Effect of Ligands on Controlled Polymerization of Methyl Methacrylate by AGET Method in Emulsion System

Mohammed Awad, Dr. Thomas Duever, Dr. Ramdhane Dhib
Department of Chemical Engineering, Ryerson University, ON M5B 2K3, Canada
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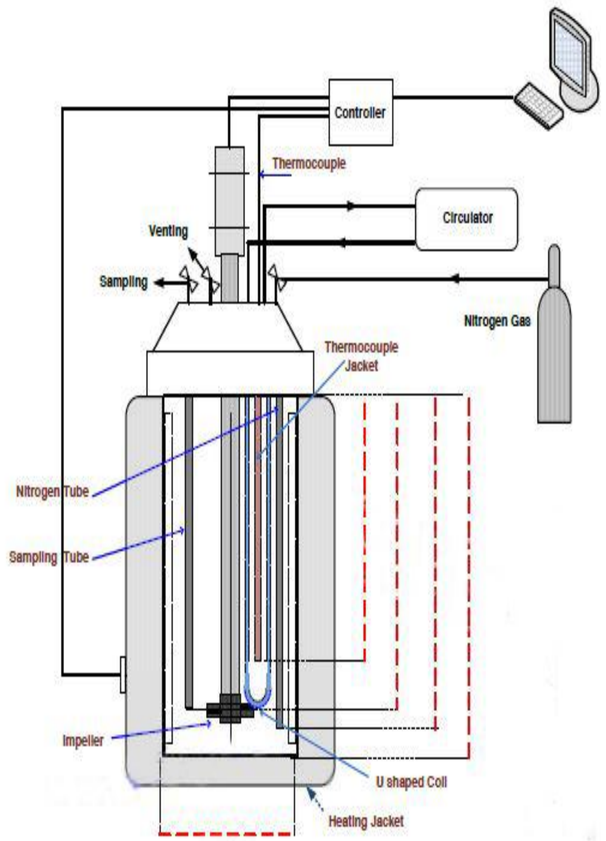
Introduction

Controlled Radical polymerization (CRP) is a dominating technique in manufacturing nano-sized polymer particles. In particular, (ATRP) Atom Transfer Radical Polymerization is one of the most growing polymerization techniques that are today extensively studied in academia and industry (Matyjaszewski et al, 1995). Actually, polymers used as lubricants, adhesives, gels, additives, and biomedical applications such as artificial bones and drug delivery are synthesized by ATRP due to its versatility in using oxidizing catalysts, reducing agents, and initiator etc (Braunecher et al, 2007; Oh, 2008). Over the past few years, ATRP has been mainly limited to bulk or solution homogeneous systems. Recently, the research emphasis is directed towards environmental and sustainable aspects for benign technology. Using water as a solvent medium for safety, environmental, and easy heat transfer reasons, ATRP can be done in aqueous media. However, unlike bulk/solution medium, maintaining the stability of 'livingness' characterization of the polymerization in an emulsion system is a major problem (Uegaki et al, 1997; Aijoka et al, 2008; Oh, 2008). The main factors affecting the polymer stability are the solubility of both initiator and reducing agent in organic and aqueous phases, the suitability of the surfactant, high reaction temperature, and side reactions.

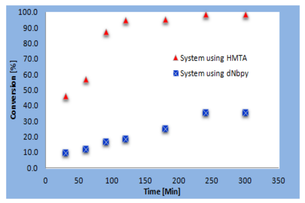
The most decisive factor in ATRP system is the ligand aptness, since it can help to adjust the catalyst solubility in both phases and have a crucial effect on the controlled polymerization. It is postulated that the ligand reduces the catalyst partitioning into the aqueous phase by improving the catalyst retention in the particle phase during the polymerization. However, it is well known that even with a 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 (Tian et al, 2012). 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 (Jia, 2008). The higher oxidation state transition metal complex reacts with the reducing agent to initiate new chains. The reducing agent plays an important role in the activator generation (Jakubowski et al, 2005; Min et al, 2006).

PMMA has been produced in this study using AGET ATRP two steps method in a 2 - Liters emulsion system. The ligand selection becomes a key for controlling the molecular weight of the polymerization reaction. The effect of the ligands Hexamethylenetetramine (HMTA) and 4,4-dinonyl-2, 2-bipyridyl (dNbpy) using AGET ATRP two steps method for Methyl Metharcylate (MMA) have been investigated for different experimental conditions on the MMA monomer conversion and the PMMA molecular weight distributions.

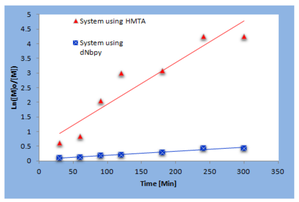
Reactor System



Results

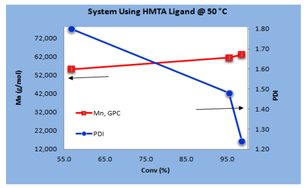


MMA conversion versus time in HMTA and dNbpy systems respectively @ 50 °C

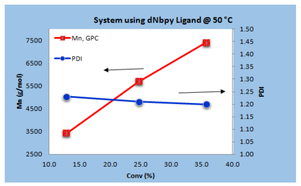


Livingness versus time in HMTA and dNbpy systems respectively @ 50 °C

Slight Coagulation in System using HMTA ligand @ 50 °C



Number-average molar mass and polydispersity index (PDI) versus MMA conversions in HMTA system @ 50 °C

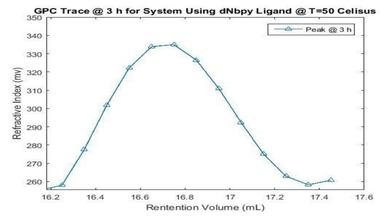


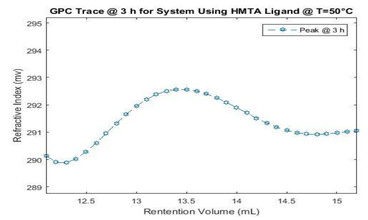
Number-average molar mass and polydispersity index (PDI) versus MMA conversions in dNbpy system @ 50 °C

Slight Coagulation in System using dNbpy ligand @ 50 °C

Results Summary for HMTA and dNbpy systems

Exp#	t/hr	Conversion	Mn, th(gmol-1)	Mn, GPC (gmol-1)	PDI
E2 HMA Used	1	56.8	12489	55,180	1.80
	3	95.4	20982	61,418	1.48
	5	98.5	21676	62,985	1.24
E2 dNbpy Used	1	12.8	2672	3426	1.23
	3	24.7	5515	5699	1.21
	5	35.7	7836	7410	1.20





Experimental Condition

Preliminary investigation was carried out. Livingness (narrow PDI and targeted molecular weight) is preserved in both systems using HMTA and dNbpy Ligands but better results were obtained from system using dNbpy due to ligand solubility in organic phase.

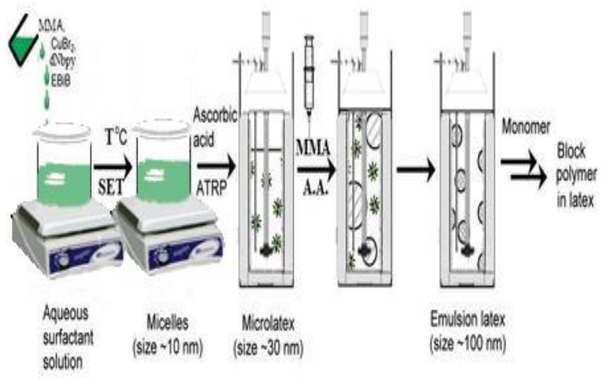
ExP#	MMAI(g)	MMAII(g)	EBiB (g)	CuBr2 (g)	HMTA (g)	AA (g)	Brij 98 (g)	Water (g)
E1	54.88001076	164.6400323	1	0.146833781	0.855645274	0.133324663	5.106682654	7580.364816
E2	54.88001076	164.6400323	1	0.146833781	0.295078974	0.133324663	5.106682654	7580.364816
E5	350.669197	1052.007591	1	0.499344481	1.000713064	0.24989372	32.63039276	49276.36784
E6	350.669197	1052.007591	1	0.499344481	1.000713064	0.24989372	32.63039276	49276.36784
E7	54.88001076	164.6400323	1	0.078147812	0.156612398	0.039108568	5.106682654	7711.791115
E8	54.88001076	164.6400323	1	0.146833781	0.295078974	0.078217136	5.106682654	7820.407892
E9	124.2450386	372.7351158	1	0.196045376	1.967078833	0.598945177	12.98556446	20438.57396

The following conditions is kept constant for all the runs .

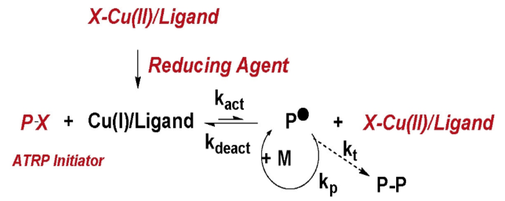
N_2 purging	(6 times with full release of pressure)
Motor Speed	250 rpm
Pressure	20 psi

Synthetic Procedure

AGET ATRP Two-step emulsion



Mechanism



Acknowledgement

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Concluding Remarks

HMTA Ligand was chosen because of its environmental friendly characteristics which is the most important and can be noticed by treating the catalyst complex which contains HMTA as a ligand with acids to purify it from the residual catalyst, also it's commercially available with cheap prices.

Experimental investigations were carried out on HMTA system to check its radical controllability by observing the effects of reducing agent, initiator, ligand and temperature. Then a comparison between two different ligands HMTA and dNbpy has been studied.

HMTA system showed a controlled radical behavior but was slightly broader than dNbpy system due to HMTA solubility in organic phase, but the conversion rate was clearly higher than dNbpy system.