Chapter 6: Starch initiated ARGET-ATRP of Methyl Methacrylate

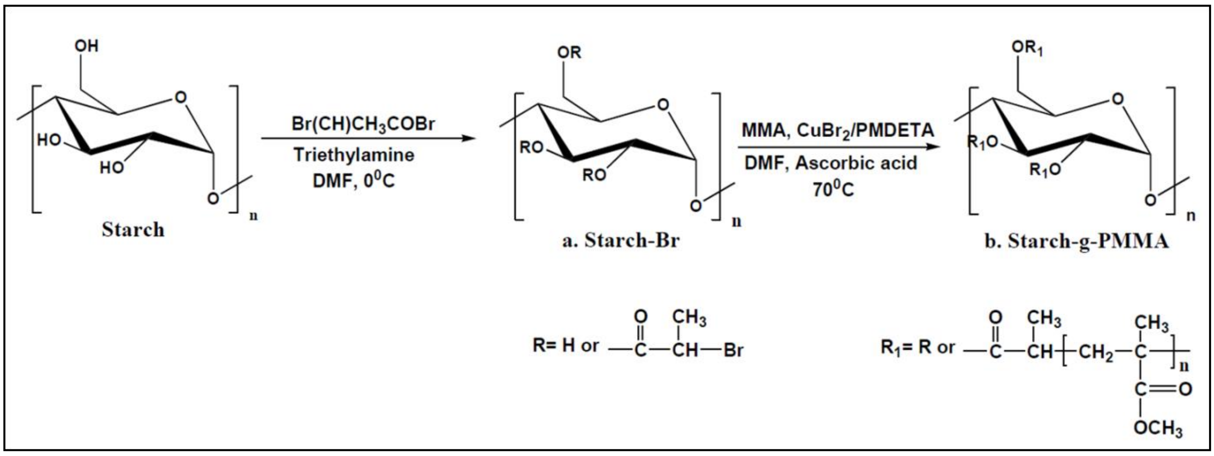
Abstract

This investigation reports the synthesis of Starch-*graft*-Poly(methyl methacrylate) graft co-PMMA) via Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP). The native starch was fabricated into an ATRP initiator via esterification reaction. The graft polymerization of methyl methacrylate (MMA) was then carried out from the ATRP initiating sites introduced in the starch. The grafting reaction was carried out at 70°C using the modified starch as macroinitiator, cupric bromide ($CuBr_2$) as catalyst, *N*,*N*,*N′*,*N″*,*N″*-pentamethyl diethylenetriamine (PMDETA) as ligand, *N*,*N*-Dimethylformamide (DMF) as solvent and ascorbic acid as reducing agent. The conversion of the monomer was carried out gravimetrically. The prepared and purified grafted co-polymer and macroinitiator were analyzed by FT-IR and ^{1}H NMR analyses for structural elucidation. Thermal properties were evaluated by TGA and DSC analyses and morphological study was carried out by SEM analysis.

6.1. Introduction:

In the past few years, there has been a rapid increase in demand of petroleum based synthetic polymer due to their outstanding properties as well as their application in numerous fields. But the excellent properties like resistance towards chemical, weathering, enzymes have led to the accumulation of this synthetic polymer as a plastic waste in earth's crust. Further, this waste proved to be one of the major factors behind the cause of environmental pollution.[130] Now, the demand has increased for a polymer which is not only having properties similar to the synthetic polymer but also environmentally friendly materials. This type of materials can be developed from naturally occurring biomaterials.[160, 164, 243] Starch as a second most abundant biomaterial with high flexibility and low cost, is commonly employed for synthesis or fabrication of starch-based polymer for various applications.[114, 177, 244] It is composed of a mixture of amylose and amylopectin which is semi crystalline in nature.[8] It contains interconnected anhydroglucose units each containing three hydroxyl units. The drawback of starch like solubility can be altered by converting this hydroxyl groups into other reactive functionalities.[244, 245] The physical or chemical modification becomes a necessary process to enhance the properties and to develop starch-based products with desired trait.[170] In the last few years, scientists were successful in making such starch based biodegradable polymers with different monomers and copolymers like Styrene, Acrylic acid, butyl acrylate, etc. via different techniques of FRP and CRP.[164, 177, 246-248] The application of this biodegradable polymer was also found in various fields in medical, in industries, in agriculture.[113, 247-251]Therefore, presently scientists along with the industrialist are focusing on the development of biodegradable polymer with wide application and enhance properties with low costs.[252] There are many works that have been reported by different researchers for the production of starch-graft-copolymers. Bansal, et. al., prepared copolymers of methyl methacrylate (MMA) and styrene by SI-ATRP and AGET-ATRP using expanded corn starch (ECS) as a support.[177] Wang, et. al., reported the synthesis of starch-based copolymers (Starch-*g*-PS and Starch-*g*-PMMA) by using starch as a macroinitiator via atom transfer radical polymerization (ATRP).[159] Cazotti et. Al. reported the synthesis of starch grafted copolymers with methyl methacrylate and styrene, acrylic acid, or methyl acrylate using functionalized starch nanoparticle as a macroinitiator via NMP.[174] Handayani et. al. also prepared grafted copolymer of PMMA onto Amylopectin via atom transfer radical polymerization using amylopectin as a macroinitiator.[178]

In this chapter, ARGET-ATRP of MMA using starch as a macroinitiator is reported. Methyl methacrylate is used as a monomer as it is commercially used monomer and can be polymerized by different polymerization techniques.[20] ARGET-ATRP is one of the methods of ATRP. Avoiding the problem of catalyst in the product ARGET-ATRP, one of the methods of ATRP is employed. It makes use of catalyst in low *ppm* level. ARGET-ATRP of MMA is shown in Scheme 6.1. Further it was characterized by IR, NMR and SEM, and thermal stability was analyzed by Thermogravimetric analysis and Differential Scanning Calorimetry. This study mainly focuses on the preparation of macroinitiator of starch with different composition and studies their effect on the conversion at different time of the polymerization of MMA.



Scheme 6.1: (a) Synthesis of starch macroinitiator and (b) ARGET-ATRP of MMA using the macroinitiator

6.2. Preparation:

6.2.1. Preparation of Starch macroinitiator

A series of starch based ATRP macroinitiator was prepared functionalized with different amounts of 2-bromopropionyl bromide. Macroinitiator Starch-Br was synthesized using 2-bromopropionyl bromide, Triethylamine and DMF as solvent. Typically, preheated starch at 70°C for 3 hours (5.0 g) was dispersed in DMF (10.0 g) with magnetic stirring at room temperature. After complete dissolution of starch in DMF, triethylamine (3g, 0.0296 mol) was added at 0°C and was allowed to stir for 45 minutes. Then 2-bromopropionyl bromide (3 g, 0.0139 mol) was added dropwise under constant stirring at 0°C. Then the mixture was allowed to react for 24 h with mechanically stirring at room temperature. The mixture was then filtered and washed with deionized water, and then the filtrate was finally dried in vacuum at 70°C for 24 h. The procedure was repeated with different amounts of starch, triethylamine and 2-bromopropionyl bromide to obtain an optimized composition which is tabulated below in Table 6.1.

Table 6.1: Preparation of macroinitiators using DMF as solvent

Starch (g)	2-Bromopropionyl bromide (g)	Triethylamine (g)	DMF (g)	Macro-initiator
5	1	3	10	A
5	2	3	10	B
5	3	3	10	C
5	4	3	10	D

6.2.2. Synthesis of Starch-*g*-PMMA co-polymer

In a typical solution polymerization reaction, the catalyst $CuBr_2$ (0.0415 g, 2.31 mmol) and the acetone (2g) were taken in a dry Schlenk tube equipped with a magnetic stirring bar and the tube was then sealed with a rubber septum. Then the ligand PMDETA (0.0515 g, 0.297 mmol) was added to the mixture after 15 mins. This mixture was stirred for 20 min to form the catalyst/ligand complex. Starch-Br was then added as an initiator to the Schlenk tube. After 10 min, a solution of MMA (2 g, 19.97 mmol) and DMF (2g) were then injected to the Schlenk reaction tube. With continuous stirring, ascorbic acid (0.2 g, 1.13 mmol) was added to start the polymerization. The reaction tube was then placed in a preheated oil bath at desired temperature. The aliquots were taken out at different polymerization times, and the conversion was calculated gravimetrically.

6.3. Characterization:

FT-IR spectra of native starch, macroinitiator and graft copolymer were recorded with a Perkin Elmer FT-IR spectrometer as a thin film on KBr plate at a range of 400 to 4000 cm^{-1}. The solid state ^1H NMR for macroinitiator was recorded on Bruker ULTRASHEILD WB 11.7 Tesla/MHz using TMS as an internal standard. Thermal study was done by STA 6000 model for Thermogravimetric analysis (TGA). Polymer approximately weight 2.048 mg was subjected to heat from 30°C to 800°C at 10°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a TA (DSC Q100 V8.1 Build

251) instrument at a heating rate of 10 °C/min under nitrogen atmosphere. In this case the sample was heated to +200 °C then cooled to -50 °C. The sample was again heated to +200 °C at the heating rate of 10°C/min. The 2nd heating cycle curve was used to calculate the T_g of the polymers. Scanning electron microscopy (SEM) images of dry solid sample of native starch, macroinitiator and graft copolymer were analyzed using silicon vapor and then coating it with gold before analysis.

6.4. Results and discussion:

The preparation of starch macroinitiator (as shown Scheme 6.1(a)) and the ARGET-ATRP of methyl methacrylate using the macroinitiator (as shown Scheme 6.1(b)) were carried at different time and monomer feed ratios at 70 °C. The monomer conversions for the polymerization were determined gravimetrically.

6.4.1. Synthesis of Starch macroinitiator: Starch-Br

The starch macroinitiator was prepared in single step via an esterification reaction using 2-Bromopropionyl bromide (2-BrPrBr) in DMF as depicted in Scheme 6.1. FT-IR spectra (shown in Figure 6.1) and ^{1}H NMR spectrums (shown in Figure 6.2) were employed to confirm the successful preparation of macroinitiator. The appearance of the new peak was assigned to C=O stretching vibration band at 1729 cm^{-1} in the FTIR spectrum (Figure 6.1b) from the initiator, and compared with the native Starch (Figure 6.1a). The hydroxyl groups of starch were reacted with 2-BrPrBr to get the bromo functional starch (Starch-Br). A comparison of the FT-IR spectra between native starch and the Starch-Br showed that the hydroxyl group stretching band which was broad and asymmetric at 3296 cm^{-1} significantly shifted to 3418 cm^{-1} and diminished after esterification reaction, which also demonstrated the successful synthesis of macroinitiator.[159] In the ^{1}H NMR spectrum of macroinitiator, similar observation as reported by Wang et al. was obtained.[159] The chemical shifts in the range of 1.7-2.2 ppm and 3.7-6.02 *ppm* (Figure 6.2) were obtained for the methyl protons of the 2-bromopropionyl bromide group (2-BrPrB),and the protons of the anhydroglucose unit, respectively.

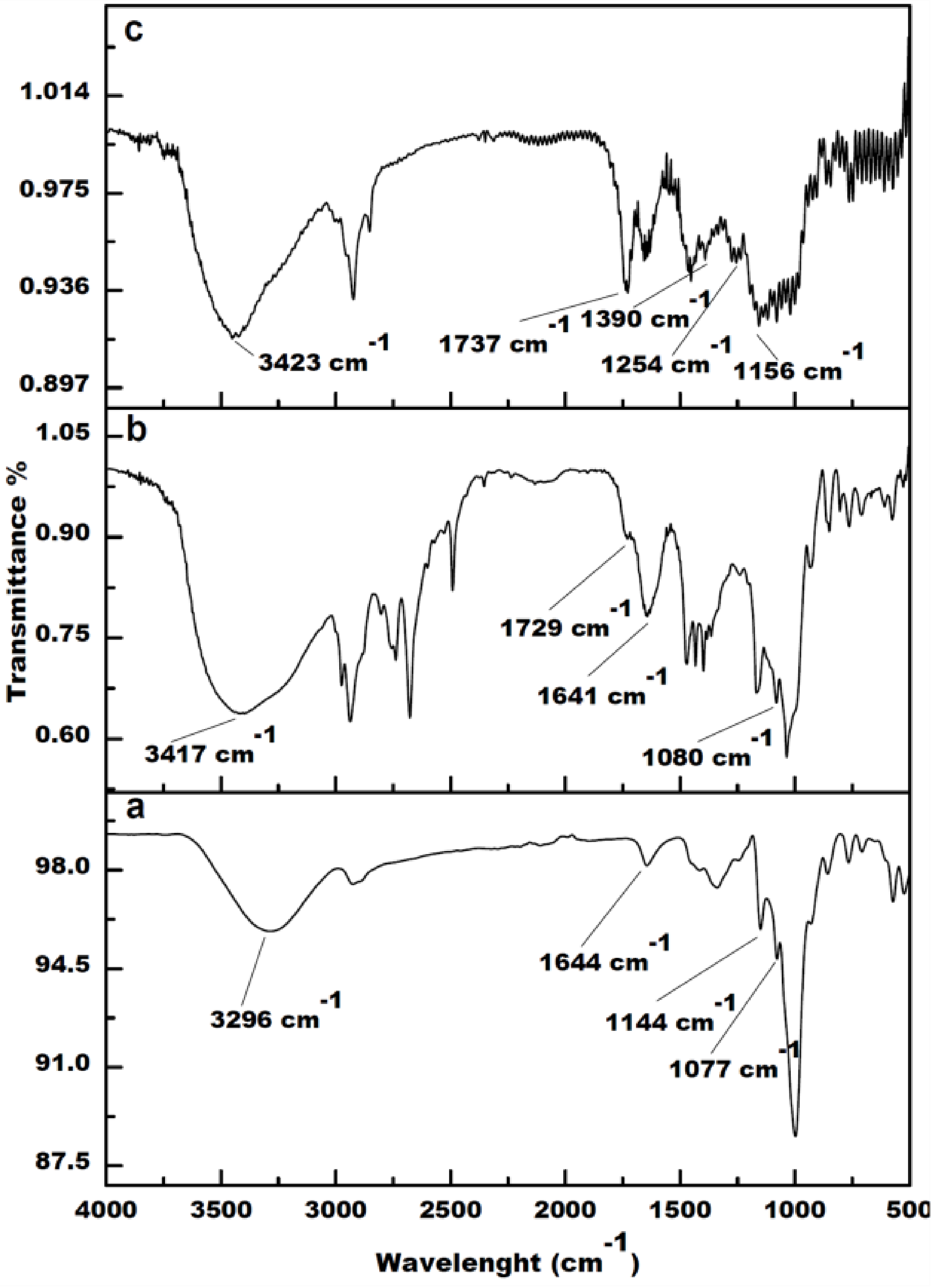


Figure 6.1: FT-IR spectra of a) Native Starch, b) Starch macroinitiator and c) Starch-*g*-PMMA

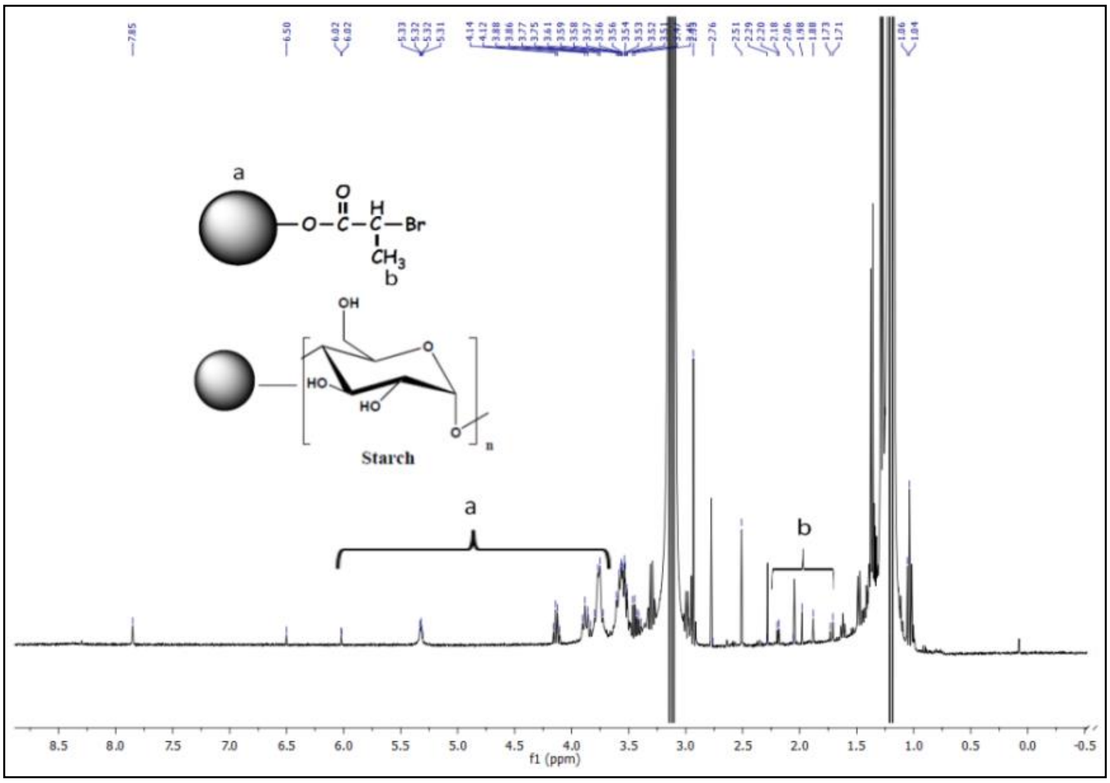


Figure 6.2: ^{1}H NMR Spectrum of starch macroinitiator

6.4.2. Kinetic study

A series of solution polymerizations of MMA with four different starch macroinitiators were carried out at 70 °C to confirm the livingness of the graft process. The polymerization kinetics of ARGET-ATRP of MMA is summarized in Table 6.1. In all cases, $CuBr_2$ was used as catalyst in combination with PMDETA as ligand at a molar ratio of [MMA]:[$CuBr_2$]:[PMDETA] = 100:1:1.5 in DMF. For all the experiments, the relative molar concentration of all the ingredients was kept constant. DMF was chosen as solvent for this study as Dhar et al. earlier reported that polar solvent accelerates the rate of polymerization of acrylates.[20] Moreover, starch macroinitiator Starch-Br has higher solubility in the solvent DMF, so for homogenous reaction and for evenly distribution of grafted chain along the starch backbone the reaction was carried out in the solvent DMF.[164]

In all the experiments, ascorbic acid was used as a reducing agent since it simply restarts the polymerization reaction if it is stopped at any time during the course of the reaction.[20]

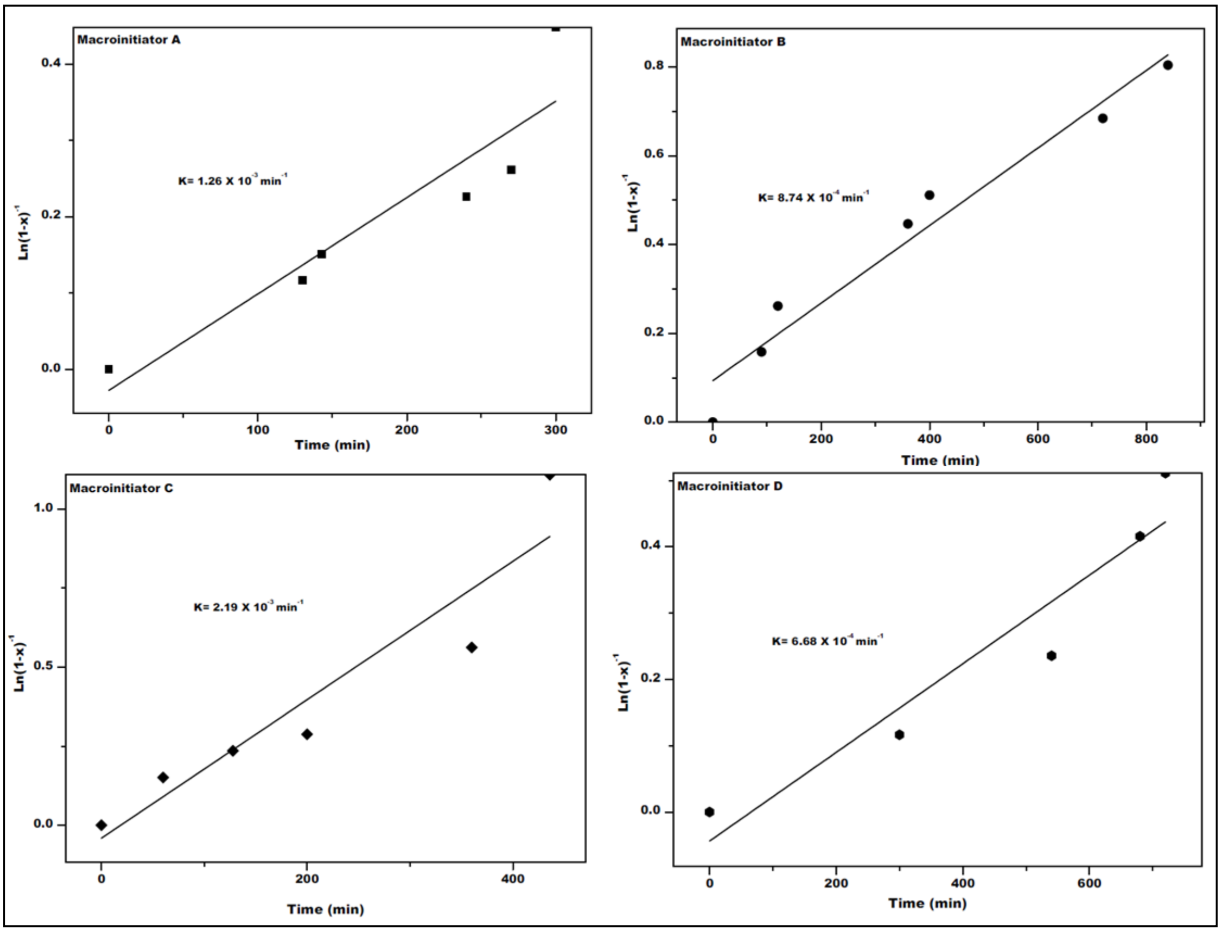


Figure 6.3: Kinetic plots for ARGET-ATRP of MMA using 0.5 g different starch macroinitiator (Starch-Br) at 70 °C, where [MMA]:[$CuBr_2$]:[PMDETA] = 100:1:1.5.

Figure 6.3 shows linear semilogarithmic kinetic plots for all the four different macroinitiator. The linear dependency of $\ln(1-x)^{-1}$ (where x is the percentage of monomer conversion) with polymerization time indicates the first-order kinetics for the polymerization. The first-order kinetics is also the characteristics of a CRP. The apparent rate constant for the corresponding reactions were calculated from the slope of the plots and are shown in Table 6.2. The highest apparent rate constant was obtained for macroinitiator C (2.19×10^{-3} min^{-1}).

Table 6.2: Apparent rate constants for ARGET-ATRP of MMA with different macroinitiators at 70 °C

Experiment No.	Macroinitiator	k_{app} (min^{-1})
1.	A	1.26×10^{-3}
2.	B	8.74×10^{-4}
3.	C	2.19×10^{-3}
4.	D	6.68×10^{-4}

6.4.3. Graft copolymerization of MMA onto Starch

ARGET-ATRP of MMA was carried out using starch as a macroinitiator and $CuBr_2$/PMDETA as the catalytic system. The effect of molar wt. of MMA/Starch-Br on the conversion of graft copolymerization, which was carried out at 70 °C was studied.

In order to confirm that PMMA was truly grafted onto the starch, the graft polymer regarding starch have been identified using Infrared. Figure 6.1 shows representative FTIR spectra of starch, Starch-Br and Starch-*g*-PMMA. In the FTIR spectrum of Starch-*g*-PMMA, the presence of PMMA gave rise to the absorption bands at 1156 and 1254 $cm^{-1}$for C-O-C stretching vibrations and the band at1737 $cm^{-1}$for C = O stretching vibrations and 1390 $cm^{-1}$for α-CH_3 stretching vibrations. These results confirmed that MMA was successfully grafted onto the starch backbone.

6.4.4. Thermal Property

TGA technique has been proved to be an important method to study the thermal stability of a graft polymer. Figure 6.4 depicts the (a) thermogravimetric curves and (b) derivative curves of native starch, Starch-*g*-PMMA and PMMA. The T_{max} for native starch, Starch-*g*-PMMA and PMMA were found to be 307 °C, 326 °C and 349 °C respectively. From the TGA plot results it can be concluded that the thermal stability of the graft copolymer, Starch-*g*-PMMA was improved in compared to native starch.

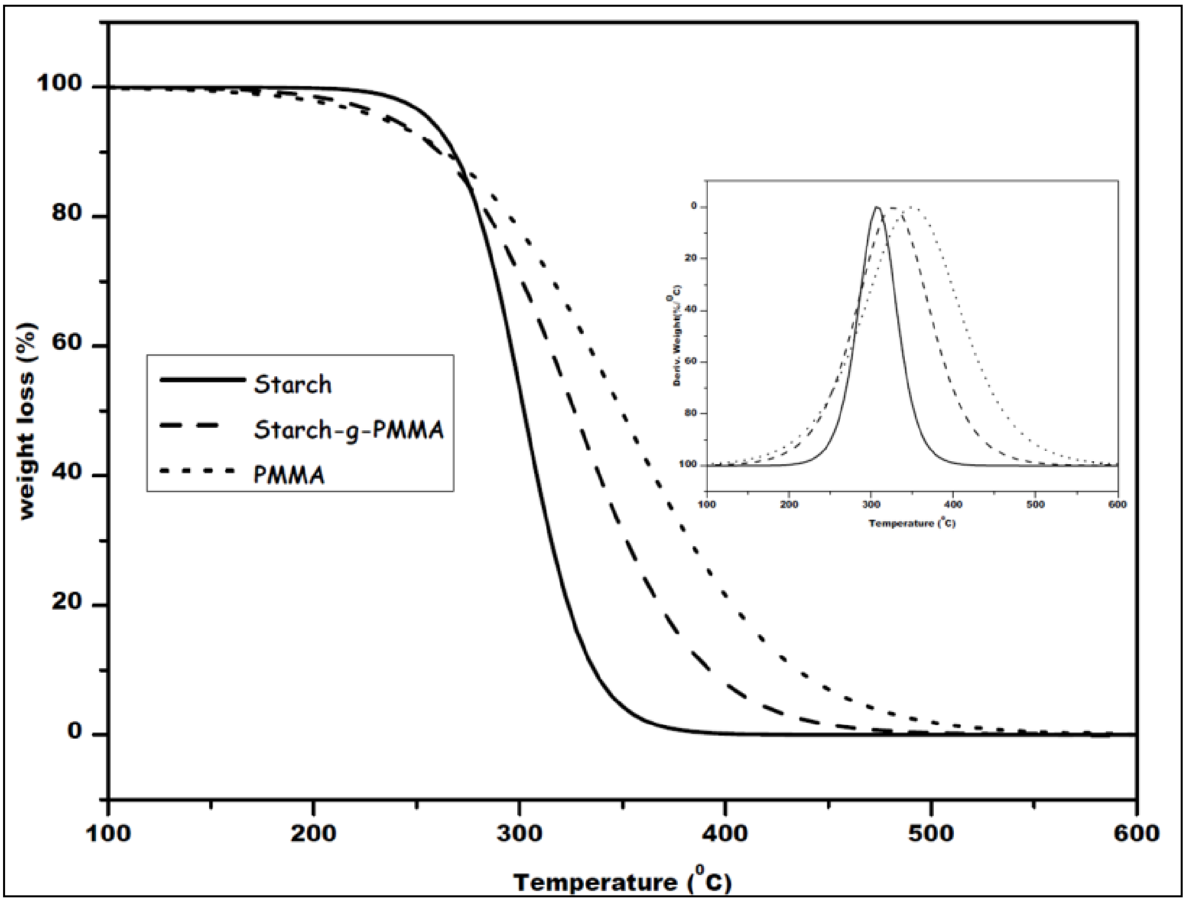


Figure 6.4: TGA and DTG curves of Starch, Starch-*g*-PMMA and PMMA

DSC analysis was used to determine the glass transition temperature of grafted copolymer of starch and MMA, Starch-*g*-PMMA and was compared with PMMA. The DSC analysis of Starch-*g*-PMMA and PMMA are shown in Figure 6.5. In this case the polymer sample was heated from -50 °C to 200 °C with a heating rate of 10 °C/min. The DSC analysis showed T_g at 138 °C for Starch-*g*-PMMA and 109 °C for PMMA.

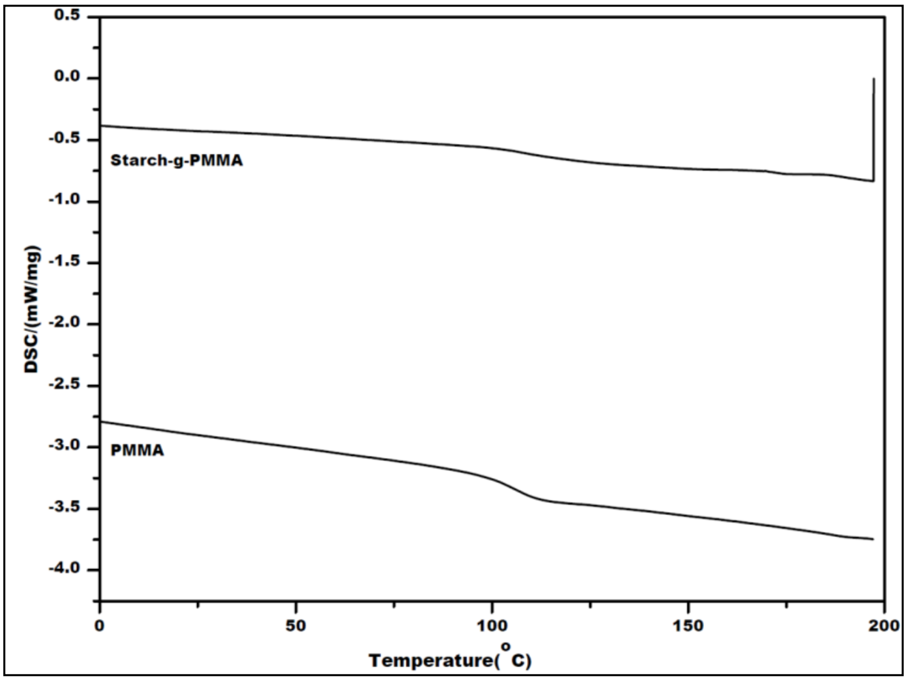


Figure 6.5: DSC thermograms of Starch-*g*-PMMA and PMMA

6.4.5. Morphological Study

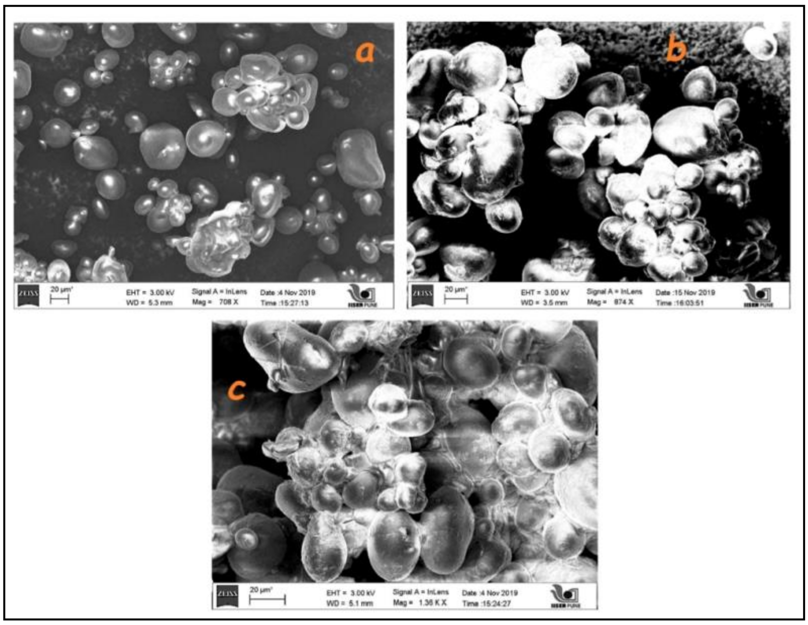


Figure 6.6: SEM images of a) Starch, b) Starch based macroinitiator and c) Starch-*g*-PMMA

The structural morphology of the dry state of starch, starch macroinitiator and Starch-*g*-PMMA was investigated by SEM as shown in Figure 6.6a, 6.6b and 6.6c. The SEM images explained that the granular structure of starch was not maintained after the esterification reaction and graft copolymerization of PMMA onto the starch backbone. The starch exhibited granular structure initially but after an esterification reaction macroinitiator exhibited a macroporous structure and similar observations were obtained in grafted polymer.

6.5. Conclusion:

In the present study, the starch based ATRP macroinitiator was successfully prepared and was confirmed by FT-IR and NMR analyses. The starch initiated graft copolymer of starch and PMMA was successfully prepared via ARGET-ATRP. The successful synthesis of Starch-*g*-PMMA was confirmed by FT-IR analysis. The kinetic plots were prepared by plotting conversion of monomer in percentage against the polymerization time. All the plots were found to be linear which is a characteristic of a first-order reaction, and eventually establishes the controlled nature of the graft co-polymerization. The thermal stability of the native starch and PMMA was compared with the graft copolymer. It was found that the graft copolymer is thermally more stable than the native starch but less stable than neat PMMA. The glass transition temperature for PMMA and the graft copolymer (Starch-*g*-PMMA) was calculated from DSC thermogram. T_g of the graft copolymer was found to be more than the neat PMMA. It was also revealed from SEM analysis that granular structure of starch was not retained after grafting in its grafted counterpart.