CHAPTER IV

Synthesis and Characterization of Nano-sized PMMA in Pure Emulsion at Room Temperation via ATRP

4.1. Introduction

Recently, nano-sized polymer particles have received increased research attention since they possess many unique and special properties. For large scale industrial applications, it is highly imperative to develop a robust method to produce nano-sized polymers with controlled molecular weight and narrow polydispersity. Ideally, the polymers are to be produced in an aqueous system because of environmental concerns hence an ideal system has to be developed and scaled to industrial production capacity. In this regard, Atom transfer radical polymerization (ATRP) becomes a versatile polymerization technique. Since its discovery in 1995[1,2] ATRP has been extensively studied for preparation of polymers with pre-determined molecular weight, narrow molecular weight distribution, high chain end functionality,[3] and desired molecular architectures.[4-10] For the past decade attempts have been made to extend ATRP to more environmental friendly aqueous dispersed medium, due to their economical and ecological importance. ATRP in aqueous dispersed media has advanced at a slower pace[11,12] compared to ATRP in both bulk and solution systems.To date, the most successful approach to aqueous dispersed ATRP has been the miniemulsion system, mainly because the polymerization environment is almost identical to that of a bulk system.[13,14]

The miniemulsion ATRP process has been successfully applied to the synthesis of numerous well-defined polymers.[15-23] However, miniemulsion is a less viable approach for large scale industrial application because it is difficult to operate high shear forces such as sonication or fluidization (which are necessary to form miniemulsion) on large volumes of biphasic liquid mixtures. A true emulsion system[11] (as distinct from miniemulsion) should be easier to manipulate and can provide direct-use latex products. The procedure of performing the polymerization in a true emulsion has been the most desirable aqueous dispersed medium for both academic study and industrial applications. A typical emulsion polymerization starts with a high concentration of monomer-swollen micelles and dispersed monomer droplets (1-20 μm). Particle nucleation occurs when radicals (generated by decomposition of free radical initiators) enter the micelles. As the micelles are depleted of monomer (forming polymerizing particles), the monomer

droplets function as a monomer reservoir with monomer diffusing through the aqueous phase to these polymerizing particles. Particles continue to grow until the monomer droplets are depleted. The unique feature of kinetics in emulsion polymerization results from the compartmentalization of the propagating radicals within separate particles, which facilitates a high polymerization rate as well as high molecular weight. Since its implementation more than half a century ago, emulsion polymerization has been the dominant aqueous dispersed polymerization process and has found numerous applications in industry.[24,25] Relative to the success of ATRP in miniemulsion, little progress has been achieved on ATRP in a true emulsion system. The extension of ATRP to an emulsion system initially attempted in 1998, led to a controlled aqueous dispersed polymerization.[26] However, the mechanisms of nucleation and particle growth during the polymerization deviated from a classical emulsion approach. Since direct ATRP was adopted and the oil-soluble initiators and catalysts preferentially stayed in the large droplets, a (mini)suspension polymerization was the more probable process, as demonstrated by the relatively large particle size and broad particle size distribution in the final product.

Recently, similar approaches were reported in which results indicating controlled polymerizations were obtained. However, colloidal stability was a serious problem, given the relatively large particle size.[27-30] A true emulsion ATRP was later approached when reverse ATRP was employed to ensure that nucleation did not occur in the monomer droplets.[31] However, most of the oil-soluble catalysts were still initially distributed in the large monomer droplets and were reluctant to diffuse across the aqueous phase to the micelles. Consequently the polymerization was not well regulated due to insufficient catalyst concentration at polymerization loci, as evidenced by the low initiation efficiency.

In short, ATRP has not yet been successfully implemented in true emulsion. Prior problems have been attributed to the inefficient transport of Cu-based catalysts from monomer droplets to micelles/polymerizing particles. To overcome this problem, a true emulsion ATRP was designed and mixed ligand system was utilized for the first time and polymerization was done at room temperature, the details are discussed in this chapter. All ATRP initiators, catalyst, ligands and a small amount of monomer were encapsulated

in emulsion micelles accomplished in the absence of any high-shear environment.[32] After activating the catalyst and initiating the reaction, the rest of the monomer was fed to the polymerization system dropwise through differential emulsion polymerization by a semi-batch operation. A semi-batch process with starved monomer feed allows control of the propagation rate and copolymer composition, avoiding the composition drift observed in batch systems.[11]

In the starving feed method, (or a semi-batch system)[19] monomer droplets cannot exist. The monomer added to the reaction system is quickly consumed by the growing chains or used to generate polymer radical particles. The differential addition of monomer gave the smallest polymer particles compared to all the addition methods.[33] During the polymerization, the diffusion of monomer from monomer droplets to the polymerizing particles containing the catalyst and growing polymer chains mimicked a true emulsion system. This chapter presents an attempt to synthesize nano-sized PMMA by a true emulsion system using mixed ligand system at room temperature.

4.2. Experimental

4.2.1. Materials

Methyl metacrylate (MMA, 99%) was purified by passing the through the column filled with basic aluminum oxide to remove inhibitor and vacuum distilled over CaH_2 before use. Ethylene glycol (Acros, 97%), 2-bromoisobutryl bromide (Aldrich, 97%), N,N,N,N',N'-pentamethyldiethylenetriamine (PMDETA, 99%) 2,2'-bipyridine (bipy) (Aldrich, 99+%), CuBr (Aldrich, 99.995+%), Polyoxyethylene (20) Oleyl Ether, Brij 98 (Aldrich) and Calcium hydride (Junsei, 97%) were used as received. Triethylamine (TEA) was dried over anhydrous $MgSO_4$.

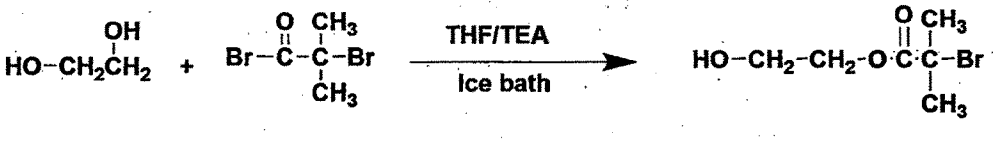
4.2.2. Methods

To determine molecular weight (M_n) and molecular weight distribution, M_w/M_n (MWD), GPC was done using Waters M 77251, M 510 with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series). The pore size of the columns was 50, 100, 10^3, and 10^4 Å, respectively, with a refractive index detector at a flow rate

of 1 mL/min. Tetrahydrofuran (THF) containing triethylamine (2%, $(C_2H_5)_3N$) was used as the elution solvent at 40 °C, and the instrument was calibrated with polystyrene standards, 0.889k, 4k, 10.4k, 30k, 44k and 104k (American Polymer Standards Corp.). ^1H NMR spectra were run on a JEOL JNM-LA300WB. All spectra were measured in $CDCl_3$ and the chemical shifts were referenced to tetramethysilane (TMS) at 0 ppm. FT-IR spectroscopy was performed with a Perkin-Elmer IR 2000 series using KBr pellets. The polymer latexes were characterized with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700)

4.2.2.1. Synthesis of 2-Hydroxyethyl-2'-Bromopropionate. (HEBI) as a hydrophilic Initiator

The initiator, 2-hydroxyethyl 2-bromoisobutyrate (HEBI), was prepared according to the following procedure[34]: 2.7 mL of 2-Bromoisobutyryl bromide (0.02175 mol) was added dropwise to a cold solution of ethylene glycol (27.7 mL, 0.49611 mol) and triethylamine (3 mL, 0.02175 mol) at 0 °C for 2 h. The reaction was continued at 0 °C for another 2 h and then at room temperature overnight. The reaction mixture was diluted with 500 mL of pure water, and extracted with chloroform three times, and then the chloroform layer was washed successively with 0.1N HCl, saturated $NaHCO_3$, and pure water. The organic layer was dried with anhydrous magnesium sulfate, filtered, and the solvent was removed under vacuum. The product was redissolved in CH_2Cl_2, and then the mixture was passed through a silica-gel column using a CH_2Cl_2/CH_3OH (95/5, v/v) mixed solvent as the eluting medium. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed. The remaining liquid was vacuum-distilled to give colorless liquid as **HEBI**, synthesis scheme is shown in Scheme 4.1 and the corresponding ^1H NMR in Figure 4.1



Scheme 4.1. Schematic illustration of the prepration of hydrophilic initiator 2-hydroxyethyl 2-bromoisobutyrate (HEBI).

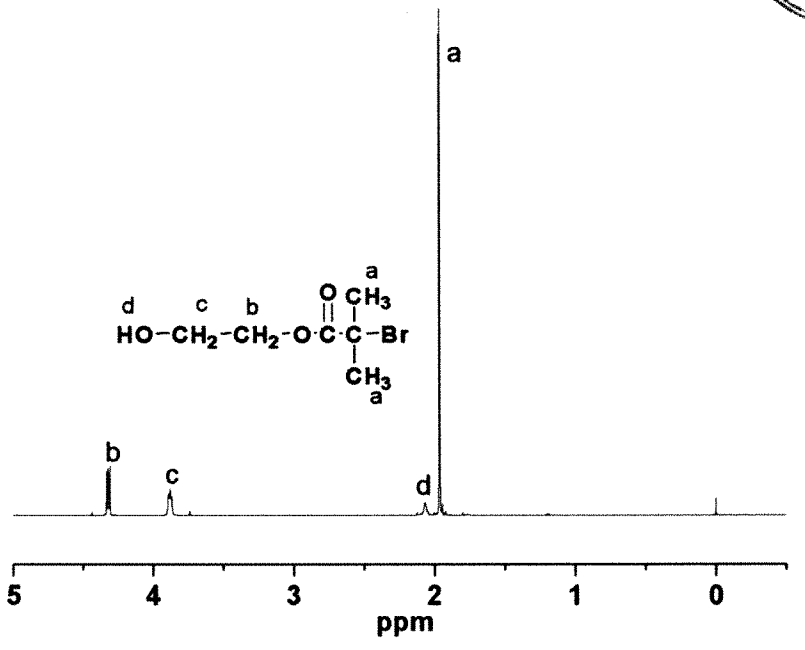


Figure 4.1 ^1H NMR spectra of HEBI in $CDCl_3$.

4.2.2.2. A True Emulsion ATRP of MMA at room Temperature (Semi-Batch Polymerization)

Before conducting the polymerization, MMA (39.9 mmol, 4.25 ml) and surfactant solution (0.092g in 28.3 ml H_2O) both were deoxygenated with Argon for 1 hour, separately. To a 2 neck rbf, CuBr (0.399 mmol, 0.057g), bipy (0.718 mmol, 0.11g) was added, under inert condition, and then PMDETA (0.079 mmol, 0.02 ml) is added via gas tight syringe. The mixture was subjected to vacuum and again argon was introduced, this process was repeated three times in order to remove any trace of oxygen in the reaction flask. To this mixture surfactant solution was cannula transferred and 0.5 ml of monomer is added. The mixture was stirred for 30 mins to form a stable emulsion, and then initiator, HEBI (0.399 mmol, 0.06 ml) is added via gas tight syringe. After allowing

the polymerization to continue for 15 minutes, the color of the copper complex changed from dark brown to green showing the onset of the polymerization. A syringe was filled with the monomer and placed in a programmable syringe pump (Model Kd Scientific) for its posterior addition in the reaction flask. For a volume of 3.75 ml of the monomer the addition profile was designed to work under starved condition, 0.5 ml in 30 min and the reaction was allowed to proceed for 4 hrs at room temperature. Different addition profiles were set to explore the time effect of monomer addition. Aliquot were withdrawn at regular intervals to measure the monomer conversion gravimetrically. The molecular weight characteristics were determined by SEC analysis after precipitating the aliquots in large excess of Water/Methanol (1:1) and dried under vacuum for 24 hr at 60 °C.

4.3. Results and Discussion

To assess the possibility of conducting an ATRP in a true emulsion, the prerequisite is to identify whether monomer and catalysts can successfully diffuse from monomer droplets across the aqueous phase to micelles/polymerizing particles. If they cannot be transported, the "emulsion" ATRP either becomes a suspension polymerization, or leads to uncontrolled polymerization, or results in low initiation efficiency. Diffusion of monomer from the monomer droplets to the polymerizing particles has been demonstrated in a conventional emulsion polymerization. As the monomer is consumed in the polymerizing particles, monomer continuously diffuses from the monomer droplets into the particles to take part in polymerization. Further evidence for the diffusion comes from semi-batch emulsion polymerization, in which only a part of the total monomers is introduced at the beginning of the reaction prior to nucleation. The remainder is added, according to a predetermined schedule, during the course of the polymerization. During this semi-batch emulsion process monomer can constantly transfer across the aqueous phase, as long as polymerization loci remain in the polymerizing particles.[19] Even if monomer transportation is successful, transportation of catalyst from monomer droplets to polymerizing particles remains the main challenge for a true emulsion ATRP system. In addition, the catalysts, especially the deactivators (Cu^{II} complexes), may decompose in water by either ligand decomplexation or hydrolysis of Cu-X bonds. To prevent the decomposition of catalysts, strongly hydrophobic ligands are used in ATRP in aqueous

dispersed media. Consequently the complexes preferentially stay in the monomer droplets and cannot be transported through aqueous phase to the polymerizing particles. For the above reasons a standard emulsion system is not a viable process for ATRP because only monomer can efficiently diffuse from monomer droplets to polymerizing particles but catalysts cannot.

To facilitate a successful ATRP, it was essential to have both the radical activator (e.g., $Cu^{I}Br$/ligand) and deactivator (e.g., $Cu^{II}Br_2$/ligand) available in the organic phase where the polymerization takes place. Thus, the selection of a suitable ligand became imperative. One of the roles that the ligand plays is adjusting the partitioning behavior of the metal complex between the oil phase and the aqueous phase. It was also realized that the use of a hydrophilic ligand greatly increased the aqueous solubility of the copper complexes, leading to uncontrolled polymerizations in the growing particles.

To solve this problem and to create a viable approach to an emulsion ATRP system, it was necessary to develop a procedure in which all catalyst components are encapsulated in the nuclei before polymerization is initiated. Then, the monomer can be added after the nucleation/initiation period is completed. We have taken bipy/PMDETA (0.9:0.1) as a mixed ligand system (bipy as hydrophobic and PMDETA as a hydrophiphilic) and the idea behind this was that the complex formed with bipy with CuBr will mainly stay in the organic phase and the complex which is formed by CuBr with PMDETA will preferentially stay in the aqueous phase and thus the there will be sufficient control over the equilibrium between dormant and the active part of the ATRP mechanism.

In addition to providing good control over the polymerization, the colloidal stability of the resulting lattices was also improved by using (2.3 wt% vs Monomer) Brij 98 as a non-ionic surfactant. Sub-micron sized polymeric nanoparticles (> 150 nm) were confirmed by SEM micrographs. The colloidal stability of the latices was satisfactory, although a minor amount of sedimentation was observed after several days.

4.3.1. Techniques for making nanoparticles

Generally, there are two ways to make polymer nanoparticles; one is polymer processing technique another is *in-situ* during polymerization. The polymer processing technique uses the existing polymers to make nanoparticles. It is a physical technique, and no chemical reaction is involved in the process. The drawback of the polymer processing methods is that special equipment is required and the final polymer must be protected from the polymer coalescence. In polymerization techniques, polymer nanoparticles are synthesized directly by the polymerization of monomers. Miniemulsion polymerization is one of the techniques to make particles in the range of 50-500 nm. In this process, high shear equipment is employed to make the smaller monomer droplets. Subsequently, initiator is added and polymerization starts to produce fine polymer particles. In order to synthesize nanoparticles, microemulsion polymerization was developed. The microemulsion is thermodynamically stable and 10 to 50 nm particle sizes can be achieved. Traditionally, a high surfactant concentration (7-15 wt. % in the solution) is required in microemulsion polymerization processes to form stable polymer latexes. High surfactant levels and low polymer contents limit the application of microemulsion latexes in industry.In order to overcome this problem, various semi-continuous microemulsion polymerizations involving drop-wise addition of monomer have been developed which utilizes less surfactant concentrations and has feasublity for industrial applicataions.[35-37]

4.3.2. A True Emulsion ATRP of MMA at room Temperature

When the polymerization was conducted alone using bipy and PMDETA keeping all other components fixed, (data not shown) it was observed that there was severe coagulation during the polymerization using conventional method at room temperature, the most possible reason for this may be the complex formed with these ligands were not sufficiently hydrophobic in order to have both the radical activator (e.g., $Cu^{I}Br$/ligand) and deactivator (e.g., $Cu^{II}Br2$/ligand) available in the organic phase where the polymerization takes place. Also when mixed ligand system was utilized by changing the ratios of the ligands as 0.5:0.5, 0.7:0.3 (bipy:PMDETA), it was observed that there was

also an uncontrolled polymerization with very high molecular weight about 300 times from the theoretical calculated molecular weight and the molecular weight distribution was broad and the SEC curves were bimodal (data not shown). But when the ratio was taken as 0.9:0.1 there was a significant effect on the stability of the colloidal solution and the the SEC curve in all polymerizations shows unimodal distribution, confirming that the polymerization has taken without any side reactions. This is the ideal ratio for a successful emulsion ATRP, using mixed ligand system, though the molecular weight was still higher compared to theoretically calculated molecular weight which was kept constant for all the polymerization as 10000 (DP_n=100) (Table 4.1)

4.3.3. Semi-Batch Emulsion ATRP of MMA at room Temperature (Monomer Starvation method)

In the differential operation, monomer was added at a very slow rate and was quickly consumed by the growing chains in the polymer particles. On the other hand, in batch polymerization, monomer droplets were formed as a reservoir and monomer molecules had to transfer from the organic phase into the aqueous phase first to reach the propagating polymer particles, leading to a slower polymerization rate. Since, we observed that Brij 98 was a very effective surfactant in forming the small particles, the particle size obtained in all cases was less than 150 nm, Figure 4.4.

Molecular weights (M_n) increased with conversion in both methods and experimental molecular weights were greater than theoretical values, suggesting inefficient initiation or possibly radical coupling termination. We observed that when the monomer is added in one shot and the polymerization is allowed to proceed in similar conditions the Molecular weight was almost 200 times (EP1) and when the addition time was varied from 60 to 180 mins, there was a substantial decrease in the molecular weight. (EP2, EP3 and EP5, Table 4.1). Figure 4.2 shows the SEC profiles of the three set of polymerization. Figure 4.3 and Table 4.2 shows the SEC profiles and the molecular weight characteristics for sample EP5 when 180 min was given for the monomer addition and aliquots were taken out for every 60 min. One can observe that there is increase in M_n with the polymerization time, but theoretical and experimental data is not matching

which is our current topic of research. The latex obtained from the samples, EP2, EP3, and EP5 were subjected to SEM measurement and in all the three case the particle size was less than 150 nm as can be seen from Figure 4.4. In addtion to this, ^{1}H NMR (Characteristic peak of -OCH_3 at 3.6 pmm) and FT-IR (carbonyl group of an ester group for MMA component appeared at 1602 and 1730 cm^{-1} respectively) study,Figure 4.5 shows that nano-sized PMMA by semi-batch emulsion polymerization utilizing mixed ligand system at room temperature was successfully synthesized.

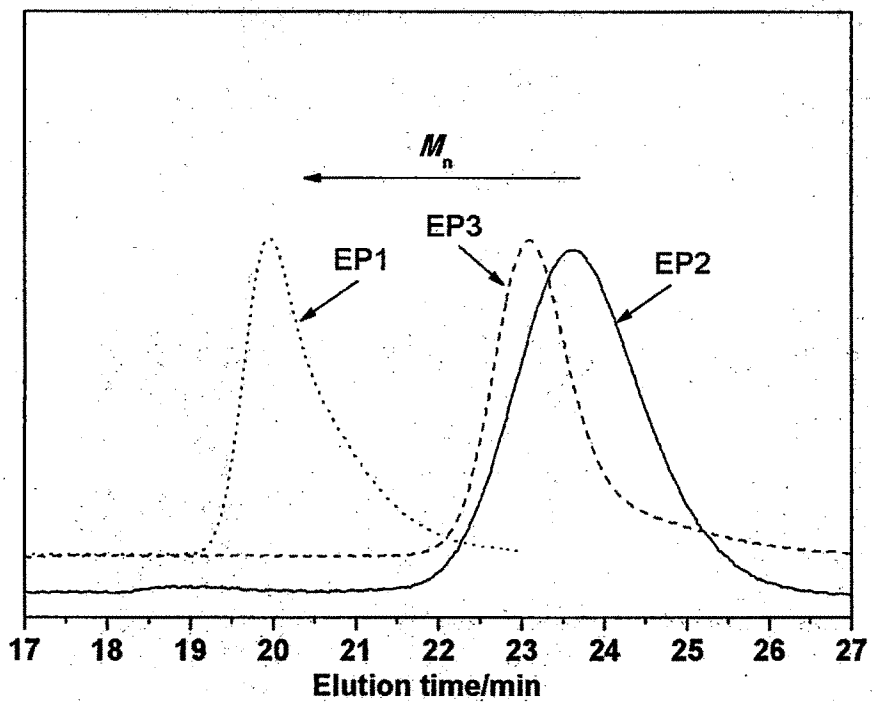


Figure 4.2. SEC traces of MMA polymerization in emulsion by varying time interval for monomer addition (EP1; one shot),(EP2; 120 min) and (EP3;60 min).

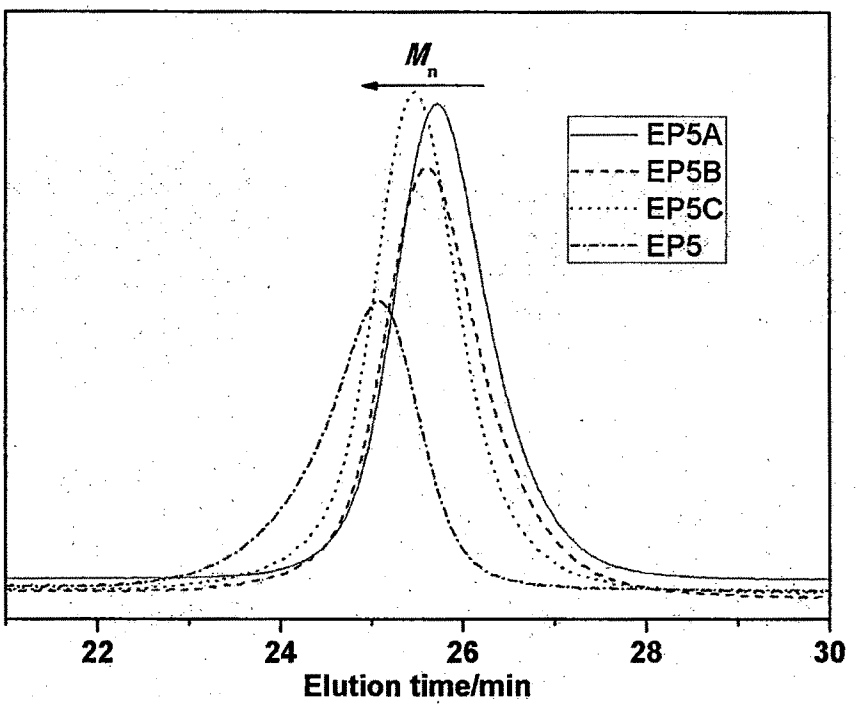


Figure 4.3. SEC traces of MMA polymerization in emulsion showing the increase in molecular weight as a function of time for EP5.

Table 4.1. Effect of Monomer Addition at different Time Intervals on Emulsion ATRP of MMA using 2-hydroxyethyl 2-bromoisobutyrate (HEBI) as an Initiator at Room Temperature.

Run	Stoichiometry $[M]_0/[I]_0/[CuBr]/[PMDETA/bipy]$	Monomer addition Time(min)	Polymerization time (min)	Yield (%)	M_n, (expt)	M_w/M_n
EP1	100/1/1/0.1/0.9	One shot	240	93	208283	1.11
EP3	100/1/1/0.1/0.9	60	240	80	40270	1.23
EP2	100/1/1/0.1/0.9	120	240	89	31161	1.18
EP5	100/1/1/0.1/0.9	180	240	90	19039	1.15

Table 4.2. SEC Results of Emulsion ATRP of MMA showing an increase in Molecular weight with Time in case of EP5.

Run	Stoichiometry $[M]_0/[I]_0/[CuBr]/[PMDETA/bipy]$	Polymerization time (min)	Yield (%)	M_n, (expt)	M_w/M_n
EP5A	100/1/1/0.1/0.9	20	-	10080	1.13
EP5B		80	-	14987	1.14
EP5C		140	-	16970	1.12
EP5		240	90	19039	1.15

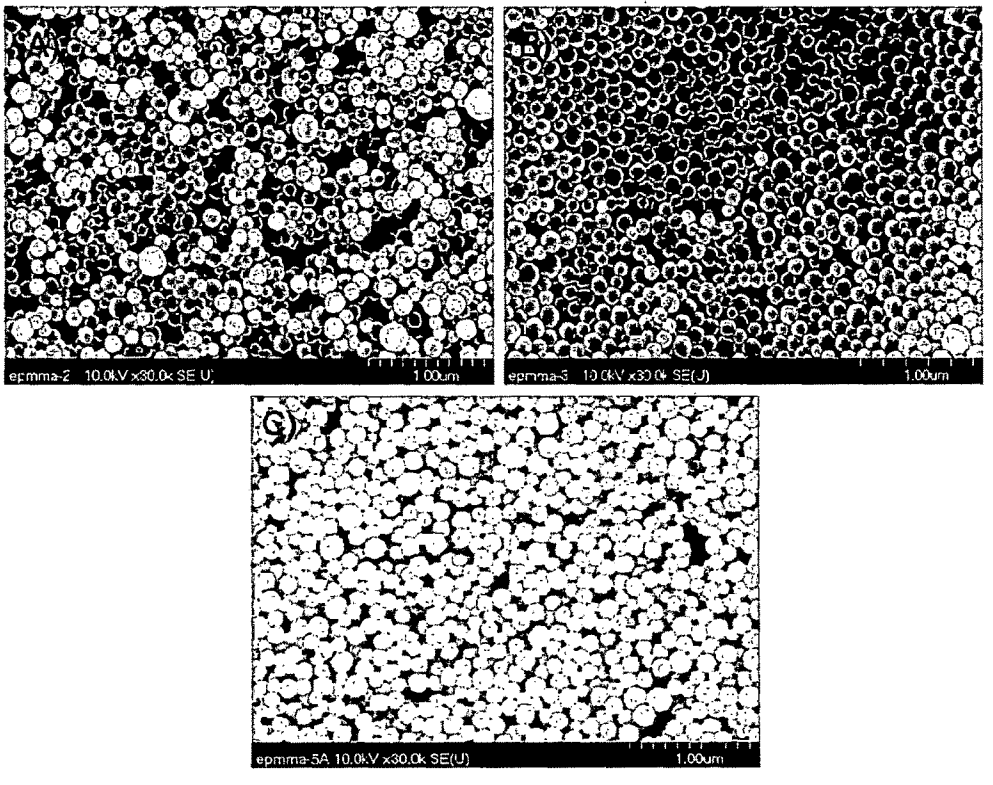


Figure 4.4. Scaning electron microscopy (SEM) images monodisperse Poly(methyl methacrylate) produced by emulsion ATRP using mixed ligand system at room temperature for (A)EP3,(B) EP2 and (C) EP5.

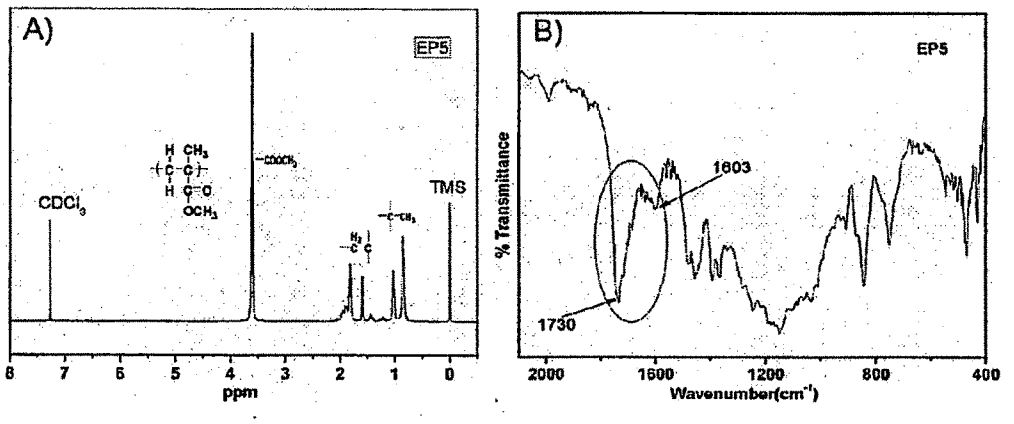


Figure 4.5.(A)1H NMR spectrum of the sample EP5 in $CDCl_3$ and (B) FT-IR spectrum of EP5.

4.4. Conclusions

The preliminary results show that ATRP by this novel methodology in a true emulsion using mixed ligand system at room temperature and by differential addition of the monomer is possible. Nano-sized poly(methyl methacryalte) of size ranging from 100±20 nm have been successfully synthesized by employing differential method with surfactant concentration as low as 2.3 wt% vs monomer. Additionally, the differential monomer addition method gave a better controlled polymerization as compared to the traditional batch method, adding monomer in one shot. Though, the theorically calculated and experimentally obtained molecular weights are not matching considerably, this may be due to the low initiator efficiency, but additional investigations are necessary to understand the role of all components involved. There are many fundamental aspects of the emulsion ATRP remaining to be understood. The polymerization mechanism is complicated by the solubility and partitioning of various species in aqueous and organic phases.The exact reason for the evolution of the decrease in the number average molecular weight with increasing the duration for the addtion of monomer dropwise is the topic that needs further investigations.

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