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Recommended Citation

Battaglia, Matthew S. () "Polymerization of Methyl Methacrylate in Supercritical Dioxide- A Review,"
Discussions: Vol. 3: Iss. 1, Article 5.

DOI: <https://doi.org/10.28953/2997-2582.1085>

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Polymerization of Methyl Methacrylate in Supercritical Carbon Dioxide: A Review

-Matthew Steele Battaglia -

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-Acknowledgements-

I would like to thank Dr. Hatsuo Ishida of the Department of Macromolecular Science and Engineering at Case Western Reserve University for his advice and advising in the writing of this paper. Also, I would like to thank Case Western Reserve University for the ability to review literature in regards to writing this paper.

ABSTRACT

Polymers and their processing are a very important part of today's world and the building block of many different industries including computer, automotive, etc. The typical industrial and laboratorial methods of processing and synthesis of these polymers have brought many environmental and cost concerns to the forefront. These concerns have brought about new types of methods of polymerization within recent years, and one such method is polymerization using supercritical fluids (SCFs) such as carbon dioxide. Polymerization using solvents such as supercritical carbon dioxide (scCO₂) have helped with the development of many polymers including polymethyl methacrylate (PMMA).

INTRODUCTION

1.1 Polymethyl methacrylate

Polymethyl methacrylate, or PMMA, is a polymer which is synthesized from methyl methacrylate. A representative diagram of PMMA is shown in figure 1.

Isotactic PMMA comprising molecules having a plane of symmetry.

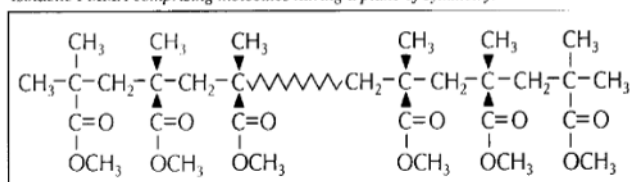


Figure 1 taken from reference Hatada.¹

It is a strong, rigid, transparent, and colorless amorphous plastic. It has a higher softening point, better weatherability, lower water absorption, good electric resistivity, and a much better impact strength than other polymers such as polystyrene^{2,3}. These characteristics of weatherability and optical clarity, along with lack of color, make PMMA an excellent tool for applications involving light transmission³. Examples of general applications include glazing, use in lighting diffusers, skylights, outdoor signs, and exterior lighting lenses in cars and trucks².

Other uses of PMMA included lithography, and PMMA is usually the typical resist film used. It has actually been the normal resist in lithography for the past twenty plus years and typically has the highest resolution available⁴. Lithograph techniques create a nanoimprinted design on a thin polymer film such as PMMA which is attached to a substrate. This is outlined in figure 2.

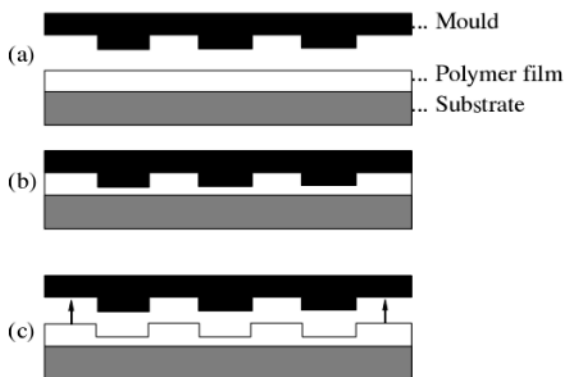


Figure 2 taken from reference Arakcheeva *et al.*⁵

- (a) Mould with polymer film substrate,
- (b) imprinting process,
- (c) mould detachment from polymer

The properties of PMMA such as its low thermal expansion coefficient of around $5 \times 10^{-5}/^{\circ}\text{C}$ and its low compression ration under pressure, around $5.5 \times 10^{-11}\text{Pa}^{-1}$, allow it to be such an excellent resist in nanoprint lithography⁵. The ability of PMMA to act as such a valuable resists assists in the production of commercial production of optical integrated circuits on a photonic crystal basis, as well as the production of semiconductor nanostructures, and many other optical applications such as microgratings for acoustic-optics, integrated optics, spectroscopy, optical interconnects, binary optics, and quantum electronics⁶.

PMMA's characteristics allow it to also act as useful in the field of optics. Such an example is the use of $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA which has been very promising in the use of rare-earth doped polymer fibers and waveguides which are instrumental in optical communication stems and sensors, such as local networks and data communications⁷. Just the same, PMMA can act as a luminescent agent when it is grafted to rare earth composite luminescent materials. It has been shown that such things have resistance to water and also produce just as much luminescence as non-PMMA grafted materials⁸.

Lastly, PMMA is a material that has had wide biomedical impacts in recent years. This includes the application to drug delivery systems and it is acting as a component of contact lenses. It has been applied in food technology and quality control systems, as well as synthetic membranes for biosensors. The list can go on from there. The application of PMMA in contact lenses is a very great contribution to society and industry as plastics such as this are light in weight, can be mass produced, and are cheaper than their counterpart, glasses⁹.

Some common properties that have been tested empirically are listed above in table 1.

Typical Properties of Poly(methyl methacrylate)	
Property	PMMA
Density (mg/m ³)	1.18–1.19
Tensile modulus (GPa)	3.10
Tensile strength (MPa)	72
Elongation at break (%)	5
Notched Izod (kJ/m)	0.4
Heat deflection temperature at 1.81 MPa (°C)	96
Continuous service temperature (°C)	88
Hardness (Rockwell)	M90–M100
Linear thermal expansion (10 ⁻⁵ mm/mm·K)	6.3
Linear mold shrinkage (in./in.)	0.002–0.008

Table 1: Taken from reference Kutz.²

1.2 Supercritical carbon dioxide as a solvent in polymerization

Over the past decades, new processing and methods of polymerization have been created and experimented with in order to reduce problems created by traditional polymerization. The problems include the use of costly, hazardous, flammable, and toxic waste, as well as the generation of large volumes of this aqueous waste. This means nearly 7.000 million metric tons of solvent is used each year, most of which becomes a waste bi-product of the reactions they are used for³. Thus, the use of supercritical fluids such as carbon dioxide (scCO₂) as a solvent can eliminate many of these problems as it does not have these effects. Other supercritical fluids exist, yet supercritical carbon dioxide is one of the most studied and easily used.

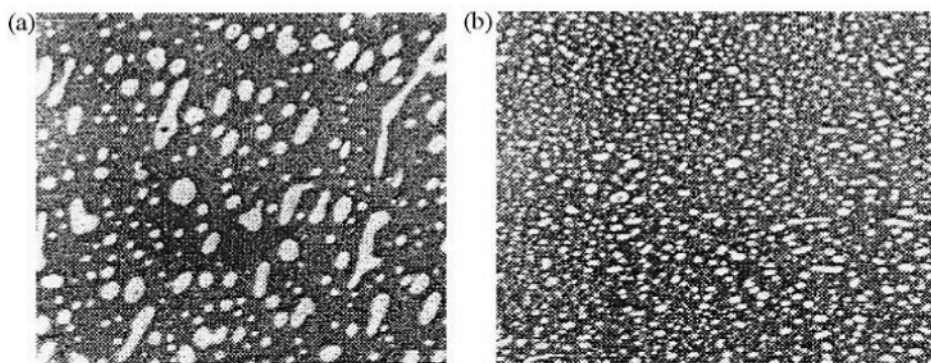
Aside from the environmental positives, supercritical carbon dioxide is great for carrying out polymerization reactions because it is also economically effective with low costs, the product can be nearly solvent free through simple venting, there is no energy intensive

drying and devolatilization processes, no chain transfer with free radical polymerizations, as well as the fact that its critical point ($T_c = 31.1^\circ\text{C}$, $P_c = 73.8$ bar) can easily be attained. Normally, it also dissolves relatively small molecular weight polymers like hydrocarbon solvents. Though it is not especially good at dissolving large molecular weight polymers, stabilizing compounds can be used in dispersion type polymerization reactions in order to synthesize the desired polymer. The surfactants either have a CO₂-philic section to react with the carbon dioxide, or a CO₂-phobic section that reacts with the polymer being made. Along with dispersion reactions, these surfactants help to stabilize the reaction and formation of high molecular weight polymers¹⁰.

Along with these high advantages to using supercritical carbon dioxide as a solvent, reactions using supercritical carbon dioxide also tend to have properties of their own. The use of scCO₂ tends to lower glass transition temperatures of the polymer which creates plasticization of this polymer. This effect allows the removal of residual monomer, incorporation of additives, and also the formation of foams. Also, molecular weight distributions can easily be controlled, as well as unreacted monomer can be regained from the system. Depending on the set up of the system and any stabilizing surfactants and copolymers used, particle size and shape can be controlled, as well as the conversion of a greater amount of monomer to polymer compared to normal synthetic methods¹². Likewise, this shape and size control element allows for the production of highly porous materials³.

A developing application of supercritical carbon dioxide as a solvent is its use with blending polymers. This is when two immiscible polymers are mixed to-

gether to form a material with new properties such as impact strength or rigidity. The use of supercritical carbon dioxide has improved the blending process as the scientist can now control the size and relative shape of the components. When blending occurs, usually polymer A and polymer B are mixed, and two phases are formed, one rich in droplets contains polymer B and the other is continuous and rich in polymer A. The viscosity ratio of B to A controls the size of the droplets, and without supercritical carbon dioxide, the shape and size of droplets is relatively uncontrolled. The use of $scCO_2$ allows the scientist to then control the size of these droplets and make a better structured blend of polymers¹¹. This is seen in figured 3.



TEM micrographs of PMMA/PS (25/75) blend: (a) without CO_2 ; (b) with supercritical CO_2 . Reproduced from Elkovitch, Lee and Tomasko by permission of the Society of Plastics Engineers, USA.

Figure 3 taken from Nalawade *et al.*¹¹

The advantages to using super critical carbon dioxide as a solvent are great. Not only can one modify the solvent for a specific purpose by changing the pressure, but these changes have also allowed for the development of polymers with specific sizes and morphologies. Also, the use of this solvent is also applicable to a wide range of polymerization reactions, including all types of chain and step-growth polymerizations such as ionic, free-radical, and metal-catalyzed reactions. Also, with the

development of surfactants, supercritical carbon dioxide is no longer limited to specific polymers, and can produce large, high weight molecular polymers.

This paper will specifically review those different methods involved in the polymerization of high molecular weight MMA in the solvent supercritical carbon dioxide, and how the challenges of its polymerization are met. The focus will be on dispersion polymerizations and the use of surfactants, though there will also focus on alternative methods currently being explored, some of which may eliminate the use of stabilizers used in dispersion polymerization.

DISCUSSION

2.1 Dispersion polymerization and the use of surfactants

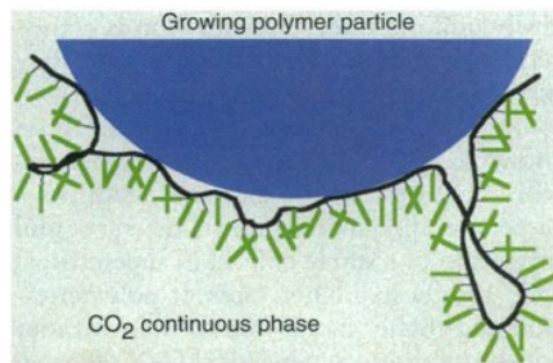
As previously mentioned, the one problem with using supercritical solvents such as carbon dioxide is that larger molecular weight polymers such as polymethyl methacrylate are not soluble in this supercritical solvents. A method thoroughly developed and researched by such scientists as DeSimone has found that dispersion polymerization is a key method to facilitating the polymerization of methyl methacrylate in supercritical carbon dioxide, though other methods can be somewhat successful.

Dispersion polymerization is defined to be the heterogeneous polymerization process based on the formation of latex particles, usually in the form of a fine powder, in the presence of a stabilizing dispersant

known as the surfactant¹⁰. The role of this surfactant is to adsorb and chemically attach to the surface of the growing polymer particle. The surfactant will then prevent the particles from aggregating by electrostatic, electrosteric, or steric mechanisms. In super critical CO₂ based systems, the surfactants provide steric stabilization because the carbon dioxide solvent has a rather low dielectric constant. The stabilizing particle tends to be a macromolecule that exists directly at the polymer-solvent interface. It prevents aggregation by coating the surface of the particles and forming long-range repulsions between them. These imparted repulsions must be greater than the attractive force of the existing van der Waals forces existing between the particles¹².

The surfactant can attach to a polymer in a multitude of ways. This includes either chemical grafting or physical adsorption. Physical adsorption is best achieved by using amphiphilic materials (ones that are both hydrophilic and hydrophobic) such as graft or block copolymers. These materials work so well because they have one component in the continuous phase, while the other component is in the polymer phase. The second route to stabilization occurs through chemical grafting of the stabilizer to the polymer particle either through chain transfer or by using such a stabilizer that acts as an initiator, monomer, or terminating agent in the reaction. These chemically grafted stabilizers provide far better colloidal stability than their physical stabilizer counterpart. Typical types of stabilizers used as surfactants include CO₂-philic polymers, block or graft copolymers with both CO₂-philic and CO₂-phobic component, or CO₂-philic reactive macromonomers¹². An example of how the surfactants interact with particles is

shown in Figure 4 where PMMA is interacting with the surfactant PFOA¹³.

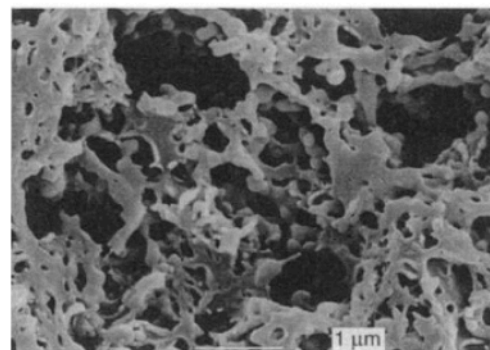


Schematic illustration of a PMMA particle stabilized by poly(FOA) in which the lipophilic backbone acts as an anchor for the fluoro-carbon steric stabilizing moieties.

Figure 4 taken from reference DeSimone *et al.*¹³

2.2.1 Poly(1,1-dihydroperfluoro-octylacrylate)

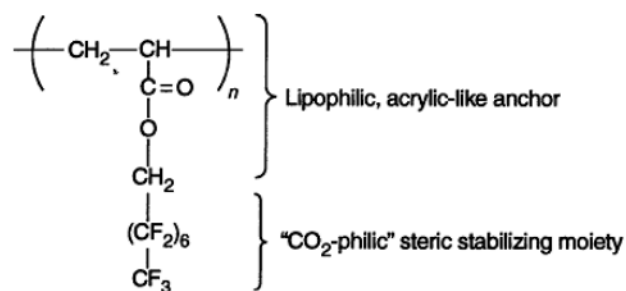
As stated before, high molecular weight polymers such PMMA cannot be formed in super critical carbon dioxides solvent without a stabilizer. PMMA produced without stabilizers tend to form polymers that form thick irregular films on the interior walls of the reaction cells denoting a precipitation reaction with very low conversions and an unstable, unrecognizable morphology¹³. Conversion percentages of less than 40% were observed¹². This unrecognizable morphology is depicted in figure 5.



Scanning electron micrograph of PMMA synthesized in CO₂ without stabilizer.

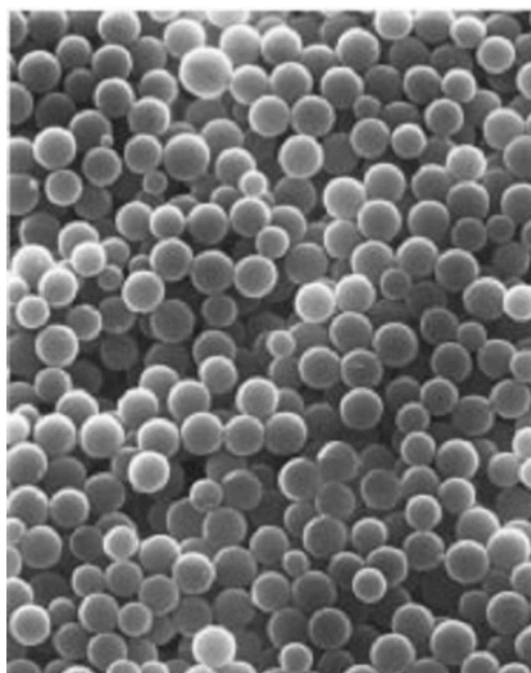
Figure 5 taken from reference DeSimone *et al.*¹³

In 1994, the novel approach to add stabilizers to the dispersion polymerization reaction was used by DeSimone and his team. They employed the use of poly(1,1-dihydroperfluorooctylacrylate) or PFOA pictured in figure 6¹². The amphiphilic nature of this homopolymer reacted well with the lipophilic monomer. The reaction ended up polymerizing MMA to high conversion rates of greater than 90% and high degrees of polymerization as well (greater than 3000) in the supercritical solvent. The experiments were conducted at 65°C and a pressure of 207 bar with AIBN or fluorinated derivative of AIBN. Not only did the polymer produced have high conversion percentage, but it formed relatively even spherical particles that had a narrow size range of one to three micrometers¹². DeSimone also found that increasing the dispersant concentration led to much finer, smaller and more uniform particles. Also increasing the overall molecular weight of the stabilizer resulted in a greater increase in particle size¹⁴. The new, finely made product is pictured in figure 7. The ending results were also significant as it was found that 83% of the solvent could be removed after drying and depressurizing of the PMMA from the carbon dioxide occurred. This is very significant as the stabilizer is of high cost, and thus can be recycled for use in following experiments¹².



The chemical structures of an-interfacially active, polymeric stabilizer [poly(FOA)], depicting the proposed site of anchorage for the CO₂-philic steric stabilizing moieties.

Figure 6 taken from reference Kendall *et al.*¹²



Scanning electron micrograph of PMMA particles produced by dispersion polymerization in CO₂ using PFOA as the stabilizer.

Figure 7 taken from reference Kendall *et al.*¹²

2.2.2 Polydimethylsiloxane

Another more recently studied stabilizer is polydimethylsiloxane (PDMS). This stabilizer has been sought after because of the relative expensive nature of fluorinated polymers¹². Despite the advantage of being cheaper, PDMS-based surfactants are less soluble in scCO₂ because monomer is continuously needed in the continuous phase, and thus these surfactants generally have to be capped with some sort of methacrylate in order to help solvate the PDMS tails and prevent flocculation, which is the formation of polymers attaching to each other, forming a fragile structure^{12,15}. Other times, the PDMS has other attachments.

Countless numbers of different forms of the stabilizers have been tested and different ones have worked at different conditions. One such example of a derivative of PDMS is PDMS-g-pyrrolidone carboxylic acid (Monasil PCA), which is a CO₂-philic stabilizer. Using this stabilizer, a 94% conversion was achieved at supercritical conditions of 338.2 K and 345 bar. Unfortunately though, this method is not perfect. It was found that when the polymer was not well stabilized the conversions were below 90%, and the polymer formed was heavily agglomerated, forming a cake-like morphology. Despite this, shape of stable particles formed were of average size, spherical in shape, and the average size decreased exponentially with increase the amount of surfactant. Also, the issue of agglomeration was solved with an increase in the amount of surfactant used. As surfactant concentration was increased, the particle size distribution narrowed, and it allowed for a more uniform polymer. This is very important as it allows for a product that is usable in both industry and the laboratory set-

tings. Figure 8 accounts for statements presented earlier about the size distribution range seen at a lower and higher concentration of the stabilizer. Stable, acceptable PMMA was polymerized when at least 7% of the Monasil PCA was used¹⁶.

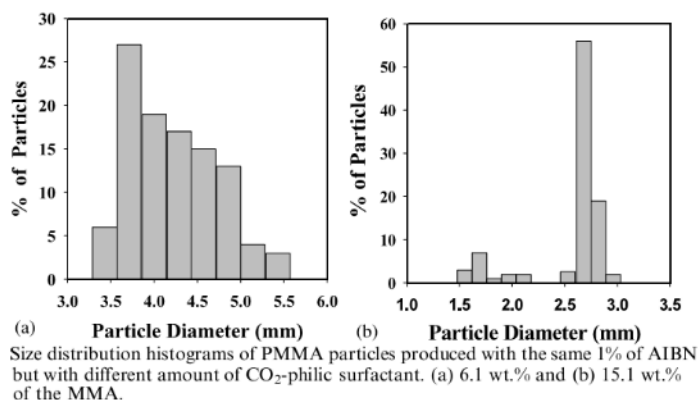


Figure 8 – Taken from Reference Park and Shim.¹⁶

Another very popular PDMS derivative that has been used in the polymerization of MMA has been polydimethylsiloxane-methyl methacrylate of PDMS-mMA macromonomer. Like other forms of PDMS, both a minimum pressure, as well as a stabilizer concentration has to be reached in order to reduce particle coagulation and prevent steric stabilization. This pressure is 3000 psia and around a 2 weight % of stabilizer to monomer. Again, greater concentrations of the macromonomer lead to a general greater percent yield of the PMMA product and also smaller, finer particles¹⁵.

These types of surfactants obviously have their advantages and disadvantages. Unlike PFOA and its derivatives, PDMS derivatives are much cheaper because they do not use fluorine associated molecules. Despite this advantage, the decreased solubility of the surfactant in the solution means PDMS cannot be used, and multitudes of derivatives have to be formed in order for the dispersion polymerization to occur and form

PMMA. In fact, it seems direct conditions such as specific pressure settings, and also much higher weight percentages of the stabilizer to monomer have to be used. Also, reaction time also plays a factor; as reaction time increases, coagulation is less frequent and stable latex particles are formed¹⁵. This is seen in table 2.

If proper conditions are not met, coagulation and agglomeration usually occur and form a product with low percent yield and a morphology that cannot be

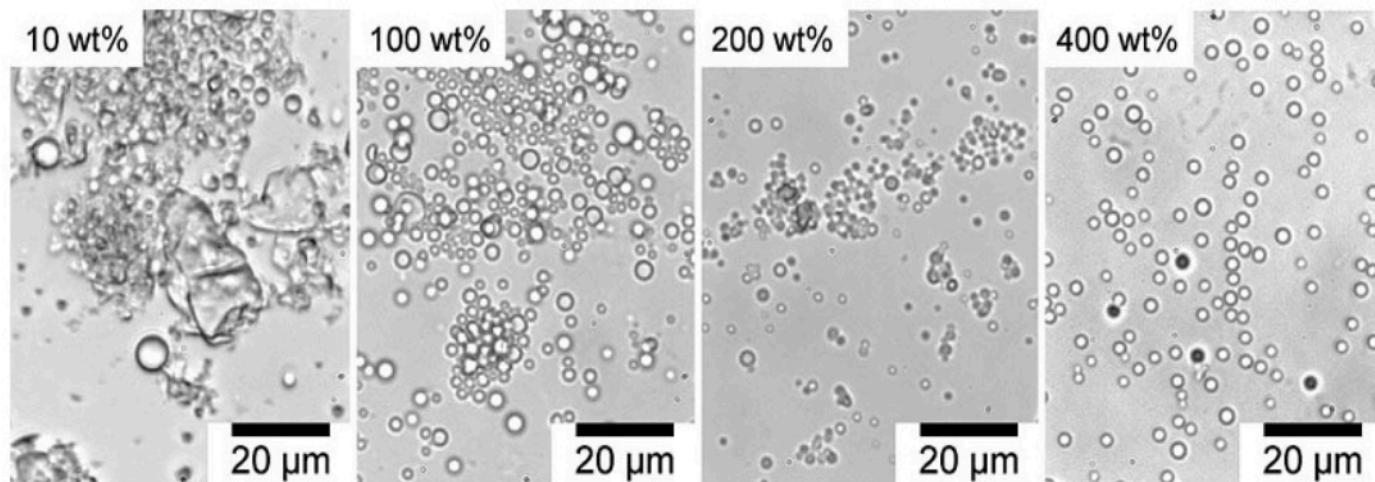
used in any real sense. An excellent example is the use of another derivative of PDMS known as trimethylsiloxy terminated PDMS (TS-PDMS). As the weight percentages of the stabilizer are increased as compared to the monomer, the morphology changes becoming much finer and the particle size decreases to a useable PMMA product¹⁷. This is clearly shown in figure 9.

Dispersion Polymerization of MMA in CO₂ at Various Pressures and Times^a

time (h)	pressure (psia)	yield (%)	M_w ($\times 10^{3g/mol}$) PDI	product morphology	approximate particle size (μm)/PDI
5	4000	88	365/3.9	uncoagulated	3.3/1.08
2	4000	68	247/4.0	n/a	n/a
1	4000	15	n/a	n/a	n/a
5	3000	93	339/4.0	partially coagulated	3.1/1.11
5	1500	90	481/4.5	coagulated	2.5/1.28
2	2000	34	203/10.9	n/a	n/a
1.25	2000	12	n/a	n/a	n/a

^a All systems were 25–30 wt % MMA/CO₂, ~5 wt % PDMS-mMAMMA, ~1 wt % AIBN/MMA, and 65 °C.

Table 2 taken from reference O'Neill *et al.*¹⁵



Optical micrographs of *n*-hexane redispersions of centrifugally washed PMMA particles with *n*-hexane, which were prepared by dispersion polymerizations with BPO (4.0 mmol/L) at different TS-PDMS concentrations (wt% based on MMA) in scCO₂

Figure 9 – Taken from reference Fujii *et al.*¹⁷

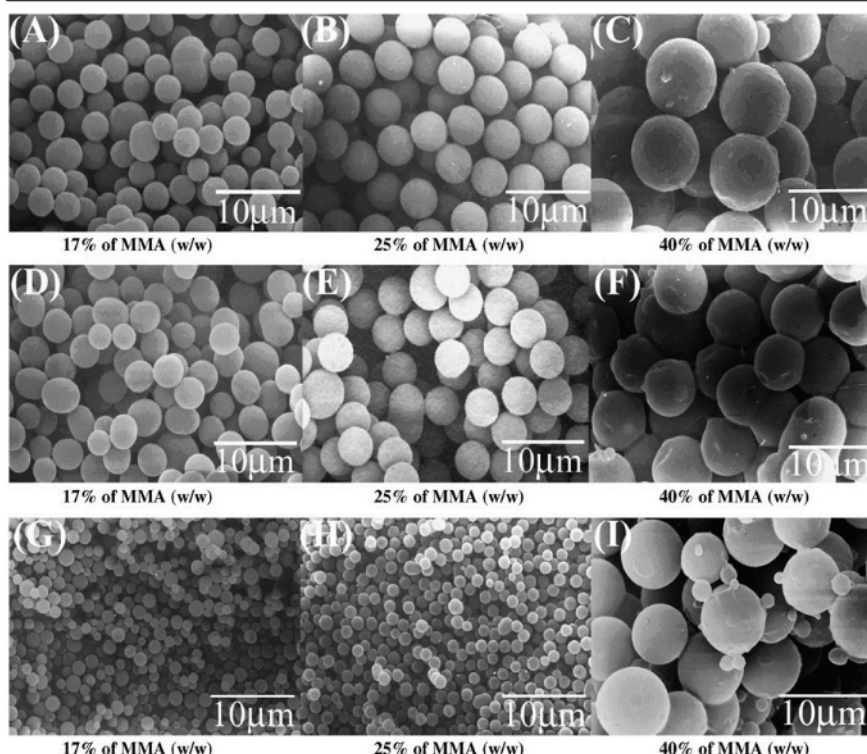
2.2.3 Random Copolymers

Though block and graft copolymers containing siloxane or fluorinated polymers such as PDMS and PFOA derivatives have been very successful in the laboratory setting when synthesizing PMMA, the small limitations to these methods have had scientists query further into the dispersion polymerization of PMMA. Fluoropolymer stabilizers are so expensive and most other graft and block copolymers such as PDMS derivatives are complex and difficult to synthesize, and they also agglomerate when conditions are not perfect¹⁸. Also, these type of block and graft polymers cannot be characterized in usually solvents because of their poor solubility¹⁹. In order to solve these problems, scientists have tested the development and use of random copolymers containing small amounts of fluorine to act as the soluble part and were incorporated with a comonomer of MMA which acted as the binding part to the MMA particles¹⁸.

One such experiment used three semi-fluorinated random copolymers using fluorinated octyl-methacrylate (FOMA) and three different comonomers of methacrylate derivatives, including n-butyl methacrylate (BMA), 2-dimethylaminoethyl methacrylate (DMAEMA), and methyl methacrylate (MMA). The three random copolymers used were poly(FOMA-co-DMAEMA), poly(FOMA-co-MMA), and poly(FOMA-co-BMA). Each of these stabilizers were used in supercritical carbon dioxide where the temperature was 65°C, a pressure of 345 bar, a reaction time of 12 hours, 2% stabilizer, and 1% of the initiator AIBN. As the reaction concluded, it was shown that only the poly(FOMA-co-DMAEMA) surfactant produced good latex stability of

the PMMA and that the particles were fine with a relatively uniform size, while the other stabilizers formed flocculated, white clumpy solids that were not usable. Thus, not all random copolymers are usable to produce stable PMMA particles, but a result that was surprising was that a poly(FOMA-co-DMAEMA) of just 34 w/w% of the FOMA was used, as compared to previous experiments which suggested that much higher weight percentages of the fluorinated polymers have to be used in the polymer in order to have a stable polymerization with high conversion percentages¹⁸.

Another experiment involved the use of poly (poly(ethylene glycol) methacrylate-co-1H,1H,2H,2H-perfluorooctylmethacrylate) or p(PEGMA-co-FOMA). This experiment incorporated the same tests as other experiments, but another characteristic put into question was the effect of the pendant chain length of the PEGMA copolymer. The stabilizers containing greater amounts of the FOMA, or fluorinated copolymer, were found to have higher conversions of PMMA as well as small, finer powders of the PMMA. The lower concentrations of FOMA in the copolymers did produce very high conversion, but the product formed somewhat irregular shapes of particles as well also small amounts of agglomerated product was formed, though it would easily be broken up. Secondly, the stabilizers containing larger pendant chain lengths of the PEGMA formed a finer powder instead of a clumpy solid. It seemed that the extended length of 1100 allowed for a greater anchoring of the PMMA particles and prevented particle aggregation. Furthermore, the smaller chain lengths of 300 and 475 were much more soluble in the supercritical carbon dioxide, while the PEGMA having a length of 1100 was less soluble, and thus able to absorb onto the



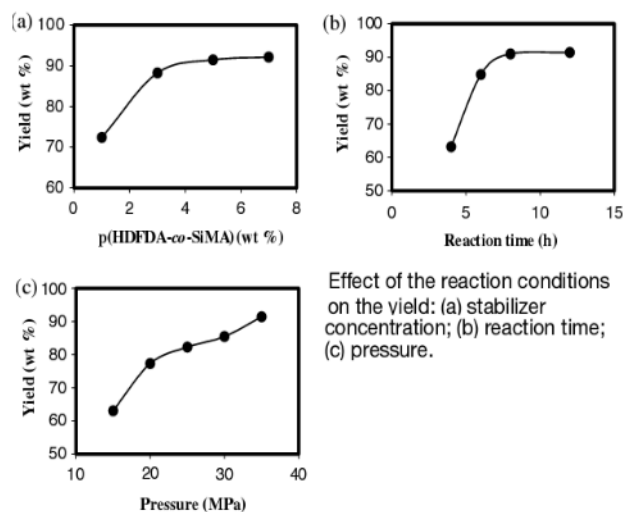
Scanning electron micrographs of PMMA particles prepared with various MMA concentrations (w/w): (A–C) PEGMA (475)-*co*-FOMA (33:67), (D–F) p(PEGMA (475)-*co*-FOMA) (16:84), and (G–I) p(PEGMA (1100)-*co*-FOMA) (12:88). Reaction conditions: 5% of stabilizer (w/w to MMA), 65 °C, 345 bar, and reaction time: 12 h.

Figure 10 – Taken from reference Hwang *et al.*¹⁹

PMMA particles and provide better anchoring. Lastly, this experiment showed that increasing concentration of the monomer, MMA, allowed for greater size of the resulting PMMA. All of this is seen in figure 10, as MMA concentration is increased the size of the PMMA particles increases, as FOMA content is increased, the particles become more spherical in nature, and as the pendant chain length is increased, the particles form finer powders¹⁹.

Like the PDMS derivatives, random copolymers and their efficiency in polymerizing MMA are affected by pressure, concentration of the stabilizer, and reaction time. Like all other random copolymer stabilizers, an experiment conducted using poly((heptadecafluorodecyl acrylate)-*co*-3-(tris(trimethylsilyloxy)silyl)propyl methacrylate, or p(HDFDA-*co*-SiMA), as the stabilizer

showed that increasing the weight percentage of the stabilizer in the solution increased the yield, number molecular average, decreased the PDI and decreased the diameter of the PMMA product creating a fine, white powder which is usable. Relatively low concentration of the copolymer, just like most reactions, produces an unusable, unrecognizable morphology in solid form. This random copolymer was also tested, as stated before, for reaction time and pressure effects as well on the yield of PMMA²⁰. The relationship between these effects and their relationship to the conversion of MMA to PMMA is seen in figure 11.



Effect of the reaction conditions on the yield: (a) stabilizer concentration; (b) reaction time; (c) pressure.

Figure 11 taken from reference Deniz *et al.*²⁰

Carole Leppilleur and Eric Beckman state it best when describing the use of random copolymers, such as p(MMA-*co*-HEMA)-*g*-PFPO which they tested. Along with pressure and reaction time, there must be a great balance between the soluble part and the anchor group of the stabilizer at hand. If properly done, the balance

should provide proper adsorption of the MMA particle leading to smaller, narrowly dispersed particles with larger molecular weights, and the proper amount of the soluble component will allow for proper stabilization, prevent larger particle sizes and greater size distributions. Of course, like all other methods used in dispersion polymerization of PMMA in supercritical carbon dioxide, concentration of the stabilizer as a whole is also very important¹⁴.

2.3 Catalytic chain transfer used in polymerizations of PMMA utilizing supercritical carbon dioxide

Polymerization in supercritical carbon dioxide has also been used by some scientists to produce small molecular weight and medium molecular weight PMMA using catalytic chain transfer instead of the typical stabilizing agents. This has been employed using transition-metal catalyst tetraphenylcobalt-oxime boron fluoride (COPhBF) as a chain transfer agent^{21, 22}.

Successful polymerization of medium ranged molecular weight PMMA product was developed using COPhBF in the presence of a PDMS-ma surfactant. It is important to note that this reaction only works with a surfactant, thus employing a dispersion polymerization. Without such a surfactant, the resulting polymer is a sticky solid or a viscous fluid. Otherwise, the use of a surfactant produces a free-flowing white powder with high conversion percentages to the product, PMMA.

Experimental results also showed that as the concentration of the catalyst was increased, molecular weight continued to decrease, producing polymers with number molecular weights of 20,000 to 50,000 depending on the concentration of the catalyst. The only prob-

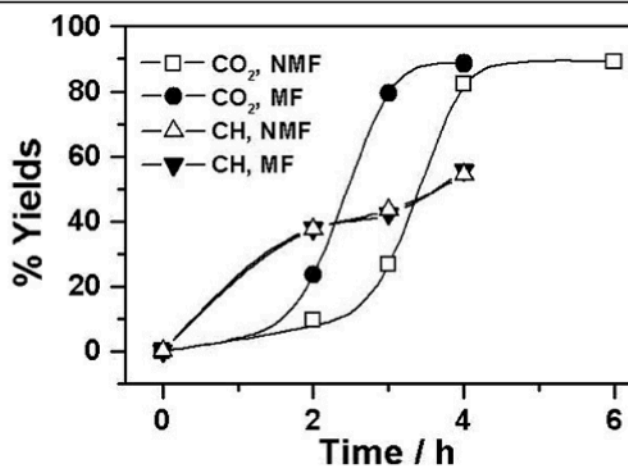
lem was the ending polymer was partially flocculated in morphology. This flocculation was most likely caused by the supercritical carbon dioxide being able to easily plasticize the polymer because of its small molecular weight. The small molecular weight distributions shown in the experimental results show that the catalytic chain transfer agent's activity was reduced, thus allowing or medium sized polymers in terms of number average molecular weight²¹.

Polymerizations using supercritical carbon dioxide and the catalytic transfer agent COPhBF, but not a stabilizing agent, produced PMMA characterized as very small, oligomeric acrylics. Though the molecular weight distributions were much narrower in supercritical carbon dioxide than other tested solvents such as toluene and bulk MMA, but the products were much smaller in number average molecular weight. This proves that the supercritical carbon dioxide solvent acts in helping the chain transfer rate as it is greatly increased, thus producing smaller polymers. As originally stated, supercritical carbon dioxide allows for control of the resulting polymer in terms of size and molecular weight. In this case, as opposed to dispersion polymerization, polymerization using a chain transfer agent in this supercritical solvent allows for the formation of a much smaller sized PMMA²².

2.4 Other methods used to change molecular weight of the PMMA product

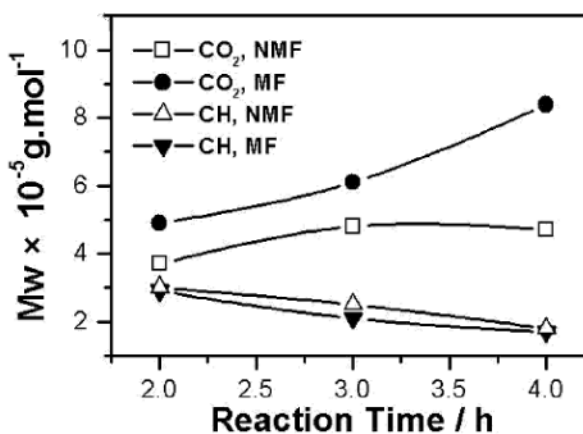
2.4.1 Magnetic fields

A recent study was conducted where magnetic fields were tested in polymerizing MMA in different solvents, including cyclohexane and supercritical carbon dioxide. Though a dispersant, or surfactant, was not used, the implication was that the resulting effects of the study could also be employed with dispersion reactions of MMA in supercritical carbon dioxide. The authors used a 3000 G external magnetic field when testing the magnetic field effect on the polymerization of MMA. The results revealed that the magnetic field effect increased the weight average molecular weights of the PMMA, and that the presence of a magnetic field produced a higher molecular weight polymer than without. The experiment also showed that at a certain time in the polymerization, percent yield was actually three times larger than the PMMA polymer produced without the magnetic field. The polymerization of MMA in the cyclohexane solvent was not affected by the magnetic field at all. These results are summarized in figures 12 and 13. The authors determined that the magnetic field actually accelerated the precipitate phase, which is significant because swelling of the PMMA caused by supercritical carbon dioxide allowed for more of the PMMA to be in the precipitate phase²³.



The yield of PMMA at different reaction times in SC CO₂ and cyclohexane with and without MF.

Figure 12 taken from reference Liu *et al.*²³



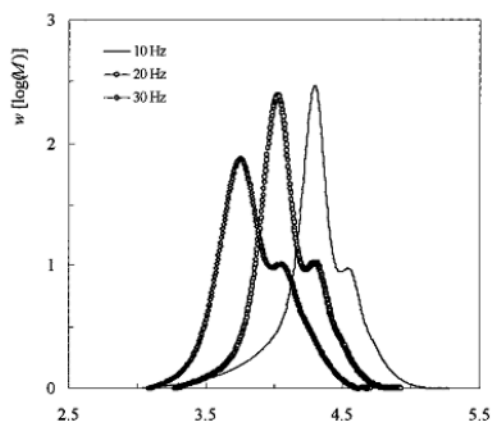
The weight average molecular weight of PMMA at different reaction times in SC CO₂ and cyclohexane with and without MF.

Figure 13 taken from reference Liu *et al.*²³

2.4.2 Pulsed lasers vary molecular weight distribution

Pulsed-laser polymerization, or PLP, works by using laser pulses to create radical from a photoinitiator. Though these radicals may combine bimolecularly, the instantaneous and large increase in radical concentration allows the growth of many new polymer chains. Just like the use of magnetic fields, this use of PLP has not been tested using surfactants, but has been used in supercritical carbon dioxide solvents with MMA. The photoinitiator makes it so no initiator is needed in the

reaction. Upon different laser repetition frequencies, the molecular weight of PMMA was changed. As the frequency of the firing increased, molecular weight decreased as more and more radicals were formed, breaking the existing polymeric chains. Laser energy and photoinitiator concentration did not seem to effect the reaction²⁴. This is seen in figure 14. Though this technique does not employ the use of surfactants and disper-



Molecular weight distribution (MWD) for PMMA produced in $scCO_2$ by pulsed-laser polymerization at various laser repetition frequencies: $[DMPA] = 6.7 \text{ mmol}\cdot\text{L}^{-1}$, $[MMA] = 6.2 \text{ mol}\cdot\text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, and $P = 180 \text{ bar}$.

Figure 14 taken from Quadir *et al.*²⁴

sion polymerization, it can be a useful method in the future because it can control and change the length and size of PMMA chains based on firing frequencies of the laser.

2.5 Future considerations

As with all techniques, many of the conditions and methods used could be improved to make the process and end product much better than they already are. For example, pressure and temperatures settings could be optimized for the supercritical carbon dioxide solvent, monomer, initiator, and surfactant concentrations

could be optimized, as well as the development of better surfactants would aid these processes.

With all these possible fine tunings to dispersion polymerization, other methods are being developed for the polymerization of MMA in supercritical carbon dioxide. As has been mentioned, pulsed-laser polymerization, the use of magnetic fields, and catalytic chain transfer agents are just some of the newly developed possibilities in the supercritical solvent. Another such future possibility is the use of ultrasound assisted polymerization.

Ultrasound assisted polymerization works by using wave frequencies ranging from 16kHz to a few megahertz. When an ultrasound of proper amplitude passes through the medium in use, large numbers of microbubbles form, grow, and collapse in a very short time. This cavitation phenomenon provides the mechanism for the sonochemistry effect. During cavitation, the bubbles collapse and produce intense local heating and high pressures during a short period of time. Cavitation creates temperatures greater than 5000°C and pressures above 1000 atm at cooling rates above 1000 K/s. These extremely harsh conditions allow for the production of excited states which are able to break chemical bonds and form free radicals. Secondly, ultrasound has unique properties which have strong dispersing, stirring, and emulsifying effects which allow for new routes of stabilization of dispersion latex²⁵.

Though the conducted experiment did not use supercritical carbon dioxide, the authors used near supercritical conditions, including very high pressures. The experiment revealed that after periods of two, four and six hours, the number and weight average molecular weights of PMMA increased. Also, the CO_2 /monomer

ratio was also significant. As the monomer concentration was raised, the molecular weight of the ending PMMA chain increased and the molecular weight distribution decreased because the resultant polymer was more soluble in solution. Though the experiment was not conducted at supercritical conditions, the authors hinted this could possibly be used in such conditions because this experiment produced a stable dispersion polymerization. They also noted the advantage that there was no necessity for a stabilizer using ultrasound irradiation in the polymerization of PMMA²⁵.

CONCLUSION

Modern methods of polymer processing have come into question because of their cost and waste producing drawbacks. The development of supercritical carbon dioxide as a solvent has acted as a monumental solution to these laboratory and industrial related polymer processing problems. Not only is it considered a "green solvent," being safe for the environment, but it is also a much cheaper solvent as it is just carbon dioxide at extreme conditions. The development of such a sol-

vent is very important as it has impacted the processing of polymethyl methacrylate. This new technique thus allows for easier processing of PMMA which is important in many important areas today, such as optics, biomedical, and glass-related products.

Due to some limitations of supercritical carbon dioxide, dispersion polymerization, the use of surfactants as stabilizers, was developed in order to incorporate PMMA into the supercritical solvent. Since the dawn of its use, many different surfactants with different properties have been developed. Scientists are continually trying to improve the process so production of more stable, higher molecular weight latex PMMA particles will be created. Other methods have been attempted, some of which employ the idea that stabilizers may not be needed. These methods include the use of catalytic chain transfer, and the possibilities of PLP, magnetic fields, and ultrasound in this supercritical solvent. Continued research and development will eventually lead to a method utilizing supercritical carbon dioxide that will produce PMMA with high conversion, very high stability, and high molecular weight.

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