Abstract

This chapter reports the synthesis of poly(methyl methacrylate) via Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) and studies the effect of solvents and temperature on its polymerization kinetics. ARGET ATRP of methyl methacrylate (MMA) was carried out in different solvents and at different temperatures using $CuBr_2$ as catalyst in combination with N, N, N´, N´´, N´´-pentamethyldiethylenetriamine (PMDETA) as a ligand. Methyl 2-chloro propionate (MCP) was used as ATRP initiator and ascorbic acid was used as a reducing agent in the ARGET ATRP of MMA. The conversion was measured gravimetrically. The semilogarithmic plot of monomer conversion vs. time was found to be linear indicating that the polymerization follows first order kinetics. The linear polymerization kinetic plot also indicates the controlled nature of the polymerization. DMF, THF, Toluene and methyl ethyl ketone were used as solvents to study the effect on the polymerization kinetics. The effect of temperature on the kinetics of the polymerization was also studied at various temperatures. It has been observed that polymerization followed first order kinetics in every case. The rate of polymerization was found to be highest (k_{app}= 6.94 x 10^{-3} min^{-1}) at a fixed temperature when DMF was used as solvent. Activation energies for ARGET ATRP of MMA were also calculated using the apparent rate constant values at two different polymerization temperatures.

3.1. Introduction:

Over past few years, controlled radical polymerization (CRP) has become one of the most versatile methods for the synthesis of well-defined polymer composition, architectures, and functionalities.[179–182] The development of CRP techniques in the past decade has attracted the synthetic polymer scientists to synthesize novel polymers with controlled and desired properties.[180, 183, 184] In past few years, it has been witnessed rapid development of few new CRP methods. All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species.[185] There are three major CRP methods. They are (1) atom transfer radical polymerization (ATRP) or degenerative transfer, when dormant species are alkyl halides, (2) reversible addition-fragmentation chain transfer process, and (3) nitroxide mediated polymerization or stable free radical polymerization, where dormant chains are thioesters and alkoxyamines, respectively.[186–190] Among the different CRP, ATRP is the most commonly used polymerization technique. It is applied to polymerize a wide range of monomers at a wide range of polymerization temperature (−20 to 200◦C).[191,192] Also, the reagents used in ATRP are commercially available.[179,193] ATRP has successfully been applied to synthesize a wide range of polymers with varied molecular weights, different architectures, functionalities, and dispersity. Transition metal catalyzed CRP (commonly known as ATRP) is an important CRP method.[92, 194] ATRP is carried out in the presence of an active alkyl halide using a transition metal halide as catalyst in combination with a suitable ligand.[192] There are several reports on the polymerization of different acrylate monomers using ATRP.[185, 193–196] ATRP is a repetitive transfer process of a halogen or pseudo-halogen atom between an alkyl halide R–X and a redox active transition metal complex Cu(I)X/ligand. The active species or radicals are generated by homolytic cleavage of alkyl halide R–X and are catalyzed by the transition metal complex (Cu(I)X/ligand). This process occurs with a rate constant for activation (ka), propagation (kp), deactivation (kd), and the growing radicals terminate either by disproportionation or recombination (rate constant kt).[179, 180, 185, 198] In this process, the atom transfer step is the key elementary reaction step responsible for the uniform growth of the polymeric chains.[185] The presence of a metal catalyst limits the wider application of ATRP. However, attempts were made to recycle and reduce the use of catalysts.[198] These catalysts may add high cost to production, which may cause undesired cost to polymer.[183] Moreover, high conversions with control of polymer molecular weight become difficult with normal or conventional ATRP.[179] So, different modified methods were developed with an aim either to reduce the concentration of catalyst or use of higher oxidation state air-stable catalyst. Few such methods are activators generated by electron transfer ATRP,[199b, c] activator regenerated by electron transfer (ARGET).[179c, 191, 199a, 200] initiators for continuous activator regeneration ATRP,[179, 201–205] supplemental activators and reducing agents ATRP,[201] etc. In this work, use of ARGET ATRP is reported. Scheme 1 shows the ARGET ATRP of MMA along with the use of other ingredients. ARGET ATRP is one of the methods of ATRP that makes use of active catalyst in the ppm level. It also uses a reducing agent.[190] In this technique, the reducing agent regenerates the activator continuously maintaining the normal ATRP.[183] It is also possible to reduce the Cu catalyst even to very low ppm levels using the starting compound as an oxidatively stable deactivator species.[206] It has also been reported that ARGET ATRP can be used to synthesize polymer with high molecular weight.[191]

The monomer methyl methacrylate (MMA) is one of the highly used commercial monomer, which can undergo polymerization by all major techniques such as free radical, anionic, and group transfer polymerization.[208, 209] The resultant homopolymer, poly(methyl methacrylate) has very high glass transition temperature (100–130 ºC) and possess the qualities that make it applicable in optics, pneumatic actuation, sensor, conductive devices, as additives in lubricants, etc.[207, 208, 210] This study mainly focuses on the effect of solvents and polymerization temperatures on the ARGET ATRP of MMA.

3.2. Preparation:

3.2.1. ARGET ATRP of MMA:

In a typical solution polymerization, the catalyst $CuBr_2$ (0.1115g, 0.50 mmol) and the ligand PMDETA (0.1298g, 0.75 mmol) were taken in a dry Schlenk tube equipped with a magnetic stirring bar and the tube was then sealed with a rubber septum. Methanol (2g) was injected to the Schlenk tube to dissolve the catalyst and ligand. This mixture was stirred for 10 minutes to form the catalyst/ligand complex. A solution of MMA (5g, 0.05 mol) and initiator MCP (0.0612g, 0.50 mmol) was then injected to the Schlenk tube. With continuous stirring, solvent toluene (5g) and ascorbic acid (0.5 g, 2.83 mmol) were then injected to the Schlenk reaction tube to start the polymerization. To carry out the polymerization at elevated temperature, the reaction tube was placed in a oil bath preheated at desired temperature. The aliquots were taken out at different polymerization time and the conversion was determined gravimetrically.

3.3. Results and discussion:

3.3.1. Polymerization kinetics

The polymerization kinetic results of ARGET ATRP of MMA are summarized in Table 3.1. The reactions were carried out in different solvents and at different temperatures. The relative molar concentrations of the ingredients were kept constant for all the experiments. Since, in ARGET ATRP, rate of polymerization and the activator concentration increases with the presence of excess amount of ligand, therefore ligand was used at higher concentration as compared to the catalyst concentration in our case.

Table 3.1: Apparent rate constants of ARGET ATRP of MMA in different solvents and temperatures[#]

Experiment No.	Solvent	Temperature (°C)	Rate constant K_{app} (min^{-1})
1	DMF	30	6.94×10^{-3}
2	Toluene	30	2.12×10^{-3}
3	THF	30	1.05×10^{-3}
4	MEK	30	1.04×10^{-3}
4a	Toluene	40	3.91×10^{-3}
4b	Toluene	50	5.71×10^{-3}
4c	Toluene	60	7.54×10^{-3}
4d	Toluene	70	1.23×10^{-2}

[#] [MMA] : [$CuBr_2$] : [PMDETA] : [MCP] : [Ascorbic Acid] = 100 : 1 : 1.5 : 1 : 5

Ascorbic acid was chosen as reducing agent as it allows the reaction to restart by simply feeding into the reaction mixture if it is stopped at any point of time during the course of polymerization reaction.[211] The concentration of ascorbic acid was calculated on the basis of weight of all the ingredients in order to ensure a constant concentration regardless the size of the reaction batch.

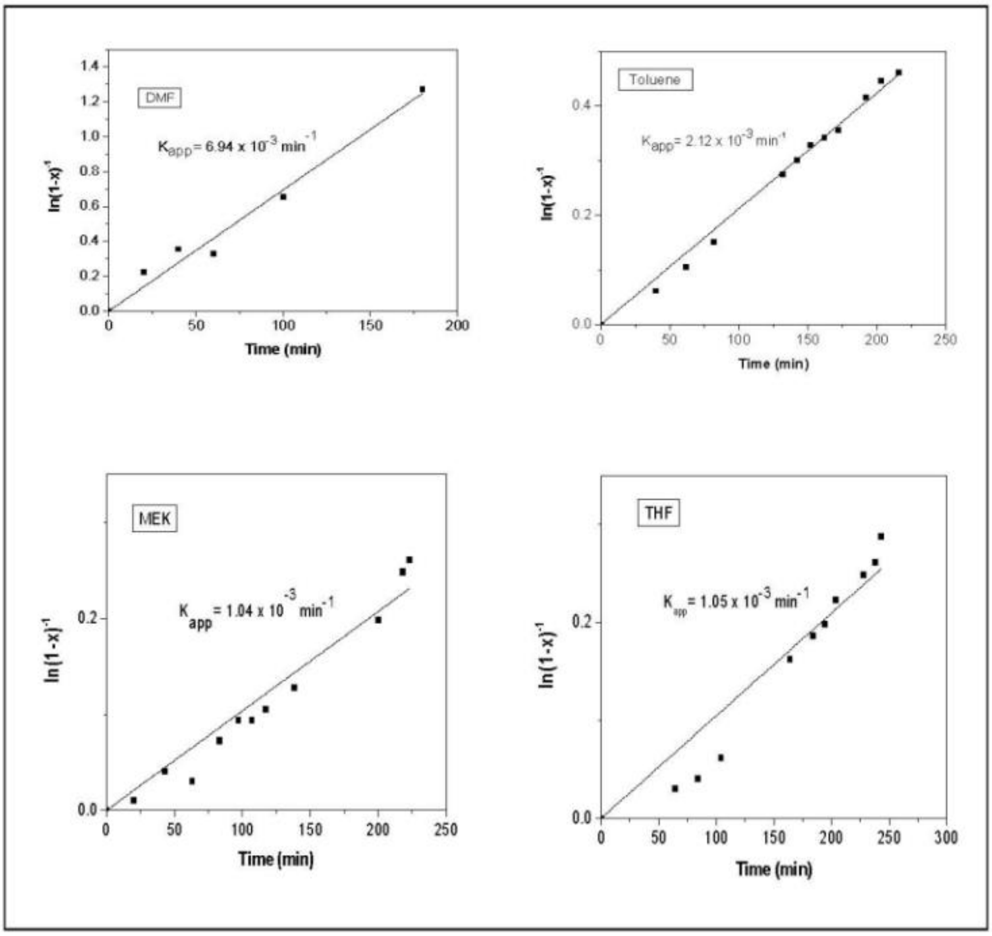

Figure 3.1: Semi-logarithmic kinetic plots of ARGET-ATRP of MMA in four solvents

3.3.2. Nature of solvents

A series of solution polymerizations of MMA in a wide variety of polar and non-polar solvents were carried out at ambient temperature to investigate the effect of the solvent on the ARGET ATRP process. In all cases, $CuBr_2$ was used as catalyst in combination with PMDETA as ligand at a molar ratio of [MMA]:[$CuBr_2$]:[PMDETA]:[MCP] is 100:1:1.5:1. DMF, Toluene, THF and Methylethyl ketone (MEK) were chosen as solvents for this study. The ambient temperature ARGET ATRP of MMA proceeds at faster rate in DMF as compared to other solvents used but toluene was chosen for studying the effect of temperature on polymerization. This is because, toluene has lower boiling point than DMF and it becomes easier to obtain the pure polymer when toluene is used as solvent. Figure 3.1 shows linear semi-logarithmic kinetic plots for all the four solvents. The linear dependency of $\ln(1-x)^{-1}$ (x is the % of monomer conversion) with polymerization time indicates the first order kinetics for the polymerization. The first order kinetics is also the characteristics of a controlled radical polymerization. The apparent rate constant for the corresponding reactions were calculated from the slope of the plots and are shown in the Table 3.1. The highest apparent rate constant was obtained for DMF (6.94×10^{-3} min^{-1}). It has been reported that on addition of a polar solvent accelerates the rate of polymerization of acrylates. The solubility of the catalyst in the reaction mixture is a very important factor to increase the polymerization rate and to reduce the polydispersity of the obtained polymer. Wang and Matyjaszewski studied the polymerization of MMA in various solvents with different polarities [212] They found that the system becomes more soluble as the polarity of the solvent increases.[212, 213] Haloi et. al. reported that addition of small amount of acetone helps in solubilising the copper catalyst in EHA and increases the rate of ATRP of EHA.[214] The second best polymerization result in terms of polymerization rate was achieved when toluene was used as solvent. It has also been reported that toluene complexes strongly with methyl methacrylate [215] and this has been reflected in the result shown in Table 3.1. Earlier, the change in reaction rate was attributed to the effect of solvent in the initiation step. [216, 217] But, Henrici-Olieve and Oleive proposed that it is the propagation step which is influenced by solvent for formation of complex between macro-radical and either monomer or solvent molecule.[218] Bamford and Brumby have showed later that termination can be diffusion-controlled and it is the aromatic solvent which affects the k_p and k_t.[219] Burnet.et.al showed that the effect of solvent is minor on initiation but has marked effect on propagation and termination.[220]

Figure 3.2 shows the linear kinetic plots for all the five reactions carried out at different temperature. In all cases, the plots are found to be linear indicating the controlled nature of the polymerization.

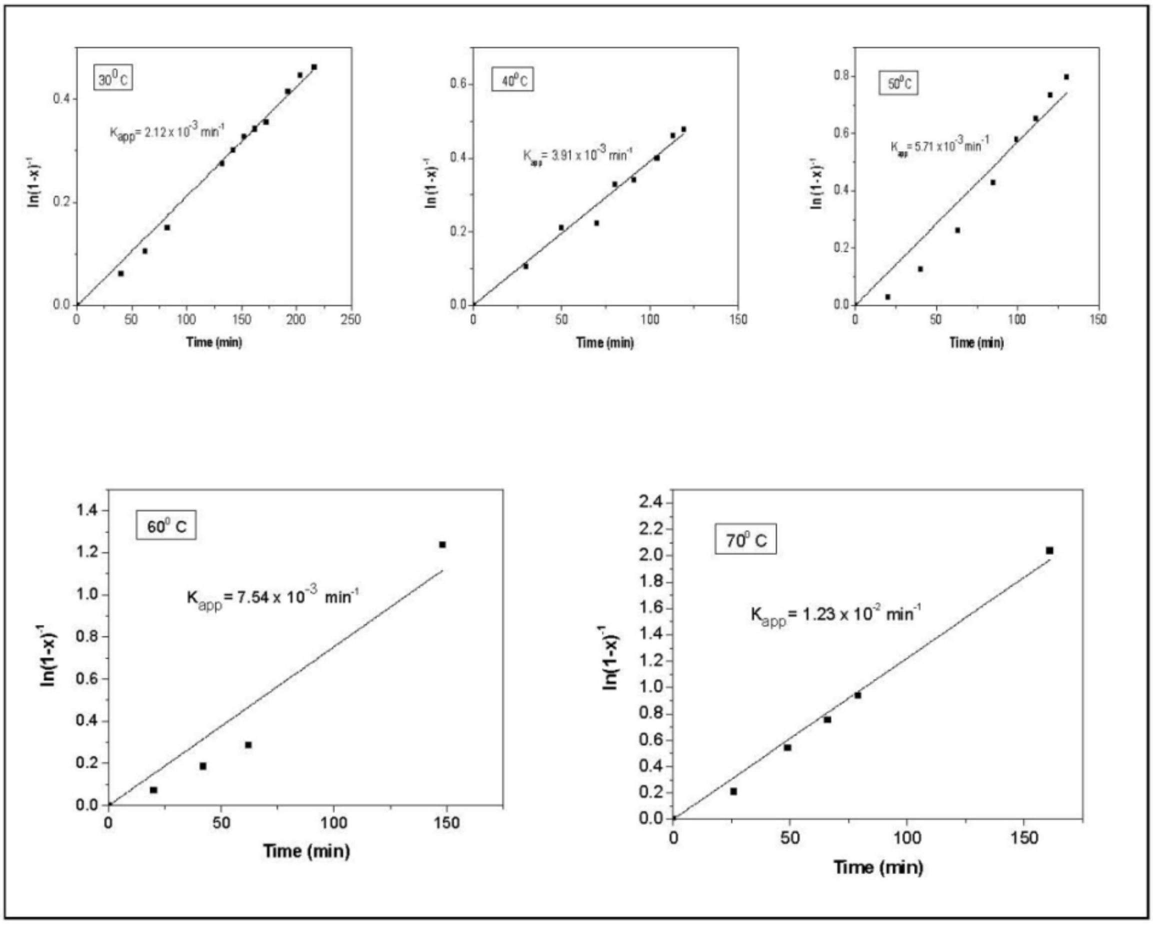

Figure 3.2: Kinetic plots of ARGET-ATRP of MMA at different temperature

From the rearranged Arrhenius equation, $[lnk = -\frac{E_{act}}{R}\frac{1}{T} + lnA]$ a plot of lnA vs $1/T$ would give a straight line of slope equal to $-\frac{E_{act}}{R}$ (where terms have their usual significances). The slop obtained from this plot can be used to calculate the activation energy for the polymerization. Figure 3.3 shows the semi-logarithmic plot of apparent rate constants vs the polymerization temperatures (in Kelvin). The slope of this linear plot (= -3984.0319) is used to calculate the activation energy. Thus the energy of activation for the ARGET ATRP of MMA in toluene is calculated to be 3.3123 X 10^4 J mol^{-1}.

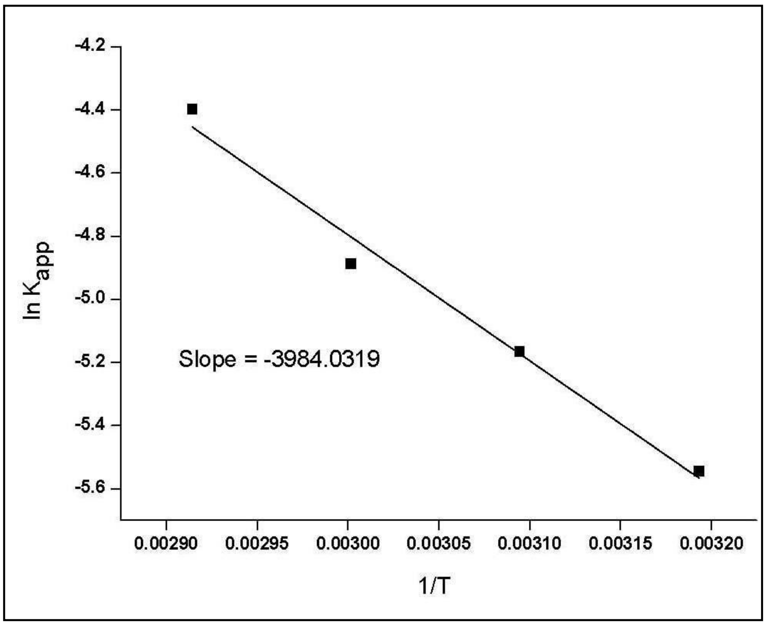

Figure 3.3: Semi-logarithmic plot of apparent rate constants vs polymerization temperatures

3.4. Conclusion:

The ARGET ATRP of MMA was carried out successfully in different solvents and at different temperatures using$CuBr_2$/PMDETA as catalyst system and MCP as initiator. The effect of solvents on the polymerization rate was studied using four different solvents. At ambient temperature, DMF offers the fastest polymerization route among the four solvents as evident by the apparent rate constant value. It has also been established that successful polymerization in solution depends on the proper selection of solvent.

The kinetics plots were prepared plotting conversion of monomer in percentage against the polymerization time. All the plots were found to be linear. This is the characteristics of a first order reaction and eventually establishes the controlled nature of the polymerization. Apparent rate constant for a particular polymerization was determined from the slop of the semi-logarithmic kinetic plot and was used subsequently to calculate the activation energy.