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Effect of Ligands in MMA AGET ATRP in 2L Stirred Tank Emulsion Reactor

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Abstract - Atom Transfer Radical Polymerization (ATRP) in a 2L emulsion batch reactor system was initiated by using the Activator Generated by Electron Transfer (AGET) technique to produce Poly (Methyl Methacrylate) (PMMA). The reactants were composed of Ethyl-2-bromoisobutyrate (EBiB) as the initiator, polyoxyethylene (20) oleyl ether (Brij98) as nonionic surfactant and ascorbic acid as the reducing agent. In addition, the catalyst complex consists of copper bromide ($CuBr_2$) and different ligands such as Triphenylphosphine (PPh_3), 1, 10-Phenanthroline (Phenol), and Vitamin D. The effect of using PPh3, Phenol and Vitamin D as novel ligands was investigated to produce PMMA polymers having the features obtained through controlled polymerization. The reaction follows a two-step experimental procedure, during which a transition from microemulsion to emulsion takes place. The mixing process between the organic phase and the aqueous phase was carried out under sufficient amount of air for simplification purposes. However, the reaction is usually sensitive to air and therefore a particular precaution was taken when purging the system inside the reactor. Gravimetric method was used to measure the monomer conversion. Characterization of PMMA samples was done by means of GPC to measure the molecular weight and the polydispersity of the product. FTIR analysis was performed to characterize the polymer product. After 5h of reaction, high monomer conversion was obtained using Phenol and gradually increasing up to 93% with low number average molecular weight of 10,158 g/mol and a relatively narrow PDI of 1.58. A narrower PDi was obtained with Phenol compared with PPh3 and Vitamin D.

Keywords: Emulsion Polymerization, Vitamin D, PPh_3, Phenol, AGET ATRP, MMA, 2L reactor.

1. Introduction

Recently, nano-sized polymer processes are dominated by Controlled Radical Polymerization (CRP) techniques. Atom Transfer Radical Polymerization (ATRP) is a simpler process compared to other CRP techniques. In addition, ATRP has versatility in using oxidizing catalysts, reducing agents, and initiator etc [1, 2]. Therefore, ATRP is one of the fastest growing polymerization techniques that is being extensively studied in academia and industry [3]. For several years, ATRP has been widely investigated for bulk or solution homogeneous systems. Recently, environmental and sustainability aspects of manufacturing technologies are becoming increasingly important. As a result, water has been chosen as a solvent medium for the reasons of safety, environment and easy heat transfer. ATRP can be done in aqueous media. However, maintaining the livingness characteristics of the polymerization in an emulsion system is a major challenge [4, 5, 2]. The main factors affecting the polymer stability in emulsion systems are the solubility of the initiator and reducing agent in both phases, the suitability of the surfactant, high reaction temperature, and side reactions.

The most crucial factor in ATRP system is the ligand suitability. The main purpose of ligand is to adjust the catalyst solubility in both phases and hence control the polymerization process. In particular, the ligand reduces the catalyst partitioning into the aqueous phase by improving the catalyst confinement in the particle phase during the polymerization. However, it is well known that even with a high hydrophobic ligand, not all of the catalyst complex can be prevented from partitioning into the aqueous phase. In another words, it can control the concentrations of the deactivator and activator in the reaction medium [6].

Activator generated by electron transfer (AGET) ATRP has been previously applied to polymerization in aqueous medium using a continuous two-step procedure, in which low surfactant amounts were used and a controlled emulsion ATRP was obtained [7]. The higher oxidation state transition metal complex reacts with the reducing agent to initiate new chains. In addition, the reducing agent plays an important role in AGET ATRP by consuming the dissolved oxygen in the system and mainly responsible for converting $CuBr_2$ to CuBr [8 - 10].

PMMA has been produced in this study using AGET ATRP and following two steps experimental procedure in a 2L emulsion tank reactor. The key of this study is the selection of commercially available, relatively inexpensive and environmentally friendly ligands to control the polymerization in the emulsion system. In addition, the ligand's ability to suppress the catalyst's solubility in the organic phase in the presence of air will be tested. This paper for the first time presents the use of 1, 10-Phenanthroline (Phenol), Vitamin D and Triphenylphosphine (PPh_3) ligands in (AGET) ATRP emulsion polymerization of MMA.

2. Experimental Procedure

The reactor setup, materials and experimental synthesis for the MMA AGET ATRP polymerization are discussed in this section.

2.1. Reactor Setup

The main parts of the reactor setup consist of a 2L stainless steel reactor, an impeller attached to a motor to drive the stirring rod and data acquisition system. The vessel has a pressure gauge, a thermocouple, a cooling pipe and a gas vent. A polymer sampling and a nitrogen purging valve are also installed in the vessel. An auto-tuning procedure takes place by running the reactor with distilled water for a few hours to ensure steady state measurements of the reactor temperature, pressure and motor speed. A detailed description about the experimental setup is reported in previous studies [10].

2.2. Materials

Table 1 shows the materials used in this study. MMA (99% purity) was purified by passage through an inhibitor removal column (Aldrich). The following materials were used without any further purification: 1, 10-Phenanthroline (Phenol), Triphenylphosphine (PPh_3) (Aldrich; 99% purity) and Vitamin D (Walmart) as ligands, copper dibromide ($CuBr_2$) (VWR; 99% purity) as a catalyst, Polyoxyethylene (20) oleyl ether (Brij98) (Aldrich) as an emulsifier, Ethyl-2-bromoisobutyrate (EBiB) (Aldrich; >98% purity) as an initiator and Ascorbic Acid (AA) (Aldrich; 99% purity) as a reducing agent.

Table 1: Reaction materials.

Reactants	Chemical Components		
	Acronym	Full name	Purity
Monomer [a]	MMA	Methyl Methacrylate	99% (≤ 30 ppm MEHQ as inhibitor)
Initiator [b]	EBiB	Ethyl-2-bromoisobutyrate	>98%
Catalyst [b]	CuBr2	Copper (II) bromide	99%
Ligand [a]	PPh3	Triphenylphosphine (PPh_3)	99%
Ligand [a]	Phenol	1, 10-Phenanthroline	99%
Ligand [c]	Vitamin D	-	-
Surfactant [a]	Brij 98	Polyoxyethylene (20) oleyl ether	Not determined
Reducing agent [a]	AA	Ascorbic Acid	99%

[a] purchased from Sigma Aldrich (Canada)
[b] purchased from VWR (Canada)
[c] purchased from Walmart (Canada)

2.3. Characterization

Gravimetry procedure was followed to calculate the monomer conversion. An aluminum cup of well known weight was used to weigh and dry the PMMA product sample in a vacuum oven (VWR, 550 watts) for 24h. Molecular weight and MWD of PMMA product were measured by using triple detector Gel Permeation Chromatography (GPC) (Viscotek TDA, Model 302). Besides, tetrahydrofuran (THF) was the GPC column mobile phase and polystyrene was the GPC standards calibration. PMMA sample at 3h of reaction and using Phenol ligand was characterized by Fourier-Transform Infrared Spectroscopy (FTIR).

2.4. Experimental Synthesis

The required amount of MMA and AA was used in two portions MMA (I) and MMA (II), AA (I) and AA (II), this is two - step method. The organic solution is made up of the catalyst complex ($CuBr_2$/ Ligand), MMA (I) and initiator. Moreover, the organic solution was poured slowly under stirring into an aqueous solution of Brij 98 to form the transparent microemulsion. The whole mixture was transferred into the reactor and purged with nitrogen. Ascorbic acid (AA) reducing agent was thawed in distilled water to make another aqueous solution. AA (I) was injected into the reactor at the set temperature to start the polymerization. After about 15 minutes, another amount of MMA (II) and AA (II) was loaded into the ongoing microemulsion polymerization to form an emulsion polymerization. The product samples were collected at desired times, then shaken and cooled to stop the polymerization. Later on, methanol was used to precipitate the PMMA product. The PMMA samples were washed and dried in an oven for FTIR analysis. For GPC analysis, these samples were treated with THF, and then filtered to remove undesired catalyst before placing them into the GPC instrument.

3. Results and Discussion

The constant generation of activator and deactivator radicals in the organic phase is a necessary condition to sustain ATRP [11]. $CuBr_2$ was added initially to overcome the air sensitivity and to facilitate the equilibrium reaction between the radical and dormant species. Herein, the ligand's main duty is to control the behavior of partitioning of the catalyst in both organic and aqueous phases. For this particular reason, this study investigates the effect of using three different ligands of PPh3, Phenol and Vitamin D that have never been used to produce PMMA through AGET ATRP in emulsion medium. The molar ratio between the three ligands and copper dibromide was kept as 2:1, as shown in Table 2.

Table 2: Experimental conditions of emulsion AGET ATRP of MMA.

Exp.	T (^oC)	MMA (g) MMA-I = 14.04 (g) MMA-II = 42.12 (g)	EBiB (g)	Brij 98 (g)	Ligand (g)	Ascorbic acid (g)	$CuBr_2$ (g)	Motor speed (rpm)	N2 Purging
PPh3	50	56.1600	0.6140	22.3820	0.1880	0.1420	0.0800	250	6 times for whole emulsion
Phenol					0.1290				
Vitamin (D)					0.2754				

Figure 1A shows the conversion of MMA monomer versus reaction time for PPh3, Phenol and Vitamin (D), respectively. The results reveal that the conversion of MMA increases rapidly with the reaction time for all three ligands. For the polymerization that used Phenol and Vitamin D, the conversion increased continuously reaching a final conversion of 93.7% and 88.3% respectively after 5h. In contrast, the system using PPh3 showed an increase in conversion up to 98% after 1h followed by a decrease and finally leveling off at 97.1% conversion after 5h. Obviously, the high conversion rate obtained from the beginning of the reaction for the three ligands indicates low initiation efficiency.

Figure 1B shows the plot of ln([Mo]/[M]) versus reaction time for PPh3, Phenol and Vitamin (D), respectively. It is obvious that the system using PPh3 showed no linear trend. However, the systems using Phenol and Vitamin (D) show linear trends which confirm the livingness of AGET ATRP polymerization of MMA in the emulsion media.

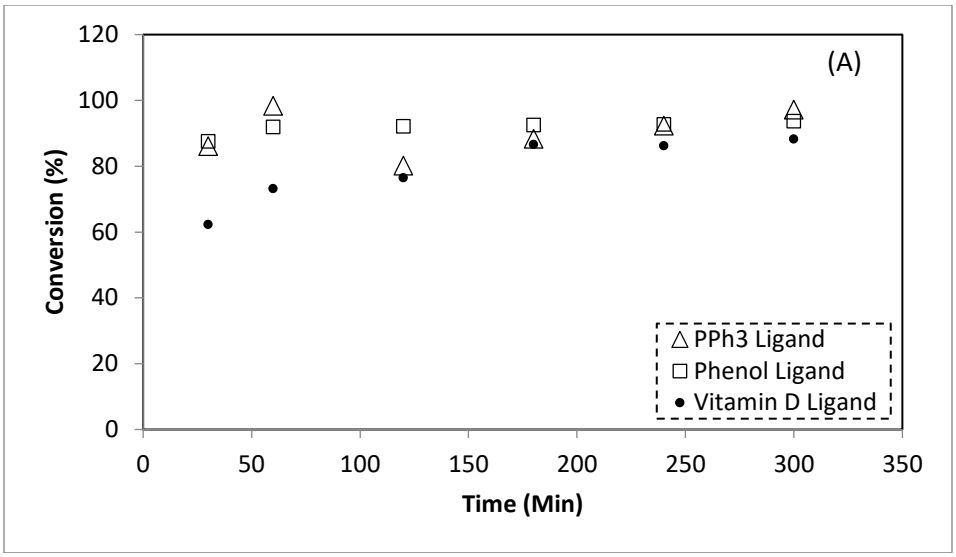

Fig. 1: (A) Methyl methacrylate (MMA) conversion versus time in emulsion polymerization in experiments using PPh3, Phenol and Vitamin D ligands (B) Variations of ln([M]o/[M]) with reaction time in experiments using PPh3, Phenol and Vitamin D ligands.

Figure 2 shows number average molecular weight (Mn) and polydispersity (Đ) of PMMA product versus conversion of MMA monomer using Phenol. Mn was gradually increased from 9,034 to 9,841 and up to 10,158 (g/mol) after 1h, 3h and 5h of the polymerization initiation. The low value of molecular weight of PMMA product may be attributed to the large amount of the initiator EBiB used in the system compared to MMA monomer [12, 13]. Đ was relatively narrow and gradually decreased from 1.71 to 1.62 and up to 1.58 after 1h, 3h and 5h of the polymerization initiation which confirms the features of controlled system using Phenol. This may be referred to the belief that it is important to use the correct ratio of reducing agent to deactivator to lower Đ values [14].

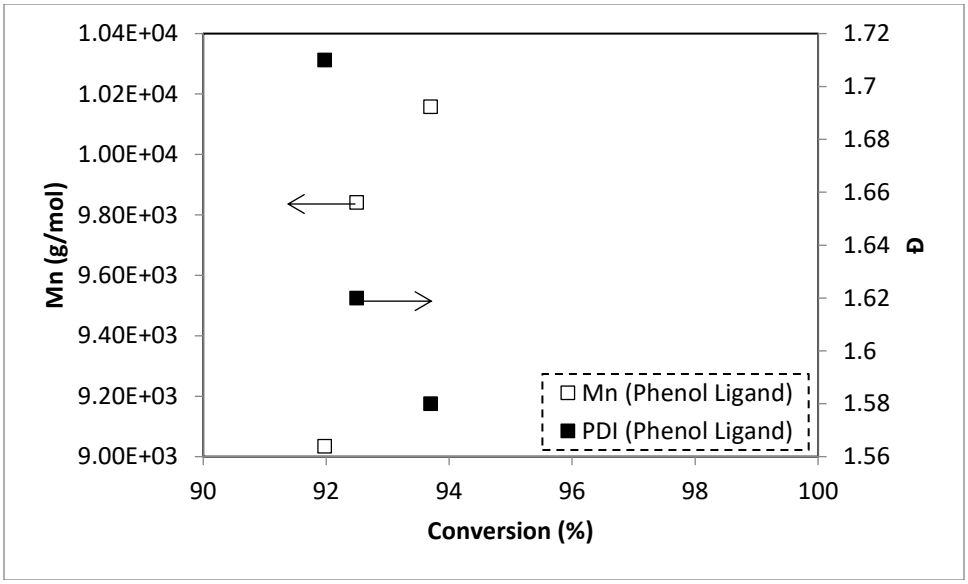

Fig. 2: Variations of experimental number-average molar mass and polydispersity index (Đ) versus methyl methacrylate (MMA) conversions in experiment using Phenol ligand @ 1h, 3h and 5h.

For the systems using PPh3 and Vitamin (D) ligands, Mn increased from 17,005 to 41, 623 (g/mol) and from 16,106 to 17,705 (g/mol) after 3h to 5h and 1h to 5 h of polymerization, respectively. In addition, Đ was broad and decreased from 4.13 to 2.36 after 3h to 5h for the system using PPh3 and increased for the system using Vitamin (D) from 2.06 to 2.51 after 1h to 5h, respectively, as shown in Table 3.

Table 3: Experimental results of emulsion AGET ATRP of MMA.

Exp.	T (h)	Conv (%)	Mn (g/mol)	Đ
PPh3	1	98.3	-	-
	3	88.4	17,005	4.13
	5	97.1	41,623	2.36
Phenol	1	91.9	9,034	1.71
	3	92.5	9,841	1.62
	5	93.7	10,158	1.58
Vitamin (D)	1	73.2	16,106	2.06
	3	86.6	-	-
	5	88.3	17,705	2.51

The increase of Mn values versus the MMA conversion indicates a controlled radical system. However, the broadness of the polydispersity indicates poor controlled systems when PPh3 or Vitamin (D) were used. There are many reasons that may explain why a poorly controlled system was obtained such as the steric hindrance of the ligand [6], the ligand compatibility with surfactant [15, 16] and the ligand hydrophobicity/ hydrophilicity characteristics.

Figure 3 shows GPC traces of PMMA product for the system using Phenol. A unimodal distribution and slight peak shift was obtained versus retention time which approves the controlled feature of PMMA system using Phenol.

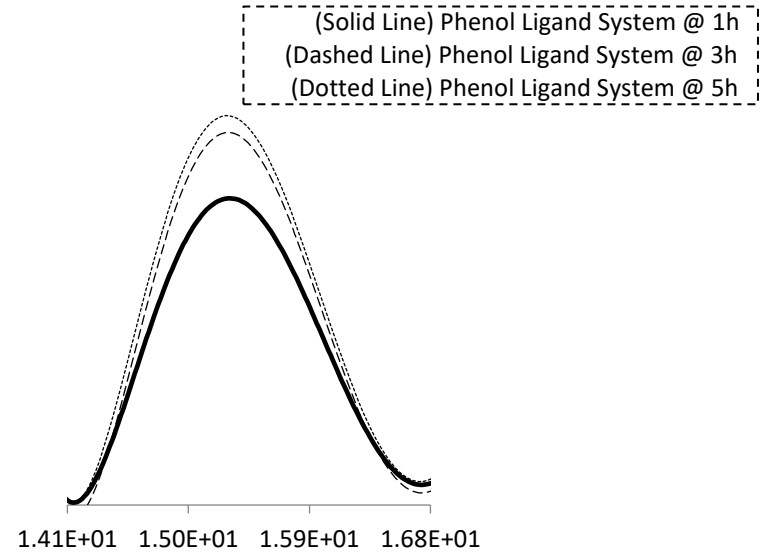

Fig. 3: Gel permeation chromatography (GPC) traces of poly (methyl methacrylate) (PMMA) molecular weight distribution (MWD) for 91.9%, 92.5% and 93.7% conversions, respectively, in experiment using Phenol ligand. (T=50 ^{o}C).

Analysis using FTIR spectrometry was done for the PMMA sample that was collected after 3h of polymerization for the system using the Phenol ligand. Figure 4 showed there is a distinct absorption band from 1,143 cm^{-1} to 1,238 cm^{-1}. This can be attributed to the C–O–C stretching vibration. The band around 1,386.6 cm^{-1} can be attributed to the α-methyl group vibrations. The band around 986 cm^{-1} is the characteristic absorption vibration of PMMA, together with the band at 840.5 cm^{-1}. The band around 1,724 cm^{-1} shows the presence of the acrylate carboxyl group. Furthermore, the band around 1,434 cm^{-1} can be attributed to the bending vibration of the C–H bonds of the –CH3 group. The two bands around 2,993 cm^{-1} and 2,948 cm^{-1} can be assigned to the C–H bond stretching vibrations of the –CH3 and –CH2- groups, respectively. Based on the above discussions, it can be concluded that the prepared polymer was indeed macromolecular PMMA [17].

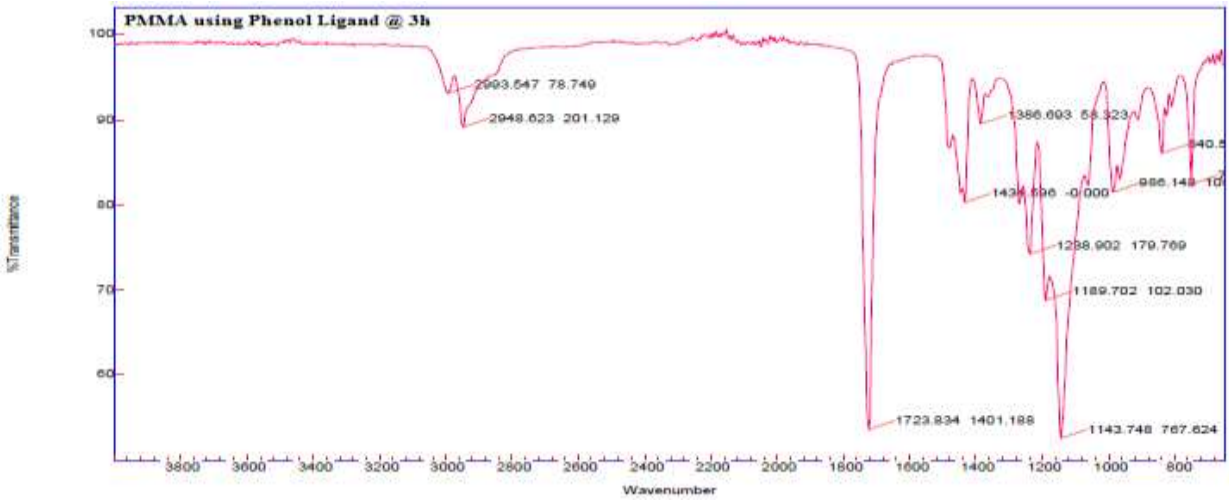

Fig. 4: Fourier - transform Infrared (FTIR) Spectrometry: Image of final polymer product of run using Phenol ligand. Image for sample collected after 3 h of polymerization initiation.

4. Conclusion

The effect of using three ligands of PPh3, Phenol and Vitamin (D) in MMA AGET ATRP emulsion polymerization in 2L well-mixed batch reactor was studied. Based on the results obtained, the system using the Phenol ligand has higher solubility in the organic phase than PPh3 and Vitamin (D). The solubility of the catalyst increases when hydrophobic ligand used in the organic phase where the polymerization takes place. Eventually, controlled polymerization will be more efficient (giving a polydispersity below 1.50). Phenol is a promising ligand which can be used in emulsion medium due to its high solubility in the organic phase. A well-controlled PMMA polymer was produced where the number average molecular weight was consistently increased to 10,158 (g/mol) with 93.7% monomer conversion and a relative narrow PDI of 1.58 was obtained after 5 h of reaction. The Phenol ligand is commercially available and affordable compared to dNbpy and BPMODA ligands which are commonly used as effective ligands for the ATRP systems in the emulsion and miniemulsion systems [18]. However, an environmental concern must be addressed when using Phenol ligand due to its toxicity. Vitamin (D) ligand showed evidence of livingness and low Mn of 17,705 (g/mol) was obtained after 5h of polymerization. The reason is possibly due to the strength of steric hindrance for Vitamin (D) ligand. Therefore, Vitamin (D) should be investigated further to prove its ability for controlling the catalyst radicals in ATRP emulsion systems due to its high hydrophobicity. As a result, the experiments demonstrated that controlled ATRP depended not only on the solubility of the catalyst complex in the organic phase, but also depended on the system radical trapping ability. In addition, suitable recipient must be chosen in two-step emulsion polymerization to increase the possibility to obtain high monomer conversion and good latex stability.

Acknowledgments

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