

Synthesis of highly cross-linked poly(diethylene glycol dimethacrylate) microparticles in supercritical carbon dioxide

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Abstract

Herein we report the synthesis of poly(diethylene glycol dimethacrylate), poly(DEGDMA), by free-radical heterogeneous polymerization in supercritical carbon dioxide (scCO₂), using a commercially available carboxylic acid end-capped perfluoropolyether oil (Krytox 157FSL) as stabiliser. The effect of initial concentration of stabiliser, monomer and initiator on the yield and morphology of the resulting polymer has been investigated. Krytox worked effectively as a stabiliser and discrete poly(DEGDMA) particles with diameters ranging from 1.28 to 2.08 µm and narrow particle size distribution were produced in supercritical carbon dioxide, in high yield and in short reaction times, without making use of harmful organic solvents.

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1. Introduction

The use of supercritical carbon dioxide (scCO₂) as a polymerisation medium offers many advantages over conventional solvents. It is environmentally friendly and relatively inexpensive, it has low viscosity, and its density and dielectric constant change rapidly with pressure and temperature. This strong density dependence enables fine adjustments in polymerisation reactions, so that polymer chains will precipitate from solution after reaching a certain threshold molecular weight. Another advantage of performing the reaction in scCO₂ is that, by simply reducing the pressure of the system, it

is possible to easily separate the solvent from the polymer, leading to highly pure materials [1,2].

In a free radical polymerisation the monomer is usually soluble in scCO₂ but the polymer is not and it readily precipitates thus requiring the use of a proper stabiliser [3]. Recent developments in the field of heterogeneous polymerisation reactions in scCO₂ have mainly focused on the search for new and more efficient stabilisers in order to optimize the preparation of spherical polymer particles for a wide range of commercial applications [4].

Although research has been intense in this area only few works reporting the production of cross-linked polymers in scCO₂ were found in literature [5–8]. Large scale bio-catalytic processes in the pharmaceutical, food and chemical industries depend on the availability of active and stable enzymes incorporated into a suitable cross-linked polymeric matrix for heterogeneous catalysis [9].

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Polymeric microspheres of poly(DEGDMA) are used to immobilise bio-molecules, such as enzymes and hormones [10,11]. Yoshida et al. [11] reported the synthesis of poly(DEGDMA) microspheres using several conventional organic solvents. Spherical particles with a mean particle diameter of 1.55 μm were obtained by radiation-induced polymerisation in methylorthoformate at temperatures between -78 and 25°C . These applications require very pure polymeric material free from residual solvent. The purification stages are often expensive and energy intensive. scCO_2 is an interesting alternative to synthesise these materials. To our knowledge this polymer was never produced in scCO_2 . Cooper et al. reported the polymerisation of other cross-linked polymers such as polydivinylbenzene [6]. In the same work these authors tested the polymerisation of the ethylene glycol dimethacrylate (EGDMA) with no added stabiliser and no microspheres were obtained. Recent works from Shiho et al. [7] and Wang et al. [8] showed the preparation of cross-linked microparticles of poly(glycidyl methacrylate), used for the same applications as poly(DEGDMA), synthesised in scCO_2 using as stabilisers PFOA, poly(1,1-dihydroperfluorooctyl acrylate), polystyrene-*b*-PFOA diblock copolymer and PDMS, poly(dimethylsiloxane).

This paper reports the heterogeneous polymerisation of diethylene glycol dimethacrylate (DEGDMA) in scCO_2 , using AIBN as initiator at 65°C and pressures up to 27 MPa. Krytox was tested as stabiliser and the effect of its initial concentration and the initial concentration of the monomer on the morphology of the synthesised polymer were investigated. Also the effect upon the reaction time, CO_2 pressure and initial concentration of AIBN are reported.

2. Experimental

2.1. Materials

Diethylene glycol dimethacrylate (DEGDMA, $\geq 99.96\%$ purity, Polysciences) was used as received. Its structure is shown in Fig. 1. Poly(hexafluoropropylene oxide) carboxylic acid end-capped (Krytox 157 FSL, DuPont) and 2,2'-azobis(isobutyronitrile) (AIBN, $\geq 98\%$ purity, Aldrich) were also used as received. Carbon dioxide was supplied by Carbueros Metalicos, with a

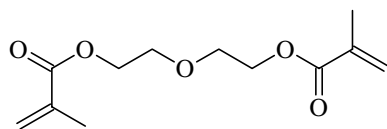


Fig. 1. Chemical structure of DEGDMA.

purity of 99.9999% and Air Liquid supplied nitrogen, with purity better than 99.995%.

2.2. Phase behaviour

Prior to the polymerization reaction, cloud point measurements for the system CO_2 + DEGDMA + Krytox were performed to define the conditions to obtain a completely homogeneous system, as it is shown in Fig. 2. No initiator was added to prevent polymerization. The measurements were performed at 65°C , the temperature of the reaction, for different percentages of Krytox with respect to the monomer (0%, 10% and 30% w/w), covering the range of the used concentrations of monomer with respect to CO_2 . At the reaction pressures (18.5–27 MPa) a single phase is observed. The measurements were carried out in a variable volume cell with a front sapphire window. The cloud point pressure recorded was the pressure at which the cell became completely cloudy (white opaque). Reproducibility within ± 1.1 bar was obtained.

2.3. Polymerisation of DEGDMA in scCO_2

Polymerisation reactions were carried out in a 33 ml stainless steel high-pressure cell equipped with two aligned sapphire windows, which allow full visualisation of the reaction mixture. The cell was built based in the one described by Corrêa de Sampaio et al. [12]. The cell is immersed in a thermostatted water bath with $\pm 0.01^\circ\text{C}$ of stability. Temperature control was made with a RTD probe contacting the cell, connected to a Hart Scientific PID controller. The cell is equipped with a Teflon coated magnetic stir bar. An immersible stirrer magnet was placed under the cell. In a typical experiment the cell is

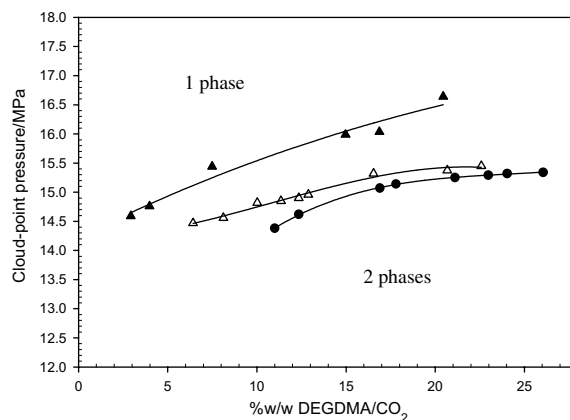


Fig. 2. Cloud point curves for CO_2 + DEGDMA + Krytox system at 338.15 K: (●) 0%; (△) 10% and (▲) 30% w/w Krytox/DEGDMA. Lines correspond to fittings using cubic polynomial equations.

loaded with the monomer (DEGDMA), stabiliser (Krytox 157 FSL) and initiator (AIBN). The cell is sealed and nitrogen is added to purge the cell and test leaks. The nitrogen is slowly released and liquid carbon dioxide is loaded into the cell using a high-pressure compressor (*NWA GmbH*). The cell is immersed in the water bath stabilised at 65 °C and temperature and pressure are allowed to rise to the required experimental conditions. Additional CO₂ may be added to reach the exact desired pressure. The reaction was allowed to proceed from 30 to 180 min under stirring. It could be seen through the sapphire windows that all polymerisations started as a completely homogeneous phase, with all reactants completely dissolved in scCO₂. At the end of the reaction, the resulting polymer was slowly washed with fresh high-pressure CO₂ in order to clean the remaining residues of stabiliser and unreacted monomer. Upon venting a fluffy, dry, white, free-flowing powder remained in the reaction vessel. The polymer yield was determined gravimetrically, assuming that all the surfactant and residual monomer were completely removed.

2.4. Polymer characterisation

Particle morphology observations were based on scanning electron microscopy (SEM) data. Samples were mounted on aluminium stubs using carbon cement (D-400, Neubauer Chemikalien) and were gold coated. SEM images were obtained on a *Hitachi, S-4100* instrument. Particle diameters and their size distributions were determined in a dry powder dispersion system (*Aerosizer LD API*).

The synthesised samples of poly(DEGDMA) were insoluble in chloroform, tetrahydrofuran, dimethylformamide, dimethylsulfoxide and mixtures of these solvents, which are usually used as eluents in GPC/SEC columns, thus making impossible to determine the molecular weight of the synthesised polymer.

Residues of monomer and stabiliser remaining in the polymer (sample produced with the highest concentration of monomer and stabiliser with respect to CO₂) were evaluated by NMR, in a *Bruker* equipment (ARX 400 MHz). The polymer was stirred in trifluoroethanol (good solvent either for the monomer and stabiliser) and the solution filtered (0.2 µm *Merck* AnatoPro filters). ¹H NMR analysis of the filtered solution showed that after washing the resulting polymer for 3 h with high-pressure CO₂ (50 °C and 22 MPa) a minimal contamination of ca. 1.3% w of monomer with respect of the initial monomer amount remained in the polymer particles. ¹⁹F NMR spectra revealed a detectable residue of Krytox and estimated to be ca. 6% w of the initial amount of Krytox. These residues could be further minimised by optimizing the extraction vessel to avoid preferential passages of CO₂ instead of using the reactor. Although no safety evaluation was found specifically

for Krytox, other similar PFPEs were found to have low toxicity and biological inertness [13–15].

DSC experiments performed in a *Setaram* equipment revealed that no degradation of the polymer occurs up to 300 °C, thus providing high thermal and chemical resistance. No *T_g* temperature was observed for all the samples produced, what is consistent with a high cross-linking degree.

3. Results and discussion

3.1. Effect of initial stabiliser concentration

In Table 1, the characteristics of polymer samples produced with concentrations of Krytox ranging from 0% to 60% w/w of the initial monomer are presented. The reactions were carried out at 18.5 MPa and 65 °C for 2 h. Two initial monomer feeds were used: 2.5 and 5 g of DEGDMA, representing 11% and 23% w/w DEGDMA with respect to carbon dioxide. High yields were obtained for all the tested stabiliser concentrations, even in the absence of stabiliser. Entry 1 shows the results with no added stabiliser while entries 2–7 and 8–10 show the increase of the initial Krytox concentration for the initial monomer feed amount of 11% and 23% w/w respectively.

When no stabiliser was added, the colour of the mixture, as it could be seen through the sapphire window, turned to yellow about 25 min after the beginning of the reaction, then to a soft orange and within a few minutes white particles of polymer started to precipitate and it was possible to see them settling in the bottom of the cell. SEM micrographs show that the polymer has an irregular bulk structure with very small primary particles agglomerated in a net. This is consistent with other precipitation reactions [11,16].

By increasing the initial concentration of stabiliser, a significant change in the morphology of the particles could be observed. In all the experiments with addition of Krytox, the Tyndall effect, due to the scattering of the light, was observed. The solutions that were initially completely clear turned to an orange colour within 15–20 min after the beginning of the reaction. The solutions gradually changed for a deeper red–orange colour and become completely opaque (black). Within minutes they changed gradually to a milky white opaque solution. The effect was less pronounced for the lower Krytox concentrations. These observations are in agreement with other dispersion polymerisations found in literature [17]. When 0.4% w/w of Krytox with respect to monomer was used (entry 2 of Table 1) the morphology of the resulting polymer changed drastically when compared with the one obtained in entry 1 with no added stabiliser. As it can be seen in Fig. 3a, particles were formed although highly irregular and agglomerated. A magnified inspection shows that each particle is indeed

Table 1

Effect of initial concentration of Krytox in the polymerization of DEGDMA in scCO₂

Entry	%DEGDMA ^a	%Krytox ^b	Yield (%) ^c	d_n (μm) ^d	PSD ^e	Polymer morphology ^f	Product ^g
1	11	0	89	–	–	Irregular structure	Powder
2	11	0.4	83	–	–	Aggregated	Powder
3	11	2	86	1.68	1.32	Slightly aggregated	Powder
4	11	4	85	1.67	1.17	Particles	Powder
5	11	10	89	1.57	1.09	Particles	Powder
6	11	20	93	1.32	1.11	Particles	Powder
7	11	60	96	1.31	1.10	Spherical	Powder
8	23	5	87	1.78	1.23	Particles	Powder
9	23	10	90	1.73	1.13	Particles	Powder
10	23	30	92	1.67	1.06	Spherical particles	Powder

^a The reactions were carried out at 18.5 MPa at 65 °C for 2 h in a 33 ml cell. Entries 1–7: 2.5 g; 8–10: 5 g of DEGDMA were used. 2% w/w of AIBN with respect to monomer was used. Percentage weight/weight with respect to CO₂.

^b Percentage weight/weight with respect to monomer.

^c Determined gravimetrically.

^d Particle diameter as determined from the *Aerosizer* technique.

^e Particle size distribution as determined from the *Aerosizer* technique.

^f As determined from SEM micrographs.

^g Appearance of the polymer after venting.

formed by smaller primary particles stuck together with approximately 0.15 μm of diameter, resulting in a “flower” morphology, which is associated to lack of stabilisation. By increasing the stabiliser concentration from 2% to 60% w/w Krytox/DEGDMA (11% w/w DEGDMA/CO₂) the diameters of the particles decrease from 1.68 μm to 1.31 μm particles and became more spherical and less aggregated. Fig. 3b shows the SEM micrograph of the sample produced with 10% w/w of Krytox with respect to monomer (entry 5), showing disaggregated and discrete polymer particles. The possible explanation of the observed trend is that when a higher amount of stabiliser is available there is a more efficient stabiliser coverage of the particles, thus the particles grow less agglomerated although with smaller diameters because there is also an increase in the number of stable nuclei. The same behaviour was also observed when 23% w/w monomer with respect to CO₂ was used. While the diameters of the particles decrease from 1.78 μm to 1.67 μm by increasing the stabiliser concentration from 5% to 30% Krytox/DEGDMA, particles became more spherical and less aggregated.

The stabilisation of the growing polymer may have two main contributions: (i) Krytox is a pseudo-graft stabiliser which interacts with the polymer through a hydrogen bond between its carboxylic end group and the ester grouping leading to a pseudo-graft copolymer, as suggested by Howdle et al. [18]; (ii) the particles of a cross-linked polymer could be stabilised against coagulation by their rigid cross-linked surfaces rather than by added stabilisers [6,19]. The carboxylic end group of Krytox can interact with the ester groups of the DEGDMA monomer, but it is not clear how the stabiliser interacts with a cross-linked polymer structure.

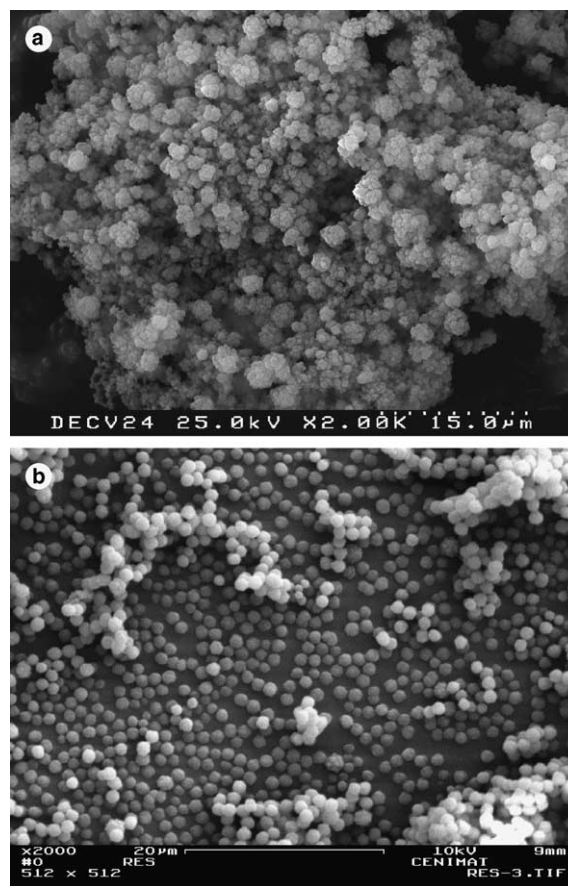


Fig. 3. SEM micrographs of poly(DEGDMA) synthesised with different initial stabiliser concentrations. (a) 0.4%; (b) 10% w/w of Krytox with respect to monomer (for 11% w/w of DEGDMA with respect to CO₂).

Table 2
Effect of the initial concentration of DEGDMA

Entry	%DEGDMA/CO ₂ ^a	Yield (%) ^b	d_n (μm) ^c	PSD ^d	Polymer morphology ^e	Product ^f
11	4	92	1.28	1.02	Particles	Powder
5	11	89	1.57	1.09	Particles	Powder
9	23	90	1.73	1.13	Particles	Powder

^a Weight percentage.

^b Determined gravimetrically.

^c Particle diameter as determined from the *Aerosizer* technique.

^d Particle size distribution as determined from the *Aerosizer* technique.

^e As determined from SEM micrographs.

^f Appearance of the polymer after venting.

IR spectroscopy of thin films of Krytox, DEGDMA and their mixture, shows the evidence for such interaction. Krytox shows a carbonyl stretching mode at 1774 cm⁻¹ [ν (C=O)], while DEGDMA shows two sharp bands, the vinyl and carbonyl stretching modes [ν (C=C) at 1635 cm⁻¹ and ν (C=O) at 1720 cm⁻¹ respectively]. When they are mixed (50:50 v/v) the carbonyl-stretching mode of the carboxylic acid head group of Krytox shifts up [ν (C=O) at 1786 cm⁻¹] while the carbonyl-stretching mode of DEGDMA shifts down [ν (C=O) at 1716 cm⁻¹]. These shifts are indicative of hydrogen bond interaction [18].

3.2. Effect of initial monomer concentration

The polymerisations were conducted at three different initial concentrations of DEGDMA (4%, 11% and 23% w/w with respect to monomer). The results obtained are summarized in Table 2. The contents of stabiliser and initiator were kept constant at 10% and 2% w/w with respect to monomer, respectively.

The trend typically observed in literature is the increase in the particle diameter with increasing monomer concentration. As more monomer is added to the reaction the solvency of the medium increases for the growing polymer and stabilizer which allows larger particles to be formed. In this work this trend was observed, with

a significant increase in the particle diameter, from 1.28 to 1.73 μm, while increasing the initial monomer concentration from 4% to 23% w/w with respect to CO₂. Although high yields were obtained, they changed very little with the initial monomer concentration, with no specific trend.

3.3. Effect of initiator concentration

In all the experiments 2% w/w (with respect to monomer) of AIBN were used. In Table 3 the results obtained for a sample using 0.6% w/w of AIBN (entry 13) are compared to a sample synthesised at the same conditions but with 2% w/w of initiator (entry 5). By increasing the initiator concentration there was a slight increase in the yield of the polymer, although no specific trend could be found in literature.

Usually, by increasing the initiator concentration there is an increase in the number of radicals in the medium and hence more nucleation sites are formed. Thus a decrease in particle size diameter is generally observed [20]. This trend was also observed in our work. By increasing the AIBN concentration from 0.6% to 2% w/w with respect to monomer the particle size diameter of the particles decreased from 2.08 to 1.57 μm. As for the lowest initiator concentration a higher PSD was

Table 3
Effect of the initial concentration of AIBN in the polymerization of DEGDMA in scCO₂

Entry	% w/w AIBN ^a	Yield (%) ^b	d_n (μm) ^c	PSD ^d	Polymer morphology ^e	Product ^f
12	0	—	—	—	—	Monomer
13	0.6	84	2.08	1.31	Particles	Powder
5	2	89	1.57	1.09	Particles	Powder

Reactions performed at 18.5 and 65 °C for 2 h using 10% w/w Krytox with respect to monomer (11% w/w DEGDMA/CO₂).

^a Percentage weight/weight with respect to monomer.

^b Determined gravimetrically.

^c Particle diameter as determined from the *Aerosizer* technique.

^d Particle size distribution as determined from the *Aerosizer* technique.

^e As determined from SEM micrographs.

^f Appearance of the polymer after venting.

Table 4
Effect of CO₂ pressure in the polymerization of DEGDMA in scCO₂

Entry	p_i (MPa) ^a	p_f (MPa) ^a	Yield (%) ^b	d_n (μm) ^c	PSD ^d	Polymer morphology ^e	Product ^f
5	18.5	21.1	89	1.57	1.09	Particles	Powder
14	23.6	24.5	86	1.51	1.17	Particles	Powder
15	27.0	31.8	91	1.49	1.02	Spherical particles	Powder

The reactions were carried out at 18.5 MPa at 65 °C for 2 h in a 33 ml cell.

^a p_i —initial pressure, p_f —final pressure.

^b Determined gravimetrically.

^c Particle diameter as determined from the *Aerosizer* technique.

^d Particle size distribution as determined from the *Aerosizer* technique.

^e As determined from SEM micrographs.

^f Appearance of the polymer after venting.

obtained we decided to carry out all the experiments with 2% w/w, maintaining this parameter constant.

3.4. Effect of reaction time

The reaction time has a strong effect upon the morphology of the resulting polymer. The reaction was stopped at certain reaction times. At 30 min no particles are formed. When the reaction time is increased up to 60 min, it is possible to see the formation of particles although with high degree of aggregation. At 180 min perfectly spherical particles were obtained with yields around 90%. During the course of the reaction the nuclei formed, which have high surface area, tend to aggregate and coalesce reducing the surface area of the particles to be covered by the available stabiliser, forming more perfect spheres.

Discrete poly(DEGDMA) microparticles are formed in high yield during a very short reaction time which contrast with the long reaction times reported by other authors for the polymerization of other cross-linked polymers [7].

3.5. Effect of CO₂ pressure

The results obtained as the initial pressure was increased from 18.5 to 27 MPa are summarized in Table 4. An increase in pressure over the course of the reaction was observed. This was also observed for other polymerisations like styrene, MMA and GMA, for initial pressures below 30 MPa. A possible explanation is that the thermodynamics of mixing favours the expulsion of CO₂ and monomer from the polymer-rich phase [7].

As the initial pressure was increased, a slightly decrease in the size of the particles was observed. However different trends can be found in literature. A similar trend was found in the polymerisation of styrene [17]. By contrast larger particles of GMA were formed by increasing the initial pressure [7].

At the highest pressure perfect spherical particles were obtained which could be explained by the increase of solvency of the medium for the fluorinated Krytox chains for higher CO₂ densities, leading to a better stabilisation [8].

4. Conclusion

It was demonstrated that discrete poly(DEGDMA) microparticles can be produced in supercritical carbon dioxide. Krytox effectively worked as stabiliser with a fundamental role in the stabilization of the poly(DEGDMA) microparticles. It is possible to obtain monodispersed micron-sized spherical particles with narrow size distribution and in short reaction times, by changing the initial concentrations of Krytox, monomer, initiator, reaction time and CO₂ pressure. The polymers were obtained in high yield as dry, fine and free flowing material directly from the reaction vessel. Low contamination of monomer and stabiliser was obtained in the final product by continuously washing the polymer at the end of the reaction with high-pressure CO₂.

Supercritical carbon dioxide is a valid greener alternative to produce cross-linked polymers for enzyme immobilization without making use of the typically used harmful organic solvents.

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