

## Production of Poly(Methyl Methacrylate) with Clariant Nuva HPC in Supercritical Carbon Dioxide as Enhanced Technology

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**Summary:** Dispersion polymerization of methyl methacrylate (MMA) was carried out in supercritical carbon dioxide (scCO<sub>2</sub>) using Clariant Nuva HPC as stabilizer. Dry, fine powdered spherical polymethyl methacrylate particles (pMMA) were produced at optimised conditions. The resulting high yield of spherical and relatively uniform micron-size pMMA particles were formed utilizing various amounts of Clariant Nuva HPC. The effects of varying the concentration of stabilizer (1-7 w%), reaction time (4-48 h) and reaction pressure (15-35 MPa) upon the polymerization yield, molar mass and morphology of pMMA were investigated. The experiments were analyzed with Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Gel Permeation Chromatography (GPC), Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The number-average particle size and particle size distributions were determined by measuring the diameters of 50–150 particles in the SEM images. The analyses results showed that the dispersion polymerization of MMA was carried out successfully by using Clariant Nuva HPC as flour-containing stabilizer.

Keywords: Dispersion polymerization; supercritical CO<sub>2</sub>; polymethyl methacrylate.

### Introduction

Supercritical carbon dioxide (scCO<sub>2</sub>) has great potential as an alternative to common volatile organic solvents because it is inexpensive, environmentally benign, nontoxic, and has tunable properties. Over the past decade, there have been extensive studies into its use as a solvent for polymerization. Heterogeneous polymerization techniques, including dispersion polymerization, have employed CO<sub>2</sub> as a solvent because it is poor solvent for most polymers but a good one for the monomers. It is environmentally benign, inexpensive, non-flammable, nontoxic, and easily separable from product. Despite CO<sub>2</sub> is a good solvent for most vinyl monomers, it is a very poor solvent for high molecular weight polymers (with the exception of silicone and fluoropolymers) under relatively mild conditions ( $P < 35$  MPa,  $T < 100$  °C). Hence the free radical polymerization of common monomers can be achieved in scCO<sub>2</sub> only through heterogeneous polymerization processes [1, 2].

A dispersion polymerization is one in which the monomer-initiator are soluble in the reaction medium, while the polymer formed is insoluble and the majority of effective CO<sub>2</sub>-soluble stabilisers for dispersion polymerisation in scCO<sub>2</sub> have been fluorinated or silicone-based polymers [3]. A polymeric surfactant is used to sterically stabilize nucleated polymer particles and prevent flocculation and precipitation of the reaction product. The key to

dispersion polymerization in carbon dioxide has been the development of surfactants with a highly CO<sub>2</sub>-soluble segment, which can stabilize the latexes that are formed by using various fluorinated materials [4]. These amphiphilic materials have a “CO<sub>2</sub>-philic” group which is highly soluble in CO<sub>2</sub>, and an “anchor” group which is adsorbed to the surface of the polymer particles. The “CO<sub>2</sub>-philic” group extends out from the surface of the polymer particles into the CO<sub>2</sub> phase, acting as a steric barrier to prevent flocculation [5, 6]. Kwon et al. [7] reported the first dispersion polymerization of N-vinyl-2-pyrrolidone (NVP) in scCO<sub>2</sub> using a highly soluble initiator and silicon based surfactant. There are other fluorinated and siloxane polymers which have been shown to be effective stabilizers for dispersion polymerization in scCO<sub>2</sub> [8, 9]. The papers described the dispersion polymerization of vinyl monomers such as styrene and methyl methacrylate (MMA) in scCO<sub>2</sub> with steric stabilizer and also succeeded in preparing of poly (methyl methacrylate) (pMMA) particles by dispersion polymerization in scCO<sub>2</sub> [10].

In this paper, the dispersion polymerization of MMA was reported by using Clariant Nuva HPC as stabilizer in scCO<sub>2</sub> [11]. The effect of varying the concentrations of stabilizer, reaction time and reaction pressure upon the polymerization yield, molar mass and morphology of the resulting pMMA have been explored.

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## Experimental

### Materials

MMA (Acros) was freed from inhibitor by washing in a 5% aqueous NaOH solution and distilled water, and drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The stabilizer, Clariant Nuva HPC was kindly supplied by Clariant (Turkey), and used as received. 2,2'-Azobis-isobutyronitrile (AIBN, Acros) was recrystallized in methanol before use.

Methanol (LabScan) and methylene chloride (LabScan) were used as received. Carbon dioxide was obtained from HABAS (Turkey) with analytical grade (purity 99.99%).

### Dispersion polymerization of MMA using Clariant Nuva HPC

Dispersion polymerization [12] reactions were carried out in a 40 ml stainless steel reactor. The reactor was charged with MMA (20 w/v% of reactor volume), desired amounts of AIBN (w% with respect to monomer), and Clariant Nuva HPC (w% with respect to monomer), and then the system was purged with CO<sub>2</sub> flow to remove oxygen for 15 min. An ISCO (Model No. 260D) automatic syringe pump was used to pressurize the reactor with CO<sub>2</sub> to approximately 9 ± 0.5 MPa, and the reaction mixture was heated to desired temperature in a heating bath (Fig. 1).

As the reaction vessel was heated, the remaining CO<sub>2</sub> was added to the system, until the desired pressure was reached. After the reaction conditions were obtained, polymerization was started with stirring by a magnetic stirrer for specified reaction times.

At the end of the reactions, the reactor was cooled in an ice bath, and CO<sub>2</sub> was vented slowly from the reactor, and bubbled through methanol in order to collect any polymer particles, which sprayed out during the venting process. The polymer product was then removed from the reactor.

To quantify the reaction yield, the reactor was rinsed with methylene chloride to collect any residual polymer product. The collected pMMA [13, 14] product was dried under vacuum, and the polymer conversion was determined gravimetrically.

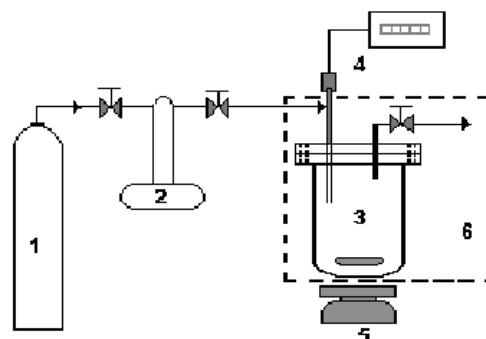


Fig. 1: Experimental setup: (1) CO<sub>2</sub> cylinder, (2) Syringe pump, (3) Reaction cell, (4) Digital pressure display, (5) Magnetic stirrer, (6) Heating bath [11]

### Polymer Characterization

The molar mass of the resulting pMMA was determined by gel permeation chromatography (GPC) [15] using a Waters Chromatograph equipped with Agilent 1100 RI detector and Waters HR 5E, 4E, 3, 2 narrowbore column set. Tetrahydrofuran (THF) was used as an eluent, and the elution rate was 0.3 ml/min.

The morphology of the polymer particles was determined with scanning electron microscope (SEM) (JEOL-5410LV).

The number-average particle size and particle size distributions were determined by measuring the diameters of 50–150 particles in the SEM images. Number ( $d_n$ ) and weight ( $d_w$ ) average particle diameters were calculated from the particle size distribution histograms using the following equations (1), (2) and polydispersity index of the molar mass distribution (PDI), dispersity index of the particle size distribution (PSD) were determined using the following equations (3), (4), respectively [16]:

$$d_n = \frac{\sum_{i=1}^N d_i}{N} \quad (1)$$

$$d_w = \frac{\sum_{i=1}^N d_i^4}{\sum_{i=1}^N d_i^3} \quad (2)$$

where  $d_i$  is the diameter of particle  $i$ , and  $N$  is the total number of particles measured in the SEM images.

$$\text{PDI} = \overline{M}_w / \overline{M}_n \quad (3)$$

$$\text{PSD} = d_w/d_n \quad (4)$$

where  $\overline{M}_w / \overline{M}_n$  is weight average molecular weight/number average molecular weight

## Results and Discussion

The effect of reaction time on the polymerization of MMA were summarized in Table-1 for dispersion polymerization of MMA in scCO<sub>2</sub> using Clariant Nuva HPC. Both the yield and the molar mass increased with reaction time although there was a slight decrease in molar mass when going for 24–48 h. This can be explained by a gel effect. In many organic solvents, gel effect occurred between 20% and 80% conversion for dispersion polymerizations [11].

Once the particles were formed, it was believed that the polymerization takes place primarily in the monomer swollen particles. Polymerization in highly viscous particles resulted in a gel effect which lead to an increase in the rate of polymerization and an increase in the molar mass of the polymer [17].

The gel effect arised relatively from retardation of termination rate, and monomer diffusion was hindered at high polymer conversion. However, polymerizations were carried out in scCO<sub>2</sub> offer the advantage of increasing the diffusivity of monomers into the growing polymer particles to maintain a sufficient rate of propagation, which in turn effectively facilitates the gel effect.

Table-1: The effect of reaction time on the polymerization of MMA<sup>a</sup> [11].

Reaction time (h)	Yield (%)	$\overline{M}_n \times 10^{-3}$ (g/mol) <sup>a</sup>	PDI <sup>a</sup>	PSD	Appearance <sup>b</sup>
4	45.14	16.6	3.10	--	Solid
12	83.64	21.9	2.17	--	Solid
24	84.27	28.9	2.06	1.082	Powder
36	84.61	37.6	2.42	1.154	Powder
48	86.45	53.6	2.60	--	Powder+Solid

<sup>a</sup> As determined by GPC

<sup>b</sup> Appearance of polymer in cell directly after venting.

As seen in Table-1, both the yield and the number-average molar mass of pMMA increased with an increase in different reaction times. The results showed that there was an increase in yield due to increasing polymerization time. A significant increase in yield was not observed after 24 h reaction. The particle distribution index values were observed between 2.06 to 3.10 (Table-1).

As expected, increasing the reaction time resulted an increase in the particle size due to the decrease in the unreacted MMA monomer. Additionally, in scCO<sub>2</sub> system, the smaller particles had a fewer number of radicals per particle, and less bimolecular termination was expected in the smaller particles than in the larger ones [16].

When the conversion was low, difficulties arose in the isolation of the pMMA particles [18] due to the high solubility of pMMA in the unreacted MMA monomer. Thus, no pMMA particles could be isolated in these experiments. The SEM images of the particles obtained from high conversion reactions (Entries 3-5 in Table-1) at different reaction times (Fig. 2).

Although higher yields as white solid were obtained in entries 1, 2 in 4 and 8 hours, an expected stabilization of pMMA was not observed as seen in SEM image of Fig. 1b and 8 h of reaction time is not sufficient for discrete particle production. Thus, SEM images of Fig. 1a,b showed aggregated particles with nonuniform distribution.

Baran Acarali [11] reported that fluorosurfactants successfully stabilized the polymerization of acrylate monomers with high yield and molar mass at very low loading.

The effect of pressure on the polymerization was clearly seen by comparing changing the density of the continuous phase by manipulating effects of the pressure on morphology. The polymer formed at 15-30 MPa did not form particles, a stabilized pMMA and high yield were not obtained at 15-30 MPa, because Clariant Nuva HPC was insoluble in CO<sub>2</sub> at this pressure, and did not stabilize the pMMA particle. The polymerization yield and the particle size distribution that expected were achieved at polymerization pressure of 35± 0.5 MPa (Table-2, Fig. 3).

Table-2: The effect of reaction pressure on the polymerization of MMA<sup>a</sup> [11]

Pressure (MPa)	Yield (%)	$\overline{M}_n \times 10^{-3}$ (g/mol) <sup>a</sup>	PDI <sup>a</sup>	PSD	Appearance <sup>b</sup>
15	96.54	75.0	2.68	--	Solid
20	90.98	66.8	2.87	--	Solid
25	84.52	66.0	2.51	1.162	Powder
30	84.08	58.2	2.39	1.187	Powder
35	84.27	28.9	2.06	1.082	Powder

<sup>a</sup> As determined by GPC

<sup>b</sup> Appearance of polymer in cell directly after venting.

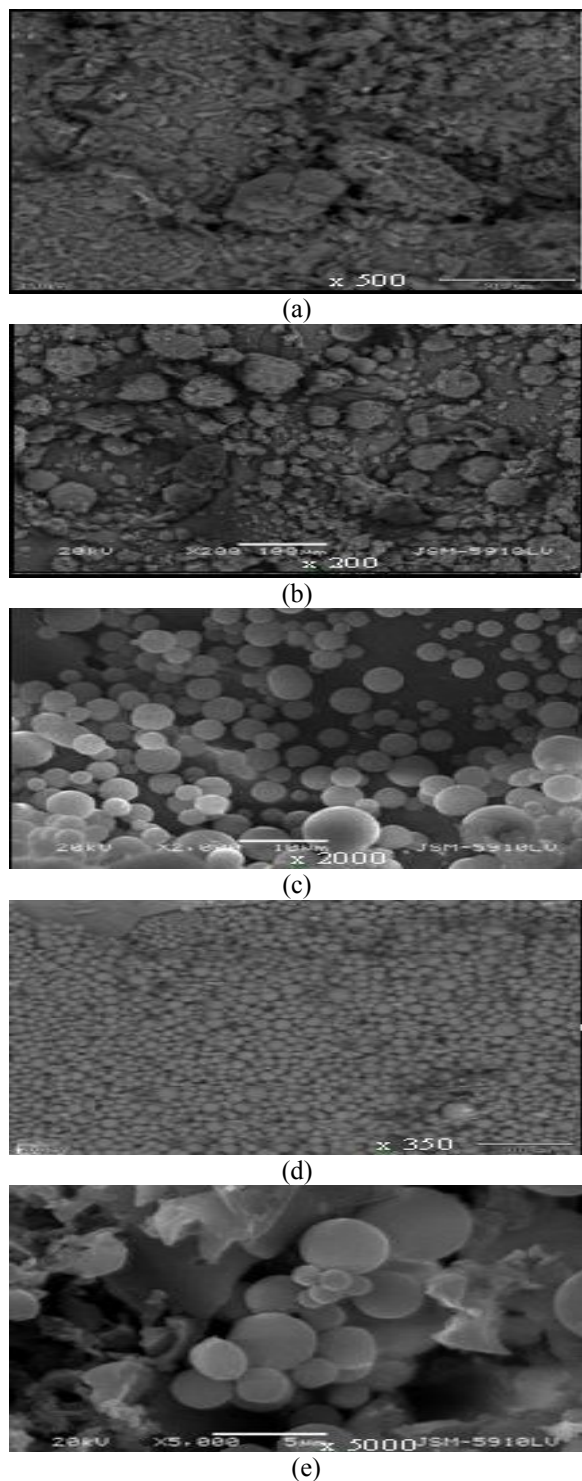


Fig. 2: SEM images of pMMA for (a) 4 h, (b) 12 h, (c) 24 h, (d) 36 h, (e) 48 h (1% of AIBN, at  $35 \pm 0.5$  MPa,  $65^\circ\text{C}$ , 5% of Clariant Nuva HPC) [11]

As discussed in the previous study [12], it was clear that the Clariant Nuva HPC provides fairly effective stabilization of the dispersion

polymerization of MMA in  $\text{scCO}_2$ . Well-defined pMMA particles with micron size were produced at the end of the studies carried out by variation of the stabilizer concentration, reaction time and pressure.

The effect of Clariant Nuva HPC on the polymerization was clearly seen by comparing Fig. 3. The polymer formed at 1% did not form particles, a stabilized pMMA and high yield were not obtained at 1%. When the concentration of Clariant Nuva HPC was increased to 7%, the yield was increased and it was obtained that the product was white powder at 5% and 7% of Clariant Nuva HPC (Table-3).

Discrete pMMA particles having a fairly narrow size distribution were formed upon increasing Clariant Nuva HPC concentrations to 1 and 7 w % (Entries 1-4 in Table 3, Fig. 4), respectively. As the stabilizer concentration increased, the diameter of particles decreased from 4.9 to  $3.5 \mu\text{m}$ . A relationship between the stabilizer concentration and the particle size had been obtained with a number of different stabilizers in  $\text{scCO}_2$  [2]. After the stabilizer concentration reached 7 w %, there was no significant effect on either the yield or particle size. Because the dispersion was completely stabilized to achieve efficient coverage of the pMMA particle surface at this concentration, where an acceptable monodispersity was obtained with  $\text{PDI} = 2.34$ .

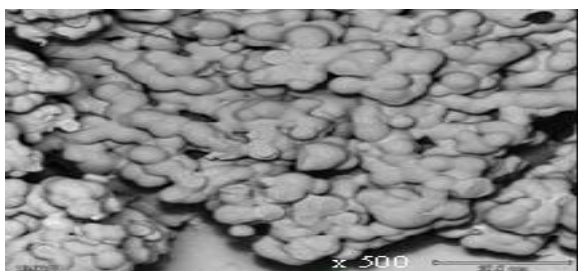
Table-3: The effect of Clariant Nuva HPC as stabilizer on the polymerization of MMA<sup>a</sup> [11]

Clariant Nuva HPC (%)	Yield (%)	$\overline{M}_n \times 10^{-3}$ (g/mol) <sup>a</sup>	PDI <sup>a</sup>	PSD	Appearance <sup>b</sup>
1	80.71	38.4	3.04	1.216	Powder
3	83.52	37.6	3.14	1.183	Powder
5	84.27	28.9	2.06	1.082	Powder
7	85.10	50.8	2.34	1.487	Powder

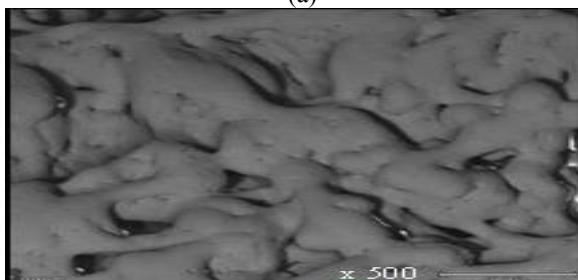
<sup>a</sup> As determined by GPC

<sup>b</sup> Appearance of polymer in cell directly after venting.

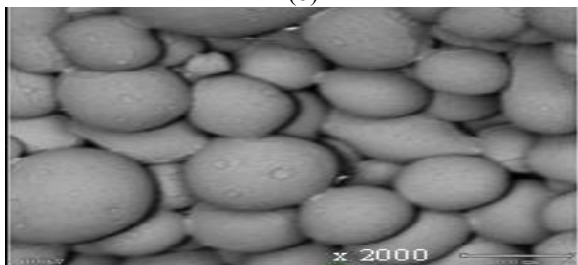
Fourier transform infrared (FT-IR) spectroscopy analyses of pMMA were performed by a Unicam Mattson 1000 spectrometer (KBr pellets; 100 scans/min, resolution  $4 \text{ cm}^{-1}$ ). The FT-IR spectrum of PMMA (Fig. 5) indicated the details of functional groups present in the synthesized PMMA. A sharp intense peak at  $1750 \text{ cm}^{-1}$  appeared due to the presence of ester carbonyl group stretching vibration as previous study [19]. The broad peak ranging from  $1300\text{-}950 \text{ cm}^{-1}$  was explained owing to the C-O (ester bond) stretching vibration. The broad band from  $950\text{-}650 \text{ cm}^{-1}$  was due to the bending of C-H. The broad peak ranging from  $3100\text{-}2900 \text{ cm}^{-1}$  was due to the presence of stretching vibrations of methylene group.



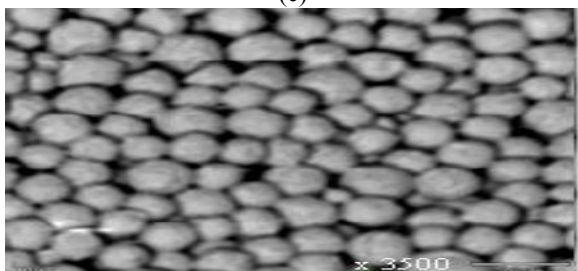
(a)



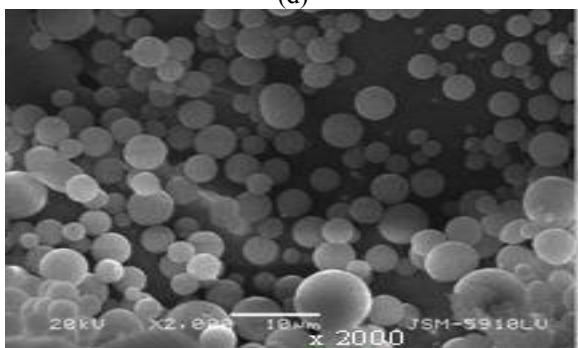
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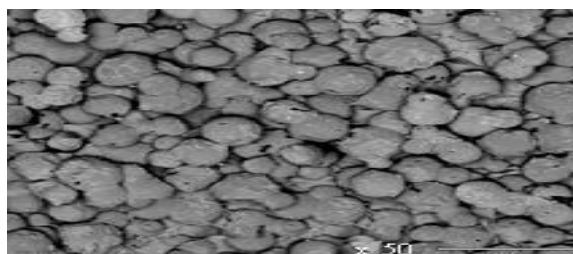


(d)

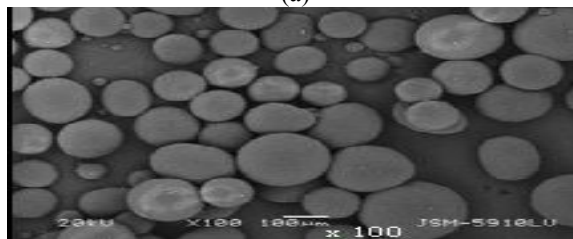


(e)

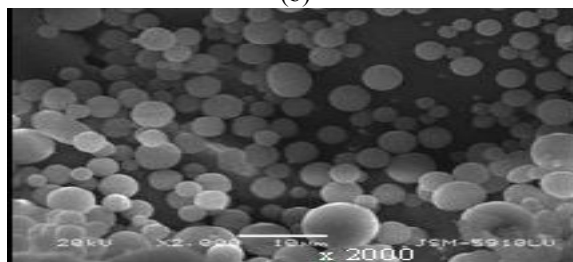
Fig. 3: SEM images of pMMA for (a) 15 MPa, (b) 20 MPa, (c) 25 MPa, (d) 30 MPa, (e) 35 MPa, (1% of AIBN, 65°C, 5% of Clariant Nuva HPC, 24 h) [11]



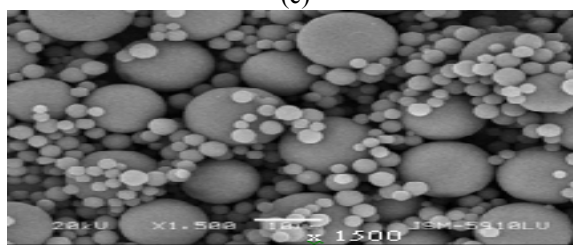
(a)



(b)



(c)



(d)

Fig. 4: SEM images of pMMA for different stabilizer concentrations: (a) 1%, (b) 3%, (c) 5%, (d) 7%, (1% of AIBN, 65°C, at 35 ± 0.5 MPa, 24 h) [11]

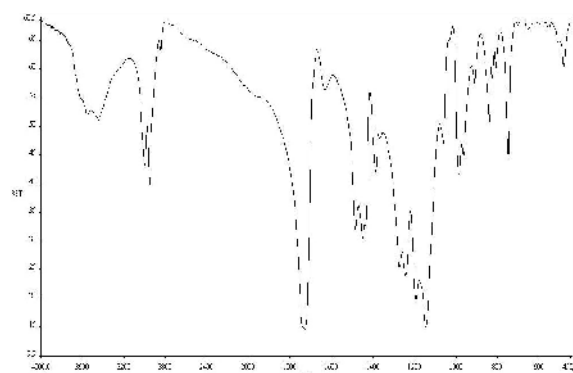


Fig. 5: FT-IR spectrum of pMMA (Polymerization conditions: 35 ± 0.5 MPa, 65°C, 1% of AIBN, 24 h, 5% of Clariant Nuva HPC)



Thermogravimetric analyses (TGA) of pMMA were carried out using a Setaram Labsys TG-DTA12. Thermal fragmentation of the pMMA synthesized was performed using TGA in nitrogen atmosphere at a heating rate of 10°C/min. The percentage weight loss reached at the end of the first derivative peak was 70% for pMMA. Decomposition of azo groups started at 200°C, and ended at 425°C. (Fig. 6).

Differential Scanning Calorimetry (DSC) of pMMA was carried out using a Perkin Elmer - Pyris 6 in N<sub>2</sub> medium with the flow-rate of 20 ml/min and the heating of 10°C/min between 80-150°C. The glass transition of pMMA was determined with 137.61°C. The crystallization of pMMA was proceeded with 140.30°C (Fig. 7).

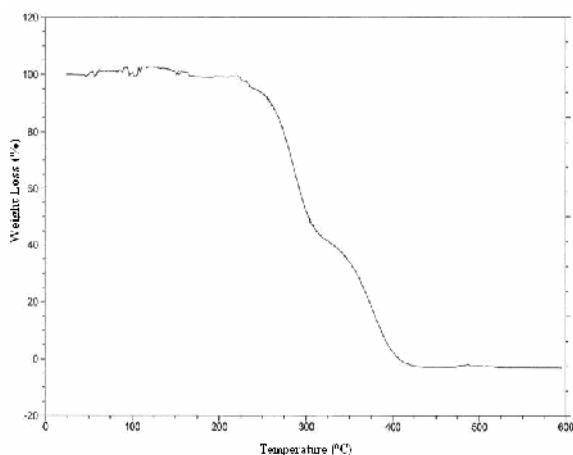


Fig. 6: TGA curve of pMMA (Polymerization conditions:  $35 \pm 0.5$  MPa, 65°C, 1% of AIBN, 24 h, 5% of Clariant Nuva HPC)

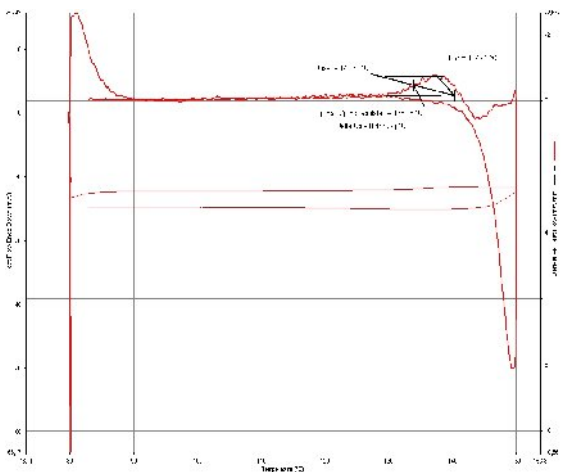


Fig. 7: DSC curve of pMMA (Polymerization conditions:  $35 \pm 0.5$  MPa, 65°C, 1% of AIBN, 24 h, 5% of Clariant Nuva HPC).

## Conclusion

The polymerization of MMA was carried out using Clariant Nuva HPC as stabilizer in supercritical CO<sub>2</sub>. The effects of the concentration of stabilizer, reaction time and pressure on the polymerization yield, molar mass and morphology of pMMA product were investigated. Clariant Nuva HPC was an effective stabilizer for the polymerization of MMA in scCO<sub>2</sub>. Dry, white, free-flowing, micron-size pMMA particles were obtained in high yields. It was observed that the yield of pMMA increased with the concentration of Clariant Nuva HPC, reaction pressure and reaction time. Molar mass of pMMA increased with reaction time and concentration of Clariant Nuva HPC. In contrast, molar mass of pMMA decreased. All results showed that Clariant Nuva HPC can be used as a fluor-containing stabilizer for dispersion polymerization of MMA in scCO<sub>2</sub>.

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