# EXPERIMENTAL AND MODELING STUDIES OF DIFFUSION-CONTROLLED REACTIONS IN ATOM TRANSFER RADICAL POLYMERIZATION AT HIGH CONVERSION

# EXPERIMENTAL AND MODELING STUDIES OF DIFFUSION-CONTROLLED REACTIONS IN ATOM TRANSFER RADICAL POLYMERIZATION AT HIGH CONVERSION

By ALI MOHAMMAD RABEA, B.SC., M.SC.

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AUTHOR: Ali Mohammad Rabea, B.Sc. (Amirkabir University of Technology), M.Sc. (Amirkabir University of Technology)

SUPERVISOR: Professor S. Zhu

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# Lay Abstract

Nowadays, polymeric materials are being used in different areas of industry and our daily life. There are different polymerization methods for producing polymers. One of the newest methods, is controlled radical polymerization (CRP), especially atom transfer radical polymerization (ATRP). Although there is about two decades of intensive study about ATRP, its significant industrial applications are still lacking. Limited monomer conversion is one of the most challenging problems in this area. In this project, the problem of reaching high monomer conversion in ATRP was studied experimentally and through performing modeling. Different strategies such as adjusting concentration of the reactants, employing a step temperature profile and using sonication waves were then investigated as the helpful methods for overcoming the problem.

# Abstract

Controlled radical polymerization (CRP), especially atom transfer radical polymerization (ATRP), has attracted great attention in the recent years. It provides a powerful tool for synthesis of functional polymers with a predetermined molecular weight and narrow molecular weight distribution (MWD). Although tremendous effort has been made in this area over the past decade, there are still many challenges that limit its industrial applications. High monomer conversion is one of the most important critical issues for commercial exploitation of CRP processes. Another important task is to eliminate organic solvents in polymerization. Most solvents are volatile organic compounds (VOCs), and are of environment and health concerns. Separating the polymer product from the solvent and removal of residual monomer are both energy intensive and costly. This thesis focused on the study of bulk ATRP at high conversion experimentally and through performing modeling. The main objectives are to elucidate the mechanism of ATRP at high conversion and to develop strategies for reaching high conversion in bulk while maintaining livingness and control of the polymerization. This sandwich-type thesis is organized based on five refereed-journal papers first-authored by the candidate.

Methyl methacrylate (MMA) was polymerized in bulk via atom transfer radical polymerization (ATRP) using initiator for continues activator regeneration (ICAR)

method. “Gel effect” started at medium conversion and it was accompanied with molecular weight distribution broadening. A dramatic increase in polydispersity was observed at high conversion. The loss of control over molecular weight was attributed to diffusion-controlled deactivation.

Model simulation of bulk ATRP revealed that it is diffusion-controlled deactivation that causes auto-acceleration in the rate (“gel effect”) and loss of the control. At high conversion, radical chains are “trapped” because of high molecular weight and high viscosity. However, the migration of radical centers through propagation (residual deactivation) can still facilitate catalytic deactivation of radicals, which improves the control of polymer molecular weight to some extent.

It was found that ICAR agents could significantly affect the rate of catalyst regeneration and consequently the rate and control of polymerization. By optimizing the ICAR agent concentration and employing step temperature profile, MMA was polymerized with ppm concentration of catalyst up to very high conversion with good livingness and control. Furthermore, it was demonstrated that employing ultrasonic waves could be helpful in order to keep the control and livingness up to high conversion through improving homogeneity of the polymerization medium and diffusivity of the reactants during the polymerization, especially after the onset of diffusion-controlled deactivation.

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# List of Abbreviations

| | |
|---|---|
| AGET | Activator Generated by Electron Transfer |
| AIBN | Azobisisobutyronitrile |
| AMRP | Aminoxyl-Mediated Radical Polymerization |
| ARGET | Activator Regenerated by Electron Transfer |
| ATRP | atom transfer radical polymerization |
| $BMPB_2$ | 1,4-(2-bromo-2-methylpropionato)benzene |
| bpy | 2,2'-bipyridine |
| $CDCl_3$ | d-Chloroform |
| CRP | Controlled Radical Polymerization |
| Đ | Dispersity |
| DC | Alkyl diethyldithiocarbamate |
| dNbpy | 4,4′-dinonyl-2,2′-dipyridyl |
| EBiB | 2-bromoisobutyrate |
| EBPA | Ethyl (α-bromophenyl)acetate |
| EBrP | Ethyl-2-bromo propionate |
| EtBriB | Ethyl 2-bromo-isobutyrate |
| FRP | Free Radical Polymerization |
| GPC | Gel Permeation Chromatography |
| HHTETA | Hexahexyltriethylenetetramine |
| HMTETA | Hexamethyltriethylenetetramine |

| | |
|---|---|
| $HONH_2HCl$ | Hydroxylamine hydrochloride |
| ICAR | Initiator for Continuous Activator Regeneration |
| $I_{eff}$ | Initiator Efficiency |
| MANDC | 1-cy-ano-1 methylethyldiethyldithiocarbamte |
| MBP | Methyl α-bromophenylacetate |
| MMA | Methyl methacrylate |
| Mn | Number average molecular weight |
| MWD | Molecular Weight Distribution |
| $NaHSO_3$ | Sodium bisulfite |
| NMP | Nitroxide Mediated Polymerization |
| PDI | Polydispersity index |
| PMDETA | N,N,N′,N″,N″-pentamethyldiethylenetriamine |
| $PPh_3$ | Triohenyl phosphine |
| RAFT | Reversible Addition Fragmentation Chain Transfer |
| RDRP | Reversible-Deactivation Radical Polymerization |
| SARA | Supplemental Activator and Reducing Agent |
| SFRP | Stable Free Radical Polymerization |
| St | Styrene |
| TBA | Tributylamine |
| TBP | tert-butyl peroxide |
| TBPB | tert-butyl peroxybenzoate |
| TDA-1 | tris-(3,6-dioxa-heptyl) amine |

| | |
|---|---|
| TEA | trimethylamine |
| TETA | triethylenetetramine |
| TPEN | N,N,N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine |
| TPMA | tris[(2-pyridyl)methyl]amine |
| VC-Na | Vitamin C sodium salt |
| VOC | Volatile Organic Compound |

## Declaration of Academic Achievement

Ali Mohammad Rabea is the principle author of all five journal articles reproduced in this thesis.

Dr. Shiping Zhu was supervisors for all five journal articles.

Each journal articles research was performed during the following timeframe:

Chapter 3: 2012 – 2013

Chapter 4: 2014 – 2015

Chapter 5: 2013 – 2014

Chapter 6: 2013 – 2014

Chapter 7: 2015

# Chapter 1

# Introduction and Research Background

Nowadays, huge amount of polymeric materials are being used in many branches of science and engineering for different purposes. This includes different forms of materials, containing linear, branched or cross-linked polymers and also polymer blends and composites. Depending on the molecular weight and molecular weight distribution (MWD) as well as the molecular structure of the synthesized polymers, the properties and applications of the final products are different. Consequently, the methods of polymerization, which give control over some or all of these parameters, are really valuable.[1]

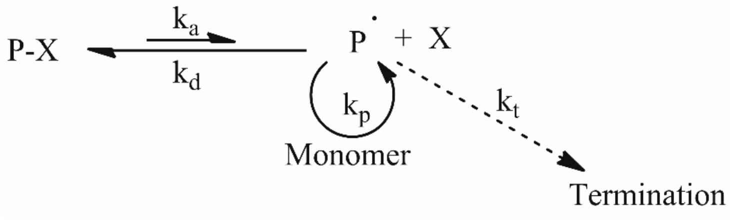
## 1-1- Free Radical Polymerization (FRP), Ionic Polymerization and Controlled Radical Polymerization (CRP)

Among different methods of polymerization, nearly 50% of all commercial polymers are synthesized using radical chemistry.[2] Free radical polymerization (FRP) is applicable to a vast number of monomers containing carbon-carbon double bonds, such as ethylene, styrene, vinyl chloride, acrylonitrile, vinyl acetate, methyl methacrylate, methyl acrylate, acrylamide, etc. Furthermore, it is tolerant toward many functional groups, impurities and solvents and can be carried out under mild reaction conditions and even in polar aqueous media.[1] In FRP, free radicals are highly active and responsible for chain propagation. However, bimolecular terminations, including combination and disproportionation, happen between two free radical centers and produce dead polymer chains, leading to a broad polydispersity in molecular weight distribution (MWD). Free radicals are continuously generated through initiator decomposition and their lifetime is typically in the order of seconds. Terminated polymer chains are produced instantly and accumulated during the polymerization. Chain transfer to small molecules such as initiator, monomer, chain transfer agent, solvent or impurities can also produce dead polymer chains. In the chain transfer reaction, the growth of a polymer chain stops and the radical center transfers to another molecule. Depending on the activity of new radical center, it could continue the polymerization. Therefore, FRP is not living and generates polymer chains with poor control over molecular weight, polydispersity and side-specific functionality.[3,4]

Living ionic polymerizations, in particular, living anionic polymerization,[5-12] are discovered in 1950’s and 1960’s, and they are used to overcome FRP’s limitations. Since carbenium ions or carbanions are active center for propagation, bimolecular termination between them does not happen, due to ionic repulsion. However, in this method of polymerization, chain transfer reactions of an active chain to couterion, solvent, monomer or any other agents, can lead to chain termination. A carbenium ion in cationic polymerization is so active and loses its activity easily through reacting with impurities without regenerating any active center. Since it is extremely difficult to get rid of all impurities especially under industrial production condition, significant percentages of the active centers are consumed by impurities and the polymerization is not living in an industrial practice.  On the other side, carbanions are relatively stable and less sensitive to impurities. By purifying the reagents, both termination and chain transfer could be prevented in anionic polymerization and thus all the active chains have the same chance to grow. Theoretically, polymer molecular weights could be controlled if all the active centers are activated simultaneously. By this method, polystyrene has been polymerized with polydispersities as low as 1.01. Furthermore, since the synthesized polymer chains using this method are still active, sequential addition of a new type of monomer leads to synthesizing well-defined block copolymers.[13,14] However, reaction conditions of living anionic polymerization are so restrictive and it is not easy to handle. It requires very low temperature, high-purified monomer and solvent, as well as anhydrous condition. Also, it is normally done as a small batch scale process for synthesizing expensive polymer products. Moreover, this kind of polymerization is just applicable to a limited range of monomer type. Only monomers with electron donating substitutes, such as 1,1-dialkyl, alkoxy, phenyl or vinyl groups can be cationically polymerized. On the other side, only monomers with electron withdrawing substitutes, such as nitrile carboxyl and phenyl groups can be anionically polymerized.[15,16]

In order to take the advantages of both FRP and ionic polymerizations, chain termination and chain transfer should be suppressed from free radical polymerization. Although it is almost impossible to omit the very fast bimolecular termination from FRP, designing controlled radical polymerization (CRP) or reversible-deactivation radical polymerization (RDRP, as recommended by IUPAC) by keeping a dynamic equilibrium between propagating radicals and large amount of dormant chain species, is possible. The most distinguished difference between controlled radical polymerization (CRP) and free radical polymerization (FRP) is the presence of a reversible activation/deactivation process. In this kind of polymerization, each active chain can be intermittently deactivated to dormant state after addition of few monomer units and reactivated (Scheme 1-1). CRP usually starts with an initiator (R-X). It produces an active radical $R^{\bullet}$ by thermal, photochemical or chemical stimuli. In the presence of monomer, the active radical can react and make a polymer radical $P^{\bullet}$ until it is deactivated to a dormant state P-X.[17-19]

**Scheme 1-1 General scheme of controlled radical polymerization (CRP)**



The reversible activation/deactivation cycle is a key factor for livingness and control of the polymerization. For effectiveness of the equilibrium, two necessary conditions must be met. First, the equilibrium between active and dormant species should be strongly in favor of the side of dormant chains in order to keep the radical concentration low and constant during the polymerization. In this way, the irreversible radical termination is minimized. Second, the rate of exchange between active and dormant species must be faster than the rate of propagation to give all the polymer chains an equal chance of adding monomers. In other words, every polymer chain in CRP grows in an intermittent manner by repeating the activation/deactivation cycles. Individual polymer chains grow slowly in a long time scale. Furthermore, every polymer chain experiences activation/deactivation cycles frequently enough over a period of time, all the polymer chains have the same or similar chance to grow, leading to a polymer product having similar chain length and narrow MWD polydispersity.[4]

## 1-2- Different Types of CRP

A number of CRP methods have been developed and the most studied ones are: stable free radical polymerization (SFRP) or aminoxyl-mediated radical polymerization (AMRP, IUPAC recommendation),[20] atom transfer radical polymerization (ATRP) or controlled reversible-deactivation radical polymerization (as recommended by IUPAC)[21,22] and reversible addition fragmentation chain transfer (RAFT) polymerization or degenerate-transfer radical polymerization (IUPAC recommendation)[23] (Figure 1-1). The livingness and control in all these methods are achieved by establishing a rapid dynamic equilibrium between the low concentration propagating chains and predominant amount dormant chains.

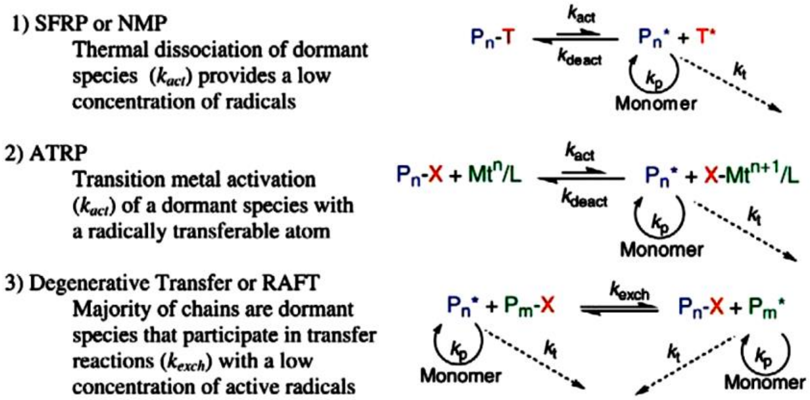


**Figure 1-1 Different CRP methods.**[3]

These techniques are among the most rapidly expanding areas of polymer chemistry due to their capability of synthesizing well-controlled functional polymers with predetermined molecular weight and narrow MWD. Over the past two decades, the number of publications using CRP methods, particularly ATRP, has been increased dramatically, proving their high potential applications in different areas.[24,25] Figure 1-2 shows the cumulative number of published papers using different CRP techniques in the past two decades. Over 25000 papers have been published based on different CRP methods and about 14000 (more than 50%) on ATRP.[25] The synthesized polymers by ATRP method are highly chain end functionalized and can therefore take part in various post-polymerization modifications, or considered as macroinitiator in the synthesis of block copolymers.[26]

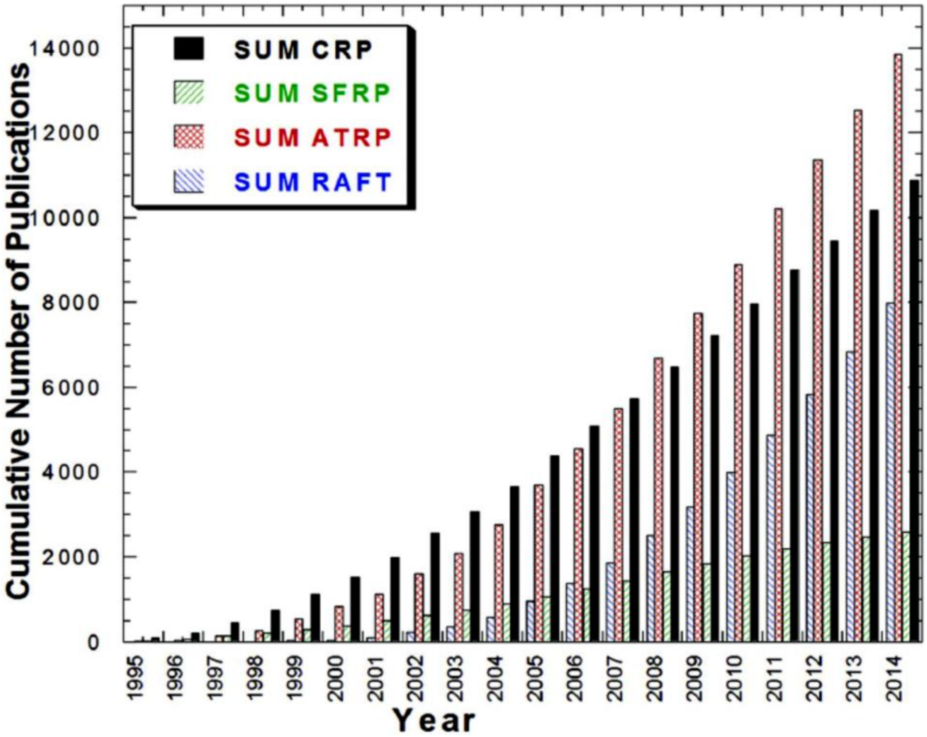
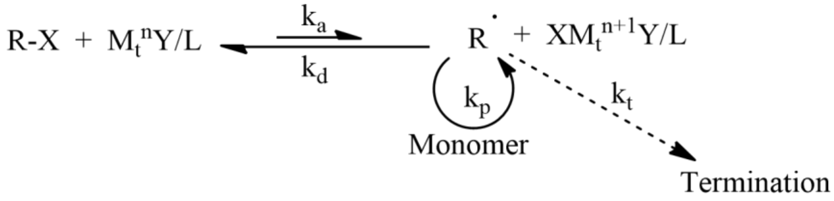


**Figure 1-2 Results of SciFinder Search on various CRP techniques.[25]**

## 1-3- Atom Transfer Radical Polymerization (ATRP)

ATRP was discovered in 1995 by Matyjaszewski's group [21] and Sawamoto's group.[22] Scheme 1-2 shows the mechanism of ATRP process,[27] which could be carried out under different conditions, such as bulk, solution, emulsion and suspension.

**Scheme 1-2 Mechanism of ATRP**



ATRP generally requires an alkyl halide (R-X) as initiator and a transition metal salt/ligand complex ($M_t^nY/L$) as catalyst. ATRP involves homolytic cleavage of R-X bond by $M_t^nY/L$ (with rate constant $k_a$), followed by propagation (rate constant $k_p$), reversible deactivation of radical ($R^\bullet$) by higher oxidation state catalyst complex ($XM_t^{n+1}Y/L$) (with rate constant $k_d$) or termination with other radicals (rate constant $k_t$). The reaction continues by repetitive transfer of halogen atom to and from the transition metal complex. Termination is minimized by decreasing the free radical concentration in favor of dormant alkyl halide in the above equilibrium (i.e., $k_a \ll k_d$).[28]

ATRP can be used to synthesize polymers with well-defined molecular weight and narrow molecular weight distribution. Furthermore, it is really effective for the preparation of reactive and functional chains, polymers with different compositions such as random, gradient and block copolymer, and polymers with a variety of topologies such as star and hyperbranched.[29-32]

## 1-4- Challenges in ATRP

Besides the advantages of ATRP method for the polymerization of a wide range of monomers with defined structure, composition, predetermined molecular weight, narrow MWD[2,24,33] and the possibility of performing polymerization in different conditions such as bulk, solution, emulsion and suspension,[34,35] ATRP has some limitations. Firstly, in order to obtain consistent results, special handling is necessary for storing the catalyst under an inert atmosphere and removing the oxygen and other oxidants from the system before and during the polymerization.[36-38] Secondly, a high concentration of catalyst is necessary for carrying out the polymerization (typically of the order of 0.1-1 mol% relative to monomer), which gives a deep color to the final product and additional polymer purification steps are required, following the reaction.[39-41] Lastly, the difficulty of reaching high conversion is another problem in ATRP technique, because of losing the control of polymerization as a result of diffusion-controlled reactions at high conversions.

Different approaches have been employed in tackling the problem of high concentration residual catalyst in the final product. These approaches can be categorized into two major classes: engineering approaches and chemistry approaches. In engineering methods, catalyst supporting is often employed. Various support systems have been developed in order to facilitate catalyst recycling.[42-45] It would be easier to purify synthesized polymer by removing catalyst embedded in solid support. However, Faucher *et al.* found that although catalytic centers on supported particle surface adequately activated dormant chains, but due to diffusion limitations, they could not effectively deactivate radicals in solution.[41] The same group also found that one catalyst center has potential to activate hundreds to thousands of chains, depending on its ability of migration.[46] There is, therefore, no need for one catalyst center to activate one chain and only ppm amount of catalyst is needed in the ATRP method.

In chemistry methods, reducing catalyst loading has been achieved by developing highly active ligands (Figure 1-3) and initiators (Figure 1-4) with a large equilibrium constant ($K_{ATRP} = \frac{k_a}{k_d}$).[47-49] However, the catalyst concentration is still considerable.[1] In the newer approach, air-stable deactivators have been used to moderate the sensitivity of ATRP to oxygen and oxidizing agents. As the first method, activator generated by electron transfer (AGET) ATRP was developed. In this method, a stoichiometric amount of reducing agents is added to the reaction medium containing deactivator ($XM_t^{n+1}Y/L$) to regenerate the activator ($M_t^nY/L$)

and the polymerization has been continued like regular ATRP. In this method, different reducing agents such as zero-valent copper, tin(II) 2-ethylhexanoate, ascorbic acid or triethylamine have been used.[50-58] However, in AGET-ATRP, although the problem of sensitivity to oxygen has been solved, a high concentration of catalyst is still present.

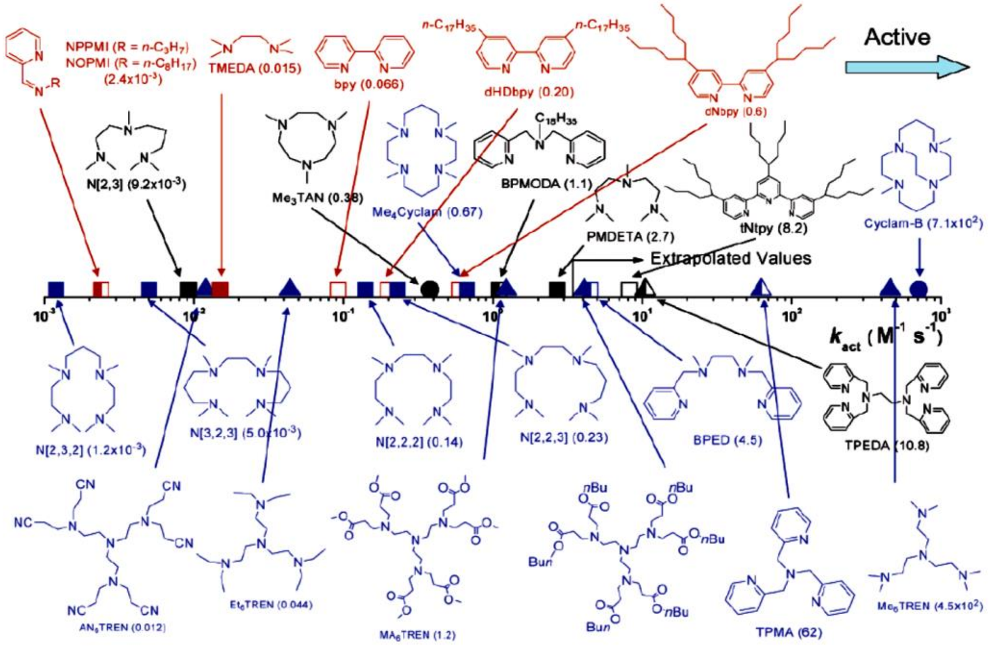


**Figure 1-3 Activation rate constants for different ligands with ethyl 2-bromo-isobutyrate (EtBriB) in the presence of $Cu^IY$(Y=Br or Cl) in acetonitrile at 35 °C.[59]**

In the newest approach, a very low concentration of catalyst (ppm level) with higher oxidation state ($XM_t^{n+1}Y/L$) is used in the presence of excess concentration of an appropriate reducing agent such as zero-valent copper, tin(II) 2-ethylhexanoate, ascorbic acid, trimethylamine or phenylhydrazine to regenerate the catalyst continuously during the polymerization, which was named as activator regenerated by electron transfer (ARGET) ATRP [60-67] or a very low concentration of catalyst (ppm level) with higher oxidation state ($XM_t^{n+1}Y/L$) is employed in the presence of normal free radical initiator (such as AIBN) to continuously regenerate the activator (initiator for continuous activator regeneration (ICAR) ATRP) [68-72] (Scheme 1-3).

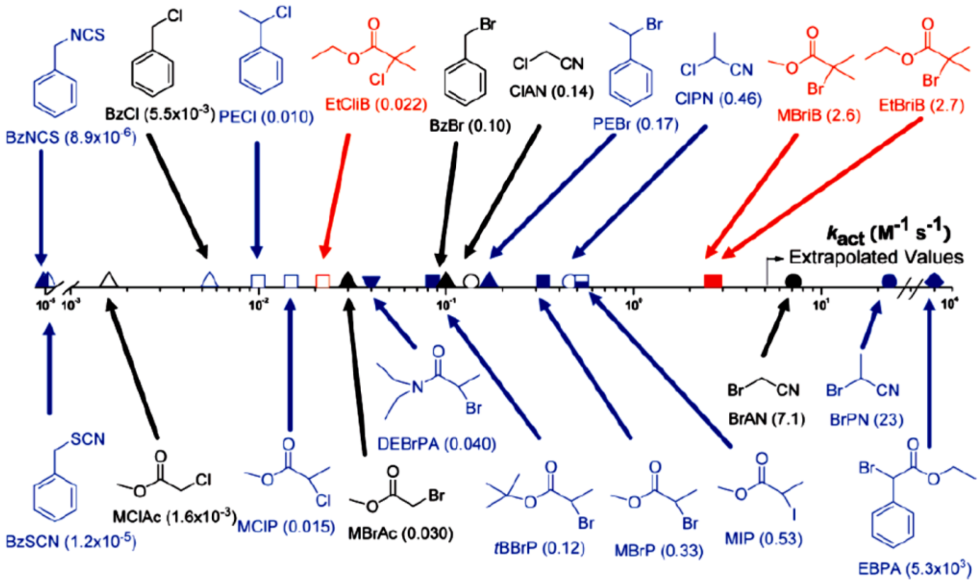
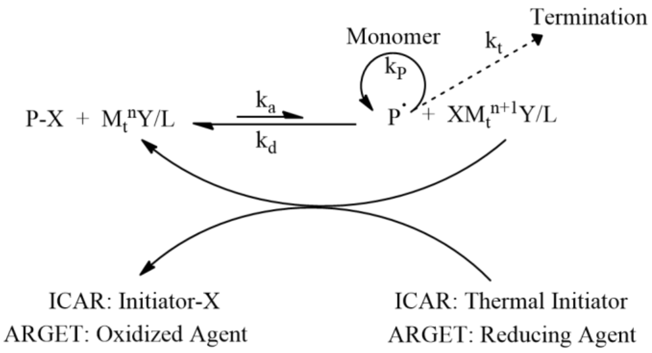


**Figure 1-4 Activation rate constants for different initiators with Cu$^{I}$X (X=Br or Cl)/ N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) in acetonitrile at 35 °C.[73]**

**Scheme 1-3 Mechanism of ARGET-ATRP and ICAR-ATRP**

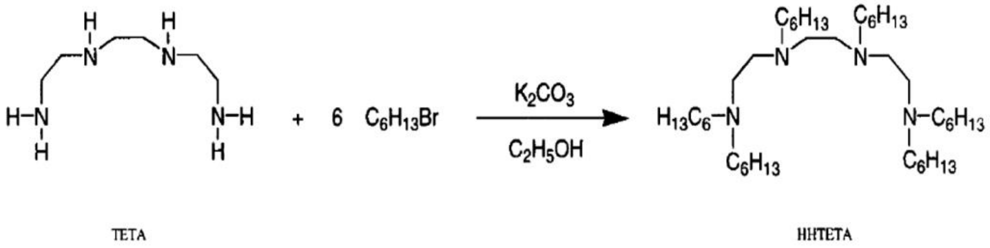


The limitation of ARGET-ATRP has been attributed to the presence of reducing agent in the system that produces acid during polymerization and increases the risk of some side reactions. On the other side, a limitation of ICAR-ATRP has also appeared in the synthesis of block copolymers, since the radicals generated by normal initiator can initiate new polymer chains.[1]

Both ARGET and ICAR ATRP overcome the limitations of normal ATRP to some extent. But still, finding better methods for improving the process is in progress such as supplemental activator and reducing agent (SARA) ATRP,[74] photochemically mediated ATRP [75] and electrochemically mediated ATRP.[76]

These approaches are effective and have provided solution to the high catalyst loading problem to some degree. However, the high monomer conversion issues is another equally important, if not more important, challenge, which has not been addressed well. Literature data over 80% conversion in bulk and solution ATRP are rarely available. Acar and his co-worker [77] tried to improve homogeneity of the catalyst/ligand complex and consequently the control of polymerization through addition of long alkyl substituents to the ligand. Hexahexyl triethylenetetramine (HHTETA) was synthesized as a new ligand through alkylation of triethylenetetramine (TETA) with 1-bromohexane (Scheme 1-4). Bulk polymerization runs of methyl methacrylate (MMA) and styrene (St) were carried out at 75 and 110 °C, respectively by employing normal ATRP and using ethyl-2-bromo propionate (EBrP) as the initiator and CuBr as the catalyst. The following molar ratios of the reactants were employed: [MMA/St]:[EBrP]:[CuBr]:[HHTETA] = 300/200:1:1:1. After 2 hours of the polymerization, about 70 and 55% conversion were obtained for St and MMA, respectively. Polydispersity index (PDI) or dispersity (Đ, as recommended by IUPAC) remained around 1.2 during the reaction for both monomers. However, there was a deviation from theoretical molecular weight during the polymerization, especially for MMA.

**Scheme 1.4 alkylation of the triethylenetetramine (TETA) with 1-bromohexane [77]**

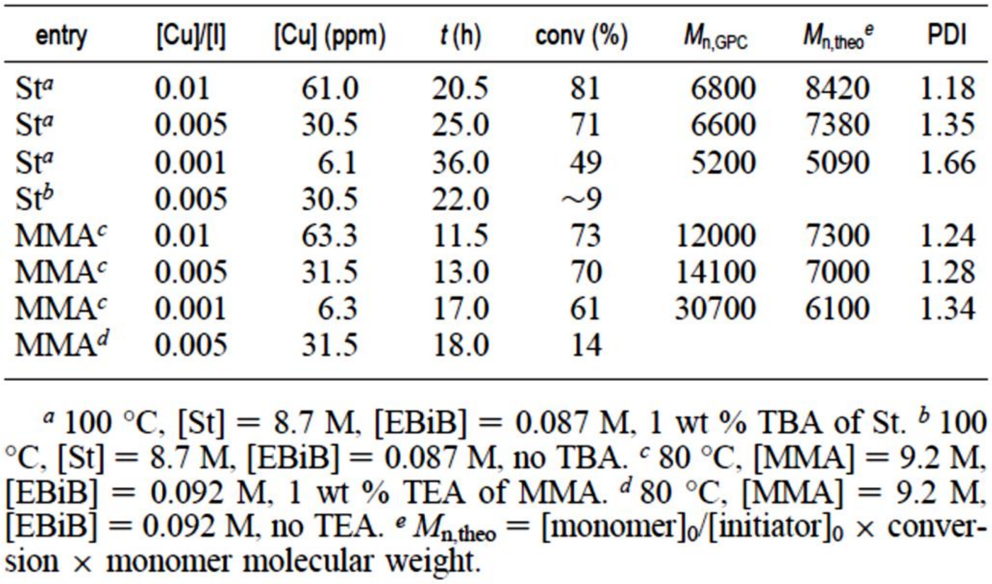


Faucher and Zhu [46] performed bulk ATRP of MMA using methyl α-bromophenylacetate (MBP) and hexamethyltriethylenetetramine (HMTETA) as the initiator and ligand. The molar ratios of the reactants were [MMA]:[MBP]:[CuBr]:[HMTETA] = 100:1:0.001:1. They obtained about 52% conversion by continuing the reaction for 4.5 hr at 90 °C. The molecular weights of the synthesized polymers increased linearly with conversion, showing the presence of livingness during the polymerization. However, high PDI was found and increased to more than 6 at the end of the polymerization. They attributed the broad MWD to high viscosity of the reacting system and its effect on the deactivation reaction. Diffusion-controlled deactivation occurred during the polymerization, leading to the loss of control and the high PDI.

It is understandable that claiming "well control" could immediately become unsupported by experimental data. Indeed, it is difficult for ATRP to reach high conversion where control of polymer molecular weight becomes very poor. Most bulk ATRP systems lose control before 80% conversion.

Matyjaszewski *et al.*[78] reported a new highly active copper based complex, CuBr/N,N,N$'$,N$'$-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN). Different concentrations of the catalyst complex have been used for the bulk ATRP of St and MMA at 100 and 80 °C, respectively, along with 2-bromoisobutyrate (EBiB) as the initiator. $Cu^{II}Br_2$/TPEN was precipitated out during the polymerization, leading to lower rate of the reaction. They found that addition of tertiary amines such as trimethylamine (TEA) or tributylamine (TBA) could prevent or retard the deactivator complex precipitation and consequently increase the rate of polymerization. Decreasing the catalyst concentration suppressed the rate of polymerization and increased the PDI (Table 1-1). A maximum 81% conversion after 20.5 hours was obtained for the polymerization of styrene with PDI around 1.2. For MMA, 73% conversion was obtained after 11.5 hours with PDI more than 1.2. They related the low initiator efficiency to highly active catalyst and very large ATRP equilibrium constant ($K_{ATRP}$), which increased the risk of the termination at the beginning of reaction.

**Table 1-1 Bulk ATRP of styrene and MMA using CuBr/TPEN as catalyst complex.[78]**

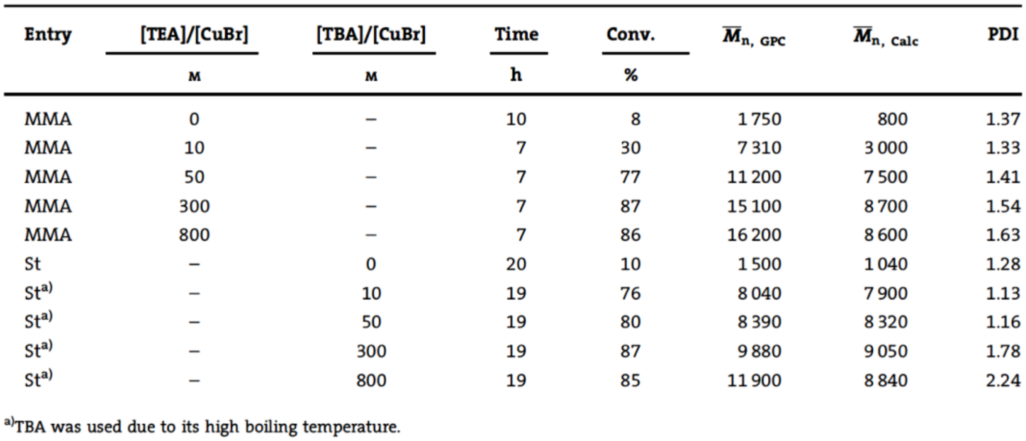


| entry | [Cu]/[I] | [Cu] (ppm) | *t* (h) | conv (%) | $M_{n,GPC}$ | $M_{n,theo}{}^{e}$ | PDI |
|---|---|---|---|---|---|---|---|
| St[a] | 0.01 | 61.0 | 20.5 | 81 | 6800 | 8420 | 1.18 |
| St[a] | 0.005 | 30.5 | 25.0 | 71 | 6600 | 7380 | 1.35 |
| St[a] | 0.001 | 6.1 | 36.0 | 49 | 5200 | 5090 | 1.66 |
| St[b] | 0.005 | 30.5 | 22.0 | ~9 | | | |
| MMA[c] | 0.01 | 63.3 | 11.5 | 73 | 12000 | 7300 | 1.24 |
| MMA[c] | 0.005 | 31.5 | 13.0 | 70 | 14100 | 7000 | 1.28 |
| MMA[c] | 0.001 | 6.3 | 17.0 | 61 | 30700 | 6100 | 1.34 |
| MMA[d] | 0.005 | 31.5 | 18.0 | 14 | | | |

[a] 100 °C, [St] = 8.7 M, [EBiB] = 0.087 M, 1 wt % TBA of St. [b] 100 °C, [St] = 8.7 M, [EBiB] = 0.087 M, no TBA. [c] 80 °C, [MMA] = 9.2 M, [EBiB] = 0.092 M, 1 wt % TEA of MMA. [d] 80 °C, [MMA] = 9.2 M, [EBiB] = 0.092 M, no TEA. [e] $M_{n,theo}$ = $[\text{monomer}]_0/[\text{initiator}]_0$ × conversion × monomer molecular weight.

Shen *et al.*[79] employed tertiary amines (TEA and TBA) to enhance the catalytic activity of CuBr/tris[(2-pyridyl)methyl]amine (CuBr/TPMA). Styrene and MMA were polymerized at 100 and 80 °C, respectively, while trying different concentrations of the tertiary amines. EBiB was employed as the ATRP initiator in the following recipe, [Monomer]:[EBiB]:[CuBr]:[TPMA] = 100:1:0.01:0.01. The results (Table 1-2) showed that rate of polymerization was improved by increasing the concentration of tertiary amines. They found that tertiary amine could reduce the deactivator to activator, leading to significant rate and catalyst activity enhancement (ARGET-ATRP). By this method, a maximum 87% conversion was obtained for MMA with PDI and initiator efficiency about 1.5 and 58%, respectively. For styrene, a maximum 87% conversion was obtained with PDI and initiator efficiency more than 1.7 and 90%, respectively.

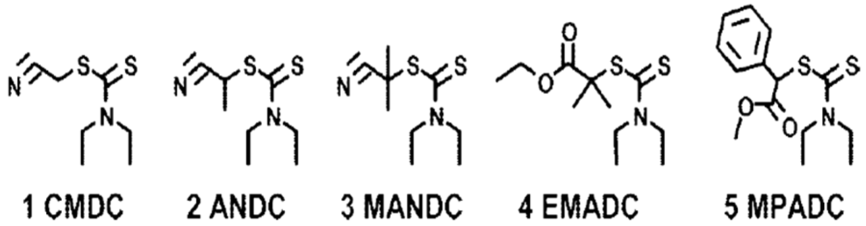
**Table 1-2 ATRP of MMA and styrene in the presence of different concentrations of the tertiary amines and CuBr/TPMA as catalyst complex.**[79]



| Entry | [TEA]/[CuBr] | [TBA]/[CuBr] | Time | Conv. | $\overline{M}_{n,\ GPC}$ | $\overline{M}_{n,\ Calc}$ | PDI |
|---|---|---|---|---|---|---|---|
| | M | M | h | % | | | |
| MMA | 0 | – | 10 | 8 | 1 750 | 800 | 1.37 |
| MMA | 10 | – | 7 | 30 | 7 310 | 3 000 | 1.33 |
| MMA | 50 | – | 7 | 77 | 11 200 | 7 500 | 1.41 |
| MMA | 300 | – | 7 | 87 | 15 100 | 8 700 | 1.54 |
| MMA | 800 | – | 7 | 86 | 16 200 | 8 600 | 1.63 |
| St | – | 0 | 20 | 10 | 1 500 | 1 040 | 1.28 |
| St[a)] | – | 10 | 19 | 76 | 8 040 | 7 900 | 1.13 |
| St[a)] | – | 50 | 19 | 80 | 8 390 | 8 320 | 1.16 |
| St[a)] | – | 300 | 19 | 87 | 9 880 | 9 050 | 1.78 |
| St[a)] | – | 800 | 19 | 85 | 11 900 | 8 840 | 2.24 |

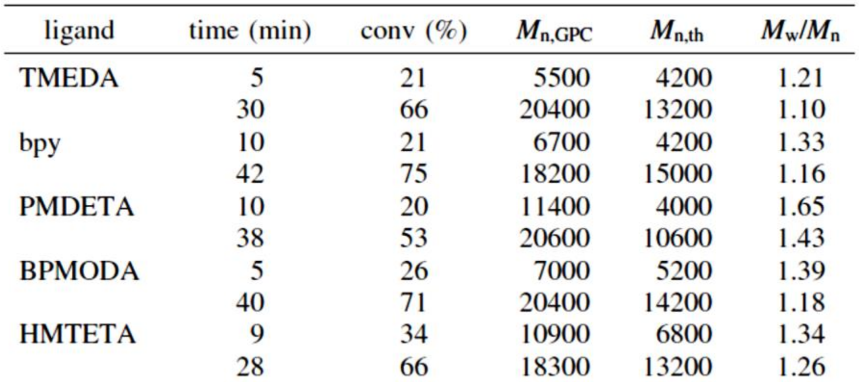
[a)] TBA was used due to its high boiling temperature.

Matyjaszewski and Kwak[80] synthesized various alkyl diethyldithiocarbamate (DC) (Scheme 1-5) and employed them as ATRP initiators for the bulk polymerization of MMA at 100 °C. They found that among different DCs, 1-cyano-1 methylethyldiethyldithiocarbamte (MANDC) could obtain the best results, based on the controllability. MANDC was used as the initiator along with different ligands in the following molar ratios, [MMA]:[MANDC]:[CuBr]:[ligand] = 100:1:1:1. A maximum 75% conversion was obtained by using 2,2'-bipyridine (bpy) as the ligand after performing the reaction for 42 hr at 100 °C with PDI about 1.16 (Table 1-3).



**Scheme 1-5 Various synthesized alkyl diethyldithiocarbamate (DC)** [80]

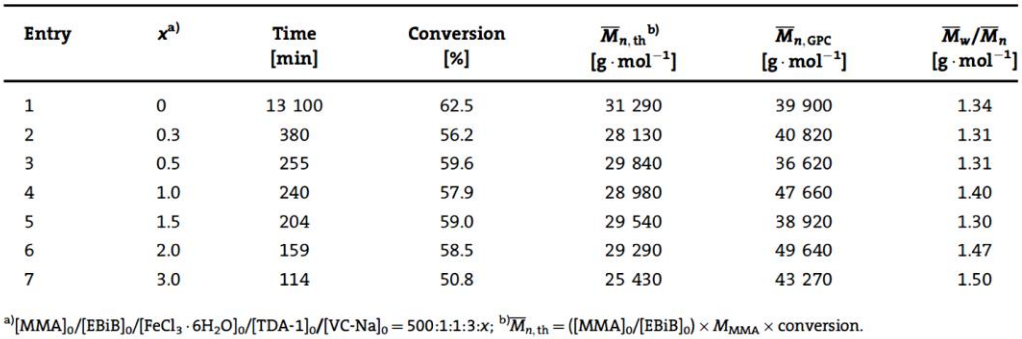
**Table 1-3 Bulk ATRP of MMA using MANDC as initiator in the presence of different ligands.**[80]



| ligand | time (min) | conv (%) | $M_{n,GPC}$ | $M_{n,th}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| TMEDA | 5 | 21 | 5500 | 4200 | 1.21 |
| | 30 | 66 | 20400 | 13200 | 1.10 |
| bpy | 10 | 21 | 6700 | 4200 | 1.33 |
| | 42 | 75 | 18200 | 15000 | 1.16 |
| PMDETA | 10 | 20 | 11400 | 4000 | 1.65 |
| | 38 | 53 | 20600 | 10600 | 1.43 |
| BPMODA | 5 | 26 | 7000 | 5200 | 1.39 |
| | 40 | 71 | 20400 | 14200 | 1.18 |
| HMTETA | 9 | 34 | 10900 | 6800 | 1.34 |
| | 28 | 66 | 18300 | 13200 | 1.26 |

Xiulin Zhu *et al.*[57] performed bulk AGET-ATRP of MMA by using vitamin C sodium salt (VC-Na) as the reducing agent (different concentrations of $NaHCO_3$). $FeCl_3.6H_2O$/tris-(3,6-dioxa-heptyl) amine (TDA-1) was employed as catalyst complex. Polymerization was carried out at 90 °C in the presence of different [VC-Na] and using the following molar ratios, [MMA]:[EBiB]:[$FeCl_3$]:[TDA-1] = 500:1:1:3. The results showed that the rate of polymerization was increased by increasing [VC-Na]. A maximum conversion of 60% was obtained for different [VC-Na] with PDI about 1.4 (Table 1-4).

**Table 1-4 Effect of [VC-Na] on bulk AGET ATRP of MMA at 90 ˚C.**[57]

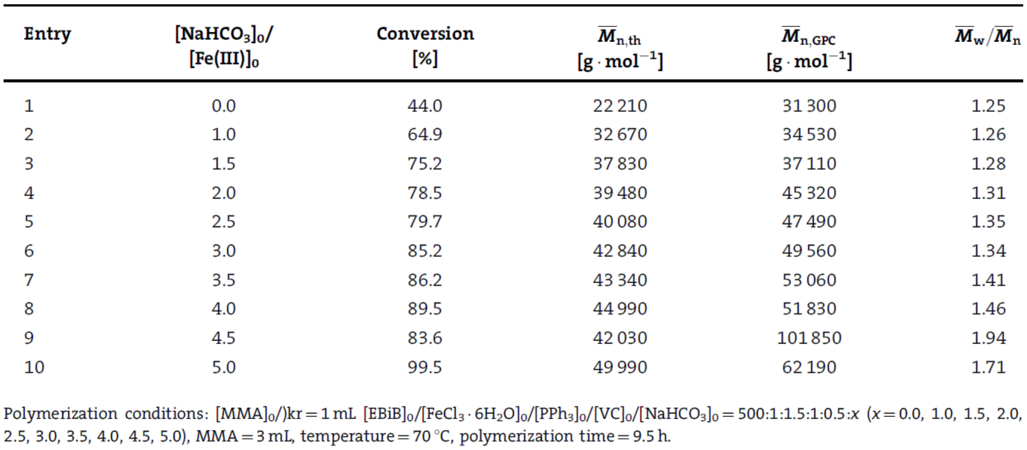


| Entry | $x^{a)}$ | Time [min] | Conversion [%] | $\overline{M}_{n,\mathrm{th}}$ $^{b)}$ [g · mol$^{-1}$] | $\overline{M}_{n,\mathrm{GPC}}$ [g · mol$^{-1}$] | $\overline{M}_w/\overline{M}_n$ [g · mol$^{-1}$] |
|---|---|---|---|---|---|---|
| 1 | 0 | 13 100 | 62.5 | 31 290 | 39 900 | 1.34 |
| 2 | 0.3 | 380 | 56.2 | 28 130 | 40 820 | 1.31 |
| 3 | 0.5 | 255 | 59.6 | 29 840 | 36 620 | 1.31 |
| 4 | 1.0 | 240 | 57.9 | 28 980 | 47 660 | 1.40 |
| 5 | 1.5 | 204 | 59.0 | 29 540 | 38 920 | 1.30 |
| 6 | 2.0 | 159 | 58.5 | 29 290 | 49 640 | 1.47 |
| 7 | 3.0 | 114 | 50.8 | 25 430 | 43 270 | 1.50 |

$^{a)}$[MMA]$_0$/[EBiB]$_0$/[FeCl$_3$ · 6H$_2$O]$_0$/[TDA-1]$_0$/[VC-Na]$_0$ = 500:1:1:3:$x$; $^{b)}\overline{M}_{n,\mathrm{th}}$ = ([MMA]$_0$/[EBiB]$_0$) × $M_{\mathrm{MMA}}$ × conversion.

In another work, Xiulin Zhu *et al.*[55] performed bulk AGET-ATRP of MMA by using vitamin C as the reducing agent in the presence of catalytic amounts of $NaHCO_3$. $FeCl_3.6H_2O$/triohenyl phosphine ($PPh_3$) and EBiB were employed as catalyst complex and initiator, respectively. Polymerization was carried out at 70 ˚C for 9.5 hr using the following recipe, [MMA]:[EBiB]:[$FeCl_3$]:[$PPh_3$]:[VC] = 500:1:1.5:1:0.5 and different [$NaHCO_3$]/[$FeCl_3$] molar ratios. The results showed that the rate of polymerization was enhanced by increasing the [$NaHCO_3$]/[Fe(III)] to 5, and 99.5% conversion was obtained with PDI and initiator efficiency about 1.7 and 80%, respectively (Table 1-5). However, they did not mention anything about the occurrence of “gel effect” and “glass effect” during the polymerization and at high conversion.

**Table 1-5 Effect of [$NaHCO_3$] on bulk AGET ATRP of MMA.**[55]



| Entry | $[NaHCO_3]_0/[Fe(III)]_0$ | Conversion [%] | $\overline{M}_{n,th}$ [$g \cdot mol^{-1}$] | $\overline{M}_{n,GPC}$ [$g \cdot mol^{-1}$] | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|
| 1 | 0.0 | 44.0 | 22 210 | 31 300 | 1.25 |
| 2 | 1.0 | 64.9 | 32 670 | 34 530 | 1.26 |
| 3 | 1.5 | 75.2 | 37 830 | 37 110 | 1.28 |
| 4 | 2.0 | 78.5 | 39 480 | 45 320 | 1.31 |
| 5 | 2.5 | 79.7 | 40 080 | 47 490 | 1.35 |
| 6 | 3.0 | 85.2 | 42 840 | 49 560 | 1.34 |
| 7 | 3.5 | 86.2 | 43 340 | 53 060 | 1.41 |
| 8 | 4.0 | 89.5 | 44 990 | 51 830 | 1.46 |
| 9 | 4.5 | 83.6 | 42 030 | 101 850 | 1.94 |
| 10 | 5.0 | 99.5 | 49 990 | 62 190 | 1.71 |

Polymerization conditions: $[MMA]_0$/)kr = 1 mL $[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[VC]_0/[NaHCO_3]_0 = 500:1:1.5:1:0.5:x$ ($x$ = 0.0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0), MMA = 3 mL, temperature = 70 °C, polymerization time = 9.5 h.

In another study from Xiulin Zhu's group,[71] bulk ICAR-ATRP of MMA was carried out using $FeCl_3.6H_2O/PPh_3$, 1,4-(2-bromo-2-methylpropionato)benzene ($BMPB_2$) and AIBN as catalyst complex, ATRP initiator and ICAR agent, respectively. Effects of temperature and catalyst and AIBN concentrations were investigated on the rate and control of polymerization. A maximum 80% conversion was obtained by employing the molar ratios of $[MMA]/[BMPB_2]/[FeCl_3.6H_2O]/[PPh_3]/[AIBN] = 500/1/0.02/1.5/0.1$ and performing the reaction for 36 hr at 60 °C. PDI and initiator efficiency were 1.51 and 98%, respectively.

Cheng *et al.* [81] performed bulk AGET-ATRP of MMA using two different types of salts, hydroxylamine hydrochloride ($HONH_2HCl$) and sodium bisulfite ($NaHSO_3$), as the reducing agents. EBiB and $FeCl_3.6H_2O/PPh_3$ were employed as initiator and catalyst complex, respectively. They found that the rate of polymerization was much faster by using $NaHSO_3$ as the reducing agent while the control of polymerization was not changed considerably. By trying the following recipe, $[MMA]/[EBiB]/[FeCl_3.6H_2O]/[PPh_3]/[NaHSO_3] = 500/1/0.5/1.5/0.5$, about 85% conversion was obtained after 20 hr at 90 °C with PDI below 1.5 during the polymerization.

It becomes clear that in order to maintain control of the polymerization, the reaction should be stopped before reaching to higher conversion. This means there is still at least around 20% residual unreacted monomer present in the system. Reclaiming such a high level of monomer residue is costly and not practical in commercial practice. It should be pointed out that the high conversion problem is common among CRP systems. Well controlled RAFT and NMP are also limited to low monomer conversions, if not more severe.

This problem in ATRP has been addressed to some extend by performing modeling and considering chain-length diffusion-controlled reactions.[72,82,83] A well behaved ATRP system relies on two factors: “livingness” and “control”. By “livingness”, it is meant the absence of irreversible chain termination or transfer. It can be quantified by the dead chain content in the final product. “Control” is determined by the number of activation/deactivation cycles that individual chains experience during polymerization. More cycles gives better control.[84]

In ATRP, as well as other CRP, radical termination and deactivation are fast reactions. Their rate constants are many orders of magnitude higher than those of initiation, propagation and activation reactions. Fast reactions could more easily become diffusion controlled. The rate constant of a diffusion-controlled reaction is proportional to the sum of the self-diffusivities of the involved reactants. Polymer diffusion is usually related to chain length of the polymer and viscosity of the media, and it becomes slower by increasing the chain length and viscosity. Bimolecular radical termination is always diffusion controlled due to the extremely high activities of free radicals. In FRP, it often causes an auto acceleration in the polymerization rate, so called Trommosdorff effect or a misnomer "gel effect" (no gels present). In ATRP, diffusion-controlled radical termination helps "livingness". It is actually the diffusion-controlled deactivation that is the trouble-maker and is responsible for loss of control of polymer molecular weight at high monomer conversion, through slowing down the deactivation of free radicals in the system ("gel Effect").[85] At very high conversions when polymerization system becomes glassy, propagation reaction can also become diffusion controlled. Because propagation and termination, as well as deactivation, are competitive reactions for a radical center, it could also significantly affect ATRP behavior. While diffusion-controlled termination at high conversion and diffusion-controlled propagation at glass state have been a matter of studies for over half a century, diffusion-controlled deactivation at high conversion and diffusion-controlled activation at glass state are new in ATRP and other CRP. Achieving high monomer conversion, as well as eliminating organic solvents, while keeping livingness and control of the polymerization, are critically important for commercial exploitation of the CRP processes.

## 1-5- References

(1) Tsarevsky, N. V.; Matyjaszewski, K. Green Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials. Chem. Rev. 2007, 107, 2270.

(2) Matyjaszewski, K.; Davis, T. P. Handbook of Radical Polymerization. 2002.

(3) Matyjaszewski, K.; Spanswick, J. Controlled/Living Radical Polymerization. Mater. Today 2005, 8 (3), 26.

(4) Patten, T. E.; Matyjaszewski, K. Atom Transfer Radical Polymerization and the Synthesis of Polymeric Materials. Adv. Mater. 1998, 10 (12), 901.

(5) Szwarc, M.; Levy, M.; Milkovich, R. Polymerization Initiated by Electron Transfer to Monomer. A New Method of Formation of Block Polymers. J. Am. Chem. Soc. 1956, 78 (11), 2656.

(6) Dreyfuss, M. P.; Dreyfuss, P. A "Living" Polymer after Cationic Initiation. Polymer (Guildf). 1965, 6 (2), 93.

(7) Bawn, C. E. H.; Bell, R. M.; Ledwith, A. Monomer-Polymer Equilibrium and Ceiling Temperature for Tetrahydrofuran Polymerization. Polymer (Guildf). 1965, 6 (2), 95.

(8) Webster, O. W. Living Polymerization Methods. Science. 1991, 251, 887.

(9) Matyjaszewski, K.; Muller, A. H. E. 50 Years of Living Polymerization. Prog. Polym. Sci. 2006, 31 (12), 1039.

(10) Smid, J.; Van Beylen, M.; Hogen-Esch, T. E. Perspectives on the Contributions of Michael Szwarc to Living Polymerization. Prog. Polym. Sci. 2006, 31, 1041.

(11) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Sakellariou, G. Synthesis of Well-Defined Polypeptide-Based Materials via the Ring-Opening Polymerization of R-Amino Acid N-Carboxyanhydrides. Chem. Eng. Sci. 2009, 109, 5528.

(12) Bielawski, C. W.; Grubbs, R. H. Living Ring-Opening Metathesis Polymerization. Prog. Polym. Sci. 2007, 32, 1.

(13) Gold, L. Statistics of Polymer Molecular Size Distribution for an Invariant Number of Propagating Chains. J. Chem. Phys. 1958, 28, 91.

(14) Litt, M. The Effects of Inadequate Mixing in Anionic Polymerization: Laminar Mixing Hypothesis. J. Polym. Sci. 1962, 58 (5), 429.

(15) Xia, J.; Xia, J.; Matyjaszewski, K.; Matyjaszewski, K. Controlled/"Living" Radical Polymerization. Homogeneous Reverse Atom Transfer Radical Polymerization Using AIBN as the Initiator. Macromolecules 1997, 30 (97), 7692.

(16) Odian, G. Principles of Polymerization, Fourth.; John Wiley & Sons, Inc.: New Jersey, 2004.

(17) Greszta, D.; Mardare, D.; Matyjaszewski, K. "Living" Radical Polymerization. 1. Possibilities and Limitations. Macromolecules 1994, 27 (3), 638.

(18) Matyjaszewski, K. Introduction to Living Polymerization. Living and/or Controlled Polymerization. J. Phys. Org. Chem. 1995, 8 (4), 197.

(19) Matyjaszewski, K.; Gaynor, S.; Greszta, D.; Mardare, D.; Shigemoto, T. "Living" and Controlled Radical Polymerization. J. Phys. Org. Chem. 1995, 8, 306.

(20) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow Molecular Weight Resins by a Free-Radical Polymerization Process. Macromolecules 1993, 26, 2987.

(21) Wang, J.; Matyjaszewski, K. Controlled/Living Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(22) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of Methyl Methacrylate with the Carbon TetrachloridelDichlorotris-(triphenylphosphine)ruthedum(II)/ Methylaluminum Bis(2,6-Di-Tert-Butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. Macromolecules 1995, 28, 1721.

(23) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; et al. Living

Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. Macromolecules 1998, 31, 5559.

(24) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. Polymers with Very Low Polydispersities from Atom Transfer Radical Polymerization. Science. 1996, pp 866–868.

(25) Matyjaszewski, K. Controlled Radical Polymerization: State-of-the-Art in 2014. In Controlled Radical Polymerization: Mechanisms; Krzysztof Matyjaszewski, Brent S. Sumerlin, Nicolay V. Tsarevsky, J. C., Ed.; 2015; 1–17.

(26) Coessens, V.; Pintauer, T.; Matyjaszewski, K. Functional Polymers by Atom Transfer Radical Polymerization. Prog. Polym. Sci. 2001, 26, 337.

(27) Wang, J. S.; Matyjaszewski, K. Controlled/“Living” Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process. Macromolecules 1995, 28, 7901.

(28) Matyjaszewski, K.; Patten, T. E.; Xia, J. Controlled /“Living” Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene. J. Am. Chem. Soc. 1997, 119, 674.

(29) Haddleton, D. M.; Crossman, M. C.; Hunt, K. H.; Topping, C.; Waterson, C.; Suddaby, K. G. Identifying the Nature of the Active Species in the Polymerization of Methacrylates: Inhibition of Methyl Methacrylate Homopolymerizations and Reactivity Ratios for Copolymerization of Methyl Methacrylate/n-Butyl Methacrylate. Macromolecules 1997, 30, 3992.

(30) Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V; Greszta, D.; Pakula, T. Gradient Copolymers by Atom Transfer Rradical Copolymerization. J. Phys. Org. Chem. 2000, 13, 775.

(31) Percec, V.; Barboiu, B.; Bera, T. K.; Sluis, M.; Grubbs, R. B.; Frechet, J. M. J. Designing Functional Aromatic Multisulfonyl Chloride Initiators for Complex Organic Synthesis by Living Radical Polymerization. J. Polym. Sci. Part A Polym. Chem. 2000, 38, 4776.

(32) Gao, X.; Feng, W.; Zhu, S.; Sheardown, H.; Brash, J. L. Kinetic Modeling of Surface-Initiated Atom Transfer Radical Polymerization. Macromol. React. Eng. 2010, 4, 235.

(33) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. Chem. Rev. 2001, 101, 2921.

(34) Cunningham, M. F. Controlled/Living Radical Polymerization in Aqueous Dispersed Systems. Prog. Polym. Sci. 2008, 33, 365.

(35) Min, K.; Gao, H.; Yoon, J. A.; Wu, W.; Kowalewski, T.; Matyjaszewski, K. One-Pot Synthesis of Hairy Nanoparticles by Emulsion ATRP. Macromolecules 2009, 42, 1597.

(36) Hong, S. C.; Matyjaszewski, K. Fundamentals of Supported Catalysts for Atom Transfer Radical Polymerization (ATRP) and Application of an Immobilized/Soluble Hybrid Catalyst System to ATRP. Macromolecules 2002, 35, 7592.

(37) Shen, Y.; Tang, H.; Ding, S. Catalyst Separation in Atom Transfer Radical Polymerization. Prog. Polym. Sci. 2004, 29, 1053.

(38) Kubisa, P. Ionic Liquids in the Synthesis and Modification of Polymers. J. Polym. Sci. Part A Polym. Chem. 2005, 43, 4675.

(39) Faucher, S.; Okrutny, P.; Zhu, S. Facile and Effective Purification of Polymers Produced by Atom Transfer Radical Polymerization via Simple Catalyst Precipitation and Microfiltration. Macromolecules 2006, 39, 3.

(40) Faucher, S.; Zhu, S. Location of the Catalytic Site in Supported Atom Transfer Radical Polymerization. Macromol. Rapid Commun. 2004, 25, 991.

(41) Faucher, S.; Zhu, S. Fundamentals and Development of High-Efficiency. J. Polym. Sci. Part A Polym. Chem. 2007, 45, 553.

(42) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. Atom Transfer Polymerisation of Methyl Methacrylate Mediated by Solid Supported Copper Catalysts. Chem. Commun. 1999, 99.

(43) Kickelbick, G.; Paik, H.; Matyjaszewski, K. Immobilization of the Copper Catalyst in Atom Transfer Radical Polymerization. Macromolecules 1999, 32, 2941.

(44) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. H. Atom Transfer Radical Polymerization of Methyl Methacrylate by Silica Gel Supported Copper Bromide / Multidentate Amine. Macromolecules 2000, 33, 5427.

(45) Shen, Y.; Zhu, S.; Pelton, R. Packed Column Reactor for Continuous Atom Transfer Radical Polymerization : Methyl Methacrylate Polymerization Using Silica Gel Supported Catalyst. Macromol. Rapid Commun. 2000, 21, 956.

(46) Faucher, S.; Zhu, S. Heterogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate at Low Metal Salt Concentrations. Ind. Eng. Chem. Res. 2005, 44, 677.

(47) De Campo, F.; Lastécouères, D.; Verlhac, J. B. New and Improved Catalysts for Transition Metal Catalysed Radical Reactions. Chem. Commun. 1998, 2117.

(48) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. Controlled/"living" Radical Polymerization. Atom Transfer Radical Polymerization of Acrylates at Ambient Temperature. Macromolecules 1998, 31, 5958.

(49) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. Optimization of Atom Transfer Radical Polymerization Using Cu (I)/ Tris (2-(Dimethylamino) Ethyl) Amine as a Catalyst. Macromolecules 2000, 33, 8629.

(50) Jakubowski, W.; Matyjaszewski, K. Activator Generated by Electron Transfer for Atom Transfer Radical Polymerization. Macromolecules 2005, 38, 4139.

(51) Min, K.; Gao, H.; Matyjaszewski, K. Preparation of Homopolymers and Block Copolymers in Miniemulsion by ATRP Using Activators Generated by Electron Transfer (AGET). J. Am. Chem. Soc. 2005, 127, 3825.

(52) Oh, J. K.; Tang, C.; Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. Inverse Miniemulsion ATRP: A New Method for Synthesis and Functionalization of Well-Defined Water-Soluble/Cross-Linked Polymeric Particles. J. Am. Chem. Soc. 2006, 128, 5578.

(53) Oh, J. K.; Dong, H.; Zhang, R.; Matyjaszewski, K.; Schlaad, H. Preparation of Nanoparticles of Double-Hydrophilic PEO-PHEMA Block Copolymers by AGET ATRP in Inverse Miniemulsion. J. Polym. Sci. Part A Polym. Chem. 20078, 45, 4764.

(54) Khan, M. Y.; Xue, Z.; He, D.; Noh, S. K.; Lyoo, W. S. Comparative Study of a Variety of ATRP Systems with High Oxidation State Metal Catalyst System. Polymer (Guildf). 2010, 51, 69.

(55) He, W.; Zhang, L.; Bai, L.; Zhang, Z.; Zhu, J.; Cheng, Z.; Zhu, X. Iron-Mediated AGET ATRP of Methyl Methacrylate in the Presence of Catalytic Amounts of Base. Macromol. Chem. Phys. 2011, 212, 1474.

(56) Qin, J.; Cheng, Z.; Zhang, L.; Zhang, Z.; Zhu, J.; Zhu, X. A Highly Efficient Iron-Mediated AGET ATRP of Methyl Methacrylate Using Fe(0) Powder as the Reducing Agent. Macromol. Chem. Phys. 2011, 212 (10), 999.

(57) Tao, M.; Zhang, L.; Jiang, H.; Zhang, Z.; Zhu, J.; Cheng, Z.; Zhu, X. Iron(III)-Mediated AGET ATRP of Methyl Methacrylate Using Vitamin C Sodium Salt as a Reducing Agent. Macromol. Chem. Phys. 2011, 212, 1481.

(58) Miao, J.; Jiang, H.; Zhang, L.; Wu, Z.; Cheng, Z.; Zhu, X. AGET ATRP of Methyl Methacrylate via a Bimetallic Catalyst. RSC Adv. 2012, 2, 840.

(59) Tang, W.; Matyjaszewski, K. Effect of Ligand Structure on Activation Rate Constants in ATRP. Macromolecules 2006, 39 (15), 4953.

(60) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP. Macromolecules 2007, 40, 1789.

(61) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents. Proc. Natl. Acad. Sci. U. S. A. 2006, 103 (42), 15309.

(62) Matyjaszewski, K.; Tsarevsky, N. V; Braunecker, W. A.; Dong, H.; Huang, J.; Jakubowski, W.; Kwak, Y.; Nicolay, R.; Tang, W. Role of Cu(0) in Controlled /“ Living ” Radical Polymerization. Macromolecules 2007, 40, 7795.

(63) Chan, N.; Cunningham, M. F.; Hutchinson, R. a. ARGET ATRP of Methacrylates and Acrylates with Stoichiometric Ratios of Ligand to Copper. Macromol. Chem. Phys. 2008, 209, 1797.

(64) Nicolay, R.; Kwak, Y.; Matyjaszewski, K. A Green Route to Well-Defined High-Molecular-Weight (Co)polymers Using ARGET ATRP with Alkyl Pseudohalides and Copper Catalysis. Angew. Chemie 2010, 122, 551.

(65) Magenau, A. J. D.; Kwak, Y.; Matyjaszewski, K. ATRP of Methacrylates Utilizing Cu(II)X2/L and Copper Wire. Macromolecules 2010, 43, 9682.

(66) Wang, Y.; Zhang, Y.; Parker, B.; Matyjaszewski, K. ATRP of MMA with Ppm Levels of Iron Catalyst. Macromolecules 2011, 44, 4022.

(67) Lou, Q.; Shipp, D. a. Recent Developments in Atom Transfer Radical Polymerization (ATRP): Methods to Reduce Metal Catalyst Concentrations. Chemphyschem 2012, 13 (14), 3257.

(68) Pintauer, T.; Matyjaszewski, K. Atom Transfer Radical Addition and Polymerization Reactions Catalyzed by Ppm Amounts of Copper Complexes. Chem. Soc. Rev. 2008, 37, 1087.

(69) Plichta, A.; Li, W.; Matyjaszewski, K. ICAR ATRP of Styrene and Methyl Methacrylate with Ru (Cp*) Cl (PPh3)2. Macromolecules 2009, 42, 2330.

(70) Machado, M.; Faucher, S.; Zhu, S. Hybrid Atom Transfer Radical Polymerization System for Balanced Polymerization Rate and Polymer Molecular Weight Control. J. Polym. Sci. Part A Polym. Chem. 2010, 48, 2294.

(71) Zhu, G.; Zhang, L.; Zhang, Z.; Zhu, J.; Tu, Y.; Cheng, Z.; Zhu, X. Iron-Mediated ICAR ATRP of Methyl Methacrylate. Macromolecules 2011, 44, 3233.

(72) D’hooge, D. R.; Konkolewicz, D.; Reyniers, M. F.; Marin, G. B.; Matyjaszewski, K. Kinetic Modeling of ICAR ATRP. Macromol. Theory Simulations 2012, 21, 52.

(73) Tang, W.; Matyjaszewski, K. Effects of Initiator Structure on Activation Rate Constants in ATRP. Macromolecules 2007, 40, 1858.

(74) Zhang, Y.; Wang, Y.; Matyjaszewski, K. ATRP of Methyl Acrylate with Metallic Zinc, Magnesium, and Iron as Reducing Agents and Supplemental Activators. Macromolecules 2011, 44 (4), 683.

(75) Tasdelen, M. A.; Uygun, M.; Yagci, Y. Photoinduced Controlled Radical Polymerization in Methanol. Macromol. Chem. Phys. 2010, 211 (21), 2271.

(76) Magenau, A. J. D.; Bortolamei, N.; Frick, E.; Park, S.; Gennaro, A.; Matyjaszewski, K. Investigation of Electrochemically Mediated Atom Transfer Radical Polymerization. Macromolecules 2013, 46, 4346.

(77) Acar, M. H.; Bicak, N. Synthesis of Hexylated Triethylenetetramine : New Ligand for Homogeneous. J. Polym. Sci. Part A Polym. Chem. 2003, 41, 1677.

(78) Tang, H.; Arulsamy, N.; Radosz, M.; Shen, Y.; Tsarevsky, N. V; Braunecker, W. a; Tang, W.; Matyjaszewski, K. Highly Active Copper-Based Catalyst for Atom Transfer Radical Polymerization. J. Am. Chem. Soc. 2006, 128, 16277.

(79) Tang, H.; Shen, Y.; Li, B.-G.; Radosz, M. Tertiary Amine - Enhanced Activity of ATRP Catalysts CuBr/TPMA and CuBr/Me6TREN. Macromol. Rapid Commun. 2008, 29, 1834.

(80) Kwak, Y.; Matyjaszewski, K. Effect of Initiator and Ligand Structures on ATRP of Styrene and Methyl Methacrylate Initiated by Alkyl Dithiocarbamate. Macromolecules 2008, 41, 6627.

(81) Wang, Y.; Bai, L.; Chen, W.; Chen, L.; Liu, Y.; Xu, T.; Cheng, Z. Iron-Mediated AGET ATRP of MMA Using Acidic/basic Salts as Reducing Agents. Polym. Bull. 2012, 70 (2), 631.

(82) Delgadillo-Velazquez, O.; Vivaldo-Lima, E.; Quintero-Ortega, I. A.; Zhu, S. Effects of Diffusion-Controlled Reactions on Atom-Transfer Radical Polymerization. AIChE J. 2002, 48 (11), 2597.

(83) D’hooge, D. R.; Reyniers, M.-F.; Marin, G. B. The Crucial Role of Diffusional Limitations in Controlled Radical Polymerization. Macromol. React. Eng. 2013, 7, 362.

(84) Mastan, E.; Zhou, D.; Zhu, S. Modeling Molecular Weight Distribution and Effect of Termination in Controlled Ratdical Polymerization: A Novel and Transformative Approach. J. Polym. Sci. Part A Polym. Chem. 2014, 52, 639.

(85) Wang, A. R.; Zhu, S. ESR Study on Diffusion-Controlled Atom Transfer Radical Polymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate. Macromolecules 2002, 35, 9926.

# Chapter 2

# Research Objectives and Thesis Outlines

## 2-1- Research Objectives

Atom transfer radical polymerization (ATRP) has been widely used for synthesizing polymers with well controlled architecture and functionality. It combines the advantages of free radical polymerization and living ionic polymerization. This method is applicable for polymerization of a wide range of monomers with predetermined molecular weight and narrow molecular weight distribution. Furthermore, it provides the possibility of performing polymerization in different conditions such as bulk, solution, emulsion and suspension. However, there are still some challenges that limit its full scale commercial exploitation. One of the most important one is high monomer conversion issues. The overall objectives of this thesis are: (1) to examine the effects of diffusion-controlled reactions on rate and control of the polymerization at high conversion, experimentally and through performing modeling; and (2) studying different strategies in order to reach to higher conversion while keeping livingness and control of the polymerization.

## 2-2- Thesis Outlines

This thesis is divided into eight chapters. The first two chapters cover the introduction and research objectives, respectively. The eighth chapter concludes the significant research contributions and provides recommendations for future study.

Chapters 3-7 are based on five published or accepted papers by various refereed journals. These chapters mainly report experimental works except chapter 4. It was planned to perform more modeling work based on the experimental results as a part of the thesis. However, because of the so many complicated reactions at high conversion and especially under diffusion-controlled reactions and also lack of experimental data, it was not successful. This is a sandwich type thesis that follows McMaster's guideline for thesis writing.

Chapter 3 consists of an investigation on bulk initiator for continuous activator regeneration (ICAR) ATRP of methyl methacrylate (MMA) at high conversion. The objectives of this work were to illustrate the effects of diffusion-controlled reactions and especially deactivation on the rate, control and livingness of the system at very high conversion. Azobisisobutyronitrile (AIBN) and tert-butyl peroxybenzoate (TBPB) were employed as ICAR agents. The ATRP was first carried out up to high conversion at 70 °C. When the system reached its glass state, the polymerization temperature was elevated to 120 °C to maximize the conversion.

Livingness of the ICAR ATRP process and control of polymer molecular weight at high conversion were carefully examined to elucidate the mechanisms of diffusion-controlled reactions.

Chapter 4 consists of a model development to study fundamental understanding of the mechanism and effects of diffusion-controlled reactions on high conversion ATRP. A kinetic model including all the possible diffusion-controlled reactions and residual termination and deactivation at high conversion were developed in order to examine their effects on the polymerization rate and the control of polymer molecular weight in a bulk ATRP using methyl methacrylate (MMA) as a model system.

Chapter 5 consists of a demonstration of good living and well controlled high-conversion bulk ATRP by the means of designing and optimizing polymerization thermal histories. Bulk ICAR ATRP of MMA was considered as a model system. Step functions in temperature were employed in order to postpone the diffusion controlled deactivation up to higher conversion and consequently keep the control of the reaction during polymerization.

Chapter 6 consists of an investigation of the effects of ICAR agent concentrations on the system livingness and control at high conversion. Binary systems of ICAR agents, containing low temperature azobisisobutyronitrile (AIBN) and high temperature tert-butyl peroxybenzoate (TBPB) or tert-butyl peroxide (TBP) were employed for bulk ICAR ATRP of MMA. Optimization of the ICAR agents' concentrations and step temperature profile were investigated as a useful strategy in order to reach to high conversion with good livingness and control while minimizing the concentration of the catalyst to ppm level.

Chapter 7 consists of a new strategy for keeping livingness and control of the ATRP at high conversion through employing ultrasonic waves. The objective of this work was to investigate the effects of ultrasonic wave's frequencies on the bulk ICAR ATRP of MMA at high conversion. It was believed that ultrasonic waves could be helpful in keeping control of the reaction up to high conversion through improving homogeneity of the polymerization medium and diffusivity of the reactants during the polymerization.

# Chapter 3

## Controlled Radical Polymerization at High Conversion: Bulk ICAR ATRP of Methyl Methacrylate

This chapter is organized based on the paper published in *Industrial & Engineering Chemistry Research*, 2014, 53(9), 3472–3477 by Ali Mohammad Rabea and Shiping Zhu

### 3-1- Abstract

Methyl methacrylate (MMA) was polymerized in bulk via atom transfer radical polymerization (ATRP) with azobisisobutyronitrile (AIBN) and tert-butyl peroxybenzoate (TBPB) as initiator for continues activator regeneration (ICAR). The ATRP was first carried out up to high conversion at 70 ˚C. When the system reached its glass state at about 94%, the polymerization temperature was elevated to 120 ˚C to maximize the conversion. Livingness of the ICAR ATRP process and control of polymer molecular weight at the high conversion were carefully examined to elucidate the mechanisms of diffusion-controlled reactions. "Gel effect" started at about 50% conversion and it was accompanied with molecular

weight distribution broadening. A dramatic increase in polydispersity was observed at above 90% conversion. The loss of control over molecular weight was caused by diffusion-controlled deactivation, which could be reduced to some extent by increasing deactivator concentration. However, despite of the loss of control at high conversion, livingness of the system did not suffer owing to diffusion-controlled termination. The polymer chains collected at very high conversion could be easily extended with a high efficiency.

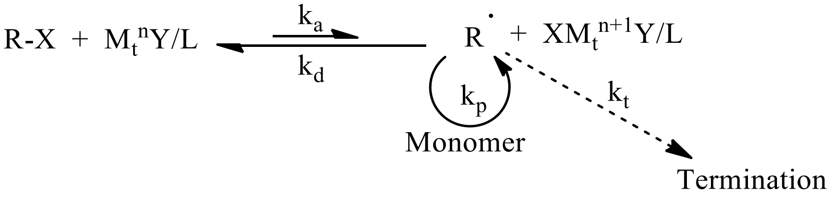
## 3-2- Introduction

Controlled radical polymerization (CRP) has attracted great attention in the recent years. It provides a powerful tool for synthesis of functional polymers with predetermined molecular weight and narrow molecular weight distribution (MWD). A number of CRP methods have been developed and the three major ones are nitroxide mediated stable free radical polymerization (SFRP or NMP),[1] transition metal mediated atom transfer radical polymerization (ATRP),[2-4] and dithioester mediated reversible addition fragmentation chain transfer (RAFT) polymerization.[5]

Over the past decade, the number of publications on the CRP methods has dramatically increased, demonstrating their applicability and potential in various areas. However, reviewing these publications reveals that in almost all of the papers the polymerization experiments were stopped at low to medium conversions. Intentionally or unintentionally, high conversion data were missed and little information about high conversion kinetics was provided. Several papers that did report some high conversion data showed severe loss of controllability (broad MWD).[6,7] This loss of controllability has been attributed to the effect of diffusion controlled deactivation reactions.[8-11]

Among the three CRP methods, ATRP has been used in >50% of the published papers.[12] Scheme 3-1 shows the mechanism of ATRP process [2,13] which could be carried out under different conditions, such as bulk, solution, emulsion and suspension.[14] However, there are still challenges that limit its full scale commercial exploitation. One of the challenges is its high catalyst loading. A typical catalyst loading is in the order of 0.1-1 mol% relative to monomer. It gives a deep color to final product and purification steps are required but costly.[15] Different approaches have been employed in tackling this problem. These approaches can be classified into two major categories: engineering approaches and chemistry approaches. In engineering approaches, catalyst supporting is often used. Various support systems have been developed that can effectively facilitate catalyst reclaiming and recycling.[16-19] It becomes easy to remove solid support materials and thus purify polymer product. However, Faucher *et al*. found that while catalytic centers on supported particle surface adequately activated dormant chains at surface they could not effectively deactivate radicals in solution due to diffusion limitations. It is particularly true for large size particles. Control over polymer molecular weight in supported ATRP is often not as good as in solution.[20] It has been advised to use nano sized particles for support. The same group also discovered that it was a trace amount of catalytic species at ppm level leached from supported particles that efficiently mediated ATRP. This discovery demonstrated that only ppm levels of catalyst loading are actually required in ATRP systems, not the previously thought 0.1-1.0%. In other words, there is no need for one catalyst center to mediate one chain. A catalyst center has potential to mediate hundreds to thousands of chains, depending on its diffusion ability.[6]

**Scheme 3-1 Mechanism of ATRP process**



In chemistry approaches, reducing catalyst loading can be accomplished by development of highly active catalysts, characteristic of a large equilibrium constant ($K_{ATRP} = \frac{k_a}{k_d}$) [21-23] or by using a ppm level of higher oxidation state catalyst ($YM_t^{n+1}Y/L$) and adding proper reducing agent (termed as "activator regenerated by electron transfer" or ARGET-ATRP) [24-26] or free radical thermal initiator (such as AIBN) (termed as “initiator for continuous activator regeneration” or ICAR-ATRP) [27] to continuously regenerate catalyst ($M_t^nY/L$) during polymerization.

These approaches are effective and have, to some extent, provided solution to the high catalyst loading problem. However, another equally important, if not more important, challenge has not been well addressed, that is, the high monomer conversion issues. We seldom found literature data over 80% conversion in bulk and solution ATRP. It is understandable that claiming of “well control” could immediately become unsupported by experimental data and be criticized by reviewers in paper submission. Indeed, it is difficult for ATRP to reach high conversions where control of polymer molecular weight becomes very poor. Most bulk ATRP systems lose control before 80% conversion. It means more than 20% residual monomer. Reclaiming such a high level of monomer residue is costly and not feasible in commercial practice. It should be pointed out that while we discuss challenges in ATRP in this work, the high conversion problem is common among CRP systems. Well controlled RAFT and NMP are also limited to low monomer conversions, if not more severe.

A well behaved ATRP system relies on two factors: “livingness” and “control”. By “livingness” it is meant absence of irreversible chain termination or transfer. It can be quantified by the dead chain content in final product. “Control” is determined by the number of activation/deactivation cycles that individual chains experience during polymerization. More cycles gives better control. Recently, Mastan *et al.*[28] developed a molecular weight distribution (MWD) theory and found that “livingness” is a “necessary condition” while “control” is a “sufficient condition” for obtaining a narrow MWD. That is, without “livingness”, it is impossible to have narrow MWD. However, “livingness” alone is not adequate and “control” is a must for narrow MWD.

In ATRP, as well as other CRP, radical termination and deactivation are fast reactions. Their rate constants are many orders of magnitude higher than those of initiation, propagation and activation reactions. Fast reactions could more easily become diffusion controlled. Bimolecular radical termination is always diffusion controlled due to the extremely high activities of free radicals. In free radical polymerization, it often causes auto acceleration in polymerization rate, so called Trommosdorff effect or misnomer “gel effect” (no gel formation). Let’s state it unambiguously that diffusion-controlled radical termination helps “livingness” in ATRP (in favor of “necessary condition”). It is actually the diffusion-controlled deactivation that trouble-makes “control” (“sufficient condition”) and is responsible for loss of control of polymer molecular weight at high monomer conversion due to lowering the number of activation/deactivation cycles.[29] The diffusion-controlled deactivation also causes an increase in the free radical concentration and thus auto acceleration in the rate of polymerization. The phenomenon is similar to Trommosdorff effect or “gel effect” in the conventional free radical polymerization. At very high conversions when polymerization system becomes glassy, propagation reaction can also become diffusion controlled.

Because propagation and termination, as well as deactivation, are competitive reactions for a radical center, it could also significantly affect ATRP behavior. While diffusion-controlled termination at high conversion and diffusion-controlled propagation at glass state have been a matter of studies for over half a century, diffusion-controlled deactivation at high conversion and diffusion-controlled activation at glass state are new in ATRP and other CRP.

High monomer conversion is critically important for commercial exploitation of CRP processes. It is costly to reclaim and recycle residual monomer. Another important task is to eliminate organic solvents in polymerization. Most solvents are volatile organic compounds (VOCs), and are of environment and health concerns. Separation polymer product from solvent and removal of residual monomer are both energy intensive and costly. Recently, we launched a research program aimed at developing strategies for achieving high monomer conversion at bulk polymerization systems while maintaining good control in CRP. Such a development must be based on good understanding of the mechanism and kinetics involved at high conversion polymerization. In this paper, we report our first experimental work and analysis for a bulk ICAR ATRP of methyl methacrylate (MMA). We target on complete monomer conversion and examine effect of thermal history on polymer molecular weight distribution.

## 3-3- Experimental

**3-3-1- Materials:** Monomer methyl methacrylate (MMA, Aldrich, 99%) was distilled under vacuum. After passing through a column of inhibitor remover, it was stored at -20 ˚C before use. Ligand 4,4′-dinonyl-2,2′-dipyridyl (dNbpy, 97%), catalyst $CuBr_2$ (99.999%), ATRP initiator ethyl (α-bromophenyl)acetate (EBPA), and initiator for continuous activator regeneration (ICAR agent) tert-butyl peroxybenzoate (TBPB, 98%) were purchased from Aldrich and used as received. Another ICAR agent azobisisobutyronitrile (AIBN, Aldrich, 99%) was recrystallized from methanol and stored at -20 ˚C.

**3-3-2- Instrumentation:** $^1H$ NMR spectra were recorded on a Bruker AV-200 spectrometer at 200 MHz. After dissolving synthesized sample in acetone, solution was diluted in d-chloroform ($CDCl_3$). Monomer conversion was calculated from the intensity ratio of methoxy group signals of polymer (3.60 ppm) and monomer (3.75 ppm).

The number average molecular weight (Mn) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) relative to narrow polymethyl methacrylate standards. A Waters 2690 autoinjector with three linear columns in series (Waters Styragel HR 2, 3 and 4) and a 2410 RI detector was used. THF was pumped through the system at a fixed flow rate of 1 mL/min. The columns and detector were heated to 35 ˚C and 40 ˚C, respectively. Data were recorded and manipulated using the Waters Millennium software package.

**3-3-3- Polymerization:** A typical bulk ICAR ATRP of MMA for the molar ratios of [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:X:2X:0.2:0.075 (X=0.01, 0.03 and 0.05) is as follow. A 25 ml bottom round flask containing a magnetic bar was loaded with varying quantities of $CuBr_2$ (0.0015-0.0075 gr), dNbpy (0.0055-0.0275 gr) and AIBN (0.0219 gr). The sealed reactor was degassed by vacuum-nitrogen cycles. Degassed MMA (13.43 gr) was then cannulated to the reactor. Required amount of TBPB (9.58 µl) was added to the flask using a nitrogen-purged syringe. The mixture was stirred at room temperature for an hour before adding initiator. EBPA (117.5 µl) was added to the flask using nitrogen-purged syringe and the reactor was placed to oil bath at 70 °C. The reaction was continued under stirring (400 rpm). For polymerization runs requiring higher temperature, a separated oil bath was set to 120 °C and the reaction was continued by switching oil bath. The polymerization was stopped by placing sample in ice water.

**3-3-4- Chain Extension Reaction:** For each catalyst concentration, polymerization was carried out at 70 °C up to glass state and then it was continued for half an hour at 120 °C. Polymer mixture was dissolved in acetone and passed through a column of alumina in order to remove catalyst residues. Purified polymer was obtained by precipitation in methanol and dried in vacuum oven. Chain extension reactions for each sample were carried out with the same molar ratio of catalyst to MMA as in the polymerization runs. However, the molar ratio of [MMA]:[PMMA] was set to 200:0.01. The recipes used in chain extension were same as in the polymerization, except for three different times, 1, 1.5 and 2 hours for the recipes containing 0.0015, 0.0045 and 0.0075 gr of $CuBr_2$, respectively.

## 3-4- Results and Discussion

Three levels of deactivator concentration (50, 150 and 250 ppm relative to monomer content) were used with their conversion versus time shown in Figure 3-1. It becomes clear that auto acceleration occurred at about 50% conversion in this system. In free radical polymerization (FRP), bimolecular termination becomes diffusion controlled with increased conversion and thus increased viscosity of the reaction medium. As a result, the concentration of free radicals increases because initiation remains unchanged. This increase in radical concentration accelerates polymerization, which is a well-known phenomenon termed as Trommsdorff effect or “gel effect”. Although it is unavoidable, radical termination in ATRP is not as significant as in FRP. Radical concentration is mainly balanced by equilibrium between activation and deactivation. The observed auto acceleration in the polymerization rate is thus caused by diffusion controlled deactivation that moved the equilibrium in Scheme 3-1 toward the right side with reduced $k_d$.[30] Furthermore, Figure 3-1 also shows limiting conversions at about 94%. This was because the polymerization temperature 70 °C was lower than the polymer glass transition temperature 105 °C. The polymerization medium became glassy. At the glass state, not only bimolecular radical termination and deactivation but also radical activation and propagation became diffusion controlled. Diffusion limitation imposed on monomer molecules eventually stopped the polymerization.

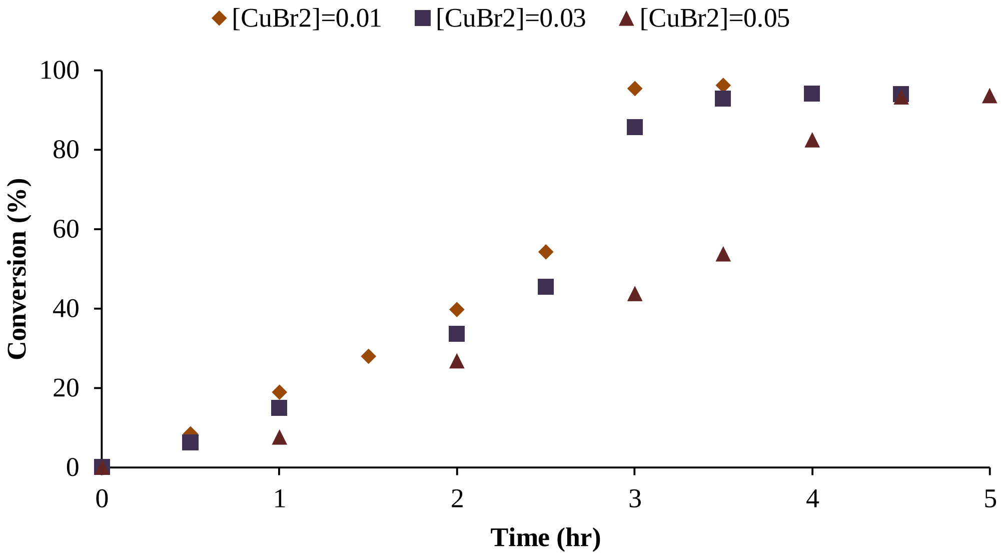


**Figure 3-1 Conversion versus time for bulk ICAR ATRP of methyl methacrylate [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:X:2X:0.2:0.075 at 70 °C. Auto acceleration and glass state happen about 50% and 94% conversion, respectively.**

Comparison between the conversion curves with three different deactivator concentrations in Figure 3-1 revealed that the rate of polymerization was higher with lower $CuBr_2$ and that higher rate started from the beginning. It was caused by a higher radical concentration through the equilibrium between activation and deactivation with the lower deactivator concentration, as expected. However, the auto acceleration was also affected by the deactivator amount. While it all started at about 50% conversion, the acceleration appeared to be milder at higher $CuBr_2$ content. In other words, decreasing deactivator content did not change onset of the auto acceleration but made the acceleration more severe.

In this ICAR ATRP, ethyl α-bromophenyl acetate (EBPA) acted as the ATRP initiator, while both azobisisobutyronitrile (AIBN) and tert-butyl peroxybenzoate (TBPB) acted as initiators for continuous activator regeneration (ICAR), with AIBN mainly for low temperature and TBPB for high temperature. At 70 °C, AIBN was responsible for generating primary radicals at the start that reduced $CuBr_2$ to CuBr. CuBr then activated EBPA for chain growth. Due to unavoidable radical termination, $CuBr_2$ was accumulated during polymerization and continuously reduced by the primary radicals generated through AIBN decomposition. After the system reached its glass state at 70 °C, we raised temperature to 120 °C, which is higher than the polymer glass transition temperature of 105 °C. By continuing the reaction for half an hour at this elevated temperature, we obtained the final conversion as high as about 98%. At 120 °C, AIBN decomposed in seconds. TBPB became the major ICAR agent that reduced deactivator to continue the ATRP process.

Figure 3-2 shows the molecular weight (Mn) versus conversion data with different $CuBr_2$ concentrations. With 250 ppm $CuBr_2$, the experimental points were very close to the theoretical line. The initiator efficiency ($I_{eff}$), solely based on the

ATRP initiator, was around 90%. The experimental data deviated from their theoretical values with decreasing deactivator concentration. $I_{eff}$ for 150 ppm $CuBr_2$ started low at the beginning and reached 80% at the final conversion. With 50 ppm $CuBr_2$, $I_{eff}$ was only 60% at the end of polymerization. Decreasing the deactivator concentration increased the radical concentration and increased termination, resulting in lower $I_{eff}$. This effect was particularly significant at low conversions. With increased conversion, the radical termination became diffusion controlled, which improved $I_{eff}$. It should be pointed out that in ICAR ATRP, the thermal initiator AIBN and TBPB could also generate polymer chains as in FRP, in addition to their role as ICAR agent to reduce $CuBr_2$. This partly contributed the increased $I_{eff}$ during polymerization.

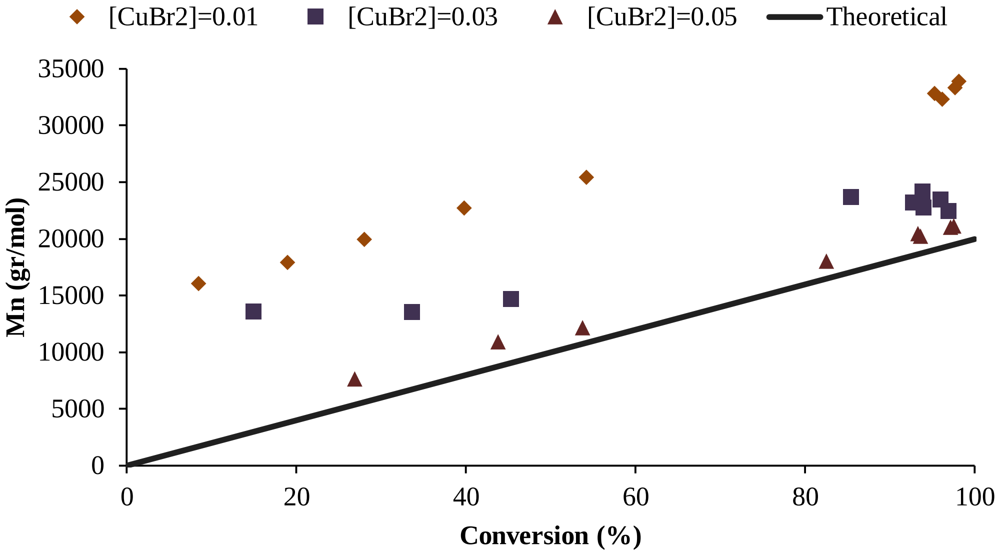


**Figure 3-2 Mn versus conversion for bulk ICAR ATRP of methyl methacrylate [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:X:2X:0.2:0.075. Initiator efficiency for 50, 150 and 250 ppm of $CuBr_2$ is about 60, 80 and 90%, respectively.**

Figure 3-3 shows PDI versus conversion. Increasing $CuBr_2$ concentration improved the control of polymer molecular weight and thus resulted lower PDI. The PDI value with 250 ppm of $CuBr_2$ was around 1.1 before the gel effect. PDI increased with decreasing deactivator concentration and reached around 1.5 with 50 ppm $CuBr_2$. The system started to lose control at higher conversions. The final PDI values with 150 and 250 ppm $CuBr_2$ were around 1.7, while that of 50 ppm $CuBr_2$ became higher than 2. Furthermore, elevating temperature to 120 ˚C increased PDI a lot with 50 ppm $CuBr_2$ but had negligible effect with 150 and 250 ppm $CuBr_2$.

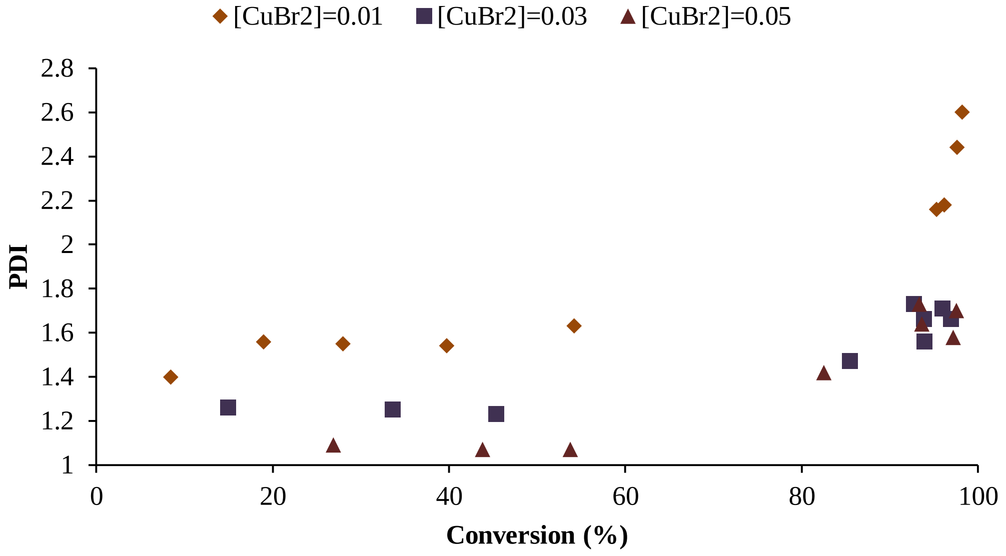


**Figure 3-3 PDI versus conversion for bulk ICAR ATRP of methyl methacrylate [MMA]:[EBPA]:[CuBr$_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:X:2X:0.2:0.075.**

Figure 3-4 shows two representative GPC curves before and after "gel effect". The sample collected in 3.5 hr at 70 ˚C (54% conversion) had a narrow peak with polydispersity of only 1.07. In comparison, the sample in 4 hr at 70 ˚C (83% conversion) had a broad peak and polydispersity of 1.42. With the increase in monomer conversion and polymer molecular weight, the polymerization system became viscous. Polymer chains experienced diffusion limitations. Radical termination involved two chain species and had the highest rate constant. It was the first reaction that became diffusion controlled. Decrease in termination rate favored livingness of the system. It also increased radical concentration and thus contributed to the gel effect. However, in ATRP, the radical concentration was mainly regulated by the equilibrium of activation and deactivation. While the diffusion-controlled termination played the major role in improving the system livingness, it was a minor contributor in gel effect.

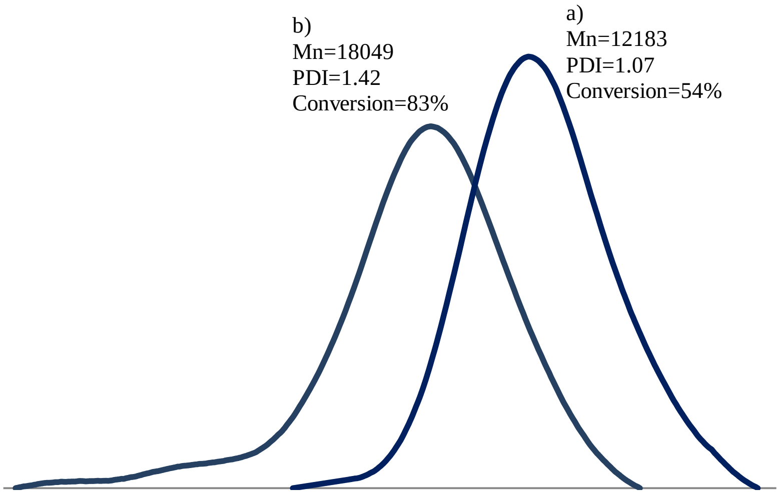


**Figure 3-4 GPC curves for [MMA]:[EBPA]:[CuBr2]:[dNbpy]:[AIBN]:[TBPB]= 200:1:0.05:0.1:0.2:0.075 a) 3.5 hr and b) 4 hr at 70 °C. “Gel effect” increased polydispersity index from 1.07 to 1.42 in 0.5 hr.**

Both deactivation and propagation reactions involved one radical chain and one small molecule reactant, $CuBr_2$ and monomer, respectively. However, the former had much higher rate constant and thus became diffusion controlled earlier. It was the diffusion-controlled deactivation that shared a major part of the causes of gel effect. It was also the diffusion-controlled deactivation that caused the loss of control over polymer molecular weight. When the glass state approached, not only chain species but also small molecule reactants experienced diffusion limitations. As a result, propagation, activation and ICAR reactions also became diffusion controlled.

Chain extension experiments were carried out to examine the livingness of polymer samples collected at high conversions. The samples were purified and used as macroinitiator for chain extension. The macroinitiator samples were prepared by carrying the ICAR ATRP at 70 °C to the glass state followed by elevating temperature to 120 °C for half an hour. These samples had about 98% conversions. Three levels of catalyst concentration were employed with X = 0.01, 0.03 and 0.05 in the recipe of [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:0.01:X:2X:0.2:0.075. The same $CuBr_2$ concentrations were used in the chain extension experiments, i.e., 50, 150, 250 ppm, with the reaction time of 1, 1.5 and 2 hours, respectively.

Figure 3-5 presents some results, which clearly showed the increase in molecular weight. It is quite impressive that the chains collected at such high conversions (ca. 98%) were still living and could be successfully extended. Starting from ca. 50% conversion, the ATRP system experienced diffusion-controlled deactivation, causing the gel effect. The polymer molecular weight distribution broadened, suggesting the loss of control. However, the termination became diffusion controlled before the deactivation and was more severe because it involved two chain species and it had higher rate constant. The diffusion control in termination saved the radical population increased by the diffusion-controlled deactivation from being terminated. This is an important observation. In practice, particularly in preparation of functional chains such as macroinitiator, preservation of the active chain end is often more important than narrow MWD. Another interesting observation could be made from Figure 3-5. The polydispersities decreased with the increased molecular weight in chain extension because of the higher molar ratio of monomer to macroinitiator (200:0.01), which decreased rate of the polymerization and viscosity of the medium. The diffusion-controlled deactivation became milder with an improvement in the control over polymer molecular weight. It became clear that these macroinitiators collected at high conversions in preparation still had high efficiencies in the chain extension experiments. Furthermore, the GPC curves of the macroinitiators with 250 and 150 ppm of $CuBr_2$ shown in Figure 3-5 are bimodal. Deconvolution of the peaks gave about 14% and 10% of the chains that were propagated to high molecular weight, respectively. The MWD became broader and overlapped more with the decreased catalyst concentration. There was only a single peak with 50 ppm of catalyst.

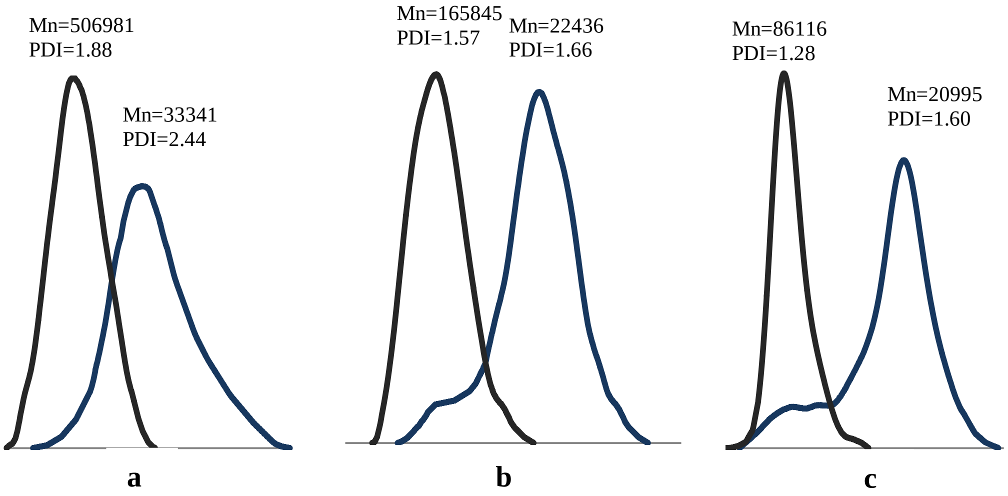


**Figure 3-5 Chain extension results with the samples collected at very high conversions (ca. 98%) as macroinitiators. The samples were prepared by running ICAR ATRP at 70 °C up to glass state, followed by elevating temperature to 120 °C for 0.5 hr. Chain extension recipes were same as in macroinitiator preparation with [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:0.01:X:2X:0.2:0.075 at 70 °C for (a) 1 hr with X = 0.01, (b) 1.5 hr with X = 0.03, (c) 2 hr with X = 0.05.**

## 3-5- Conclusion

Bulk ICAR ATRP of MMA up to high conversion was conducted with different deactivator concentrations from 50 to 250 ppm. Two thermal initiators, AIBN and TBPB, were used as ICAR agents. The polymerization was run at 70 °C up to the glass state. High conversions were achieved by elevating temperature to 120 °C. AIBN acted as the low temperature ICAR agent, while TBPB was for the high temperature.

The bulk system behaved very well at low monomer conversions, with good livingness and control. However, it experienced “gel effect” and the autoacceleration in rate started about 50% conversion. The gel effect was caused by diffusion-controlled deactivation. It was accompanied with the loss of control over polymer molecular weight, evident from the broadening of molecular weight distribution. Increasing deactivator concentration compensated to some extent the loss of molecular weight control, but decreased the rate of polymerization.

The system also experienced glass effect about 94% conversion at 70 °C. At this stage, not only termination and deactivation became diffusion controlled, but also propagation and activation as well as ICAR reaction became diffusion controlled because all reactants suffered severe diffusion limitations. Elevating temperature to 120 °C released the diffusion constraints and pushed the final conversions up to 98%.

The ultimate concern of this work was the livingness and control of the ATRP system at high conversions, which could be improved through design and optimization of thermal history in the polymerization. Chain extension experiments demonstrated that the chains collected at the final conversions could extended with high efficiencies. The polymers were still living, though did not have very narrow molecular weight distributions. In other words, bulk ATRP systems can be run to high conversions to eliminate monomer residues, if living chains are the targeted product. The molecular weight distribution can be broad due to diffusion-controlled deactivation, but the chains are protected from termination by diffusion-controlled termination, which is more severe than diffusion-controlled deactivation.

## 3-6- Acknowledgment

We thank the Natural Science and Engineering Research Council of Canada (NSERC) for supporting this research and the Canada Foundation of Innovation who support our research facilities.

## 3-7- References

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow Molecular Weight Resins by a Free-Radical Polymerization Process. Macromolecules 1993, 26, 2987.

(2) Wang, J.; Matyjaszewski, K. Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(3) Wang, J. S.; Matyjaszewski, K. Controlled/"Living" Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process. Macromolecules 1995, 28, 7901.

(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of Methyl Methacrylate with the Carbon. 1995, 28, 1721.

(5) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H.; South, C. Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer : The RAFT Process. Macromolecules 1998, 31, 5559.

(6) Faucher, S.; Zhu, S. Heterogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate at Low Metal Salt Concentrations. Ind. Eng. Chem. Res. 2005, 44, 677.

(7) He, W.; Zhang, L.; Bai, L.; Zhang, Z.; Zhu, J.; Cheng, Z.; Zhu, X. Iron-Mediated AGET ATRP of Methyl Methacrylate in the Presence of Catalytic Amounts of Base. Macromol. Chem. Phys. 2011, 212, 1474.

(8) Shipp, D. A.; Matyjaszewski, K. Kinetic Analysis of Controlled/“Living” Radical Polymerizations by Simulations. 1. The Importance of Diffusion-Controlled Reactions. Macromolecules 1999, 32, 2948.

(9) Butte, A.; Storti, G.; Morbidelli, M. Kinetics of "Living" Free Radical Polymerization. Chem. Eng. Sci. 1999, 54, 3225.

(10) Yu, Q.; Zeng, F.; Zhu, S. Atom Transfer Radical Polymerization of Poly(Ethylene Glycol) Dimethacrylate. Macromolecules 2001, 34, 1612.

(11) Delgadillo-Velazquez, O.; Vivaldo-Lima, E. Effects of Diffusion-Controlled Reactions on Atom-Transfer Radical Polymerization. AIChE J. 2002, 48, 2597.

(12) Matyjaszewski, K. Controlled Radical Polymerization : State-of-the-Art in 2011. In Controlled Radical Polymerization: Mechanisms and Techniques; American Chemical Society: Washingtom, DC, 2012; pp. 1.

(13) Matyjaszewski, K.; Patten, T. E.; Xia, J. Controlled/“Living” Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene. J. Am. Chem. Soc. 1997, 119, 674.

(14) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. Chem. Rev. 2001, 101, 2921.

(15) Tsarevsky, N. V.; Matyjaszewski, K. “Green” Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials. Chem. Rev. 2007, 107, 2270.

(16) Haddleton, D. M.; Kukulj, D.; Radigue, A. P. Atom Transfer Polymerisation of Methyl Methacrylate Mediated by Solid Supported Copper Catalysts. Chem. Commun. 1999, 99.

(17) Kickelbick, G.; Paik, H.; Matyjaszewski, K. Immobilization of the Copper Catalyst in Atom Transfer Radical Polymerization. Macromolecules 1999, 32, 2941.

(18) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. H. Atom Transfer Radical Polymerization of Methyl Methacrylate by Silica Gel Supported Copper Bromide/Multidentate Amine. Macromolecules 2000, 33, 5427.

(19) Shen, Y.; Zhu, S.; Pelton, R. Packed Column Reactor for Continuous Atom Transfer Radical Polymerization: Methyl Methacrylate Polymerization Using Silica Gel Supported Catalyst. Macromol. Rapid Commun. 2000, 21, 956.

(20) Faucher, S.; Zhu, S. Fundamentals and Development of High-Efficiency. J. Polym. Sci. Part A Polym. Chem. 2007, 45, 553.

(21) De Campo, F.; Lastécouères, D.; Verlhac, J. B. New and Improved Catalysts for Transition Metal Catalysed Radical Reactions. Chem. Commun. 1998, 2117.

(22) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. Controlled/“living” Radical Polymerization. Atom Transfer Radical Polymerization of Acrylates at Ambient Temperature. Macromolecules 1998, 31, 5958.

(23) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. Optimization of Atom Transfer Radical Polymerization Using Cu(I)/Tris(2-( Dimethylamino) Ethyl) Amine as a Catalyst. Macromolecules 2000, 33, 8629.

(24) Jakubowski, W.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers. Angew. Chemie 2006, 118, 4594.

(25) Jakubowski, W.; Min, K.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization of Styrene. Macromolecules 2006, 39, 39.

(26) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP. Macromolecules 2007, 40, 1789.

(27) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A; Tsarevsky, N. V. Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents. Proc. Natl. Acad. Sci. U. S. A. 2006, 103, 15309.

(28) Mastan, E.; Zhou, D.; Zhu, S. Modeling Molecular Weight Distribution and Effect of Termination in Controlled Radical Polymerization: A Novel and Transformative Approach. J. Polym. Sci. Part A Polym. Chem. 2014, 52, 639.

(29) Wang, A. R.; Zhu, S. ESR Study on Diffusion-Controlled Atom Transfer Radical Polymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate. Macromolecules 2002, 35, 9926.

(30) Wang, A. R.; Zhu, S. Effects of Diffusion-Controlled Radical Reactions on RAFT Polymerization. Macromol. Theory & Simulations 2003, 12, 196.

# Chapter 4

## Modeling the Influence of Diffusion-Controlled Reactions and Residual Termination and Deactivation on the Rate and Control of Bulk ATRP at High Conversions

This chapter is organized based on the paper published in *polymers*, 2015, 7(5), 819–835 by Ali Mohammad Rabea and Shiping Zhu

### 4-1- Abstract

In high-conversion atom transfer radical polymerization (ATRP), all the reactions, such as radical termination, radical deactivation, dormant chain activation, monomer propagation, *etc.* could become diffusion controlled sooner or later, depending on relative diffusivities of the involved reacting species. These diffusion-controlled reactions directly affect the rate of polymerization and the control of polymer molecular weight. A model is developed to investigate the influence of diffusion-controlled reactions on the high conversion ATRP kinetics. Model simulation reveals that diffusion-controlled termination slightly increases the rate, but it is the diffusion-controlled deactivation that causes auto-acceleration in the rate ("gel effect") and loss of control. At high conversions, radical chains are “trapped” because of high molecular weight. However, radical centers can still migrate through (1) radical deactivation–activation cycles and (2) monomer propagation, which introduce “residual termination” reactions. It is found that the “residual termination” does not have much influence on the polymerization kinetics. The migration of radical centers through propagation can however facilitate catalytic deactivation of radicals, which improves the control of polymer molecular weight to some extent. Dormant chain activation and monomer propagation also become diffusion controlled and finally stop the polymerization when the system approaches its glass state.

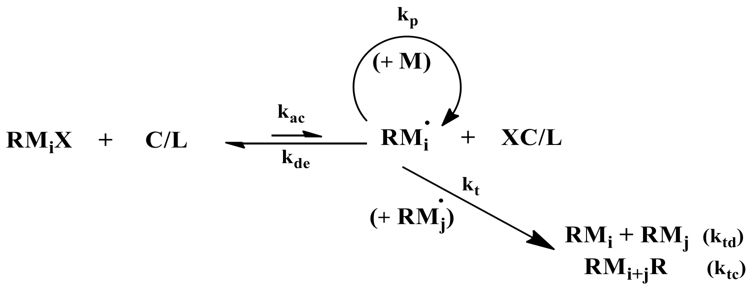
**4-1-1- Keywords:** modeling; ATRP; high conversion; diffusion-controlled reactions; radical termination; radical deactivation; dormant chain activation; monomer propagation

## 4-2- Introduction

Controlled radical polymerization (CRP) (or equivalently, reversible-deactivation radical polymerization, RDRP), such as stable free radical polymerization (SFRP) (or equivalently, aminoxyl-mediated radical polymerization, AMRP),[1] atom transfer radical polymerization (ATRP) (or equivalently, controlled reversible-deactivation radical polymerization),[2,3] and reversible addition fragmentation chain transfer (RAFT) polymerization (or equivalently, degenerate-transfer radical polymerization),[4] has attracted great attention in synthesis of well-controlled functional polymers. Among different CRP methods, ATRP is of particular interest for its high potential of applications in various areas.[5] Control over chain microstructure such as molecular weight distribution (MWD) (or equivalently, molar mass distribution) and polymerization system livingness depend on the polymerization recipes and conditions, which determine the rates of radical termination, radical deactivation, dormant chain activation, and monomer propagation. Numerous studies have been carried out to investigate the influences of chemical recipes,[6-8] catalyst solubility and catalyst supporting,[9-12] as well as thermal history,[13,14] on the ATRP kinetics and polymer molecular weight control. There have been also many modeling efforts made to predict the polymerization behaviors.[15-20]

An important objective of our research program is to tackle the challenges that face commercial exploitations of the CRP processes. Minimizing the catalyst concentration[21,22] and maximizing monomer conversion and eliminating organic solvent as much as possible represent some of the major challenges in this area. Both solvent and residual monomer impose high costs and energy consumption in their separation and purification. High monomer conversions and high solid content polymerization systems are thus most desirable. The problem has been attributed to the diffusion-controlled deactivation reaction which occurs at high conversions.[23] It decreases the radical deactivation rate and causes a “gel effect” in the polymerization rate, leading to the loss of control over polymer molecular weight and resulting in a high polydispersity index (PDI) (or equivalently, dispersity, Đ) for the synthesized polymers. The most important reactions in an ATRP system are termination, deactivation, activation and propagation as shown in Scheme 4-1.

**Scheme 4-1 Schematic presentation of the most important reactions in atom transfer radical polymerization (ATRP).**



In Scheme 4-1, M, C, L and XC represent the monomer, catalyst, ligand and deactivator; $RMi^{\bullet}$, RMiX, RMi and RMi+jR are the living chain, dormant chain, dead chain formed by disproportionation termination and dead chain by combination termination; i and j denote the number of monomeric units in the polymer chain; k is a rate coefficient with subscript ac indicating activation; de, deactivation; p, propagation; t, termination; td, termination by disproportionation and tc, termination by combination, respectively. The reactants are monomer, initiator and catalyst with the initial concentrations of $[M]_0$, $[RX]_0$ and $[C]_0$, respectively.

In our previous study,[13] the bulk ATRP of methyl methacrylate (MMA) was carried out up to very high conversions. The results showed that although the livingness of polymer chains was preserved because of the diffusion-controlled termination, the control over polymer molecular weight was lost because of the diffusion-controlled deactivation. The final products had broad MWDs with high PDIs. In another study,[14] it was found that by elevating polymerization temperature at high conversions, it was possible to postpone the diffusion-controlled deactivation and obtain highly living and well controlled polymer chains at an almost complete conversion.

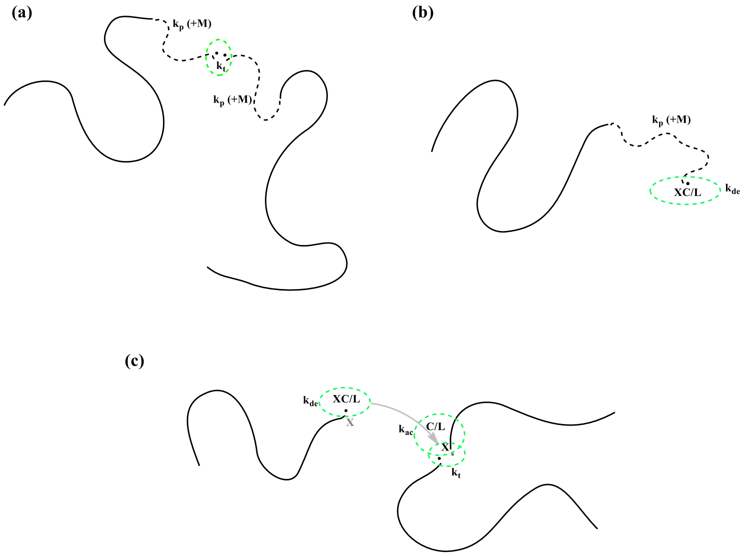
We focus on developing experimental strategies for high livingness and good control of CRP at high conversions. The molecular processes involved in the high conversion polymerization are indeed very complicated. In general, any reaction could become diffusion controlled. The fast reactions become diffusion controlled earlier. Typically, radical termination is the first reaction that experiences diffusion limitations, because the reaction involves two chain species of low diffusivity. It is also because of the termination rate coefficient which is the highest among all the reactions. Radical deactivation is the second reaction that onsets diffusion control, because it has a lower rate coefficient than termination and also because it involves one chain and the other small catalytic deactivator. In conventional free radical polymerization, diffusion-controlled termination causes an auto-acceleration in the polymerization rate (named Trommsdorff effect or a misnomer "gel effect"). In CRP, it is the diffusion-controlled deactivation that is responsible for the "gel effect" occurring. Diffusion-controlled termination in CRP is considered as an asset that helps the livingness of polymer chains.[13,16]

By further increasing the conversion, the system becomes more viscous, small reactants such as catalytic activator and deactivator as well as monomer also experience diffusion limitations. This is particularly true when the system approaches its glass state when the glass transition temperature of the synthesized polymer is higher than the temperature of the polymerization. In the conventional free radical polymerization, diffusion-controlled monomer propagation is responsible for the termination of polymerization at an incomplete conversion (termed "glass effect"). However, it is much more complicated in CRP processes. At this stage, all the small molecule reactants are limited by diffusion. Monomer propagation and dormant chain activation reactions also become diffusion controlled. Depending on the relative sizes and diffusivities of monomer and catalytic activator, as well as the rate coefficients of propagation and activation, one can undergo diffusion control earlier than the other. Either diffusion controlled propagation or diffusion controlled activation can stop the polymerization.

It is also well known that at intermediate and high conversions, while radical chains are limited by diffusion, the radical centers can be still mobile. One mechanism is through monomer propagation. When one monomer is added to a chain end, the radical center moves one step further. This migration of radical center by propagation facilitates residual termination and deactivation. The residual “termination by propagation” has been well studied in the conventional free radical polymerization (Scheme 4-2a).[24] However, its effect on CRP has not been investigated thoroughly. The residual “deactivation by propagation” is a totally new concept of the present work. Based on intuition, the residual deactivation should help to improve the control at high conversions (Scheme 4-2b).

Furthermore, the recent advent in surface-initiated CRP research reveals additional possible mechanisms of radical center migration. Radicals growing from the surface are constrained by their chains covalently bonded to the surface. The radicals cannot reach each other to be terminated. However, there were some experimental data that supported radical termination. A new “hopping” mechanism was thus proposed by Zhu *et al.*.[25,26] A radical center can be deactivated in one spot by a catalytic deactivator. The latter quickly moves to another spot to activate a radical center. A net outcome of this deactivation/activation cycle is migration of the radical center from one spot to another, which can facilitate radical termination, if another radical center happens to be at the vicinity. This “hopping” migration can also exist in the bulk or solution CRP at high conversions (Scheme 4-2c). The residual termination caused by the radical “hopping” could also affect the control of ATRP, which has not been investigated.

**Scheme 4-2 Schematic presentation of (a) termination by propagation, (b) deactivation by propagation, and (c) termination by activation/deactivation, which can possibly occur in ATRP at high conversions when small reactants experience diffusion limitations. M, C, L and XC represent the monomer, catalyst, ligand and deactivator; k is a rate coefficient with subscript ac indicating activation; de, deactivation; p, propagation and t, termination, respectively.**



Considering all the complicated mechanisms outlined above, one must resort to the use of modeling approaches to investigate their influences in CRP processes. In this paper, we develop a kinetic model that includes all the possible reactions at high conversions and examine their effects on the polymerization rate and the control of polymer molecular weight in a bulk ATRP using methyl methacrylate (MMA) as a model system.

## 4-3- Theoretical Development

Mass balance equations for living, dormant and dead chains formed by radical termination by disproportionation and combination (Scheme 4-1) have been shown in Equations 1–4, respectively.[15] No chain transfer has been considered during polymerization.

$$\frac{d[RM_i^\bullet]}{dt} = k_p[RM_{i-1}^\bullet][M] - k_p[RM_i^\bullet][M] + k_{ac}[RM_iX][C] - k_{de}[RM_i^\bullet][XC] - k_t[RQ_0^\bullet][RM_i^\bullet] \tag{1}$$

$$\frac{d[RM_iX]}{dt} = -k_{ac}[RM_iX][C] + k_{de}[RM_i^\bullet][XC] \tag{2}$$

$$\frac{d[RM_i]}{dt} = k_{td}[RQ_0^\bullet][RM_i^\bullet] \tag{3}$$

$$\frac{d[RM_iR]}{dt} = \frac{k_{tc}}{2}\sum_{j=0}^{i}[RM_j^\bullet]\,[RM_{i-j}^\bullet] \tag{4}$$

By using the conservation Equations 5–8 and applying the method of moments, the zeroth-, first- and second-order moment equations were derived.[15]

$$[RQ_0^\bullet] + [RQ_0X] + [RQ_0] + 2[RQ_0R] = [RX]_0 \tag{5}$$

$$[RQ_0X] + [XC] = [RX]_0 \tag{6}$$

$$[C] + [XC] = [C]_0 \tag{7}$$

$$[RQ_1^\bullet] + [RQ_1X] + [RQ_1] + [RQ_1R] = [M]_0 - [M] \tag{8}$$

For the zeroth-order moments,

$$\frac{d[RQ_0^\bullet]}{dt} = k_{ac}[RQ_0X]([C]_0 - [RX]_0 + [RQ_0X]) - k_{de}[RQ_0^\bullet]([RX]_0 - [RQ_0X]) - k_t[RQ_0^\bullet] \tag{9}$$

$$\frac{d[RQ_0X]}{dt} = -k_{ac}[RQ_0X]([C]_0 - [RX]_0 + [RQ_0X]) + k_{de}[RQ_0^\bullet]([RX]_0 - [RQ_0X]) \tag{10}$$

$$\frac{d[RQ_0]}{dt} = k_{td}[RQ_0^\bullet][RQ_0^\bullet] \tag{11}$$

$$\frac{d[RQ_0R]}{dt} = \frac{k_{tc}}{2}[RQ_0^\bullet][RQ_0^\bullet] \tag{12}$$

For the first-order moments,

$$\frac{d[RQ_1^\bullet]}{dt} = k_p[RQ_0^\bullet][M]_0(1 - X) + k_{ac}[RQ_1X]([C]_0 - [RX]_0 + [RQ_0X]) - k_{de}[RQ_1^\bullet]([RX]_0 - [RQ_0X]) - k_t[RQ_0^\bullet][RQ_1^\bullet] \tag{13}$$

$$\frac{d[RQ_1X]}{dt} = -k_{ac}[RQ_1X]([C]_0 - [RX]_0 + [RQ_0X]) + k_{de}[RQ_1^\bullet]([RX]_0 - [RQ_0X]) \tag{14}$$

$$\frac{d[RQ_1]}{dt} = k_{td}[RQ_0^\bullet][RQ_1^\bullet] \tag{15}$$

$$\frac{d[RQ_1R]}{dt} = k_{tc}[RQ_0^\bullet][RQ_1^\bullet] \tag{16}$$

For the total moment of the second order,

$$\begin{aligned}&\frac{d([RQ_2^\bullet]+[RQ_2X]+[RQ_2]+[RQ_2R])}{dt}\\&\qquad=k_p[RQ_0^\bullet][M]+2k_p[RQ_1^\bullet][M]+k_{tc}[RQ_1^\bullet][RQ_1^\bullet]\end{aligned}\tag{17}$$

For the conversion (X),

$$\frac{dX}{dt}=k_p[RQ_0^\bullet](1-X)\tag{18}$$

Number-average chain length, weight-average chain length, and PDI are calculated by using the Equations 19–21.

$$\overline{r_N}=\frac{[RQ_1^\bullet]+[RQ_1X]+[RQ_1]+[RQ_1R]}{[RQ_0^\bullet]+[RQ_0X]+[RQ_0]+[RQ_0R]}\tag{19}$$

$$\overline{r_w}=\frac{[RQ_2^\bullet]+[RQ_2X]+[RQ_2]+[RQ_2R]}{[RQ_1^\bullet]+[RQ_1X]+[RQ_1]+[RQ_1R]}\tag{20}$$

$$PDI=\frac{\overline{r_w}}{\overline{r_N}}\tag{21}$$

### 4-3-1- Diffusion-Controlled Reactions

When a polymerization proceeds to higher monomer conversions, especially in bulk situation, the system becomes viscous and the rate coefficients of reactions involving chain reacting species could become chain-length dependent. For the termination reaction, as it involves two radical chains, diffusion-controlled termination starts at almost low conversions.[27] The reaction rate coefficients do not remain constant but change during polymerization. There are different ways to account for this effect in modeling the polymerization kinetics, as summarized by D'hooge *et al.*.[28] In this work, the simple approach based on the free volume theory was employed.[28] In this model, the relative contributions of chemical activation and diffusion to reaction rate coefficients can be expressed as Equation 22,

$$\frac{1}{k_j} = \frac{1}{k_{j,C}} + \frac{1}{k_{j,D}} \tag{22}$$

In Equation 22, subscript j can be termination (t), deactivation (de), activation (ac) and propagation (p). Subscript C and D indicate the chemical and diffusion contributions to the reaction rate coefficient, respectively. The diffusion-controlled rate coefficient ($k_{j,D}$) is proportional to the diffusion coefficients of the reactants, which are a function of viscosity (polymer concentration) and molecular weight.

In this study, for the diffusion part of the rate coefficients, the free volume-based semi-empirical equations are used, Equations 23 and 24 give the $k_{j,D}$ for polymer chains and small molecule reactants (catalyst and monomer), respectively.[29] $(\overline{r_N})^{-2}$ is incorporated in Equation 23, as the $k_{j,D}$ for polymer chains is chain-length dependent as well.

$$k_{j,D} = k_{j,D}^{0} (\overline{r_N})^{-2} exp\left(\frac{-1}{\upsilon_f}\right) \tag{23}$$

$$k_{j,D} = k_{j,D}^{0} exp\left(\frac{-1}{\upsilon_f}\right) \tag{24}$$

where $k_{j,D}^{0}$ is considered as an adjustable parameter, which is sensitive to the onset of the corresponding diffusion-controlled reactions. $\overline{r_N}$ is the number-average chain length as defined by Equation (19). Also, $\upsilon_f$ is the free volume fraction, which is related to polymer concentration (Equation 25),[29,30]

$$\upsilon_f = \left[0.025 + \alpha_P\left(T - T_{gP}\right)\right]X + \left[0.025 + \alpha_M\left(T - T_{gM}\right)\right](1 - X) \tag{25}$$

where $\alpha$, $X$ and $T_g$ are the coefficients of thermal expansion, conversion and glass transition temperature, with the subscripts P and M indicating polymer and monomer, respectively. In addition, as $T_g$ of the polymer is related to the polymer type and changes with conversion, Equation 26 has been used for the polymerization of methyl methacrylate (MMA).

$$T_{gP} = 378 - \frac{2.11 \times 10^4}{\overline{r_N} \times 100} \tag{26}$$

### 4-3-2- Residual Termination and Deactivation

In high-conversion ATRP, when radical chains are trapped (*i.e.*, zero translational diffusion), the catalyst complexes can still move around and activation and deactivation reactions continue to occur. Deactivation of a radical at one site, followed by activation of a dormant chain end at another site through diffusion of the catalyst species, is equivalent to migration of the radical center from one site to the other site. This radical "hopping" migration increases the chance of radical termination. So, faster deactivation and activation reactions mean faster migration of radical centers and higher radical termination rate. A simple equation, $k_{t,D}$ ($= z_{tde}k_{de}[CuBr_2]$), was proposed to account for contribution of the "hopping" mechanism toward residual radical termination.[26]

In the high conversion free radical polymerization, when all reactants, except for monomer, are trapped, radicals can still be terminated due to propagation diffusion: $k_{t,D}$ ($= z_{tp}k_p[M]$), where $z_{tp}$ is a constant.[24] This termination by propagation concept has been employed in modeling ATRP at high conversion.[16] In this study, in addition to the residual termination by propagation, the residual deactivation by propagation is also included. Furthermore, when polymer chains and catalytic deactivators are trapped at high conversion, the radical chains can still propagate, and upon reaching the deactivator molecules, the deactivation reaction occurs. Similar to termination, the residual deactivation can be expressed as $k_{de,D}$ ($= z_{de}k_p[M]$), which contributes to the diffusion-controlled deactivation rate coefficient.

### 4-3-3- Parameters and Initial Conditions

Table 4-1 gives the parameters and initial conditions for solving the above moment equations. The parameters are for the bulk ATRP of MMA with a monomer/initiator molar ratio of 200 and CuBr/4,4'-Dinonyl-2,2'-dipyridyl (dNbpy) as the catalyst complex. From the previous study,[14] it is known that with this recipe the diffusion-controlled deactivation occurs around 50% conversion and the maximum monomer conversion at 70 °C is around 90%.

**Table 4-1 Initial conditions and parameters used in the model simulation.**

| Parameters | Value | Reference or Comments |
|---|---|---|
| $k_{ac,C}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | 0.37 | 16 |
| $k_{de,C}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | $5.28 \times 10^5$ | 16 |
| $k_{p,C}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | 1051 | 31 |
| $k_{tc,C}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | $10^7$ | 16 |
| $k_{td,C}$ ($L \cdot mol^{-1} \cdot s^{-1}$) | $9.21 \times 10^7$ | 16 |
| $\alpha_M$ ($K^{-1}$) | 0.001 | 16 |
| $\alpha_P$ ($K^{-1}$) | 0.00048 | 16 |
| $T_{gM}$ (K) | 167 | 16 |
| $[M]_0$ ($mol \cdot L^{-1}$) | 9.35 | Bulk MMA |
| $[RX]_0$ ($mol \cdot L^{-1}$) | 0.0488 | Initiator |
| $[C]_0$ ($mol \cdot L^{-1}$) | 0.0244 | CuBr |
| T (K) | 343 | Reaction Temperature |

## 4-4- Results and Discussion

The influences of the various diffusion-controlled reactions, residual termination and deactivation on the polymerization rate and polymer molecular weight control are examined using the model simulation, in the order that they could potentially occur during polymerization. The radical termination reaction has the highest rate coefficient and involves two chains, which readily experience diffusion limitations. It thus becomes diffusion controlled at relatively low monomer conversions. Figure 4-1 compares the kinetic behaviors of the bulk ATRP of MMA with and without diffusion-controlled termination, with and without residual termination, but excluding the other diffusion-controlled reactions.

Figure 4-1a shows that for the system without any diffusion-controlled reaction, the polymerization rate is slower. The onset of diffusion-controlled termination slightly increases the radical concentration, resulting in a minor increase in the rate. However, the influences of the residual termination by "hopping" mechanism and that by propagation on the rate are negligible. In contrast to the conventional free radical polymerization, in which diffusion-controlled termination can cause a dramatic auto-acceleration (*i.e.*, "gel effect"), the diffusion-controlled termination in ATRP does not have as much influence. The reason is that the radical concentration in the former is determined by the initiation and termination reactions, while that in the latter is mainly regulated by the activation and deactivation reactions. The termination does not significantly change the equilibrium of activation and deactivation. Figure 4-1b shows that PDI remains lower than 1.2 because of negligible influence of the termination reaction.

Radical deactivation in ATRP involves a large radical chain and a small catalytic deactivator. Second to termination, it can easily become diffusion controlled at medium conversions (in this case, around 50% conversion). One might argue that activation and deactivation should onset diffusion control at the same time because both reactions are between large chains and small catalytic molecules. However, it is indicated that because of lower diffusivity of larger deactivator, diffusional limitation on deactivation reaction is more severe than activation.[18] Furthermore, the deactivation rate coefficient is typically much higher than that of activation. A faster reaction becomes diffusion controlled earlier than a slower one, which is evident from Equation 22. Figure 4-2 shows the influence of diffusion-controlled deactivation with or without residual deactivation on the rate and control of polymerization, in the presence of diffusion-controlled termination ($\mathrm{k_{t,D}^{0}} = 10^{14}$) and residual termination ($\mathrm{z_{tde}} = 100$ & $\mathrm{z_{tp}} = 10$). It also shows the change of $\mathrm{k_{de}}$ in a log scale with conversion.

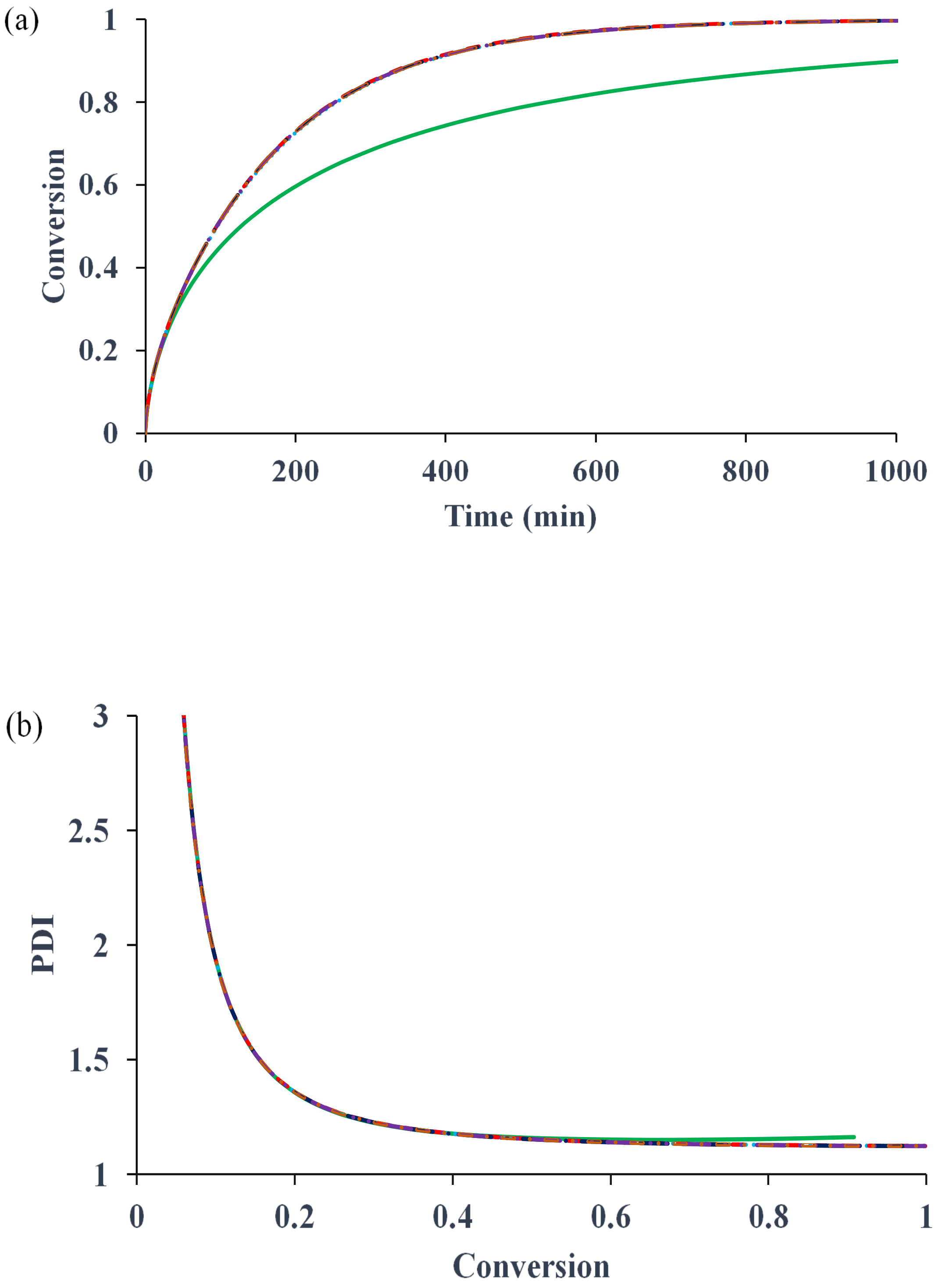


**Figure 4-1** ***Cont.***

**Figure 4-1 Effects of diffusion-controlled termination and residual termination on (a) conversion *versus* time (b) polydispersity index (PDI) *versus* conversion. No diffusion-controlled termination (——), translational diffusion-controlled termination ($k^{0}_{t,D} = 10^{14}$) but no residual termination (⋯⋯), translational diffusion-controlled termination ($k^{0}_{t,D} = 10^{14}$) with residual termination by radical hopping via deactivation/activation reactions ($z_{tde} = 10$ ) (– – –) & ($z_{tde} = 100$) (–·–), and translational diffusion-controlled termination ($k^{0}_{t,D} = 10^{14}$) with residual termination by radical hopping ($z_{tde} = 100$) and monomer propagation ($z_{tp} = 1$) (–··) & ($z_{tp} = 10$) (-·-·).**

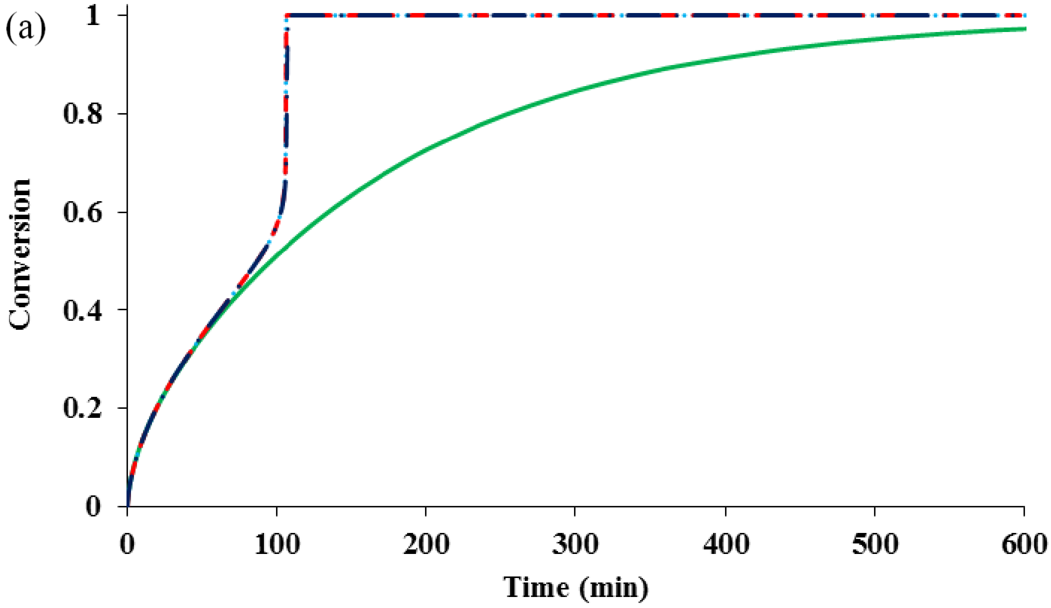


Figure 4-2 *Cont.*

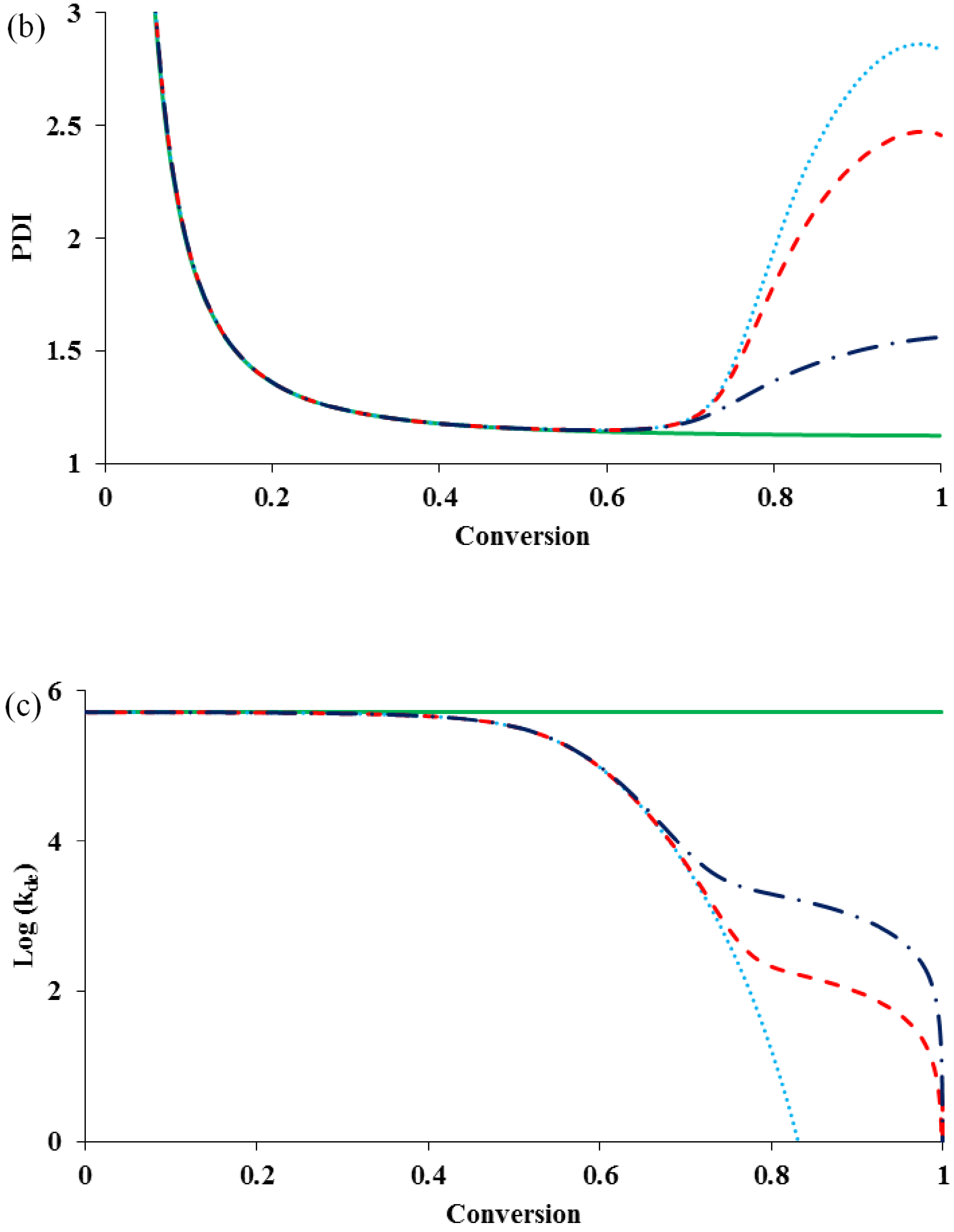
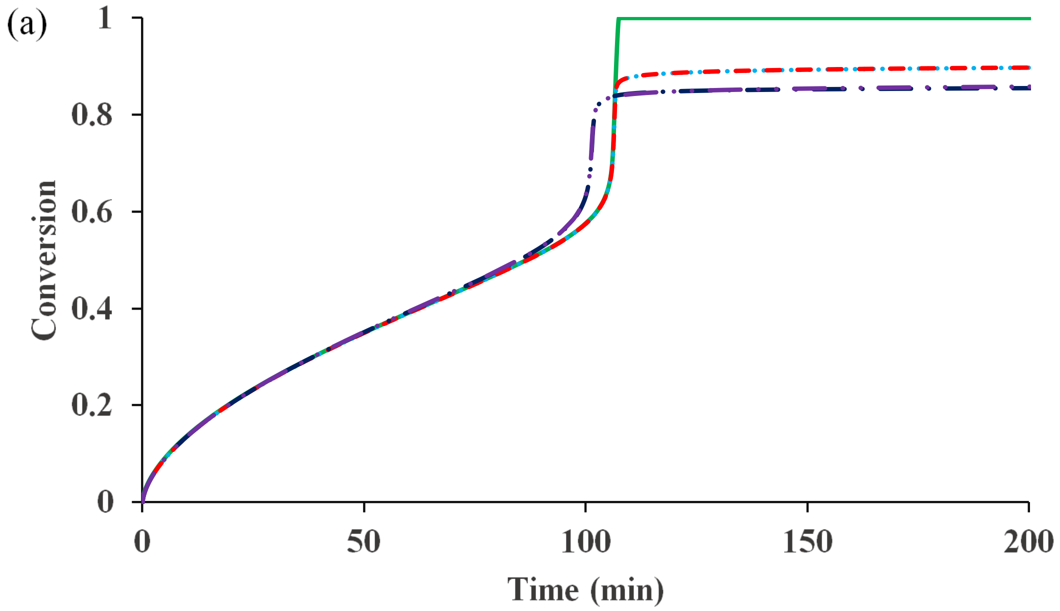


**Figure 4-2** ***Cont.***

**Figure 4-2 The influence of diffusion-controlled deactivation and residual deactivation on (a) conversion *versus* time; (b) PDI *versus* conversion; and (c) log ($k_{de}$) *versus* conversion for an ATRP system having diffusion-controlled termination ($k^{0}_{t,D}=10^{14}$) and residual termination ($z_{tde} = 100$ & $z_{tp} = 10$). No diffusion-controlled deactivation (——), diffusion-controlled deactivation ($k^{0}_{de,D} = 10^{10}$) but no residual deactivation (⋯⋯), diffusion-controlled deactivation ($k^{0}_{de,D} = 10^{10}$) with residual deactivation by monomer propagation ($z_{de} = 0.1$) (– – –) & ($z_{de} = 1$) (–·–).**

It can be seen that the diffusion-controlled deactivation causes a severe auto-acceleration in the polymerization rate ("gel effect"). This is because the radical concentration increases dramatically in the absence of adequate deactivation. The residual deactivation by propagation does not help to compensate the situation. There is no significant difference in the rate profiles with and without the residual deactivation. When the deactivation becomes diffusion controlled, the radical freely propagates with monomer and the chain quickly grows to a high molecular weight, without regulation of the equilibrium of activation and deactivation. This results in the loss of control over polymer molecular weight and leads to the dramatic increase in PDI, as shown in Figure 4-2b. It is also clear from the simulation result that the residual deactivation compensates the loss of control to certain extents. Introducing the residual deactivation decreases the PDI at high conversions. Figure 4-2c shows the $k_{de}$ profile during polymerization. The residual deactivation becomes dominant at very high conversions.

After termination and deactivation of radicals, dormant chain activation and monomer propagation can become diffusion controlled as well. Figure 4-3 shows the influence of diffusion-controlled activation and propagation on the rate and control of polymerization for the ATRP system having diffusion-controlled termination ($\mathrm{k}_{\mathrm{t,D}}^{0} = 10^{14}$) and deactivation ($\mathrm{k}_{\mathrm{de,D}}^{0} = 10^{10}$), as well as residual termination ($\mathrm{z}_{\mathrm{tde}} = 100$ & $\mathrm{z}_{\mathrm{tp}} = 10$) and deactivation ($\mathrm{z}_{\mathrm{de}} = 1$). It can be clearly seen from Figure 4-3a that both diffusion-controlled activation and diffusion-controlled propagation can lead to dead-end polymerization with limited conversion. Depending on their rate coefficients, as well as the relative sizes of monomer and catalyst complex, either activation or propagation can onset diffusion control first and dominate the influence on the high-conversion kinetic behavior. When activation onsets first, it reduces the radical concentration and slows down the polymerization rate. After that, diffusion-controlled propagation cannot make any difference. The opposite is also true, when propagation onsets diffusion control first, the diffusion controlled activation has no further influence. In contrast to the conventional free radical polymerization, in which diffusion-controlled propagation is responsible for the occurrence of "glass effect", both diffusion-controlled activation and diffusion-controlled propagation can stop the polymerization in ATRP. Furthermore, both diffusion-controlled activation and diffusion-controlled propagation cannot significantly affect the control of molecular weight at high conversions, as evident in Figure 4-3b.



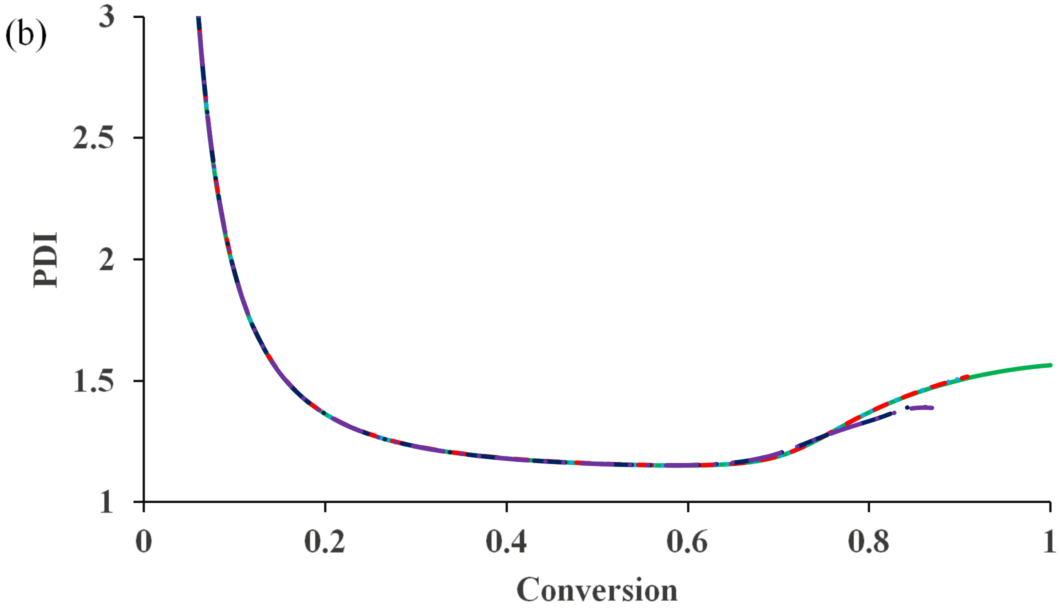


**Figure 4-3** ***Cont.***

**Figure 4-3 The influence of diffusion-controlled activation and propagation on (a) conversion *versus* time and (b) PDI *versus* conversion for an ATRP system having diffusion-controlled termination ($k^0_{t,D}$=$10^{14}$) and deactivation ($k^0_{de,D}$=$10^{10}$), as well as residual termination ($z_{tde} = 100$ & $z_{tp} = 10$) and deactivation ($z_{de} = 1$). No diffusion-controlled activation and propagation (——), diffusion-controlled activation ($k^0_{ac,D} = 10^{10}$) (······), diffusion-controlled activation and propagation ($k^0_{ac,D} = 10^{10}$ & - $k^0_{p,D} = 10^{16}$) (− − −), diffusion-controlled propagation ($k^0_{p,D} = 10^{10}$) (−·−) and diffusion-controlled propagation and activation ($k^0_{p,D} = 10^{10}$ & $k^0_{ac,D} = 10^{10}$) (−··).**

Figure 4-4 shows the change of various rate coefficients with monomer conversion during the polymerization. The radical termination onsets diffusion control first, at a low monomer conversion. This is because the reaction involves two chains, which easily experience diffusion limitations. It is also because termination has the highest rate coefficient among all the reactions involved in ATRP and the diffusion of reacting species easily becomes a rate-determining step. Diffusion control of radical chains decreases $k_t$ until the “hopping” mechanism through activation/deactivation cycles dominates the radical termination. With further progress of monomer conversion, small catalytic deactivator molecules start to experience diffusion limitations and the deactivation onsets diffusion control. The “hopping” mechanism becomes negligible. At this stage the residual termination is dominated by migration by propagation. This residual termination is at a much lower order of magnitude $k_t$ and it continues until the propagation onsets diffusion control, which often occurs when the system approaches its glass state. It is evident from Figure 4-4 that there exist three steps of reduction in $k_t$: at a low conversion corresponding to the translational diffusion control of radical chains, at a middle conversion due to the residual termination by “hopping” mechanism, and at a high conversion because of diffusion-controlled propagation.

During the polymerization, the radical termination, radical deactivation and monomer propagation become diffusion-controlled one after another. Similar to termination, diffusion-controlled deactivation decreases $k_{de}$ at a middle conversion. After that, it remains almost constant up to a high conversion because of residual deactivation by propagation. At the high conversion when the system approaches its glass state and the propagation becomes diffusion-controlled, $k_{de}$ decreases considerably, in response to $k_p$. The catalytic species for activation and deactivation have similar molecular sizes and thus diffusivities. Because of its much higher rate coefficient, deactivation onsets diffusion control earlier than activation. Activation becomes diffusion-controlled at a very high conversion, similar to propagation.

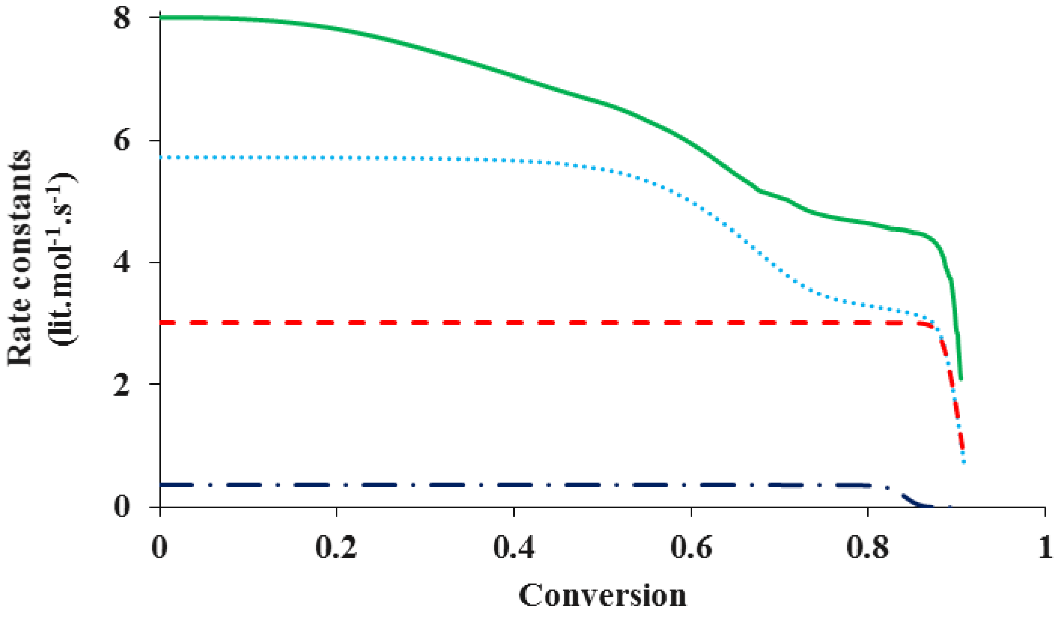


**Figure 4-4 The rate coefficients in logarithmic scale of termination ($k^0_{t,D}$=$10^{14}$, $z_{tde} = 100$ & $z_{tp} = 10$) (——), deactivation ($k^0_{de,D}$=$10^{10}$ & $z_{de} = 1$) (······) and propagation ($k^0_{p,D}$=$10^{16}$) (– – –), as well as activation ($k^0_{ac,D}$=$10^{10}$) (– · –), as a function of monomer conversion.**

It should be pointed out that the residual deactivation has an important role in keeping the control of polymer molecular weight at high conversions. Without it, the polymerization would be totally out of control. Figure 4-5 shows that although its influence on the polymerization rate is negligible, the residual deactivation reduces PDI value at the high conversion considerably. With $z_{de} = 10$, the PDI is below 1.2, despite the occurrence of a “gel effect”.

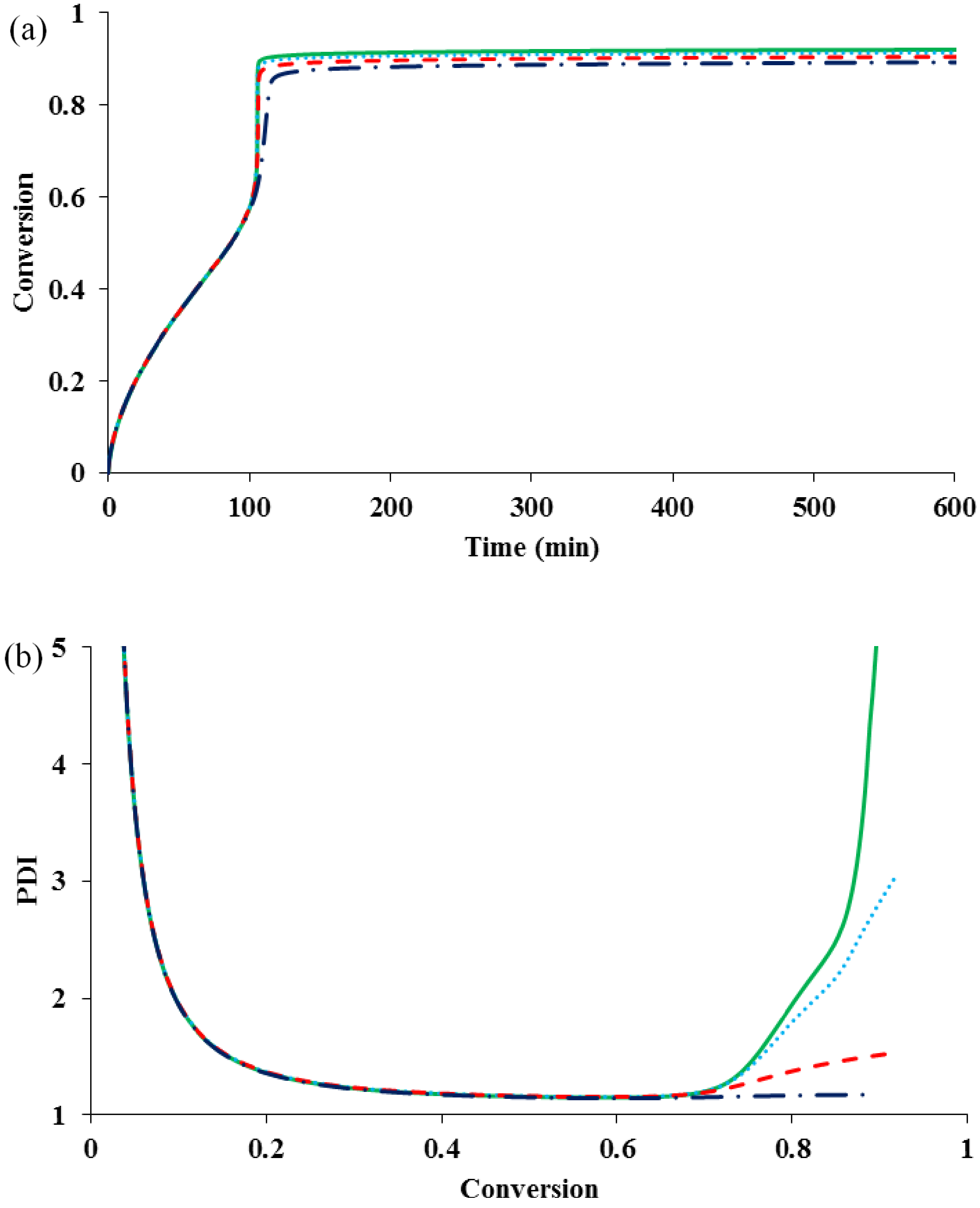


**Figure 4-5 The influence of residual deactivation ($z_{de} = 0$) (——), ($z_{de} = 0.1$) (······), ($z_{de} = 1$) (− − −) and ($z_{de} = 10$) (−·−) on (a) conversion *versus* time and (b) PDI *versus* conversion for a system having diffusion-controlled termination ($k^0_{t,D}$=$10^{14}$), deactivation ($k^0_{de,D}$=$10^{10}$), activation ($k^0_{ac,D}$=$10^{10}$), propagation ($k^0_{p,D}$=$10^{16}$) and residual termination ($z_{tde} = 100$ and $z_{tp} = 10$).**

## 4-5- Conclusions

High-conversion bulk controlled radical polymerization such as ATRP represents a great challenge. Various reactions, including radical termination, radical deactivation and activation, monomer propagation, can become diffusion controlled at high conversions. Diffusion-controlled reactions significantly influence the rate of polymerization and the control of polymer molecular weight. Using the modeling and simulation approach, these influences are systematically investigated in this work.

Radical termination onsets diffusion control first, at a relatively low conversion. It is because termination involves two chains, which easily experience diffusion limitations. It is also because termination has the highest rate coefficient among all the reactions, which makes diffusion easily become the rate-determining step. Diffusion-controlled termination increases radical concentration and thus polymerization rate slightly. Unlike conventional radical polymerization where diffusion-controlled termination causes “gel effect”, the radical concentration in ATRP is mainly regulated by the equilibrium of activation and deactivation. At high conversions, translational diffusion of chains may be totally limited but the radical centers can still move around by the “hopping” mechanism via the activation/deactivation cycles, and by propagation. However, influence of the residual termination on polymerization rate and molecular weight control is negligible.

After termination, deactivation becomes diffusion controlled. Although both deactivation and activation reactions involve large chain and small catalyst species, the deactivation rate coefficient is several orders of magnitude higher than that of activation and thus it onsets diffusion control earlier. Diffusion-controlled deactivation dramatically increases the radical concentration, causing a severe auto-acceleration in rate ("gel effect"). It is also responsible for the loss of polymer molecular weight control. However, as along as monomer molecules can still move around, the migration of radical centers through propagation can also facilitate the deactivation to some extent. This residual deactivation helps to lower PDI and improves the control at high conversions. Diffusion-controlled activation and propagation happen at very high conversions when the system approaches to its glassy state. Depending on the relative sizes and diffusivities of monomer and catalytic species, either one can onset diffusion control earlier than the other to stop polymerization, leading to a "dead-end polymerization".

## 4-6- Acknowledgments

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## 4-7- Author Contributions

Ali Mohammad Rabea wrote the first draft after discussing about the results with Shiping Zhu. Shiping Zhu revised the manuscript. The authors declare no conflict of interest.

## 4-8- References

(1) Georges, M.K.; Veregin, R.P.N.; Kazmaier, P.M.; Hamer, G.K. Narrow molecular weight resins by a free-radical polymerization process. Macromolecules 1993, 26, 2987.

(2) Wang, J.; Matyjaszewski, K. Controlled "living"/radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of methyl methacrylate with the carbon tetrachloridel dichlorotris-(triphenylphosphine)ruthedum(II)/methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system: Possibility of living radical polymerization. Macromolecules 1995, 28, 1721.

(4) Chiefari, J.; Chong, Y.K.B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T.P.T.; Mayadunne, R.T.A.; Meijs, G.F.; Moad, C.L.; Moad, G.; et al. Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process. Macromolecules 1998, 31, 5559.

(5) Matyjaszewski, K. Controlled radical polymerization: State-of-the-art in 2011. Controlled Radical Polymerization: Mechanisms and Techniques; American Chemical Society: Washingtom, DC, USA, 2012; 1.

(6) Tang, W.; Matyjaszewski, K. Effect of ligand structure on activation rate constants in ATRP. Macromolecules 2006, 39, 4953.

(7) Tang, W.; Matyjaszewski, K. Effects of initiator structure on activation rate constants in ATRP. Macromolecules 2007, 40, 1858.

(8) Kwak, Y.; Matyjaszewski, K. Effect of initiator and ligand structures on ATRP of styrene and methyl methacrylate initiated by alkyl dithiocarbamate. Macromolecules 2008, 41, 6627.

(9) Faucher, S.; Okrutny, P.; Zhu, S. Catalyst solubility and experimental determination of equilibrium constants for heterogeneous atom transfer radical polymerization. Ind. Eng. Chem. Res. 2007, 46, 2726.

(10) Fu, Y.; Mirzaei, A.; Cunningham, M.F.; Hutchinson, R.A. Atom-transfer radical batch and semibatch polymerization of styrene. Macromol. React. Eng. 2007, 1, 425.

(11) Shen, Y.; Zhu, S.; Zeng, F.; Pelton, R. Supported atom transfer radical polymerization of methyl methacrylate mediated by CuBr–tetraethyldiethylenetriamine grafted onto silica gel. J. Polym. Sci. 2001, 39, 1051.

(12) Shen, Y.; Zhu, S.; Pelton, R. Effect of ligand spacer on silica gel supported atom transfer radical polymerization of methyl methacrylate. Macromolecules 2001, 34, 5812.

(13) Mohammad Rabea, A.; Zhu, S. Controlled radical polymerization at high conversion: Bulk ICAR ATRP of methyl methacrylate. Ind. Eng. Chem. Res. 2014, 53, 3472.

(14) Mohammad Rabea, A.; Zhu, S. Achieving high-conversion bulk ATRP with good livingness and well controlled by design and optimization of polymerization temperature profile. Macromol. React. Eng. 2014, 8, 771.

(15) Zhu, S. Modeling of molecular weight development in atom transfer radical polymerization. Macromol. Theory Simul. 1999, 8, 29.

(16) Delgadillo-Velazquez, O.; Vivaldo-Lima, E.; Quintero-Ortega, I.A.; Zhu, S. Effects of diffusion-controlled reactions on atom-transfer radical polymerization. AIChE J. 2002, 48, 2597.

(17) Tang, W.; Matyjaszewski, K. Kinetic modeling of normal ATRP, normal ATRP with [CuII]0, reverse ATRP and SR&NI ATRP. Macromol. Theory Simul. 2008, 17, 359.

(18) D’hooge, D.R.; Reyniers, M.F.; Marin, G.B. Methodology for kinetic modeling of atom transfer radical polymerization. Macromol. React. Eng. 2009, 3, 185.

(19) D’hooge, D.R.; Konkolewicz, D.; Reyniers, M.F.; Marin, G.B.; Matyjaszewski, K. Kinetic modeling of ICAR ATRP. Macromol. Theory Simul. 2012, 21, 52.

(20) Van Steenberge, P.H.M.; D’hooge, D.R.; Wang, Y.; Zhong, M.; Reyniers, M.F.; Konkolewicz, D.; Matyjaszewski, K.; Marin, G.B. Linear gradient quality of ATRP copolymers. Macromolecules 2012, 45, 8519.

(21) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W.A.; Tsarevsky, N.V. Diminishing catalyst concentration in atom transfer radical polymerization with reducing agents. PNAS 2006, 103, 15309.

(22) Payne, K.A.; D’hooge, D.R.; van Steenberge, P.H.M.; Reyniers, M.R.; Cunningham, M.F.; Hutchinson, R.A.; Marin, G.B. ARGET ATRP of butyl methacrylate: Utilizing kinetic modeling to understand experimental trends. Macromolecules 2013, 46, 3828.

(23) Wang, A.R.; Zhu, S. ESR study on diffusion-controlled atom transfer radical polymerization of methyl methacrylate and ethylene glycol dimethacrylate. Macromolecules 2002, 35, 9926.

(24) Russell, G.T.; Napper, D.H.; Gilbert, R.G. Termination in free-radical polymerizing systems at high conversion. Macromolecules 1988, 21, 2133.

(25) Gao, X.; Feng, W.; Zhu, S.; Sheardown, H.; Brash, J.L. Kinetic modeling of surface-initiated atom transfer radical polymerization. Macromol. React. Eng. 2010, 4, 235.

(26) Zhou, D.; Gao, X.; Wang, W.; Zhu, S. Termination of surface radicals and kinetic modeling of ATRP grafting from flat surfaces by addition of deactivator. Macromolecules 2012, 45, 1198.

(27) Derboven, P.; D’hooge, D.R.; Reyniers, M.F.; Marin, G.B.; Barner-Kowollik, C. The long and the short of radical polymerization. Macromolecules 2015, 48, 492.

(28) D’hooge, D.R.; Reyniers, M.F.; Marin, G.B. The crucial role of diffusional limitations in controlled radical polymerization. Macromol. React. Eng. 2013, 7, 362.

(29) Wang, A.R.; Zhu, S. Effects of diffusion-controlled radical reactions on RAFT polymerization. Macromol. Theory Simul. 2003, 12, 196.

(30) Bueche, F. Physical Properties of Polymers; Interscience: New York, NY, USA, 1962; Volume 16.

(31) Taylor, D.R.; van Berkel, K.Y.; Alghamdi, M.M.; Russell, G.T. Termination rate coefficients for radical homopolymerization of methyl methacrylate and styrene at low conversion. Macromol. Chem. Phys. 2010, 211, 563.

# Chapter 5

# Achieving High-Conversion Bulk ATRP with Good Livingness and Well Controlled by Design and Optimization of Polymerization Temperature Profile

This chapter is organized based on the paper published in *Macromolecular Reaction Engineering*, 2014, 8(11), 771–776 by Ali Mohammad Rabea and Shiping Zhu

## 5-1- Abstract

Controlled radical polymerization (CRP) such as atom transfer radical polymerization (ATRP) is often conducted in solution processes and stopped at medium monomer conversions to yield well controlled polymer samples. A great challenge lies in running bulk CRP up to high conversions but still retaining system livingness and molecular weight control. In this work, we demonstrated the achievement of good living and well controlled high-conversion bulk ATRP by the means of design and optimizing polymerization thermal histories. We used the initiator-for-continues-activator-regeneration (ICAR) ATRP of methyl methacrylate (MMA) as a model system. Employing step functions in temperature,

we pushed MMA conversions up to 98% and obtained the PMMA samples having polydispersities <1.3. Chain extension experiments confirmed good livingness of synthesized polymers collected at the high conversions.

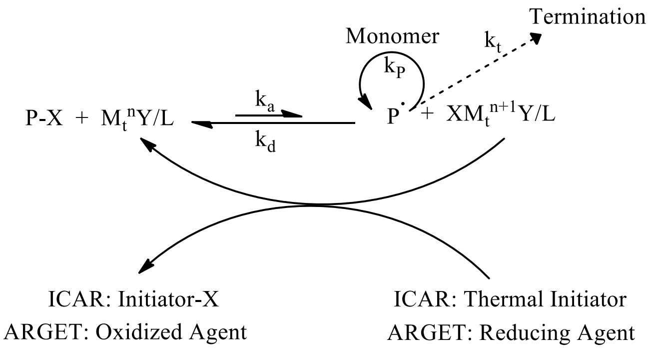
**5-1-1- Keywords**: ATRP, bulk polymerization, high conversion, system livingness, molecular weight control, thermal history

## 5-2- Introduction

In the recent decades, controlled radical polymerization (CRP) has been employed in many fields of polymer chemistry and engineering. By using CRP, it is possible to synthesize different polymers with desired molecular weight and narrow molecular weight distribution (MWD). Among different methods of CRP, the most promising are stable free radical polymerization (SFRP),[1] transition metal mediated atom transfer radical polymerization (ATRP),[2,3] and dithioester mediated reversible addition fragmentation chain transfer (RAFT) polymerization.[4]

The number of publications on CRP methods has been increasing considerably year by year. Among published papers, more than 50% are based on ATRP, which shows the great potential of this kind of polymerization for different applications.[5] ATRP generally requires an alkyl halide (R-X) as initiator and a transition metal salt/ligand complex ($M_t^nY/L$) as catalyst. Homolytic cleavage of R-X bond happens by $M_t^nY/L$ (with rate constant $k_a$) and follows by propagation (rate constant $k_p$), reversible deactivation of radical ($R^{\bullet}$) by higher oxidation state catalyst complex ($XM_t^{n+1}Y/L$) (with rate constant $k_d$) or termination with other radicals (rate constant $k_t$). The reaction continues by repetitive transfer of halogen atom to and from the transition metal complex. Also, by adjusting $k_a << k_d$, termination is minimized through decreasing the concentration of free radicals.[2,6] Furthermore, the problem of high catalyst loading in the initial ATRP recipes has been solved to some extent by applying newer methods. In these methods, a ppm level of $M_t^nY/L$ is continuously regenerated through reaction of $YM_t^{n+1}Y/L$ with a proper reducing agent (activator regenerated by electron transfer or ARGET-ATRP)[7,8] or free radical thermal initiator (initiator for continuous activator regeneration or ICAR-ATRP)[9] (Scheme 5-1). There are several papers in this area in order to decrease the concentration of catalyst as much as possible and make ATRP appropriate for industrial applications.[10-12]

**Scheme 5-1 Mechanism of ARGET and ICAR ATRP**



Nowadays, one of the important setbacks in ATRP and other CRP commercialization could be the difficulty of achieving high conversion in bulk systems, to avoid the use of solvents and to minimize the monomer residues. Both solvent and residual monomer are challenging in practice, in terms of cost and energy consumption in separation and purification, as well as environment concerns. Most of the literatures about ATRP reported polymer data of low to medium conversions. Few papers, which did present some high conversion data, gave high polydispersity indexes (PDI) in molecular weight distribution, indicating severe loss of controllability.[13,14] This problem in ATRP has been addressed by performing modeling and considering chain-length diffusion-controlled reactions[15-17] and by carrying out experiment[18,19] and investigating the effects of diffusion-controlled deactivation reaction at high conversion which causes “gel effect”. There is thus a major challenge between controlled polymerization and high conversion. Keeping good control means stopping reaction early. As a consequence, the system contains a high content of residual monomer, which imposes extra cost in separation/purification in industrial application. On the other hand, pushing the system to high conversion means losing the control and synthesizing polymers with broad MWD, which is in direct contrast with the purpose of CRP methods.

In a previous study,[19] bulk ICAR ATRP of methyl methacrylate (MMA) was carried up to high conversions by employing two thermal initiators, azobisisobutyronitrile (AIBN) and tert-butyl peroxybenzoate (TBPB), as ICAR agents. High conversion (98%) was achieved by carrying the reaction at 70 ˚C up to the glass state and then elevating temperature to 120 ˚C. Chain extension reaction showed that there was good livingness for the chains collected at 98% conversion. Diffusion-controlled termination was believed to suppress the rate of radical termination during the polymerization. While the work demonstrated that the system livingness could be maintained, the controllability remained to be a serious issue at the high conversions. Diffusion-controlled deactivation started about 50% conversion. It was followed by the loss of control over polymer molecular weight through decreasing the deactivation reaction for the activated chains. The chains thus propagated freely to higher molecular weights in the absence of adequate deactivation cycles.

High-conversion solvent-free bulk polymerization has clear advantages in the environmental protection and cost-saving production aspects. Achieving high conversion in bulk ATRP while remaining good livingness and good controllability provides a great challenge in polymerization research. Recently, we took the challenge and organized a program aimed at improving the controllability in ATRP at high conversions without sacrificing the livingness. As the first approach, we found that thermal history is important not only for reaching to high conversions, but also for adjusting controllability during the reaction. All the reactions in radical polymerization could become diffusion controlled at very high conversions. In general, the faster reactions become diffusion controlled earlier.[15] In an ICAR

ATRP, they probably are in the order of termination, deactivation, activation, propagation and regeneration. The diffusion-controlled termination and deactivation are the two key reactions. The former facilitates livingness while the latter damages controllability. In this work, we tried to optimize the temperature profile during the bulk ICAR ATRP of MMA. The target was to reach to higher conversions while keeping livingness and controllability. For this purpose, the temperature of the polymerization was increased in order to reach to high conversions in a reasonable time and also postpone diffusion-controlled deactivation reaction to higher conversions.

## 5-3- Experimental Section

**5-3-1- Materials:** Methyl methacrylate (MMA, Aldrich, 99%) was distilled under vacuum and stored at -20 °C before use. Ligand 4,4′-dinonyl-2,2′-dipyridyl (dNbpy, 97%), catalyst $CuBr_2$ (99.999%), ATRP initiator ethyl (α-bromophenyl)acetate (EBPA), thermal initiator (ICAR agent) tert-butyl peroxide (TBP, 98%) were purchased from Aldrich and used as received. Another thermal initiator azobisisobutyronitrile (AIBN, Aldrich, 99%) was recrystallized from methanol and stored at -20 °C.

**5-3-2- Instrumentation:** $^1$H NMR spectra were recorded on a Bruker AV-200 spectrometer at 200 MHz. polymer solution in acetone was diluted in d-chloroform

($CDCl_3$). Monomer conversion was measured from the intensity ratio of methoxy group signals of polymer (3.60 ppm) and monomer (3.75 ppm).

The number average molecular weight ($M_n$) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) relative to narrow PMMA standards. A Waters 2690 autoinjector with three linear columns in series (Waters Styragel HR 2, 3 and 4) and a 2410 RI detector was employed. The flow rate of THF which was pumped through the system was 1 mL/min. The temperature of columns and detector was set at 35 ˚C and 40 ˚C, respectively. Waters Millennium software package was used for recording and manipulating the data.

**5-3-3- Polymerization:** The experiment on the bulk ICAR ATRP of MMA with the molar ratios of [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:1:0.05:0.1:0.2:0.2 was as follow. $CuBr_2$ (0.0075 gr), dNbpy (0.0275 gr) and AIBN (0.0219 gr) were added to a 25 ml bottom round flask containing a magnetic bar. Different cycles of vacuum-nitrogen were applied to the sealed reactor. Degassed MMA (13.43 gr) was added to the reactor through cannulating. A nitrogen-purged syringe was used to add TBP (24.7 µl) to the flask. Stirring at room temperature was done for an hour before adding initiator. A nitrogen-purged syringe was used to add EBPA (117.5 µl) to the flask and the reactor was placed to oil bath. Stirring was continued during the reaction in order to dissolve the catalyst and make a homogenous solution. Although the magnet bar stopped from stirring by increasing the viscosity during the polymerization. Different oil baths with different temperatures (70, 90 and 120 ˚C) were prepared. For trying different temperature profiles, the reactions were continued by switching oil baths. Ice water was used to stop the polymerization.

**5-3-4- Chain Extension Reaction:** Polymerization was carried out for 4.5 hours at 70 ˚C and followed by 15 minutes at 90 ˚C and half an hour at 120 ˚C. Catalyst residue was removed by passing polymer solution in acetone through a column of alumina. The polymer was precipitated in methanol and dried in vacuum oven. Dried purified polymer was used as macroinitiator. Chain extension reaction was performed for 3 hours at 70 ˚C by trying the molar ratios of [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:0.01:0.05:0.1:0.2:0.2.

## 5-4- Results and Discussion

Three different temperature profiles were applied with their conversion versus time shown in Figure 5-1. In 70TP, the reaction was carried out at 70 ˚C to the end; in 70-90TP, the reaction was started at 70 ˚C for 4.5 hours and the temperature was then elevated to 90 ˚C; in 70-120TP, the reaction was started at 70 ˚C for 4.5 hours and the temperature was then elevated to 120 ˚C.

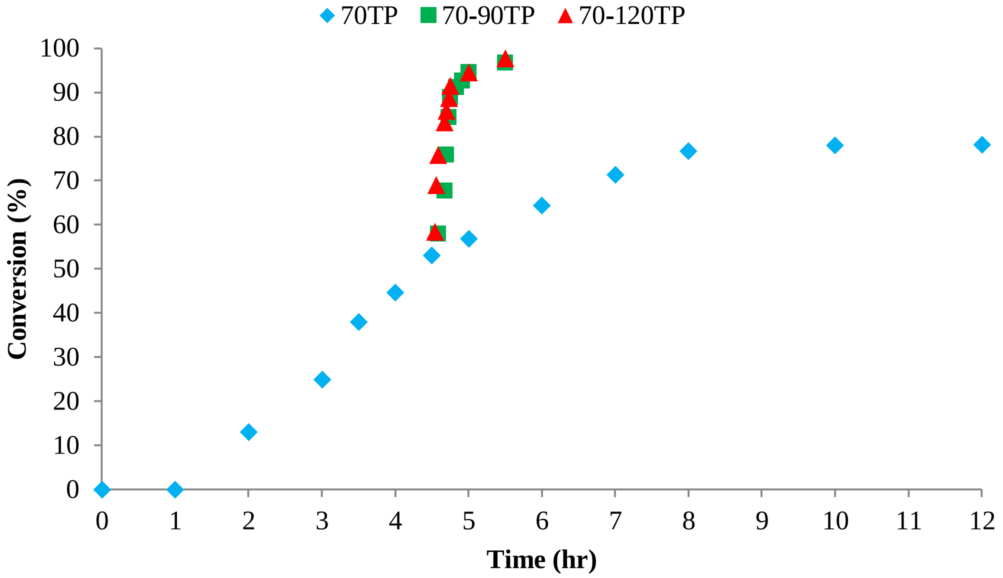


**Figure 5-1 Conversion versus time for the bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:1:0.05:0.1:0.2:0.2. ◆ 70TP: reaction carried out at 70 ˚C, ■ 70-90TP: reaction for 4.5 hr at 70 ˚C and then temperature raised to 90 ˚C, ▲ 70-120TP: reaction for 4.5 hr at 70 ˚C and then temperature raised to 120 ˚C.**

The results showed that in 70TP, around 78% conversion was obtained after polymerized for 8 hours at 70 ˚C. The conversion did not increase much by continuing the reaction further at this temperature. The possible reason is lack of AIBN concentration. At 70 ˚C, just AIBN works as ICAR agent. AIBN generates primary radicals at the start of the reaction by reducing $CuBr_2$ to CuBr. CuBr then activates the ATRP initiator EBPA for chain growth. $CuBr_2$ is accumulated during polymerization because of unavoidable radical termination and the free radicals generated by AIBN decomposition continuously reduce $CuBr_2$ to CuBr. The low concentration of AIBN could not adequately regenerate the catalyst after 10 hr and thus the conversion did not increase anymore. With this temperature profile, the rate of increase in conversion reduced after around 4.5 hours (55% conversion) because of AIBN exhaustion and reduced monomer concentration. Furthermore, a "gel effect" did not occur after around 50% conversion which was in contrast to the result found in the previous work,[19] in which a higher concentration of ICAR agent was used. The accumulated deactivator would effectively suppress chain activation, resulting a "dead-end" polymerization, which is also a phenomenon often observed in conventional free radical polymerization due to an inadequate level of thermal initiator.

In both 70-90TP and 70-120TP, the rates of polymerization became so fast upon the elevation of temperature that the conversion reached to around 98% in just one additional hour. At the high temperatures, AIBN decomposed very rapidly and TBP became the major contributor as ICAR agent. The decomposition of TBP increased the concentration of primary radicals, which reduced $CuBr_2$ to CuBr. The concentration of radical chains thus increased through chain activation by CuBr. Furthermore, elevating temperature also increased the rate of propagation constant. As a result, the rate of polymerization increased considerably.

Figure 5-2 presents the number-average molecular weight ($M_n$) and PDI versus conversion data with the different temperature profiles. In each case, a good agreement between the experimental and theoretical values of molecular weights was observed. The initiator efficiency based on ATRP initiator, $I_{eff}$, was found to be around 70% at the beginning, suggesting the presence of termination at low conversions before the radical termination became diffusion controlled. The efficiency increased to around 100% during the polymerization. It should be pointed out that the initiator efficiency was solely based on the ATRP initiator, that is, the molar ratio of polymer chains over EBPA or equivalently, the ratio of theoretical $M_n$ over experimental $M_n$. Theoretical $M_n$ was calculated by multiplying the conversion of the polymerization by the ratio of monomer to ATRP initiator and molecular weight of MMA. The increase in $I_{eff}$ during polymerization could be contributed to the ICAR agent acting as thermal initiator as in free radical polymerization and generating new polymer chains.

In 70TP, PDI was around 1.1 throughout of the reaction, demonstrating good controllability. But, it was impossible to reach high conversions (> 80%) at this temperature because of the “dead-end” polymerization. In 70-90TP, after temperature increased to 90 ˚C, the PDI remained around 1.1 for around 15 min up to 90% conversion. Then, it started to increase and reached to around 1.6 at the end of polymerization. It suggested that after 90% conversion, the deactivation reaction became diffusion controlled and “gel effect” occurred, which broadened molecular weight distribution due to lack of activation/deactivation cycles in chain growth. In 70-120TP, the PDI started to increase at 80% conversion and reached to around 1.6 at the end of polymerization.

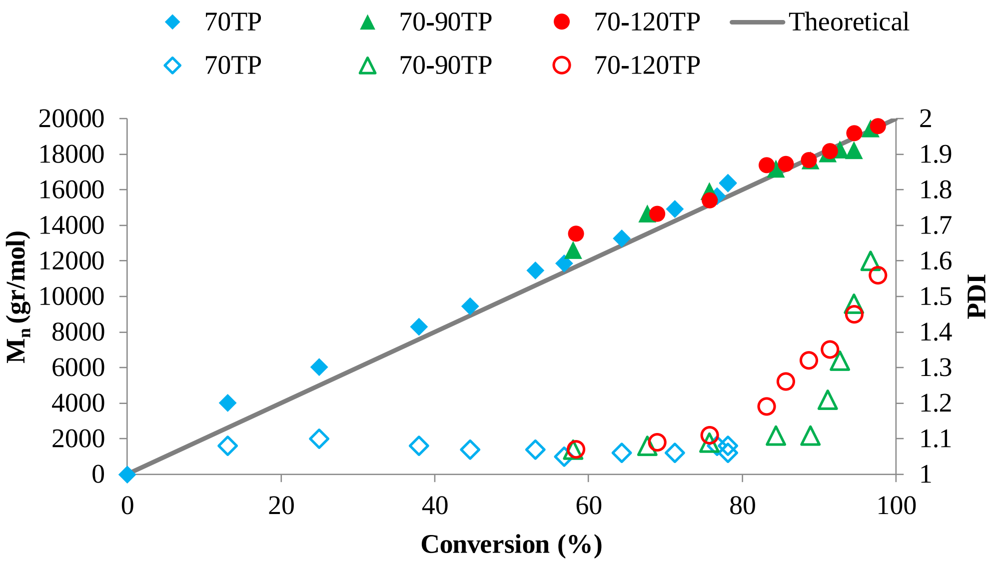


**Figure 5-2 $M_n$ and PDI versus conversion for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:1:0.05:0.1:0.2:0.2. ◆ 70TP: carried out at 70 ˚C, ▲ 70-90TP: reaction for 4.5 hr at 70 ˚C and then temperature raised to 90 ˚C, ● 70-120TP: reaction for 4.5 hr at 70 ˚C and then temperature raised to 120 ˚C (filled markers show $M_n$ and hollow ones show PDI).**

The difference in the PDI responses to temperature elevation between 70-90TP and 70-120TP caught our attention. We carried many repeated experiments and confirmed the difference. In 70-90TP, the reaction was well controlled between 80 to 90% conversion, while in 70-120, the lack of control became obvious in the same conversion interval. The rate of PDI increase with conversion was slower in 70-90TP than in 70-120TP. It could be caused by a too high decomposition rate of the ICAR agent at 120 ˚C that reduced almost all $CuBr_2$. A very low $CuBr_2$ concentration led to insufficient deactivation reaction and loss of the control.

Indeed, the control of polymer molecular weight is determined by $CuBr_2$ concentration, which is regulated by the ICAR reaction. There exists an optimal rate of ICAR that allows us to produce well controlled polymers at a reasonable rate of polymerization. Neither too fast nor too slow would work for a well-controlled polymerization system.

Figure 5-3 shows the representative GPC curves for the sample collected in 4.5 hr at 70 °C (55% conversion), the sample prepared by doing ATRP for 4.5 hr at 70 °C followed by 1 hr at 90 °C (97% conversion) and the sample prepared by carrying out ATRP for 4.5 hr at 70 °C followed by 1 hr at 120 °C (98% conversion). The sample which was prepared by doing 4.5 hr at 70 °C had a narrow peak with polydispersity of only 1.07. In comparison, the other samples had a broad peak and polydispersity of about 1.6. This problem has been attributed to diffusion-controlled deactivation reaction which has been discussed in detail in previous paper[19] also the lack of catalyst concentration because of high decomposition rate of the ICAR agent. They led to lack of deactivation reaction for the activated chains which would propagate to higher molecular weights.

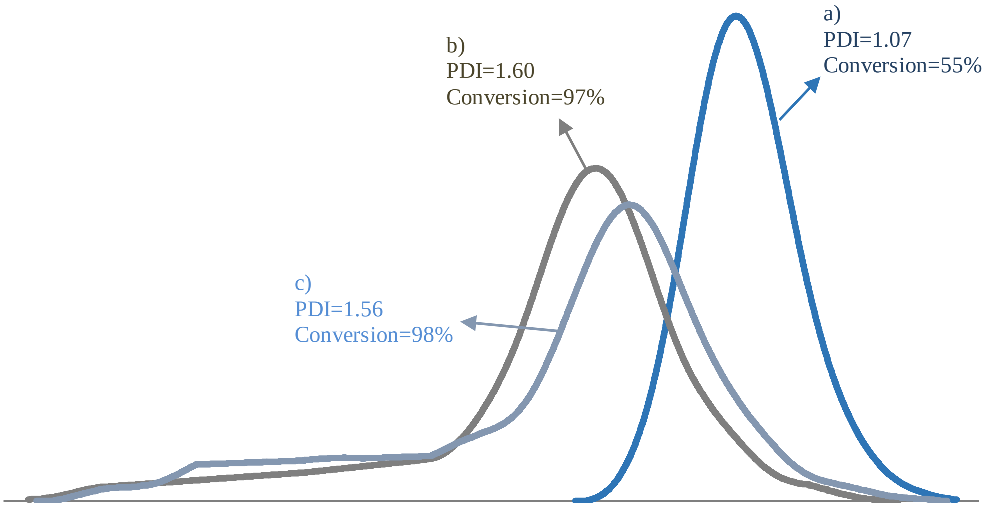


**Figure 5-3 GPC curves for [MMA]:[EBPA]:[ $CuBr_2$]:[dNbpy]:[AIBN]:[TBP]= 200:1:0.05:0.1:0.2:0.2 a) 4.5 hr at 70 ˚C , b) 4.5 hr at 70 ˚C followed by 1 hr at 90 ˚C and c) 4.5 hr at 70 ˚C followed by 1 hr at 120 ˚C .**

Inspired by the above experimental observation and data analysis, we foresaw an opportunity in design and optimizing the temperature profile during polymerization for a high-conversion bulk ATRP with good control and livingness. In 70-90-120TP, we run the reaction for 4.5 hours at 70 ˚C, followed successive temperature elevations. Temperature was raised to 90 ˚C for 15 min, allowing us to reach 90% conversion with good controllability. It was then raised to 120 ˚C to complete the residual monomer. Figure 5-4 shows the conversion versus time data of 70-90-120TP. By applying the new temperature profile, 98% conversion was reached within 5 hours.

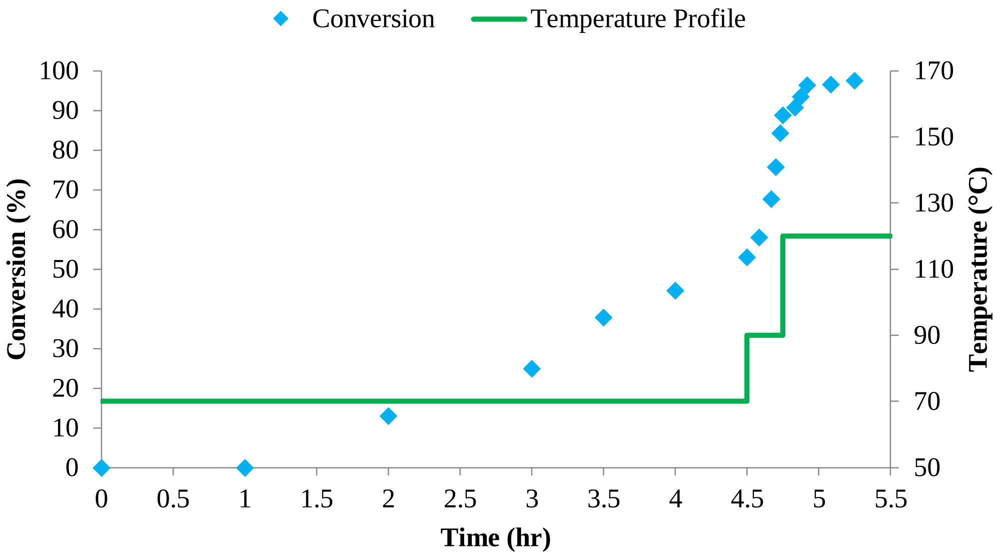


**Figure 5-4 Conversion and adjusted temperature of the polymerization versus time for bulk ICAR ATRP of methyl methacrylate [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:1:0.05:0.1:0.2:0.2.**

Figure 5-5 shows molecular weight and PDI versus conversion data. There was a good correlation between the experimental and theoretical molecular weights calculated by multiplying conversion of the reaction by ratio of monomer to ATRP initiator and molecular weight of MMA. The initiator efficiency was around 90% up to 90% conversion and increased to >100% at the end. It was clear that some new chains were generated through ICAR agents at the final step. To our satisfaction, PDI's of the final polymer samples at 98% conversion were around 1.3, suggesting a good control throughout the polymerization.

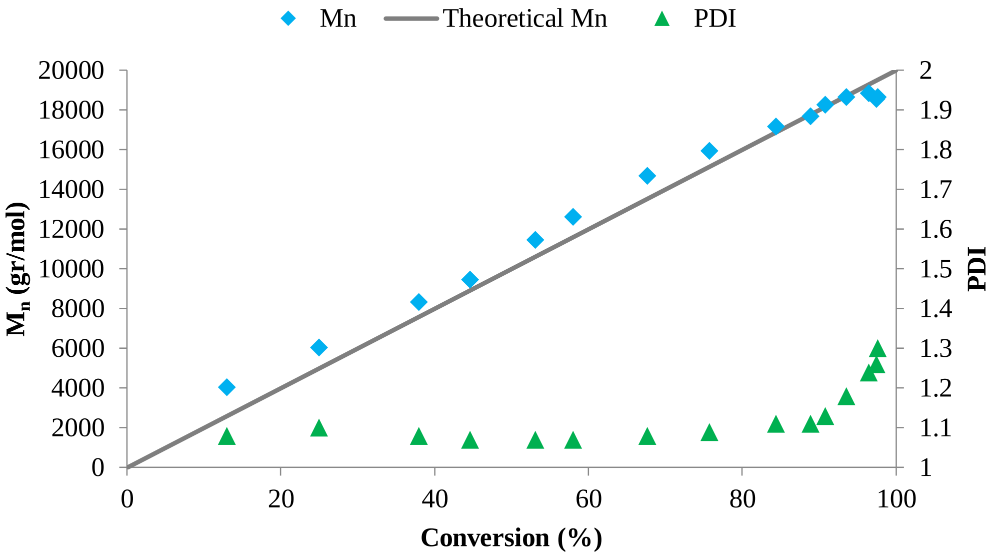


**Figure 5-5 $M_n$ and PDI versus conversion for bulk ICAR ATRP of methyl methacrylate [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:1:0.05:0.1:0.2:0.2.**

Polymer livingness of the samples collected at high conversions was examined by chain extension experiments. Several new polymer samples were prepared by the ICAR ATRP at 70 ˚C for 4.5 hr followed 90 ˚C for 15 min and 120 ˚C for half an hour. About 98% conversions were reached. The samples were purified and used as macroinitiator for the chain extension. The following recipe was employed: [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:0.01:0.05:0.1:0.2:0.2 with the reaction at 70 ˚C for 3 hr.

Figure 5-6 shows a chain extension result. The molecular weight was clearly increased, which could be considered as a hard evidence for the livingness of polymer chains. There was no low molecular weight shoulder in the GPC curve, indicating no significant amount of dead chains present. This helped us in reaching the conclusion that well-controlled living polymers can be achieved in bulk ATRP run up to high conversion, through manipulating the polymerization thermal history. A final point worth mentioning is that not all diffusion-controlled reactions in ATRP are troublesome. Diffusion-controlled termination at high conversion actually favors a lot to polymer livingness, by suppressing chain termination. It is the diffusion-controlled deactivation of propagating radicals that causes the loss of control and thus needs to be regulated by ICAR reaction.

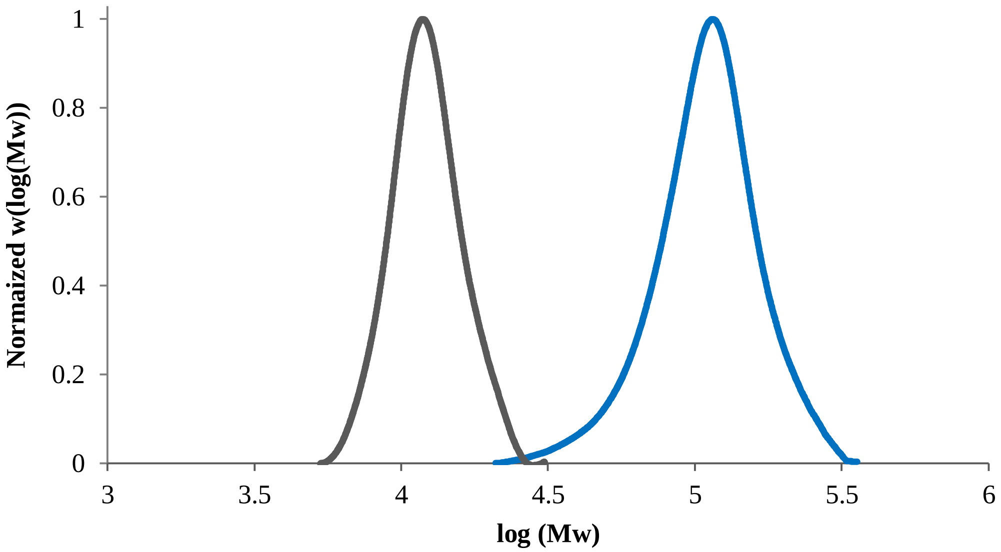


**Figure 5-6 Chain extension result for the sample collected at about 98% conversion as macroinitiator. The sample was prepared by carrying ICAR ATRP at 70 °C for 4.5 hr, continued by raising temperature to 90 °C for 15 min and 120 °C for 0.5 hr. Chain extension recipe was [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 200:0.01:0.05:0.1:0.2:0.2 at 70 °C for 3 hr.**

## 5-5- Conclusion

Bulk ICAR ATRP of MMA was carried out up to high conversions with different temperature profiles. Both thermal initiators, AIBN and TBP, were employed as ICAR agents. High conversions were achieved by running the polymerization for 4.5 hours at 70 ˚C continued at elevated temperature at 90 ˚C and/or 120 ˚C. The ATRP at 70 ˚C behaved very well with good livingness and control. However, the final conversion was limited to 78% with the used low concentration of AIBN as ICAR agent. Running the polymerization at 70 ˚C for 4.5 hours followed by a temperature elevation to 90 ˚C (70-90TP) or 120 ˚C (70-120TP) could push the conversion up to 98% in less than an hour. In 70-90TP, the PDI remained around 1.1 up to 90% conversion and then quickly increased to 1.6 at the end, while in 70-120TP, it started to increase at 80% conversion and gradually increased to 1.6.

The different behaviors in polymer molecular weight control between 70-90TP and 70-120TP inspired the design of temperature profile for well-controlled high conversion bulk ATRP. Running the polymerization for 4.5 hours at 70 ˚C followed by 15 min at 90 ˚C and then 30 min at 120 ˚C, we reached 98% conversion and obtained the polymer products with PDI's <1.3. The polymers are living, confirmed by chain extension experiments.

At high conversions, various reactions become diffusion controlled sooner or later. While diffusion-controlled termination helps polymer livingness by suppressing termination of radical chains, the diffusion-controlled deactivation trouble-makes the control of polymer molecular weight. In ICAR ATRP, the concentration of deactivator $CuBr_2$ must be precisely regulated by the ICAR reaction. If the regeneration of CuBr is too slow, too much $CuBr_2$ would be accumulated and thus stop the polymerization. In the opposite, if CuBr regeneration is too fast, the rate of polymerization would increase but at the cost of losing control. Through optimizing the ICAR rate by designed temperature profile, a well-controlled good living high conversion bulk ATRP has been achieved in this work.

## 5-6- Acknowledgment

We thank the Natural Science and Engineering Research Council of Canada (NSERC) for supporting this research and the Canada Foundation of Innovation who support our research facilities. Ali Mohammad Rabea acknowledges McMaster University for the Ontario trillium scholarship.

## 5-7- References

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow Molecular Weight Resins by a Free-Radical Polymerization Process. Macromolecules 1993, 26, 2987.

(2) Wang, J.; Matyjaszewski, K. Controlled/Living Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of Methyl Methacrylate with the Carbon TetrachloridelDichlorotris-(triphenylphosphine)ruthedum(II)/ Methylaluminum Bis(2,6-Di-Tert-Butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. Macromolecules 1995, 28, 1721.

(4) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H.; South, C. Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. Macromolecules 1998, 31, 5559.

(5) Matyjaszewski, K. Controlled Radical Polymerization : State-of-the-Art in 2011. In Controlled Radical Polymerization: Mechanisms and Techniques; American Chemical Society: Washingtom, DC, 2012; 1.

(6) Matyjaszewski, K.; Patten, T. E.; Xia, J. Controlled /“ Living ” Radical Polymerization . Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene. J. Am. Chem. Soc. 1997, 119, 674.

(7) Jakubowski, W.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers. Angew. Chemie 2006, 118, 4594.

(8) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP. Macromolecules 2007, 40, 1789.

(9) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. a; Tsarevsky, N. V. Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents. Proc. Natl. Acad. Sci. U. S. A. 2006, 103, 15309.

(10) Pintauer, T.; Matyjaszewski, K. Atom Transfer Radical Addition and Polymerization Reactions Catalyzed by Ppm Amounts of Copper Complexes. Chem. Soc. Rev. 2008, 37, 1087.

(11) Bai, L.; Zhang, L.; Cheng, Z.; Zhu, X. Activators Generated by Electron Transfer for Atom Transfer Radical Polymerization: Recent Advances in Catalyst and Polymer Chemistry. Polym. Chem. 2012, 3, 2685.

(12) Jakubowski, W. Adapting Atom Transfer Radical Polymerization to Industrial Scale Production: The Ultimate ATRPSM Technology. ACS Symp. Ser. 2012, 1100, 203.

(13) Faucher, S.; Zhu, S. Heterogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate at Low Metal Salt Concentrations. Ind. Eng. Chem. Res. 2005, 44, 677.

(14) He, W.; Zhang, L.; Bai, L.; Zhang, Z.; Zhu, J.; Cheng, Z.; Zhu, X. Iron-Mediated AGET ATRP of Methyl Methacrylate in the Presence of Catalytic Amounts of Base. Macromol. Chem. Phys. 2011, 212, 1474.

(15) Delgadillo-Velazquez, O.; Vivaldo-Lima, E.; Quintero-Ortega, I. A.; Zhu, S. Effects of Diffusion-Controlled Reactions on Atom-Transfer Radical Polymerization. AIChE J. 2002, 48, 2597.

(16) D’hooge, D. R.; Konkolewicz, D.; Reyniers, M.-F.; Marin, G. B.; Matyjaszewski, K. Kinetic Modeling of ICAR ATRP. Macromol. Theory Simulations 2012, 21, 52.

(17) D’hooge, D. R.; Reyniers, M.-F.; Marin, G. B. The Crucial Role of Diffusional Limitations in Controlled Radical Polymerization. Macromol. React. Eng. 2013, 7, 362.

(18) Shipp, D. A.; Matyjaszewski, K. Kinetic Analysis of Controlled/“Living” Radical Polymerizations by Simulations. 1. The Importance of Diffusion-Controlled Reactions. Macromolecules 1999, 32, 2948.

(19) Mohammad Rabea, A.; Zhu, S. Controlled Radical Polymerization at High Conversion: Bulk ICAR ATRP of Methyl Methacrylate. Ind. Eng. Chem. Res. 2014, 53, 3472.

# Chapter 6

## Pushing Monomer Conversions High in Bulk ATRP: the Effects of ICAR Agents Concentrations on the System Livingness and Polymer Molecular Weight Control

This chapter is organized based on the chapter published in *ACS Symposium Series: Controlled Radical Polymerization: Mechanisms*, 2015, 1187, Chapter 9, 159–169 by Ali Mohammad Rabea and Shiping Zhu

### 6-1- Abstract

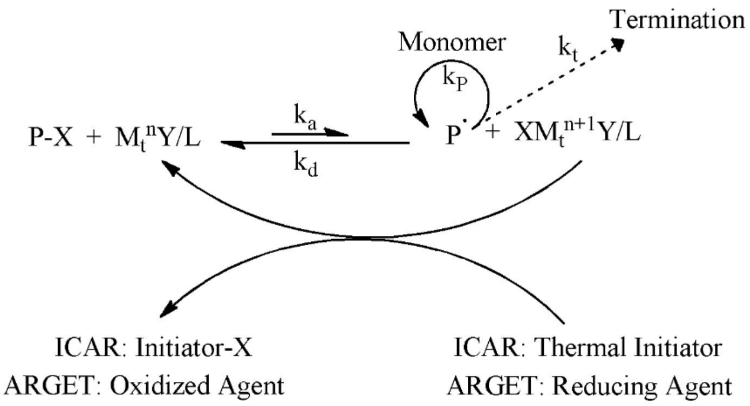
Controlled radical polymerization often loses control over polymer molecular weight at high monomer conversions due to diffusion-controlled reactions. This is particularly true for bulk polymerization systems. In this work, bulk atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) was carried out by employing an initiator for continuous activator regeneration (ICAR) method. Binary systems of ICAR agents, that is, low temperature azobisisobutyronitrile (AIBN) and high temperature tert-butyl peroxybenzoate (TBPB) or tert-butyl peroxide (TBP) were used. The polymerization was run at 70 ˚C at the beginning and completed at an elevated temperature. The objective was to investigate the effects of ICAR agent concentration on the system livingness and control at high conversions. It was found that both ICAR agents significantly affected the rate of catalyst regeneration and consequently the rate and control of polymerization. By optimizing the concentrations of the ICAR agents and employing step temperature profile, MMA was polymerized with 50 ppm $CuBr_2$ up to 98% conversion in less than 5 hours. The final products had dispersity (Đ) about 1.3.

**6-1-1- Key words**: ATRP, high monomer conversion, gel effect, glass effect, diffusion-controlled reactions, thermal initiator, catalyst regeneration

## 6-2- Introduction

Controlled radical polymerization (CRP), mostly nitroxide-mediated polymerization (NMP),[1] atom transfer radical polymerization (ATRP),[2,3] and reversible addition fragmentation chain transfer (RAFT) polymerization,[4] have provided great potential for synthesis of functional polymers with predetermined molecular weight and narrow molecular weight distribution (MWD). The number of publications on the CRP methods, ATRP in particular, has increased dramatically in the recent decade,[5] but their commercial exploitation is rather limited.[6,7] Among many others, high catalyst loading and limited conversion represent two significant challenges. The high catalyst loading gives deep color to the final ATRP products and makes the post purification costly.[8] The high conversion in bulk causes diffusion control problem for those reactions involving chain species and loss of control of the reaction.[9] Solution polymerization is often employed. However, both solvent and residual monomer are costly in terms of separation and purification and have environmental concern as well. With numerous efforts, the catalyst loading problem has been solved to some extent by catalyst supporting or by introducing new ATRP methods, such as the activator regenerated by electron transfer (ARGET ATRP) and the initiator for continuous activator regeneration (ICAR ATRP),[10-12] as shown in Scheme 6-1. In contrast, the problem associated with high conversion has not been addressed thoroughly. The high conversion problem is attributed to diffusion-controlled reactions, which cause “gel effect” and “glass effect” and make the system suffer from loss of control and result in high dispersity (Đ).[9,13,14]

**Scheme 6-1 ATRP with the activator regenerated by electron transfer (ARGET ATRP) and the initiator for continuous activator regeneration (ICAR ATRP).**



Recently, we launched a research program aiming to tackle the problems that limit commercial exploitation of controlled radical polymerization processes. One of the objectives is to push monomer conversion high in the most challenging bulk systems. Polymerization up to a complete conversion but still living and controlled serves as an ultimate target. On the fundamental side, we tried to investigate the effects of diffusion-controlled reactions on bulk polymerization in order to develop strategies to keep system livingness and control up to high conversions. In our first study,[9] the effect of deactivator concentration ($CuBr_2$), from 50 to 250 ppm, on the bulk ICAR ATRP of methyl methacrylate (MMA) was examined. Two thermal initiators (azobisisobutyronitrile (AIBN) and tert-butyl peroxybenzoate (TBPB)) were employed as the ICAR agents. The polymerization runs were performed at 70 ˚C up to the glass state. The results showed good livingness and control at low monomer conversions. However, diffusion-controlled deactivation occurred at medium conversion, causing "gel effect" and loss of control over polymer molecular weight. Loading higher concentration of the deactivator (250 ppm) compensated the loss of control to some extent but decreased the rate of the polymerization. Also, the polymer chains were protected from termination because of the diffusion-controlled termination.

In another study,[15] the bulk ICAR ATRP of MMA was performed up to high conversions by using AIBN and tert-butyl peroxide (TBP) as the ICAR agents in the presence of 250 ppm catalyst concentration. Temperature profile was employed to postpone the diffusion-controlled deactivation reaction to higher conversion. The results showed that increasing temperature before the onset time of diffusion-controlled deactivation could help to keep the control of polymerization up to higher conversions, while polymer chains were still preserved from termination because of diffusion-controlled termination. This was due to a difference in the onset times between diffusion controlled deactivation and termination. The former involved one chain species with the other small molecule catalyst complex, while the latter involved two chain species and thus became diffusion controlled earlier. Using this method, we obtained polymer products having Đ smaller than 1.3 at about 98% conversion.

It is well known that ICAR agent adjusts the rate and control of polymerization through reducing catalyst of higher oxidation state (deactivator) (mostly $CuBr_2$) to a lower oxidation state (CuBr). When the radical concentration generated through thermal initiator decomposition is low, the regeneration of catalyst is slow as well, causing accumulation of the deactivator and finally stopping the polymerization. On the other side, when the radical concentration is high, most deactivator molecules are reduced to catalyst, increasing the rate of polymerization but at the cost of losing control over polymer molecular weight. Therefore, the deactivator concentration must be precisely regulated through the ICAR reactions for an optimal balance of control and rate of polymerization.

In this work, the effects of concentration of ICAR agents on the control and rate of polymerization are investigated. We focus on high conversions and target to achieve the optimal ICAR concentration for the livingness of polymerization system and the control of polymer molecular weight at high conversions. It must be pointed out that diffusion-controlled reactions at high conversion are very complicated. It is worth of much effort in research to understand their mechanisms. There are so many reactions involved, namely, ATRP initiation, propagation, termination, activation, deactivation, catalyst regeneration and thermal initiator decomposition. Any of the reactions could become diffusion controlled at very high conversions, particularly when the system approaches its glass stage. The relative onset times and magnitudes of diffusion limitations are very important in determining the system livingness and control. In our program, we make effort to investigate the effects of each of the major parameters on the bulk polymerization, with the final objective of a comprehensive understanding of the high conversion mechanisms and a possible computer model that could be used to design and control the polymerization operation for achieving targeted polymer products. This paper report the result of the effect of ICAR agent type and concentration.

## 6-3- Experimental Section

**6-3-1- Materials:** Methyl methacrylate (MMA, Aldrich, 99%) was distilled under vacuum. After passing through a column of inhibitor remover, it was stored at -20°C before use. 4,4′-Dinonyl-2,2′-dipyridyl (dNbpy, 97%) as ligand, $CuBr_2$ (99.999%) as deactivator and ethyl (α-bromophenyl)acetate (EBPA) ATRP initiator were purchased from Aldrich and used without any further purification. Initiators for continuous activator regeneration (ICAR agents), tert-butyl peroxybenzoate (TBPB, 98%), tert-butyl peroxide (TBP, 98%) and azobisisobutyronitrile (AIBN, 99%) were purchased from Aldrich and used as received, except for AIBN which was recrystallized from methanol and stored at -20 ˚C.

**6-3-2- Instrumentation:** $^1$H NMR spectra were recorded through running diluted polymer-acetone solution in d-chloroform ($CDCl_3$) on a Bruker AV-200 spectrometer at 200 MHz. The intensity ratio of the methoxy group signals of polymer (3.60 ppm) and monomer (3.75 ppm) was employed for estimate of monomer conversions. Gel permeation chromatography (GPC) was used for determining the number average molecular weight (Mn) and dispersity (Đ) relative to a set of narrow polymethyl methacrylate standards. The polymer samples were run through a Waters 2690 autoinjector with three linear columns in series (Waters Styragel HR 2, 3 and 4) and a 2410 RI detector, with THF as effluent at a fixed flow rate of 1 mL/min. The columns and detector were heated to 35 ˚C and 40 ˚C, respectively. Data were recorded by Waters Millennium software package for further manipulation.

**6-3-3- Polymerization:** The bulk ICAR ATRP runs of MMA with the molar ratios of [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB]=200:1:0.05:0.1:X:Y (X=0.1 and 0.2) (Y=0.075 and 0.2) and [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:

[TBP]=1000:1: 0.05:0.1:0.375:0.5 was carried out as follow. A 25 mL bottom round flask containing a magnetic bar was loaded with appropriate amount of $CuBr_2$ (0.0015 or 0.0075 gr), dNbpy (0.0055 or 0.0275 gr) and AIBN (0.0082, 0.0109 or 0.0219 gr). The sealed reactor was degassed by several cycles of vacuum-nitrogen. Degassed MMA (13.43 gr) was then added to the reactor. Required amount of TBPB (9.6 or 25.5 µL) or TBP (12.3 µL) was added to the flask using a nitrogen-purged syringe. Proper amount of EBPA (23.5 or 117.5 µL) was added to the flask using syringe after the mixture was stirred for an hour at room temperature. The reactor was then placed to an oil bath at 70 ˚C. The reaction was continued under stirring at the speed of 400 rpm. For the polymerization runs requiring other temperatures, separated oil baths were set to 90 and 120 ˚C. The reaction was continued by switching oil baths. Ice water was employed to stop the reaction.

**6-3-4- Chain Extension Reaction:** The sample used for chain extension experiments was prepared with the molar ratio of [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP]=1000:1:0.05:0.1:0.375:0.5. The polymerization was performed for 4.5 hours at 70 ˚C and followed by 10 min at 90 ˚C and 10 min at 120 ˚C. The polymer was purified by passing the polymer solution in acetone through a column of alumina, then was precipitated out in methanol and dried in vacuum oven. The dried polymer was used as macroinitiator for the chain extension with the molar ratios of [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] =1000:0.001:0.05:0.1:0.375:0.5. Chain extension reaction was carried out at 70 ˚C for 3 hours.

## 6-4- Results and Discussion

Three different concentrations of ICAR agents (AIBN and TBPB) were applied in the following recipe: [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB]=200:1 :0.05:0.1:X:Y containing 250 ppm catalyst. Their conversion versus time profiles are shown in Figure 6-1. It can be seen that the run with a low concentration of the ICAR agents (X=0.1 and Y=0.075) reached only 77% conversion after 12 hours at 70 ˚C. It did not show any "gel effect". Because of the low ICAR concentrations, little catalyst could be regenerated after 12 hours. The conversion did not increase much with time in further reaction. Increasing the ICAR concentrations significantly accelerated the rate of polymerization, with "gel effect" occurred at about 50% conversion. For X=0.2 and Y=0.075, a maximum conversion of 94% was obtained in about 4.5 hours. For X=0.2 and Y=0.2, the rate of polymerization was even faster and the same conversion was achieved in 3 hours. It is clear that both ICAR agents decomposed at 70 ˚C and contributed the rate of polymerization. Lowering the ICAR agents concentrations decreased the concentration of primary radicals, so the rate of $CuBr_2$ reduction to CuBr slowed down, which accumulated the concentration of $CuBr_2$ during the polymerization. When deactivation reaction became diffusion-controlled, the higher deactivator concentration could partly compensate the decreased rate constant of deactivation. As a result, the rate of deactivation remained, to some extent. At the same time, because of the lower regenerated catalyst (CuBr) concentration, the rate of activation and consequently the rate of polymerization decreased. Therefore, the run with X=0.1 and Y=0.075

did not show “gel effect”. Increasing the ICAR agent concentrations led to faster regeneration of catalyst from deactivator. The higher CuBr concentration increased the rate of activation and that of polymerization as well. Furthermore, with the onset of diffusion-controlled deactivation, the concentration of radical chains increased and thus “gel effect” occurred in the system.

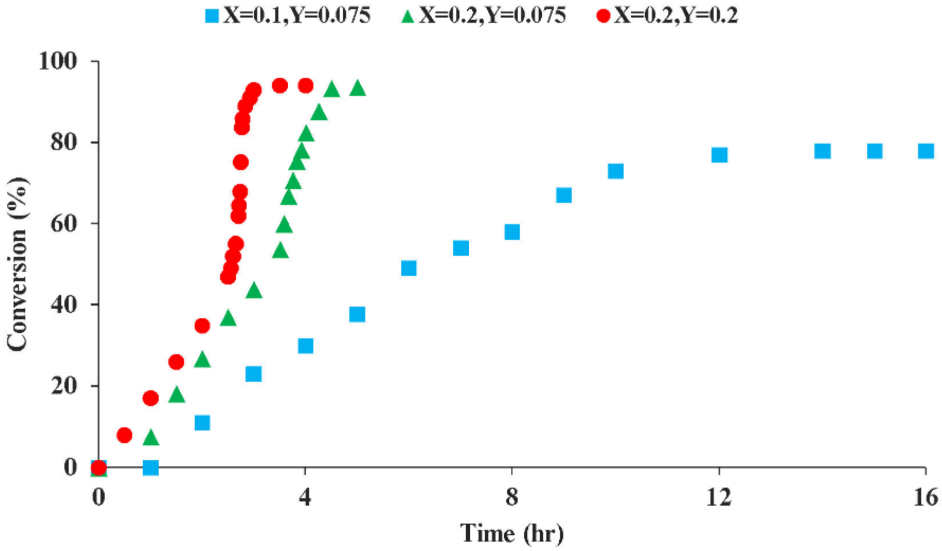


**Figure 6-1 Conversion versus time for the bulk ICAR ATRP of methyl methacrylate with [MMA]:[EBPA]:[CuBr$_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:0.05:0.1:X:Y at 70 °C.**

Figure 6-2 shows the number-average molecular weight (Mn) versus conversion data with different concentrations of the ICAR agents. For X=0.1, Y=0.075 and X=0.2, Y=0.075, a good correlation between experimental and theoretical Mn values was observed. With these two recipes, the initiator efficiencies ($I_{eff}$), estimated from the ATRP initiator only, were about 70% at the start and reached over 90% at the end of polymerization. For comparison, with X=0.2 and Y=0.2, the $I_{eff}$ was about 20% at the low conversion and increased to about 80% at the end. Loading higher ICAR agents concentrations increased the catalyst concentration and consequently increased the rate of activation reaction and thus the concentration of radicals, which increased termination and resulted in the lower $I_{eff}$. At the increased conversions, radical termination became diffusion controlled and suppressed, thus improving the initiator efficiency $I_{eff}$. The polymer chains generated from the ICAR agents also contributed the increase in $I_{eff}$ during polymerization.

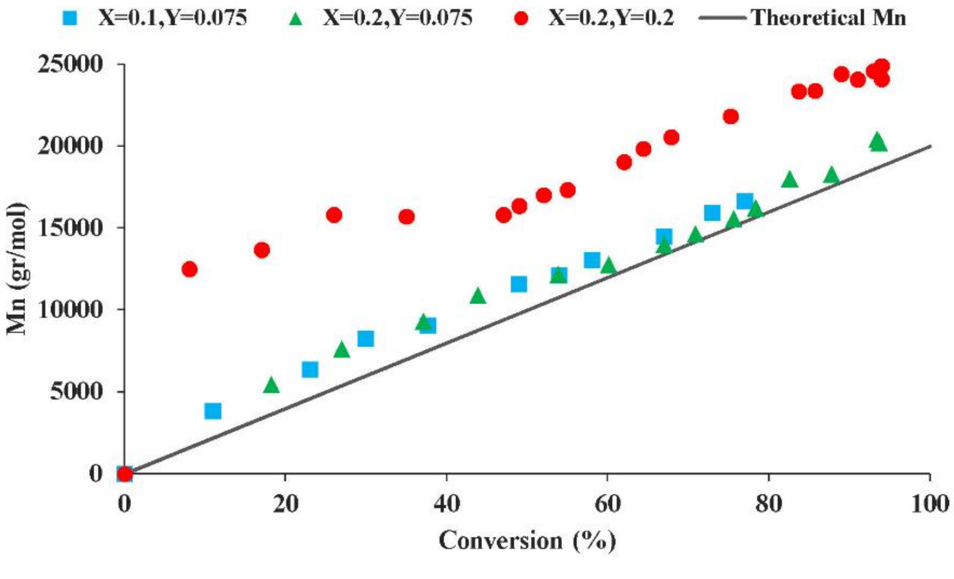


**Figure 6-2 Mn versus conversion for bulk ICAR ATRP of methyl methacrylate with [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:0.05:0.1:X:Y at 70 °C.**

Figure 6-3 shows dispersity (Đ) versus conversion for different concentrations of the ICAR agents. Decreasing the ICAR concentration improved the control of polymer molecular weight and resulted in lower dispersity's. For X=0.1 and Y=0.075, the Đ was around 1.1 throughout the course of polymerization. For X=0.2 and Y=0.075, there was a good control until about 65% conversion with Đ about 1.1. After that, the system started to lose the control. The Đ value reached to > 1.7 at the end of reaction. For X=0.2 and Y=0.2, the Đ was around 1.3 at low conversion, but increased continuously and reached about 3 at the end. This could be because of some side reactions between TBPB and catalyst, as well.[16]

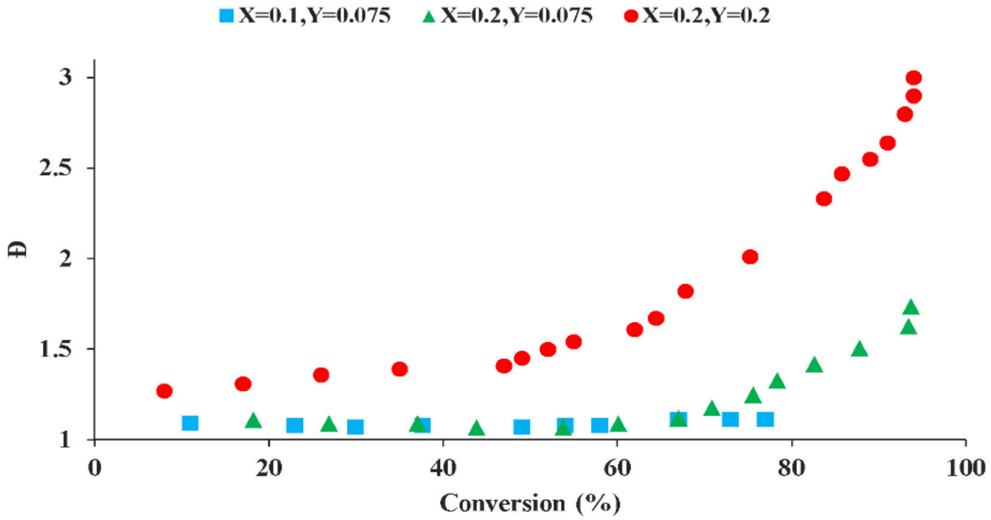


**Figure 6-3 Đ versus conversion for the bulk ICAR ATRP of methyl methacrylate with [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:0.05:0.1:X:Y at 70 °C.**

In our previous study,[15] we found that employing two ICAR agents with varying operating temperature could be helpful in regulating rate and control of the polymerization. It allowed us to lower the thermal initiator concentration at each temperature in order to keep the control of polymerization while there was adequate ICAR action to reach to high conversions at an elevated temperature, which postponed diffusion-controlled deactivation and improved the control over polymer molecular weight. As TBPB affected the rate of the polymerization even at 70 ˚C, TBP was employed which had higher decomposition temperature and did not affect the rate of the polymerization at 70 ˚C.

In this work, this temperature elevation method was employed with the following recipe: [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP]=1000:1:0.05: 0.1:0.375:0.5. It contained 50 ppm $CuBr_2$ and a ratio of 1000 monomer to ATRP initiator. AIBN and TBP were used as the ICAR agents, which had very different decomposition temperatures. AIBN was mostly responsible for ICAR at 70 ˚C, while TBP for 120 ˚C. Different concentrations for the ICAR agents were evaluated in order to find the optimal values for the control over polymer molecular weight, within a reasonable time duration. Figure 6-4 shows a representative conversion result. At 70 ˚C and remaining constant, a maximum conversion of 96% was reached in about 6 hours. The "gel effect" occurred after 3.5 hours at around 30% conversion. About 52% conversion was obtained by carrying out the reaction for 4.5 hours at 70 ˚C. Continuing the polymerization for 10 minutes at 90 ˚C led to 78% conversion. Final increasing the temperature to 120 ˚C resulted in more than

98% conversion in about 10 minutes. The temperature elevation significantly shortened the polymerization duration.

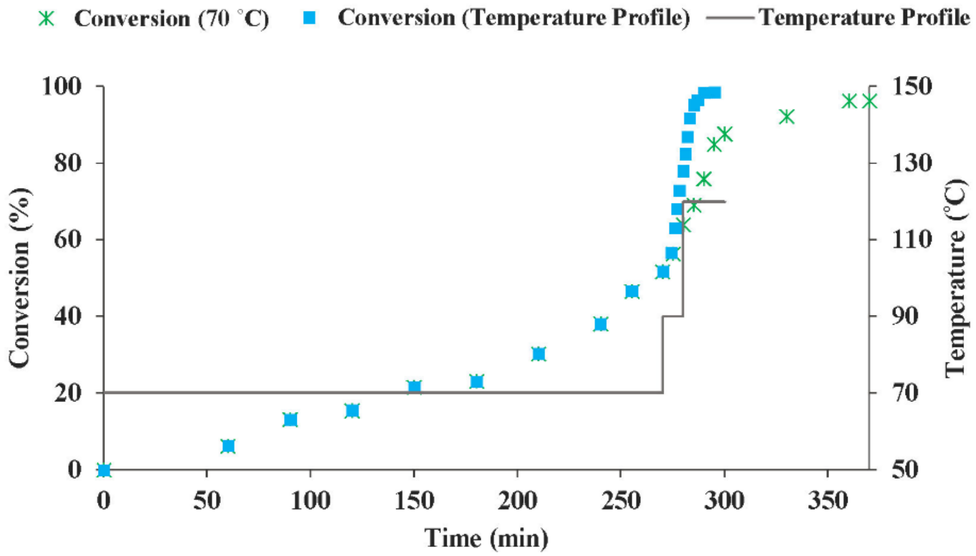


**Figure 6-4 Conversion and adjusted temperature versus time for the bulk ICAR ATRP of methyl methacrylate with [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 1000:1:0.05:0.1:0.375:0.5.**

Figure 6-5 shows the corresponding molecular weight and Đ versus conversion data. In both cases of remaining temperature versus varying temperature, there were good correlations between the experimental molecular weights with their theoretical values. The initiator efficiencies ($I_{eff}$), based on ATRP initiator only, were higher than 80% at lower conversions and reached to about 115% at the end of polymerization. It is evident that some new chains were generated through ICAR agents, causing $I_{eff}$ over 100%.

In the case of remaining temperature at 70 ˚C, Đ remained below 1.2 up to 70% conversion. It then started to increase dramatically, because of the diffusion-controlled deactivation. It reached to 2.5 at the end of reaction. In a strong contrast, increasing the temperature from 70 ˚C to 90 ˚C at 52% conversion and continuing the reaction at 90 ˚C for 10 min gave a Đ about 1.2 at 78% conversion. A final push of the temperature to 120 ˚C for another 10 min resulted in a Đ about 1.3 at 98% conversion. It was also found that, if remaining 90 ˚C for 15 min, Đ increased considerably to 1.75 at 95% conversion.

Through a systematical study, we found that by optimizing the concentrations of ICAR agents and temperature profile, it was possible to decrease the deactivator concentration to 50 ppm $CuBr_2$ but still achieve the good control over polymer molecular weight up to very high conversions in a reasonable time duration.

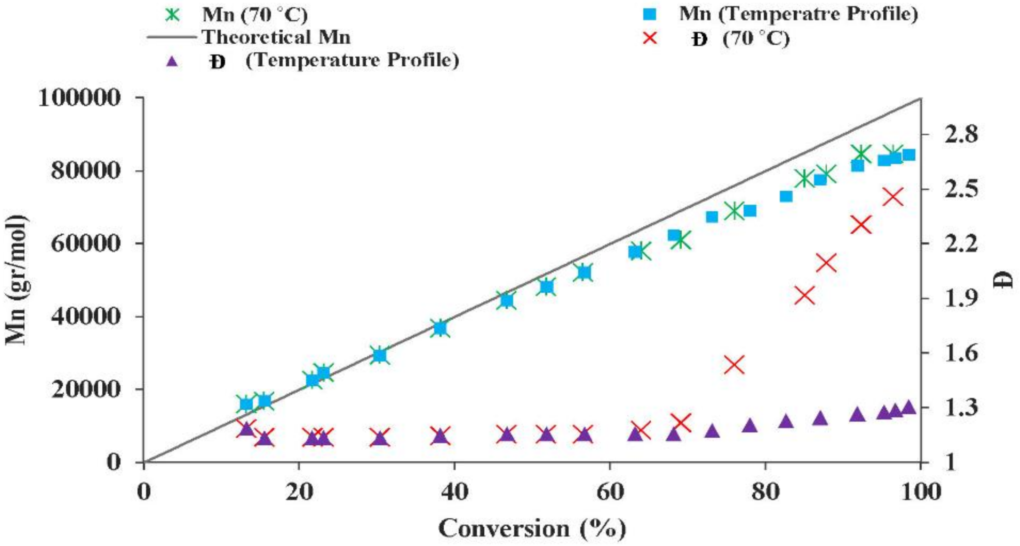


**Figure 6-5 Mn and Đ versus conversion for the bulk ICAR ATRP of methyl methacrylate with [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 1000:1:0.05:0.1:0.375:0.5 at 70 ˚C and under temperature profile.**

The polymers collected at 98% conversion were used in chain extension experiments to examine their livingness. The dried purified samples were used as a macroinitiator with the following recipe: [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP]=1000:0.001:0.05:0.1:0.375:0.5 run for 3 hours at 70 ˚C and 35% conversion. Figure 6-6 shows the chain extension result. The molecular weight increased to higher values, which proved livingness for the synthesized polymers collected at very high conversions. Diffusion-controlled termination at high conversions improved the livingness.[9,15] Furthermore, GPC curve of the macro initiator showed a very small peak at high molecular weight region, caused by the diffusion-controlled deactivation in the macro-initiator preparation,[9] where Đ increased from 1.15 to 1.3. This peak was almost disappeared after the chain extension reaction.

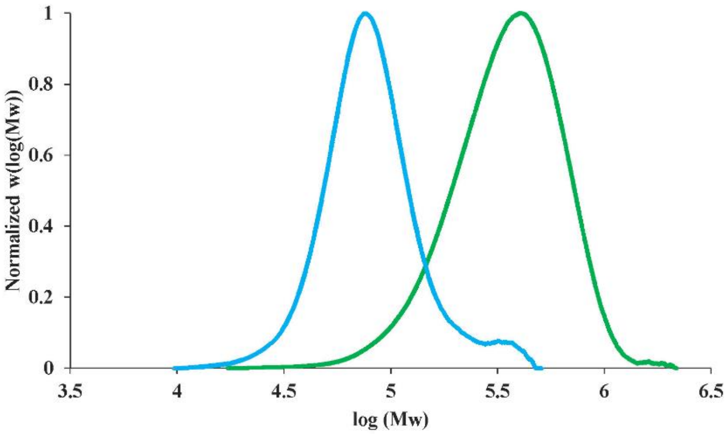


**Figure 6-6 Chain extension result of the polymer collected at 98% conversion and used as macroinitiator. Chain extension recipe was [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] = 1000:0.001:0.05:0.1:0.375:0.5 run for 3 hours at 70 °C.**

## 6-5- Conclusion

Bulk ICAR ATRP of MMA at 70 ˚C was carried out up to high conversions with different concentrations of AIBN and TBPB as ICAR agents. The system of low ICAR concentrations (X=0.1, Y=0.075 in [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBPB] = 200:1:0.05:0.1:X:Y) behaved very well with Đ about 1.1 throughout of the reaction. However, the maximum conversion was only 77% after 12 hours. Increasing the ICAR agent concentrations improved the rate of polymerization but at the cost of control over polymer molecular weight because of diffusion-controlled deactivation. With X=0.2, Y=0.075, Đ started to increase after 67% conversion and reached to 1.7 at the end of polymerization (94% conversion). With X=0.2, Y=0.2, Đ was around 1.3 at the beginning but continuously increased to 3 at 94% conversion. With [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]:[TBP] =1000:1:0.05:0.1:0.375:0.5, the monomer to initiator ratio was pushed to 1000, with only 50 ppm $CuBr_2$. The reaction was first carried out at 70 ˚C for 4.5 hours, followed by a temperature elevation to 90 ˚C for 10 min and to 120 ˚C for another 10 min. The rate of polymerization was improved significantly with the step temperature profile. A conversion of 98% was reached in less than 5 hours. The molecular weight data were very close to their theoretical values. The polymers collected at 98% conversion had Đ about 1.3. The chains were living, confirmed by a chain extension experiment. This work demonstrated that the ICAR agent concentration plays a critical role in determining the livingness of ATRP system and the control of polymer molecular weight. By optimizing the concentrations and temperature profile, high conversion bulk ATRP with fast rate and good control becomes feasible. The key is to balance the diffusion controlled reactions such as termination and deactivation, through relaxing the diffusion limitations of various reacting species and regulating the ICAR action.

## 6-6- Acknowledgement

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## 6-7- References

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow Molecular Weight Resins by a Free-Radical Polymerization Process. Macromolecules 1993, 26, 2987.

(2) Wang, J.; Matyjaszewski, K. Controlled/“Living” Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of Methyl Methacrylate with the Carbon Tetrachlorideldichlorotris (triphenylphosphine)ruthedum(II)/ Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. Macromolecules 1995, 28, 1721.

(4) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H.; South, C. Living Free-Radical Polymerization by Reversible Addition - Fragmentation Chain Transfer : The RAFT Process. Macromolecules 1998, 31, 5559.

(5) Matyjaszewski, K. Controlled Radical Polymerization : State-of-the-Art in 2011. In Controlled Radical Polymerization: Mechanisms and Techniques, American Chemical Society: Washington DC, 2012, 1.

(6) Destarac, M. Controlled Radical Polymerization: Industrial Stakes, Obstacles and Achievements. Macromol. React. Eng. 2010, 4, 165.

(7) Jakubowski, W. Adapting Atom Transfer Radical Polymerization to Industrial Scale Production: The Ultimate ATRP$^{SM}$ Technology. ACS Symp. Ser. 2012, 1100, 203.

(8) Tsarevsky, N. V.; Matyjaszewski, K. “Green” Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials. Chem. Rev. 2007, 107, 2270.

(9) Mohammad Rabea, A.; Zhu, S. Controlled Radical Polymerization at High Conversion: Bulk ICAR ATRP of Methyl Methacrylate. Ind. Eng. Chem. Res. 2014, 53, 3472.

(10) Jakubowski, W.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers. Angew. Chemie 2006, 118, 4594.

(11) Jakubowski, W.; Min, K.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization of Styrene. Macromolecules 2006, 39, 39.

(12) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP. Macromolecules 2007, 40, 1789.

(13) Faucher, S.; Zhu, S. Heterogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate at Low Metal Salt Concentrations. Ind. Eng. Chem. Res. 2005, 44, 677.

(14) He, W.; Zhang, L.; Bai, L.; Zhang, Z.; Zhu, J.; Cheng, Z.; Zhu, X. Iron-Mediated AGET ATRP of Methyl Methacrylate in the Presence of Catalytic Amounts of Base. Macromol. Chem. Phys. 2011, 212, 1474.

(15) Mohammad Rabea, A.; Zhu, S. Achieving High-Conversion Bulk ATRP with Good Livingness and Well Controlled by Design and Optimization of Polymerization Temperature Profile. Macromol. React. Eng. 2014, 8, 771.

(16) Xia, J.; Matyjaszewski, K. Homogeneous Reverse Atom Transfer Radical Polymerization of Styrene Initiated by Peroxide. Macromolecules 1999, 32, 5199.

# Chapter 7

## Ultrasonically Enhanced Bulk ATRP of Methyl Methacrylate at High Conversion with Good Livingness and Control

This chapter is organized based on the paper submitted to *AIChE Journal* by Ali Mohammad Rabea and Shiping Zhu

### 7-1- Abstract

A great challenge in controlled radical polymerization (CRP) such as atom transfer radical polymerization (ATRP) has been related to keep the livingness and molecular weight control of the reaction at high conversion, especially in bulk polymerization. The objective of this work is to investigate the effects of ultrasonic wave's frequencies on the polymerization at high conversion. The initiator for continuous activator regeneration (ICAR) ATRP is used for bulk polymerization of methyl methacrylate (MMA) as the model system. Good livingness and control up to high conversion are obtained through employing ultrasonic waves. By this method, MMA is polymerized in bulk up to "glass state" (88%) at 70 ˚C with polydispersity about 1.2 under an operating frequency of 40 kHz. Chain extension reaction proves the livingness of the synthesized polymers at glassy state.

**7-1-1- Keywords:** ATRP; high monomer conversion; gel effect; ultrasonic wave; diffusion-controlled reactions.

## 7-2- Introduction

Controlled/living radical polymerization (CRP) or reversible-deactivation radical polymerization (RDRP, as recommended by IUPAC) techniques mainly include stable free radical polymerization (SFRP) or aminoxyl-mediated radical polymerization (AMRP, IUPAC recommendation),[1] atom transfer radical polymerization (ATRP) or controlled reversible-deactivation radical polymerization (as recommended by IUPAC)[2,3] and reversible addition fragmentation chain transfer (RAFT) polymerization or degenerate-transfer radical polymerization (IUPAC recommendation).[4] These techniques are among the most rapidly expanding areas of polymer science and engineering due to their capability of synthesizing well-controlled functional polymers. The number of publications using CRP methods and particularly ATRP, has been increased notably during recent years, proving their high potential applications in different areas.[5] However, in spite of enormous industrial interest in employing these methods and especially ATRP, its commercial application is still limited particularly because of high catalyst loading and limited conversion.[6-9] High catalyst concentration problem has been solved to some extent by developing newer ATRP methods such as activator regenerated by electron transfer (ARGET) ATRP,[10,11] initiator for continuous activator regeneration (ICAR) ATRP,[12] supplemental activator and reducing agent (SARA) ATRP,[13] photochemically mediated ATRP[14] and electrochemically mediated ATRP.[15] Limited conversion problem has been attributed to diffusion-controlled deactivation reaction, which happens at high conversion especially in bulk polymerization, causing loss of control of the reaction.[9,16] In order to moderate this problem, solution polymerization is mostly employed or the reaction is stopped at medium conversion. However, separation of polymer from solvent and residual monomer is costly and not environmental friendly.

Recently, we launched a research program in order to find strategies to achieve high conversion in bulk system while keeping livingness and control of the polymerization. It was found that temperature profile could be employed as a useful method in order to postpone the diffusion-controlled deactivation reaction to higher conversion.[17] The results showed that increasing the polymerization temperature before the deactivation reaction became diffusion controlled, could help to preserve the control of polymerization up to higher conversion, while diffusion-controlled termination guaranteed the livingness of polymerization. In another study,[18] it was observed that in ICAR ATRP, ICAR agents could significantly affect the rate and control of polymerization through influencing the rate of catalyst regeneration. Also, by optimizing both ICAR agent concentration and reaction temperature profile, it could be possible to decrease the catalyst concentration to a ppm level and synthesize polymers at high conversion with good livingness and control.

In this work, as another strategy, ultrasonic (US) waves are employed in order to improve homogeneity of the reaction medium and diffusivity of the reactants, in hope of enhancing the control of polymerization. Ultrasound irradiations with frequencies between 20 kHz and 1 MHz have been employed in different chemical reactions[19] and polymerizations[20-22] to improve the rate and selectivity. The major benefits of using US arise from the acoustic cavitation phenomenon and acoustic streaming. Acoustic cavitation causes the formation, growth and implosive collapse of bubbles in a liquid medium, leading to extremely high local temperature and pressure. Under this condition, the efficiency of conventional chemical reactions is improved. Acoustic streaming enhances the transport rates of heat, mass and momentum, and provide more homogeneous medium.[23] In this paper, ultrasonic waves are employed in order to improve the control of polymerization at high conversion.

## 7-3- Experimental Section

**7-3-1- Materials:** Methyl methacrylate (MMA, 99%) as monomer, 4,4′-dinonyl-2,2′-dipyridyl (dNbpy, 97%) as ligand, $CuBr_2$ (99.999%) as deactivator, ethyl (α-bromophenyl) acetate (EBPA) ATRP initiator and azobisisobutyronitrile (AIBN, 99%) as ICAR agent were purchased from Sigma-Aldrich and used without any further purification except for MMA which was distilled under vacuum and AIBN which was recrystallized from methanol and stored at -20 °C.

**7-3-2- Instrumentation:** Monomer conversion was estimated using $^1$H NMR spectra. Diluted polymer-acetone solution in d-chloroform ($CDCl_3$) was run on a Bruker AV-200 spectrometer at 200 MHz. The intensity ratio of methoxy group signals of polymer (3.60 ppm) over the polymer and monomer (3.75 ppm) was announced as the conversion.

Gel permeation chromatography (GPC) was used for measuring the number average molecular weight (Mn) and polydispersity index (PDI) (or dispersity Đ, as recommended by IUPAC). GPC was built of Waters 2690 autoinjector with three linear columns in series (Waters Styragel HR 2, 3 and 4) and a 2410 RI detector, calibrated with a set of narrow polymethyl methacrylate standards and with THF as effluent at a fixed flow rate of 1 mL/min. The polymer samples were run through the machine and data were recorded by Waters Millennium software package for further manipulation.

**7-3-3- Polymerization:** The bulk ICAR ATRP of MMA with the molar ratios of [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 was performed as follow. A disposable borosilicate glass tube with inner diameter, height and thickness of 11.34, 125 and 0.6 mm, respectively, was loaded with appropriate amount of $CuBr_2$ (0.00175 gr), dNbpy (0.00641 gr), AIBN (0.00767 gr) and MMA (3.135 gr). The reactor was sealed with rubber septum and degassed by several cycles of vacuum-nitrogen. Then, the sample was placed in a Branson Bath Sonicator CPX2800H operating at 40 kHz for 15 min at room temperature in order to make a homogeneous solution. Required amount of EBPA (27.4 µL) was added to the flask using a nitrogen-purged syringe. The reactor was then placed in the sonication bath (Branson Bath Sonicator CPX2800H) at 70 ˚C. A four-Hotwatt cartridge immersion heater with power of 300 W, connected to a Benchtop Temperature Controller Omega CSi32 was used in order to keep the temperature of the sonication bath at 70 ˚C during the polymerization. Three different ultrasonic frequencies of 0 (no sonication), 28 and 40 kHz were applied and the reactions were continued and repeated for different times. Ice water was used to stop the reaction. For measuring the temperature inside the reactor during the polymerization, a Teflon covered T-type thermocouple connected to a Temperature Data Logger OM-CP-TC101A, was placed in the middle of the reactor and inside the polymerization medium. The temperature was recorded every second.

**7-3-4- Chain Extension Reaction:** For operating frequencies of 0, 28 and 40 kHz, polymerization was carried out at 70 ˚C for 5, 4 and 4.5 hours, respectively, until the conversion was about 88%. The purified polymers were obtained by passing the polymer solutions in acetone through a column of alumina, precipitating in methanol and drying in vacuum oven. The dried polymers were used as macroinitiator in the recipe with the molar ratios of [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN] = 200:0.01:0.05:0.1:0.3. Chain extension reactions were carried out inside the sonication bath with the operating frequency of 40 kHz at 70 ˚C for 2.5 hours.

## 7-4- Results and Discussion

Polymerization runs were carried out under three different ultrasonic frequencies (0, 28 and 40 kHz). Figure 7-1 shows their conversion versus time curves. As evident, there was an induction period for around one hour in the beginning of all polymerization conditions. This was because it took time for the AIBN to decompose and reduce Cu(II) to Cu(I) in order to start the polymerization and establish a dynamic equilibrium between species.[24] Comparison between the conversion curves at different ultrasonic frequencies revealed that the rate of polymerization was faster at frequency of 28 kHz than the other frequencies. Ultrasonic waves improve the homogeneity of the polymerization medium and increase the collision rate of the reactants, leading to higher rate of the polymerization. On the other side, higher frequencies increase the concentration of the dissolved deactivator (Cu(II)) in the polymerization medium. So, it makes the induction period longer and moderates the effects of the “gel effect” on the rate of polymerization.[9] Therefore, the rate of polymerization was faster under the frequency of 28 kHz than the situation without any sonication. However, by increasing the frequency to 40 kHz, because of higher concentration of the dissolved catalyst, the rate of reaction was slower and the induction period was longer. The difference was confirmed by many repeated experiments.

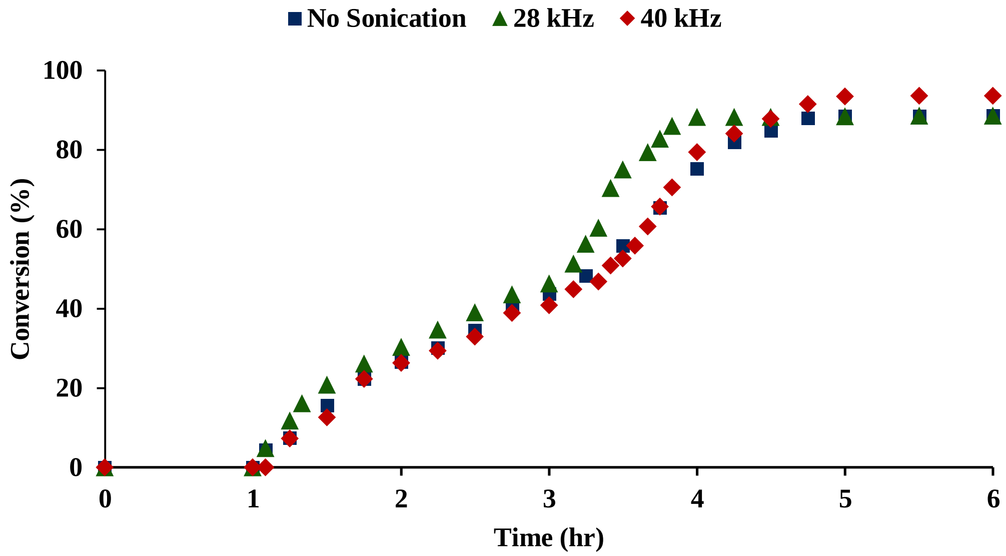

**Figure 7-1 Conversion versus time for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 under different ultrasonic frequencies at 70 °C.**

It is clear that autoacceleration occurred at about 50% conversion under different frequencies. At this conversion, diffusion-controlled deactivation happened in the system, leading to higher concentration of the free radicals and consequently higher rate of the polymerization which was discussed in detail in previous study.[9]

For the polymerization without any sonication and that under the operating frequency of 28 kHz, the limited conversions of 89% were obtained. For the ultrasonic frequency of 40 kHz, about 88% conversion was obtained after performing reaction for 4.5 hr at 70 ℃, then the limited conversion of 94% was reached after additional 2 hr. This was because the polymerization temperature was below the glass transition temperature of the synthesized polymer and “glass effect” happened in the system.

Figure 7-2 shows the temperature profiles inside the reactors and in the middle of the polymerization medium during the polymerization.

The temperature was about 70 °C throughout of the reaction and even when autoacceleration happened in the system. As the purpose of this study was about the investigation of using ultrasonic waves for the rate and control of ATRP, different reactor types had been tried for the polymerization and temperature profiles inside the reactors were measured, in order to find the best one based on the heat transfer. When “glass effect” happened during the polymerization, for the systems under ultrasonic operation, the temperature increased inside the reactor and the situation was more severe under higher ultrasonic frequency. Under operating frequency of 28 kHz, the temperature increased after about 4 hr (around 88% conversion) and reached to a maximum of 74 °C. For the other system, under ultrasonic frequency of 40 kHz, the temperature was increased after about 4.5 hr (88% conversion) and reached to more than 90 °C. This increase in temperature pushed the polymerization to higher conversion (about 94%).

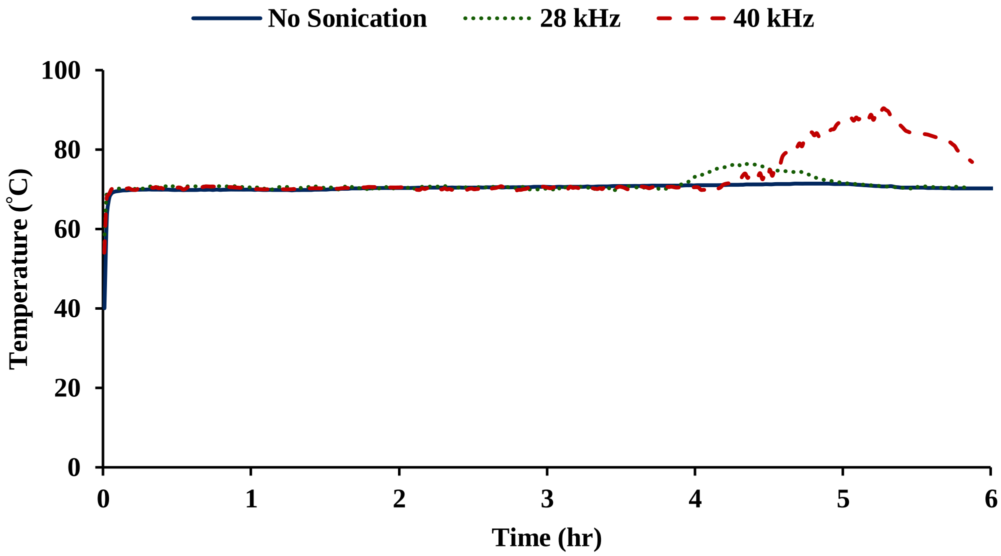

**Figure 7-2 Temperature profiles inside the reactors for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 under different ultrasonic frequencies at 70 °C.**

Figure 7-3 shows the number-average molecular weight (Mn) and Figure 7-4 shows PDI versus conversion, respectively. Under different conditions, a good correlation between the Mn experimental and theoretical values was observed. The initiator efficiency ($I_{eff}$) was increased slightly during the polymerization, which could be attributed to the ICAR agent.[9,17] Figure 7-4 shows that PDI was around 1.1 under different ultrasonic frequencies before "gel effect". When diffusion-controlled deactivation happened during the polymerization, PDI started to increase. For the system without any sonication, PDI increased to more than 2 at the end of the reaction. Using ultrasonic waves moderated the rate of PDI increase after "gel effect". For the ultrasonic frequency of 28 kHz, the PDI was around 1.7 at glassy state and for 40 kHz, the PDI was about 1.2 at 88% conversion which showed the good control of the polymerization in that high conversion. However, when the temperature inside the reactor was increased, leading to higher conversion (about 94%) and lack of control. The PDI at the end was around 1.6. It is clear that when the temperature inside the reactors was 70 ˚C, using higher ultrasonic frequency was lead to better control all over the polymerization.

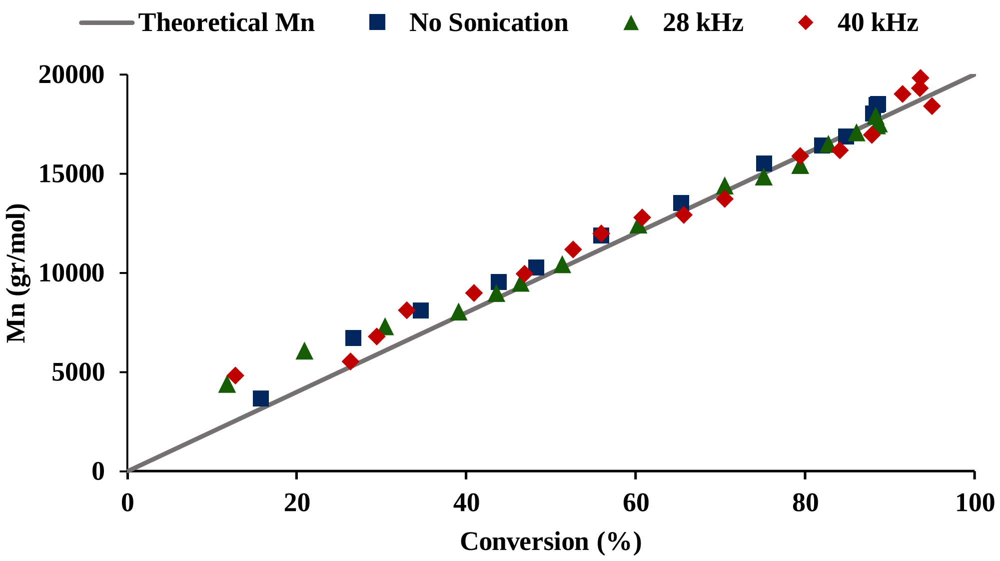

**Figure 7-3 Mn versus conversion for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 under different ultrasonic frequencies at 70 ˚C.**

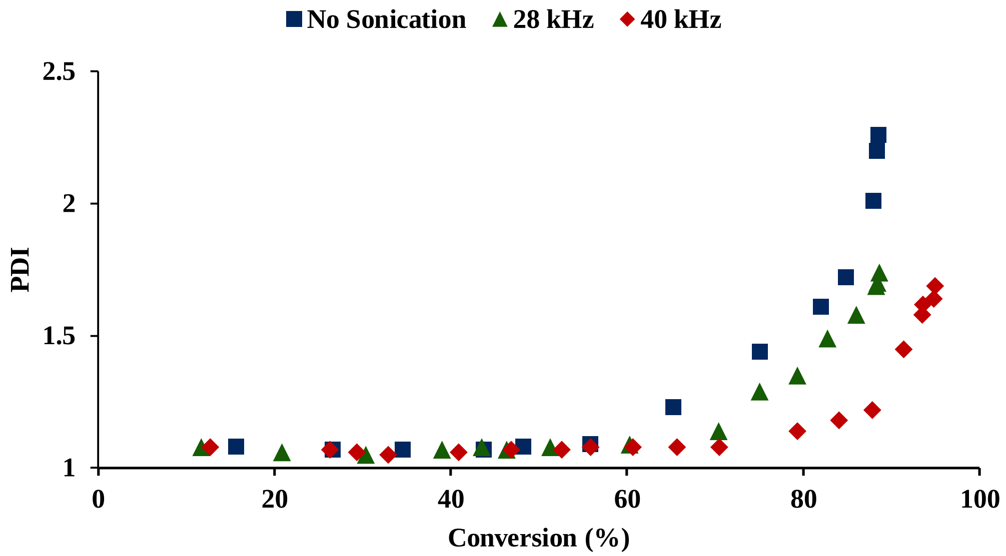

**Figure 7-4 PDI versus conversion for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[$CuBr_2$]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 under different ultrasonic frequencies at 70 °C.**

Figure 7-5 shows the representative GPC curves for the samples collected at 88% conversion under different ultrasonic frequencies. The sample without sonication had a bimodal broad peak with PDI more than 2. This problem had been attributed to diffusion-controlled deactivation reaction, which was discussed before.[9,17] For the sample under operating frequency of 28 kHz, the result was better and the PDI was about 1.7. However, the presence of the high molecular weight tail was still clear, because of the “gel effect”. The best result was obtained by using ultrasonic frequency of 40 kHz. It showed a narrow peak with PDI around 1.2. It becomes clear that using ultrasonic waves can develop the control of polymerization up to high conversion through enhancing homogeneity and solubility of the catalyst and also improving diffusivity of the reactants inside the reactor.

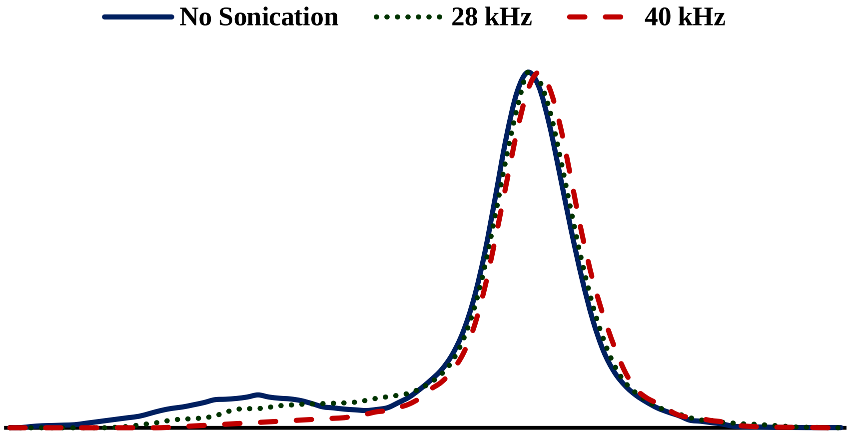

**Figure 7-5 GPC curves for bulk ICAR ATRP of MMA [MMA]:[EBPA]:[CuBr2]:[dNbpy]:[AIBN]=200:1:0.05:0.1:0.3 under different ultrasonic frequencies at 88% conversion.**

Polymer livingness of the samples collected at 88% conversion under different ultrasonic frequencies was examined by chain extension experiment. The samples were purified and used as macroinitiator for the chain extension using the following recipe: [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN] = 200:0.01:0.05:0.1:0.3. Chain extension reaction was performed inside the sonication bath with the ultrasonic frequency of 40 kHz for 2.5 hours at 70 ˚C. Figure 7-6 shows the chain extension results. Molecular weights of the polymers, synthesized under different ultrasonic frequencies, were clearly increased, proving the livingness of the polymer chains. Diffusion-controlled termination, which occurs during the polymerization, suppresses chain termination and keeps the livingness of the chains. It somewhat compensates the loss of control and the increase in PDI caused by the diffusion-controlled deactivation of the propagating radicals.[9,17]

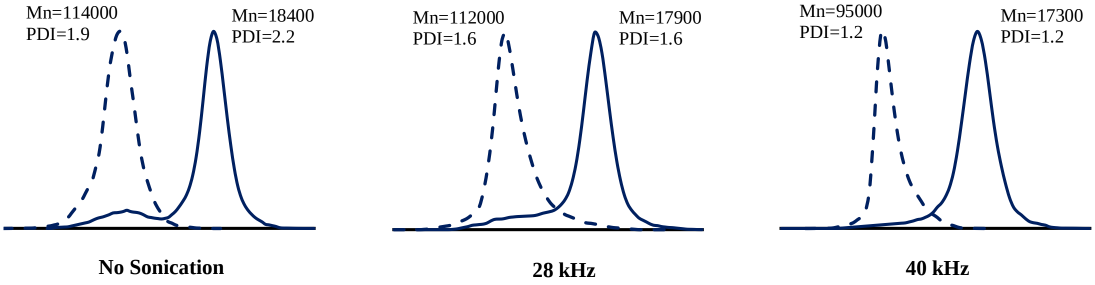

**Figure 7-6 Chain extension results with the samples collected at 88% conversion as macroinitiators under different ultrasonic frequencies. Chain extension recipe was [MMA]:[PMMA]:[$CuBr_2$]:[dNbpy]:[AIBN] = 200:0.01:0.05:0.1:0.3 under operating frequency of 40 kHz at 70 ˚C for 2.5 hours.**

### 7-5- Conclusion

Bulk ICAR ATRP of MMA was performed up to high conversions under different ultrasonic frequencies at 70 ˚C. The rate of the polymerization was faster by employing ultrasonic frequency of 28 kHz than the situation without sonication. However, the rate of the reaction was decreased by further increasing the frequency to 40 kHz. Under different situations, “gel effect” and “glass state” were occurred at about 50% and 88% conversion, respectively. For the polymerization under the operating frequency of 40 kHz, after reaching to “glass state” at 70 ˚C, the conversion was further increased to 94% due to the temperature increase inside the reactor.

Under different frequencies, there was a good correlation between the experimental and theoretical molecular weights of the synthesized polymers. At low to medium conversion, the PDI was around 1.1 for the polymerization using different ultrasonic waves. However, because of the diffusion-controlled deactivation reaction, for the situations without sonication and under the frequency of 28 kHz, the PDI was increased to more than 2 and 1.7 at the “glass state”, respectively. For the frequency of 40 kHz, the PDI was about 1.2 at about 88% conversion, showing the good control of molecular weight under this condition. After the increase in temperature inside the reactor, PDI was increased to about 1.6 at 94% conversion. Chain extension experiment confirmed the livingness of the polymer chains, collected at glassy state.

This work demonstrated that employing ultrasonic waves could be helpful in order to keep the control and livingness of the reaction up to high conversion through improving homogeneity of the polymerization medium and diffusivity of the reactants during the polymerization and especially after on the onset of diffusion-controlled deactivation in the system.

### 7-6- Acknowledgements

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### 7-7- References

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow Molecular Weight Resins by a Free-Radical Polymerization Process. Macromolecules 1993, 26, 2987.

(2) Wang, J.; Matyjaszewski, K. Controlled/“Living” Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. J. Am. Chem. Soc. 1995, 117, 5614.

(3) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimuras, T. Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris(triphenylphosphine)ruthedum(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization. Macromolecules 1995, 28, 1721.

(4) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. Macromolecules 1998, 31, 5559.

(5) Matyjaszewski, K. Controlled Radical Polymerization: State-of-the-Art in 2014. In Controlled Radical Polymerization: Mechanisms. ACS Symposium Series 2015, 1.

(6) Destarac, M. Controlled Radical Polymerization: Industrial Stakes, Obstacles and Achievements. Macromol. React. Eng. 2010, 4, 165.

(7) Jakubowski, W. Adapting Atom Transfer Radical Polymerization to Industrial Scale Production: The Ultimate ATRP$^{SM}$ Technology. ACS Symposium Series 2012, 1100, 203.

(8) Tsarevsky, N. V.; Matyjaszewski, K. “Green” Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials. Chem. Rev. 2007, 107, 2270.

(9) Mohammad Rabea, A.; Zhu, S. Controlled Radical Polymerization at High Conversion: Bulk ICAR ATRP of Methyl Methacrylate. Ind. Eng. Chem. Res. 2014, 53, 3472.

(10) Jakubowski, W.; Matyjaszewski, K. Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers. Angew. Chemie 2006, 118, 4594.

(11) Min, K.; Gao, H.; Matyjaszewski, K. Use of Ascorbic Acid as Reducing Agent for Synthesis of Well-Defined Polymers by ARGET ATRP. Macromolecules 2007, 40, 1789.

(12) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. a; Tsarevsky, N. V. Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents. Proc. Natl. Acad. Sci. U.S.A. 2006, 103 (42), 15309.

(13) Zhang, Y.; Wang, Y.; Matyjaszewski, K. ATRP of Methyl Acrylate with Metallic Zinc, Magnesium, and Iron as Reducing Agents and Supplemental Activators. Macromolecules 2011, 44 (4), 683.

(14) Tasdelen, M. A.; Uygun, M.; Yagci, Y. Photoinduced Controlled Radical Polymerization in Methanol. Macromol. Chem. Phys. 2010, 211 (21), 2271.

(15) Magenau, A. J. D.; Bortolamei, N.; Frick, E.; Park, S.; Gennaro, A.; Matyjaszewski, K. Investigation of Electrochemically Mediated Atom Transfer Radical Polymerization. Macromolecules 2013, 46, 4346.

(16) Mohammad Rabea, A.; Zhu, S. Modeling the Influence of Diffusion-Controlled Reactions and Residual Termination and Deactivation on the Rate and Control of Bulk ATRP at High Conversions. Polymers 2015, 7, 819.

(17) Mohammad Rabea, A.; Zhu, S. Achieving High-Conversion Bulk ATRP with Good Livingness and Well Controlled by Design and Optimization

of Polymerization Temperature Profile. Macromol. React. Eng. 2014, 8, 771.

(18) Mohammad Rabea, A.; Zhu, S. Pushing Monomer Conversions High in Bulk ATRP: The Effects of ICAR Concentration on the System Livingness and Polymer Molecular Weight Control. In Controlled Radical Polymerization: Mechanisms. ACS Symposium Series 2015, 159.

(19) Cravotto, G.; Cintas, P. Power Ultrasound in Organic Synthesis: Moving Cavitational Chemistry from Academia to Innovative and Large-Scale Applications. Chem. Soc. Rev. 2006, 35, 180.

(20) Liao, Y.; Wang, Q.; Xia, H.; Xu, X.; Baxter, S. M.; Slone, R. V.; Wu, S.; Swift, G.; Westmoreland, D. G. Ultrasonically Initiated Emulsion Polymerization of Methyl Methacrylate. J. Polym. Sci. Part A Polym. Chem. 2001, 39, 3356.

(21) Kojima, Y.; Koda, S.; Nomura, H. Effect of Ultrasonic Frequency on Polymerization of Styrene under Sonication. Ultrason. Sonochemistry 2001, 8, 75.

(22) Kojima, Y.; Koda, S.; Nomura, H.; Kawaguchi, S. Effect of Sonication on Nitroxide-Controlled Free Radical Polymerization of Styrene. Ultrason. Sonochemistry 2001, 8, 81.

(23) Crum, L. A.; Mason, T. J.; Reisse, J. L.; Suslick, K. S. Sonochemistry and Sonoluminescence; Springer 1998.

(24) Zhu, G.; Zhang, L.; Zhang, Z.; Zhu, J.; Tu, Y.; Cheng, Z.; Zhu, X. Iron-Mediated ICAR ATRP of Methyl Methacrylate. Macromolecules 2011, 44, 3233.

# Chapter 8

# Research Contributions and Recommendations for Future Work

## 8-1- Significant Research Contributions of Thesis Work

This thesis work has made a number of significant contributions to the atom transfer radical polymerization (ATRP) area. These contributions are summarized as follow:

In Chapter 3, the bulk ICAR ATRP of MMA up to high conversion was conducted with different deactivator concentrations from 50 to 250 ppm. Two thermal initiators, AIBN and TBPB, were employed as ICAR agents. The polymerization was run at 70 °C up to the glass state and then higher conversion was achieved by elevating temperature to 120 °C. AIBN acted as the low temperature ICAR agent, while TBPB was for the high temperature. The bulk system behaved very well at low monomer conversions, with good livingness and control. However, it experienced “gel effect” (autoacceleration in the rate) started at about 50% conversion. The gel effect was caused by diffusion-controlled deactivation, it was accompanied with the loss of control over polymer molecular weight, leading to the broadening of molecular weight distribution. Increasing deactivator concentration compensated the loss of molecular weight control to some extent for a price of decreasing the rate of polymerization. The system also experienced glass effect about 94% conversion at 70 °C. At this stage, not only termination and deactivation, but also propagation and activation as well as ICAR reactions became diffusion controlled. Elevating temperature to 120 °C released the diffusion constraints and pushed the final conversion up to 98%. The ultimate concern of this work was the livingness and control of the ATRP system at high conversions, which could be improved through design and optimization of thermal history in the polymerization. Chain extension experiments demonstrated that the polymers were still living, although they did not have very narrow molecular weight distributions.

In Chapter 4, the influences of diffusion controlled reactions and residual termination and deactivation were systematically investigated on bulk ATRP using modeling approach. It was found that radical termination becomes diffusion controlled at a relatively low conversion. It is because termination involves two chain species and, at the same time, it has the highest rate constant among all the reactions. Diffusion-controlled termination increases radical concentration and thus polymerization rate slightly. At higher conversion, translational diffusion of chains may be totally limited but still the radical centers can move around through the activation/deactivation cycles, and by propagation. However, influence of the residual termination on polymerization rate and molecular weight control is negligible. After termination, deactivation becomes diffusion controlled. Although both deactivation and activation reactions involve large chain and small catalyst species, the deactivation onsets diffusion control earlier because its rate constant is several orders of magnitude higher than that of activation. Diffusion-controlled deactivation dramatically increases the radical concentration, causing a severe auto-acceleration in the rate of polymerization ("gel effect"). It is also responsible for the loss of control over polymer molecular weight. However, the migration of radical centers through propagation can also facilitate the deactivation to some extent. This residual deactivation helps to lower PDI and improves the control at high conversions. Diffusion-controlled activation and propagation happen at very high conversion when the system approaches to its glassy state. Depending on the relative sizes and diffusivities of monomer and catalytic species, either one can become diffusion controlled earlier than the other to stop polymerization, leading to a "dead-end polymerization".

In Chapter 5, the bulk ICAR ATRP of MMA was carried out up to high conversion with different temperature profiles. Both thermal initiators, AIBN and TBP, were employed as ICAR agents. High conversions were achieved by running polymerization at 70 ˚C and continuing at elevated temperature of 90 ˚C and/or 120 ˚C. The ATRP at 70 ˚C behaved very well with good livingness and control. However, the final conversion was limited because of low concentration AIBN as ICAR agent. Running the polymerization at 70 ˚C and increasing the temperature to 90 ˚C and then 120 ˚C, before the onset of diffusion-controlled deactivation in the system, resulted in 98% conversion with polymer products having PDI's <1.3.

The polymers were living, confirmed by chain extension experiments. It was concluded that at high conversions, various reactions become diffusion controlled sooner or later. While diffusion-controlled termination suppresses termination of radical chains and helps polymer livingness, diffusion-controlled deactivation causes problems for the control of polymer molecular weight. In ICAR ATRP, the deactivator concentration must be precisely regulated by the ICAR reaction. If the regeneration of CuBr is too slow, too much $CuBr_2$ would be accumulated and thus stop the polymerization. On the other side, if CuBr regeneration is too fast, the rate of polymerization would increase at the cost of losing control. Through optimizing the ICAR rate by designed temperature profile, the bulk ATRP with good livingness and control is achievable.

In Chapter 6, the bulk ICAR ATRP of MMA at 70 ˚C was carried out up to high conversions with different concentrations of AIBN and TBPB as ICAR agents. The system of low ICAR concentrations behaved very well with PDI about 1.1 throughout of the reaction with a limited conversion of 77%. Increasing the ICAR agent concentrations improved the rate of polymerization but at the cost of losing control over polymer molecular weight because of diffusion-controlled deactivation. By optimizing the ICAR agents concentrations and employing step temperature profile, MMA was polymerized in bulk using 1000 molar ratio of monomer to initiator and in the presence of only 50 ppm catalyst. A maximum 98% conversion was reached in less than 5 hours with PDI about 1.3. The chains were living, confirmed by chain extension experiment. It was demonstrated that ICAR agent concentration plays a critical role in the control of polymer molecular weight. By optimizing the concentrations and temperature profile, high conversion bulk ATRP with fast rate and good control becomes feasible.

In Chapter 7, the bulk ICAR ATRP of MMA was performed up to high conversions under different ultrasonic frequencies at 70 ˚C. Under different situations, “gel effect” and “glass state” occurred at about 50% and 88% conversions, respectively. At low to medium conversion, the PDI was around 1.1 for the polymerization using different ultrasonic waves. However, because of the diffusion-controlled deactivation reaction, for the situations without sonication and under the frequency of 28 kHz, the PDI was increased to more than 2 and 1.7 at glassy state, respectively. For the frequency of 40 kHz, the PDI was about 1.2 at about 88% conversion, showing the good control of molecular weight under this condition. Chain extension experiment confirmed the livingness of the synthesized polymers collected at “glass state”. This work demonstrated that employing ultrasonic waves could be helpful in order to keep the control and livingness of the polymerization up to high conversion through improving homogeneity of the polymerization medium and diffusivity of the reactants during the polymerization, especially after the onset of diffusion-controlled deactivation in the system.

## 8-2- Recommendations for Future Research

This thesis consists of studies on the effects of diffusion controlled reactions on the rate and control of ATRP systems at high conversion experimentally and through modeling. It also demonstrated some strategies in order to keep the control of the polymerization up to high conversion. The future research activities in this area should be directed to, 1) investigating the similar strategies for other methods of the ATRP as well as other CRP such as NMP and RAFT, and 2) developing models for high-conversion ATRP processes.

### 8-2-1- Investigating the Similar Strategies for Other Methods of the ATRP and CRP

This thesis focused on ICAR ATRP in order to find the methods to keep the control of polymerization up to high conversion. The presence of ICAR agents gives the possibility of adjusting the rate of deactivator reduction and consequently the rate of polymerization through changing the polymerization temperature. Furthermore, it would be possible to use different ICAR agents at the same time with different temperature dissociation. However, as it has been mentioned in Chapter 1, the limitation of ICAR-ATRP appeared, during the synthesis of block copolymers, that the radicals generated by normal initiator can initiate new polymer chains. Finding similar strategies for other methods of the ATRP, especially ARGET-ATRP, could be helpful for synthesizing different block co-polymers. We tried regular reducing agents for ARGET-ATRP in this study, but unfortunately none of them led to a successful polymerization up to high conversion. It means that designing or finding special reducing agents could be critical in order to reach to high conversion with good livingness and control. Employing different reducing agents with different solubility in monomer and synthesized polymer, or with various operating temperatures would be helpful, as well. The work can also be extended to the other types of CRP such as NMP and RAFT.

### 8-2-2- Developing Models for High-Conversion ATRP Process

It must be pointed out that diffusion-controlled reactions at high conversion are very complicated. In Chapter 4, it was tried to investigate the effects of different diffusion-controlled reactions and residual termination and deactivation on the rate and control of polymerization. It was found that because of the lack of experimental data about the values of different parameters during the polymerization, especially at high conversion, generalizing the model to the experimental data was impossible. Measuring the values of different rate constants during the polymerization at high conversion could be really helpful in order to model the experimental values. The developed model could be employed to investigate the effects of different parameters such as reactants concentrations and temperature on the rate and control of polymerization. Furthermore, the developed model could be used for the investigation of different monomers in order to find the optimum situations for the reactants concentrations and temperature without running so many different experiments.