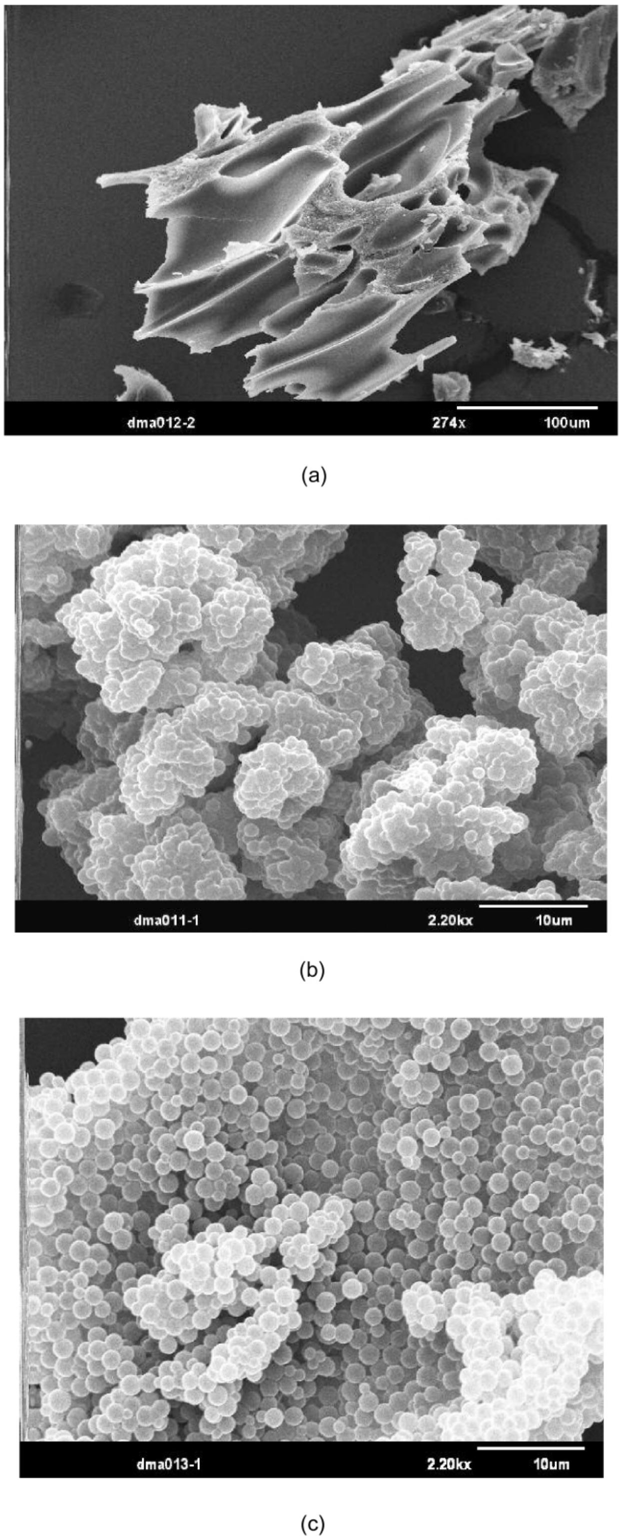
Entry	Reaction time (h)	MMA in the polymer[a] (%)	DMA in the polymer[a] (%)	Yield (%)	M_n[b]	M_w[b]	PDI[b]	Polymer appearance[c]
1	6	65	35	35	11,300	33,600	2.9	White fine powder
2	20	74	26	89	11,800	31,200	2.6	White solid

Polymerisations were carried out at 65 °C at 4000 psi, initial monomer ratio of MMA/DMA (75:25), using 10% PDMS-mma as stabiliser.

[a] As determined by ^{1}H NMR.

[b] As determined by GPC.

[c] Appearance of polymer in cell directly after venting.



(a)

(b)

(c)

Fig. 3. SEM images of poly(MMA-*co*-DMA) composed of (a) 75:25, (b) 90:10 and (c) 95:5 MMA/DMA molar ratios, entries 2–4 in Table 2.

consistent with our observation of the initial formation of particles in the present study. However, we think this is not the only explanation for the aggregation of the particles at high conversions, especially in those cases in which a low T_g copolymer is formed. This observation has important implications for the synthesis of polymeric particles of controlled morphology via dispersion polymerisation in $scCO_2$.

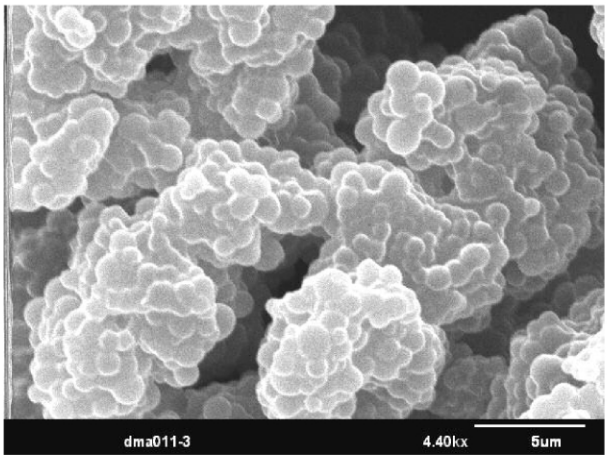


Fig. 4. SEM images of poly(MMA-*co*-DMA) (MMA/DMA = 75:25) at 6 h, entry 1 in Table 3.

3.2.3. Effect of reaction pressure

A primary advantage of employing $scCO_2$ as a reaction medium lies in the ability to tune the solvent density and dielectric constant by simply changing either temperature or pressure [5,6]. Therefore, the effect of initial pressure of the reaction medium on the particle size and size distribution was investigated. The effect of pressure on the polymerisation can be clearly seen by comparing Fig. 5 with Fig. 3(c): changing the density of the continuous phase by manipulating the pressure affects morphology.

At 4000 psi pressure ($scCO_2$ density = 0.79 g/ml) well-defined, non-flocculated particles were isolated after 20 h, with a final conversion of over 90% (entry 3 in Table 4, Fig. 3(c)). These particles were monodisperse (PSD = 1.05)

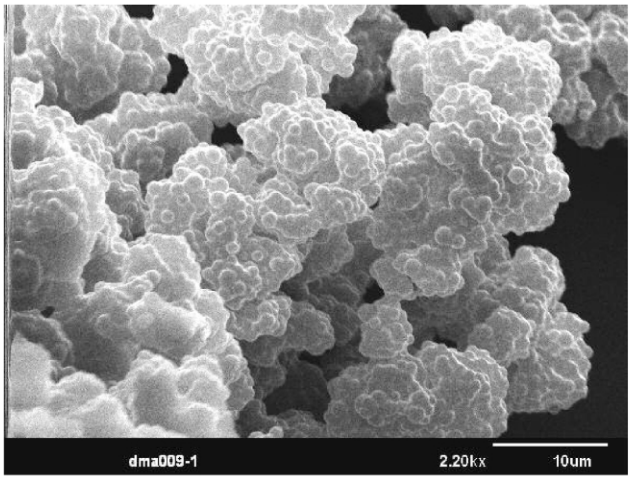


Fig. 5. SEM images of poly(MMA-*co*-DMA) (MMA/DMA = 95:5) at 2800 psi, entry 4 in Table 4.

Table 4
Copolymers of MMA and DMA under different reaction pressures

Entry	Reaction pressure (psi)	Ratio of MMA/DMA[a]	Yield (%)	M_n[b]	M_w[b]	PDI[b]
1	4000	90:10	92	25,500	95,300	3.7
2	2800	90:10	93	28,100	108,000	3.8
3	4000	95:5	93	41,700	162,100	3.9
4	2800	95:5	91	47,500	190,700	4.0

Polymerisations were carried out at 65 °C. 20 h, using 10% PDMS-mma as stabiliser.

[a] The molar ratio of monomers at the beginning of the reaction.

[b] As determined by GPC.

with an average diameter of about 2.1 μm. However, at 2800 psi pressure ($scCO_2$ density = 0.68 g/ml) agglomeration was observed (entry 4 in Table 4, Fig. 5). At lower pressures, the solubility of the stabiliser in $scCO_2$ was reduced. Thus, at high monomer conversions (i.e. low cosolvent concentration) the PDMS-mma chains become less efficient steric stabilisers, leading to agglomeration. Another result that must be mentioned here is that although increasing the pressure prevents aggregation in this particular high T_g copolymer (DMA/MMA = 5:95), aggregation still occurs when a lower T_g copolymer (DMA/MMA = 25:75, entry 2 in Table 2, Fig. 3(a)) is synthesised. This is a further proof that T_g is a very important factor in particle morphology.

Despite this effect on the final morphology, Table 4 shows that the change in pressure had relatively little effect on the final molecular weight of the copolymer. According to our earlier experimental results [31], if the free radical polymerisation in $scCO_2$ was carried out under precipitation conditions, i.e. in the absence of stabiliser, lower molecular weight polymers were obtained. So it appears that, although the morphology of polymers formed at low reaction pressure was aggregated, the low density of the $scCO_2$ still provided an effective reaction medium for dispersion polymerisation using PDMS-mma stabiliser. This implies that cheaper, less efficient stabilisers and milder conditions could be used if the molecular weight and polydispersity of the final copolymer are deemed more important than its morphology. High reaction pressures and the relatively high cost of the stabiliser are two very important considerations if dispersion polymerisations in $scCO_2$ are to be used on an industrial scale.

4. Conclusions

The homopolymerisation of DMA and copolymerisation of DMA with MMA have been achieved in $scCO_2$. The homopolymer of DMA tends to agglomerate because of its low T_g. The copolymerisation is comparable to that observed in conventional solvents, which indicates that the relative reactivity ratios for these two monomers are not changed significantly in $scCO_2$. The morphology of the resulting copolymers can be influenced via control of the initial feedstock monomer ratio and reaction pressure. A lower copolymer T_g under high DMA feed ratio increases the probability of aggregation during polymerisation. Dry, fine powdered product was produced for the copolymer as increasing MMA monomer feed ratio.

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