Chapter 5

ATRP using functionalized nanotubes /Acetyl Chloride as radical initiators

Chapter- 5

ATRP using functionalized nanotubes/acetyl chloride as radical initiators

5.1 Introduction

It has been found that recently developed atom transfer radical polymerization (ATRP)[184-188] is one of the most versatile methods to control the structure, chain length, distribution and chain end functionality of polymers. This method of polymerization gives functional and "living " end groups and helps produce various nanocomposites of immense importance[189,190]. A three-component initiating system for *Atom transfer radical polymerization (ATRP)* contains halide-type true initiator, catalyst – a transition metal salt in the lower oxidation state, and a complexing ligand, based on amine-type or organophosphorus compounds[191,192].Initiator systems such as alkyl or aryl halides, esters on haloorganic acids, polyhalogenated compounds[193] have been reported. General scheme for CRP method is shown in Figure 5.1.

It involves a reversible redox process whereby a transition metal complex [Mtn – Y/Ligand] catalyses the reaction. After accepting the (pseudo halogen) from the initiator species, the transition metal-ligand complex in its lower oxidation state converts to higher oxidation state. Y is either a ligand or counter ion. This process occurs at a rate constant of activation K_{act} and deactivation K_{deact} . Establishing a rapid dynamic equilibration between a very small amount of growing free radicals and a large majority of dormant species (initiators) is the most essential requirement of ATRP for controlled polymerization. Temperature and solvent types also greatly effect the polymer properties.

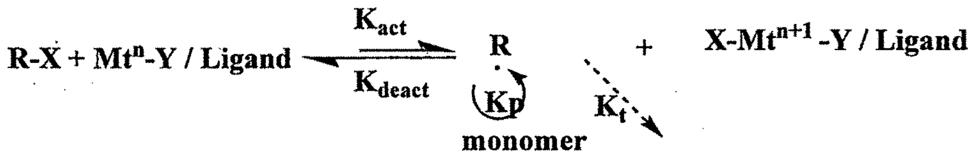

Figure 5.1 Schematic presentation of general mechanism of controlled radical polymerization (CRP) method.

The rate of polymerization in ATRP increases with increase in temperature due to increase in radical propagation and atom transfer equilibrium constant, but at the same time side reactions also become dominant, which gives high PD. Various initiating systems such as halogenated alkanes, benzylic halides, α-Haloketones, α-Haloesters etc. can be used which facilitate the transfer of halogen to catalyst-ligand complex. Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) has been reported at room temperature (25 °C) under 60Co γ-irradiation environment. The polymerization proceeded smoothly with high conversion (>90%) within 7h[194]. Surface initiated ATRP of MMA has been reported at 80°C using modified PANI as macroinitiator[195]. A new ATRP initiator, viz, 2-oxo-1,3-dioxolan-4-yl-(methyl-2-bromo-2-methylpropanoate) (ODMBMP) was used to carry out ATRP reactions of methyl methacrylate (MMA) in the presence of copper chloride/N,N′,N′,N″N″-pentamethyldiethylenetriamine to give low molecular weight cyclic carbonate-terminated poly(methyl methacrylate)s with relatively narrow molecular weight distribution[196]. Various such experiments on ATRP of MMA[197-200] and styrene[201-203] have been reported using various catalyst and ligand systems like 2-pyridinecarbaldehyde imine copper(I) complexes, alkyl pyridylmethanimine, CuI(bpy)nCl or Wilkinson catalyst , but the initiator system had terminal free halide group.

The α,ω-dichloro-PMMA prepared by ATRP of MMA using 1,3-bis{1-methyl-1-[(2,2,2-trichloroethoxy)carbonylamino]ethyl}benzene as bifunctional initiator were used as macroinitiators for ATRP of tert-butyl acrylate (t-BuA), giving the corresponding triblock copolymers with narrow MWDs and molecular weights controllable in a wide range[204-206]. Controlled functionalization of multiwalled carbon nanotubes by in Situ ATRP has been performed by generating terminal bromine on CNT by reaction with 2-bromo-2-methylpropionyl bromide. Similar work has been done to produce polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) grafted MWNTs[207]. Construction of polymer brushes on multiwalled carbon nanotubes by in situ reversible addition fragmentation chain transfer polymerization has been done to generate poly(methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS)[208].

In present study compounds of the general formula RCO-Cl were used as ATRP initiators, for polymerization of MMA and styrene, in which –R can be a alkyl group of any number of carbon atoms. Use of acetyl chloride groups as initiating systems is a totally as RCO-Cl bond is highly reactive and dissociates readily to form radicals and thus producing halogen radical for further transfer reactions. Apart from various alkanoyl chlorides, acylated nanotubes have also been used as macro initiators.

Free radical polymerization is a method by which a polymer is formed from the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following creation of free radical monomer units, polymer chains grow rapidly with successive addition of building blocks onto free radical sites. Free radical polymerization is a key synthesis route for obtaining a wide variety of different polymers and material composites. The relatively non-specific nature of free radical chemical interactions makes this, one of the most versatile forms of polymerization available and allows facile reactions of polymeric free radical chain ends and other chemicals or substrates.

Poly(methyl methacrylate) and polystyrene were synthesized by emulsion polymerization with Methyl Methacrylate and styrene as monomers respectively, acetyl chloride as initiator in one reaction set and acylated nanotubes as initiator in other set , Brij-98 as the emulsifier and distilled water as a medium. Similar reactions using pentanoyl chloride and hexanoyl chloride as initiators have also been performed.

PMMA is a versatile material and has been used in a wide range of fields and applications. The German chemist Fittig and Paul discovered in 1877 the polymerization process that turns Methyl Methacrylate into poly Methyl Methacrylate (Lovell 1997). Water born polymerization such as emulsion polymerization are of great importance in industry application as they provide environmental friendly process, remove the reaction heat easily during polymerization and assume the feasible handling of the final product having a low viscosity.

Emulsion polymerization involves the propagation reaction of free radicals with monomer within the monomer–swollen polymer particle dispersed in the hydrophobic particles stabilized by surfactant. Micelles are formed when the level of surfactant is greater than its critical micelles concentration (CMC). Particle nucleation are generated via the capture of radicals by micelles. These absorb monomer to achieve a critical chain length.

5.2. Materials

Methyl methacrylate(>99%, Aldrich), Styrene (Sty, >99%, Aldrich) were passed through alumina in order to remove inhibitor and stored under argon in freezer. CuCl (>99%, Aldrich) was purified by washing with glacial acetic acid, absolute ethanol, and finally with diethyl ether. The ligand 2-2' bipyridyl (>99%, Aldrich) , initiator acetyl chloride (MERCK) ,Carbon nanotubes (multi-walled carbon nanotubes, MWNTs) manufactured by HiPCO , $SOCl_2$, methanol(>92%, Aldrich) and chloroform were used as obtained.

5.3 Experimental

5.3.1 Polymerization of MMA

All reagents were nitrogen purged before use. Emulsion of MMA (6.2 mL /5.78 gm, 0.0289mmol) with 28.0 mL of distilled water and 4.6 gm of Brij 98 surfactant was prepared. The solution was stirred for 1.5 h using magnetic stirrer. This emulsion was found to be stable.

In a typical experiment, CuCl (0.0288 g, 0.14 mmol) and a bidentate ligand 2,2'-bipyridyl (0.0872 g,0.28 mmol) were added to a two neck 100 mL round bottom flask, equipped with a magnetic stirring bar. After sealing with a three way stopcock, the flask was degassed and backfilled with argon three times.

To this, emulsion of monomer was transferred by means of cannula using vacuum, keeping flask stirring by use of magnetic stirrer.

After three freeze–thaw-pump cycles *initiator (Acetyl Chloride)* was injected dropwise under nitrogen purging. The reaction mixture was stirred for 20 hours.

(1) at room temperature and

(2) at temperature 60°C.

The reaction was quenched by intensive cooling and diluted with tetrahydrofuran (THF). The formed polymer was recovered by precipitation in acidic methanol/water mixture = 80/20 (v/v) and dried in vacuum at 40°C to constant weight.

For purification it was dissolved in chloroform and reprecipitated it in methanol 3-4 times. Figure 5.2 shows the reaction scheme followed. Similar procedures were followed for polymerization of MMA and Styrene using Acylated Nanotubes as initiators. *Acylated nanotubes could be only used as emulsion, due to their insolubility in water.* Acylated nanotubes were prepared by reaction of carboxylated nanotubes with 20 mL of thionyl chloride and 2mL of DMF (dimethyl formamide). The system was properly sealed with grease and teflon, to prevent any moisture contamination and then refluxed for 36 hrs. at 60°C.The product obtained was washed with toluene .The sample was then dried in a vacuum oven at 80 °C for 4 h to get the macro initiator.

$$\underset{\text{Initiator}}{CH_3COCl} \longrightarrow CH_3CHO\bullet + Cl\bullet$$

$$CH_3COCl + M_t{}^{s}L_yX \underset{K_{da0}}{\overset{K_{a0}}{\rightleftarrows}} CH_3CO\bullet + M_t{}^{s+1}L_yX_2$$

$$CH_3C\dot{O} + M \xrightarrow{K_{p0}} CH_3CO\dot{M}$$

$$CH_3CO\dot{M} + M_i \xrightarrow{K_{pi}} CH_3CO\dot{M}_{i+1}$$

$$CH_3CO\dot{M}_{i+1} + CH_3CO\dot{M}_{i+j} \xrightarrow{K_{tij}} \text{Dead Polymer}$$

Figure 5.2 Reaction scheme employed in the process where K_a, K_p, K_t are rate coefficients for activation, propagation and termination.

For preparation of emulsion of initiator initially distilled water (14.0 ml) was added to 2.3 gm of Brij 98 surfactant and 6 mg of acylated MWCNTs. The solution was sonicated for 1 hr and stirred for 1 hour and 30 minutes using magnetic stirrer. The prepared nanotube emulsion could be used as macro initiator for polymerization process, for either MMA or Styrene. The processes carried out are listed in Table 5.1.

5.4 Characterization

FT-IR was carried out on Perkin-Elmer spectro photometer at 20 scans using the KBr pellet method. The polymer was confirmed by 13C NMR. NMR spectra of 10% (w/w) solutions in $CDCl_3$ were measured at 330K with a Bruker Avance DPX300 spectrometer at 300.13 and 75.45 MHz resonance frequency, respectively. All polymers were characterized by SEC (WATERS) in THF at room temperature at a flow rate of 1 ml/min using a PSS column (5 lm; 103 and 105A °) (PSS, AUSTRIA), equipped with RI detector . Polystyrene standards and the Mark–Houwink constants for the PS/THF system ($K = 1.17x10^4$ mL g^{-1}, $a = 0.717$) were used to establish the number average molecular weights (Mn) and molecular weight distributions (MWD). The apparent molecular weights (Mn) were obtained from here. The TGA data were obtained in Nitrogen atmosphere with mettle Teledo Star SW 7.01 thermo gravimetric analyzer with 7.4640 mg of the specimen at 10 degree centigrade per minute.

Table 5.1 Various sets performed to obtain polymers.

Monomer	Initiator		Catalyst	Ligand	Temperature
MMA	Acetyl chloride	AC	CuCl	2,2' bipyridyl	28°C 60°C
	Acylated nanotubes	ANT			
	Pentanoyl chloride	PC			
	Heptanoyl chloride	HC			
Styrene	Acetyl chloride	AC			28°C, 60°C
	Acylated nanotubes	ANT			

5.5 Results and Discussion

5.5.1 Polymerization of MMA and Styrene

In a 100 mL round bottom flask, catalyst/ligand complex was nitrogen purged for three times, and to it emulsion of monomer was added under nitrogen atmosphere through cannula, followed by addition of initiator. In present work, a novel initiator, acetyl chloride (CH_3COCl) and acylated nanotubes were used.

5.5.2 Characterization

5.5.2.1 IR Spectra

In the IR spectra (Figure 5.3a) of the polymer PMMA the peaks corresponding to C=O stretching (1737.92 cm^{-1}), C-O stretching (1242 cm^{-1}),C-H stretching (2850-2960 cm^{-1}) and C-C stretching (1450-1550 cm^{-1}) and absence of peak corresponding to C=C stretching at 1500-1600 cm^{-1} confirm the formation of polymer . Peak at 752.26 cm^{-1}corresponds to presence of C-Cl terminal end group in growing (living) polymer chain. In the IR spectra (Figure 5.3b) of the Polystyrene strong bands at 3021.81cm^{-1}/3029.47cm^{-1} show C-H stretching of aromatic ring and at 2917.72cm^{-1}/2925.03cm^{-1} showing C-H stretching of aliphatic chain present in polystyrene. The bands shown in from 1650-2000cm^{-1} and near about 3600cm^{-1} are overtone and combination bands mainly of aromatic C-H *def* absorption. Overtone bands appear at integer multiples of fundamental vibrations, so that strong absorptions at, say, near 800 cm^{-1} and 1750cm^{-1} will also give rise to weaker absorptions at 1600cm^{-1} and 3500cm^{-1} respectively. Band between 1400-1600cm^{-1} indicates aromatic C=C bending and between 860-680 cm^{-1} indicates aromatic C-H bending.

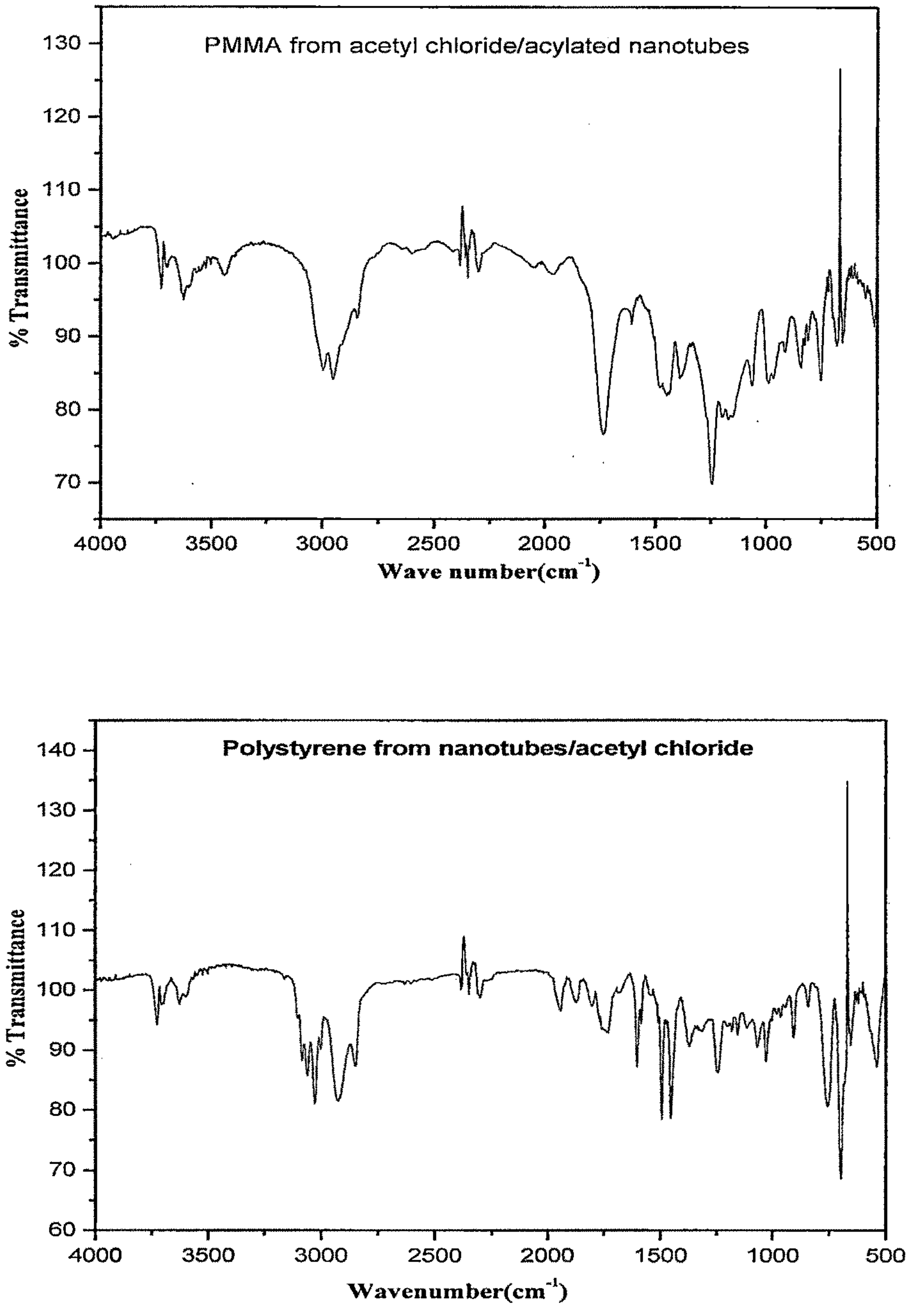

Figure 5.3 FTIR of (a) PMMA (b) Polystyrene initiated from acetyl chloride/ acylated nanotubes.

5.5.2.2 ^{13}C-NMR

Figure 5.4 shows ^{13}C-NMR of acetyl initiated PMMA. Peak at 177.938 ppm shows the presence of carbonyl group. Peak at 77.322 ppm shows solvent peak. Peak at 54.479 ppm shows methylene ($-CH_2-$) group. Peak at 52.174 ppm shows $-OCH_3$ group is present. Peak at 44.871 ppm shows quaternary carbon is present. Peak at 19.113 ppm and 16.850 ppm shows two types $-CH_3$ groups are present.

The peaks obtained confirm the formation of polymer.

The similar ATRP setup was used with labeled acetyl chloride as initiator . An extra peak (four instead of three) in the range 170-190cm^{-1} owing to presence of carbonyl group with labeled carbon ($^{13}C=O$) in the end group functionality in NMR spectra of the polymer was obtained (Figure 5.5a). The presence of peaks due to terminal functionalities in the polymer confirms the formation of a living polymer. The results have been verified with standard ^{13}C NMR PMMA where peaks are matching with the NMR obtained in the study, hereby confirming the formation of polymer using acetyl chloride or acylated nanotubes as initiators(Figure 5.5b).

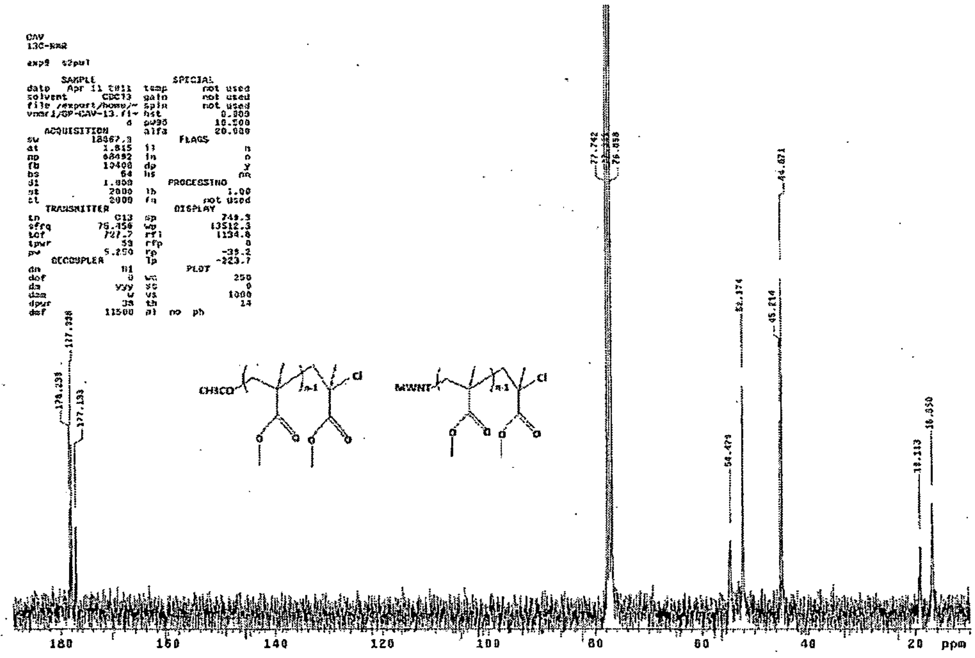

Figure 5.4 NMR of acetylchloride/acylated nanotubes initiated PMMA.

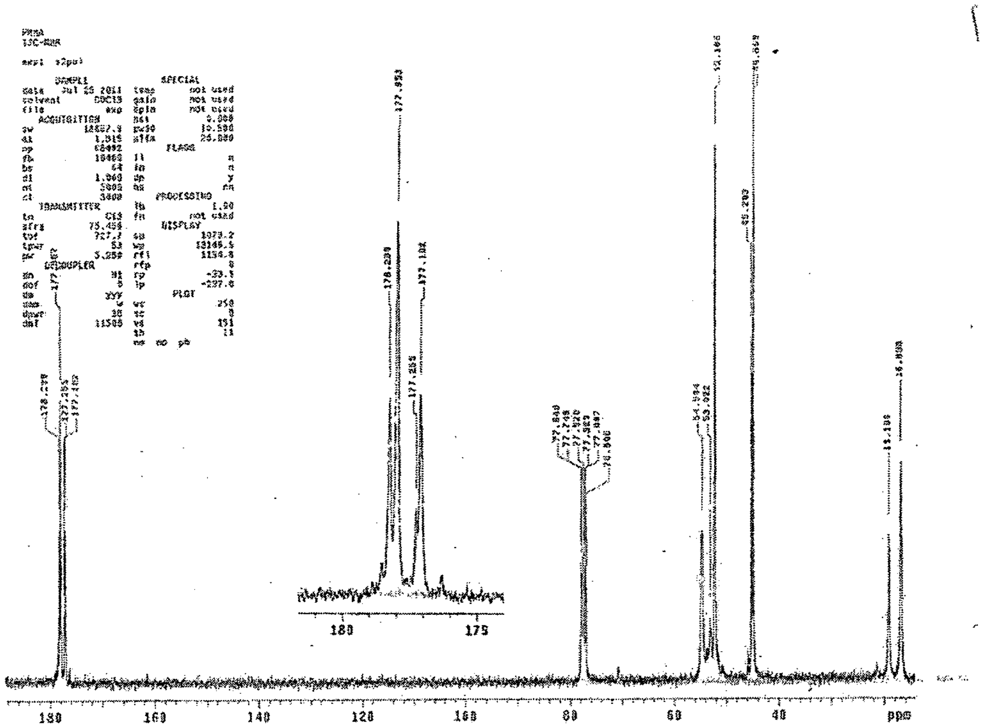

Figure 5.5 (a)^{13}C NMR of PMMA obtained from labeled acetyl chloride as initiator

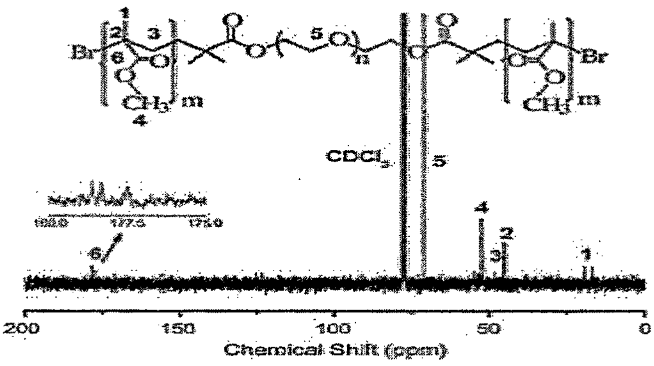

Figure 5.5 (b) Standard PMMA (Dandan Wang et.al *European Polymer Journal* **2007**, *43,* 2799-2808)

Presence of CH_3CO- as one of the terminal groups was confirmed by presence of peaks in range 177-178cm^{-1} in ^{13}C NMR of polystyrene prepared by using acetyl chloride as initiator (Figure 5.6). Peak at 128.154/127.880/125.846 cm^{-1} is obtained due to phenyl ring. Peak at 46.164/45.237/44.890 cm^{-1} points to presence of Methylene ($-CH_2-$) group. Peak at 19.094 cm^{-1} and 16.983 cm^{-1} indicates the presence of Methyl halide ($-CH_2-X$), and Methyl group ($-CH_3$) groups.

Thus acetyl chloride was confirmed to act as active radical generating initiator molecule both for MMA and Polystyrene.

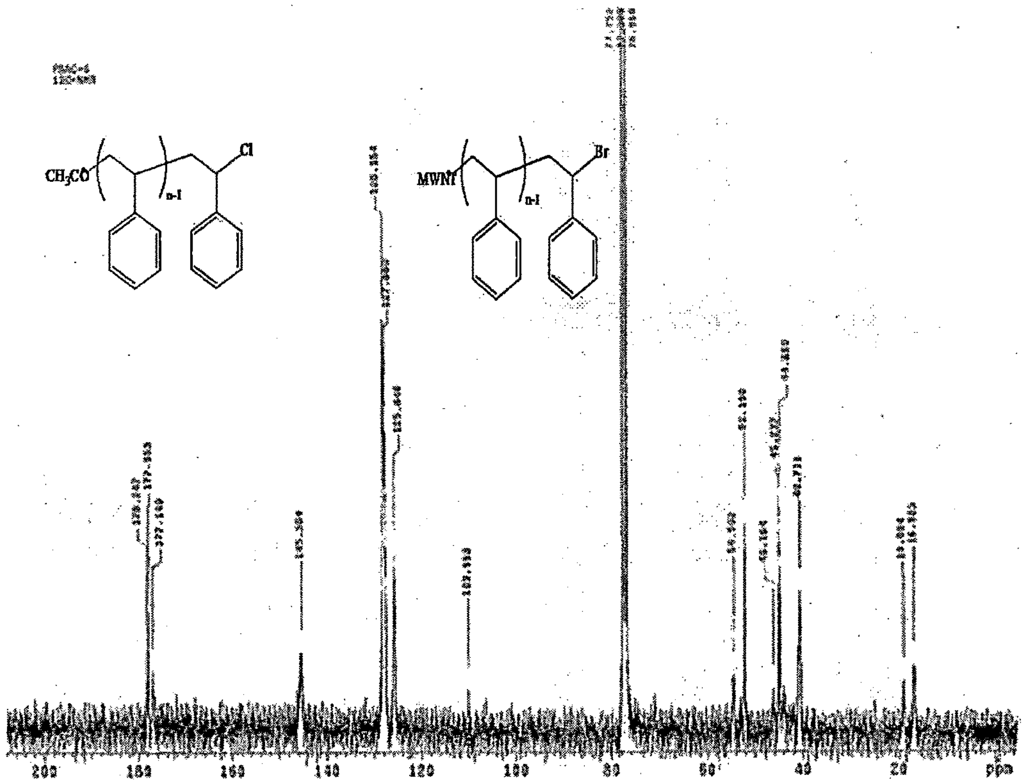

Figure 5.6 ^{13}C NMR of Polystyrene obtained from acetyl chloride used as initiator.

5.5.2.3 Thermo-gravimetric analysis

Figure 5.7a shows TGA thermogram of acetyl initiated PMMA polymer. From thermogram it is interpreted that polymer decomposes around 240°C after 22 minutes to around 400°C after 38 minutes. No loss (or decomposition) after around 400°C. The polymer PMMA obtained at 28°C appears to have nearly similar thermal stability as that of the polymer prepared at 60°C. For polymer initiated by acylated nanotubes thermal stability appears to increase as in Figure 5.7b.

From thermogram (Figure 5.8) of polystyrene prepared by acylated nanotubes as initiator, it is seen that polymer decomposition starts at around 308° C to around 421° C. No loss (or decomposition) after 422°C. Polystyrene polymer from conventional methods starts decomposition at around 274° C. From the above results we can say that by using CNTs as an initiator the thermal stability of polymer is increased.

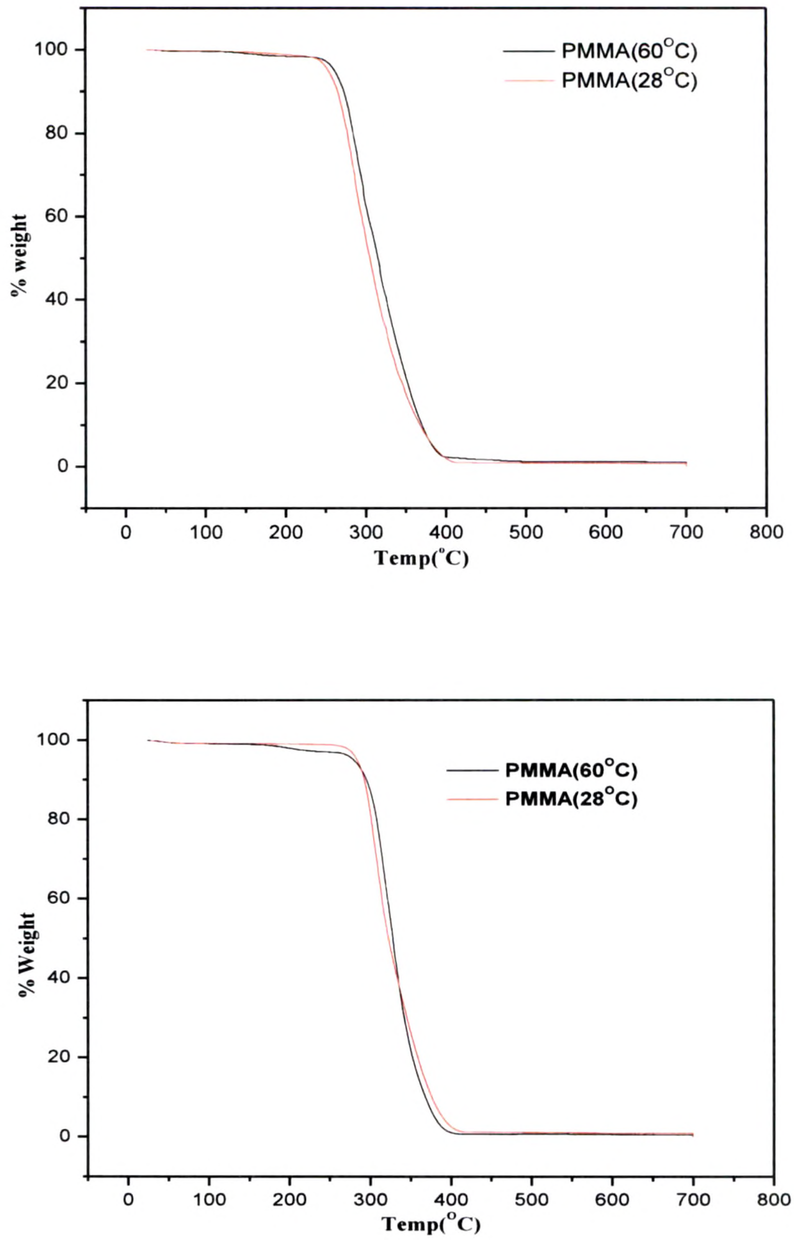

Figure 5.7 Thermogravimetric analysis of PMMA, obtained by (a) acetyl chloride (b) acylated nanotubes as initiator.

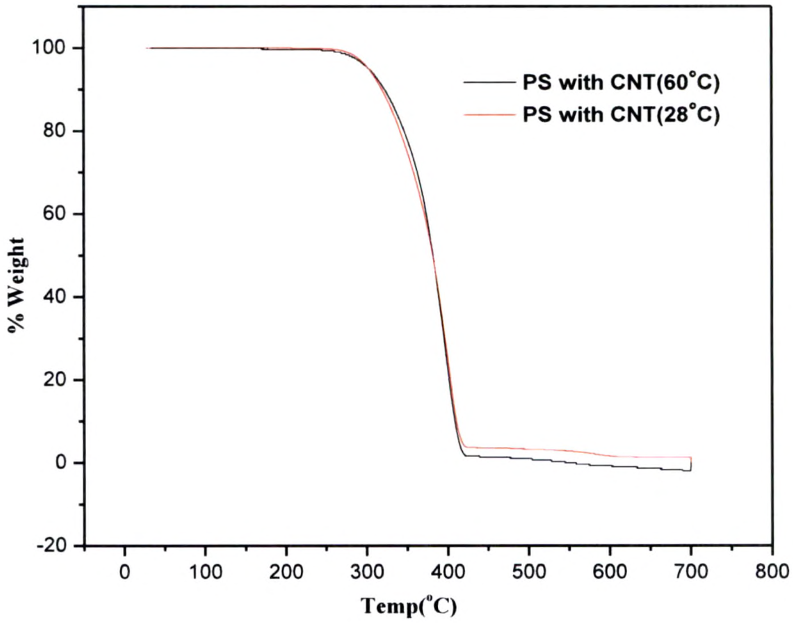

Figure 5.8 Thermogravimetric analysis of Polystyrene by acylated nanotubes as initiator.

5.5.2.4 DSC :

PMMA can exhibit stereoisomerism tacticity. Changes in tacticity have a significant effect on the glass transition temperature and hence mobility of chain backbone. The T_g of isotactic polymer is nearly 48°C , and is significantly lower than that for syndiotactic PMMA(T_g=160°C). Syndiotactic PMMA has been reported to possess lower intramolecular energy, and isotactic PMMA has lower intermolecular energy[209].The difference in T_g's has been attributed to conformational energy difference by MacKnight and Karasz [210], and to intermolecular interactions by O'Reilly and Mosher[211].The polymers obtained in present work were observed to possess high glass transition temperature (Figure 5.9 & 5.10) T_g=135°C for PMMA and T_g=109°C for Polystyrene. This signifies the formation of a highly syndiotactic structure, with high intermolecular and intramolecular interactions and thus effecting the packing structure. As a consequence of these interactions, a fringe micelle structure may be formed with dimensions several times larger than region of specific polymer chain interaction (cross linked structure). This is in accordance with the abnormally high molecular weights obtained by SEC.

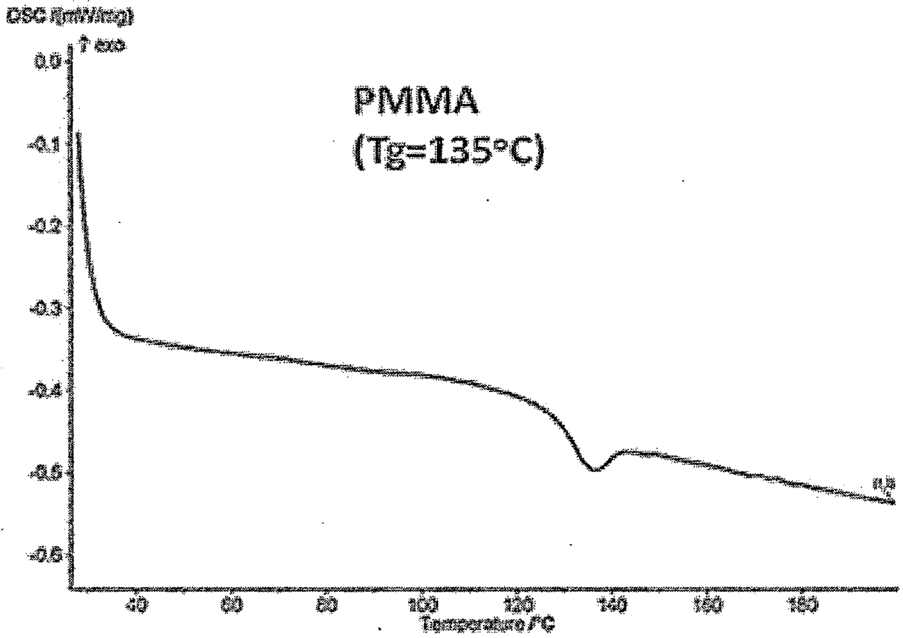

Figure 5.9 DSC curve for PMMA (glass transition temperature:135°C).

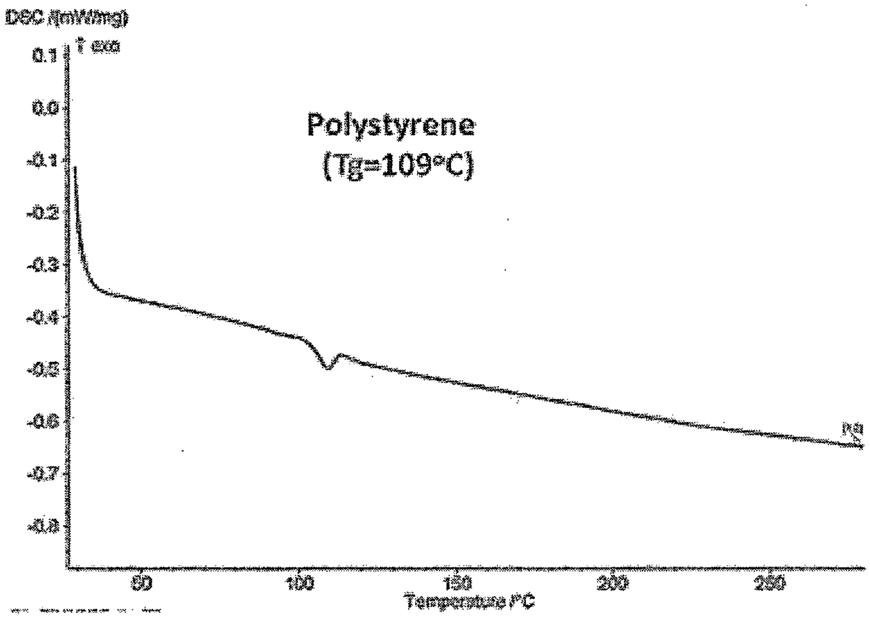

Figure 5.10 DSC curve for PS (glass transition temperature:109°C).

5.5.2.5 Scanning electron microscopy (SEM)

Scanning electron microscopy provides information for the shape, morphology and purity of compound. It is also advantageous for investigation of the changes that occurred upon various treatments.SEM photographs (Figure 5.11) of obtained polymer confirm the foamy fibrous texture of polymer. The surfaces are clean and seem to possess no external impurity or traces of side products or unused catalyst/ligand materials.

SEM photographs of PMMA initiated with CNTs clearly show the presence of nanotubes in it's texture (Figure 5.12).

SEM photographs of Polystyrene initiated with CNTs have a glassy appearance and a hard texture. The presence of CNT is visible in the SEM images.

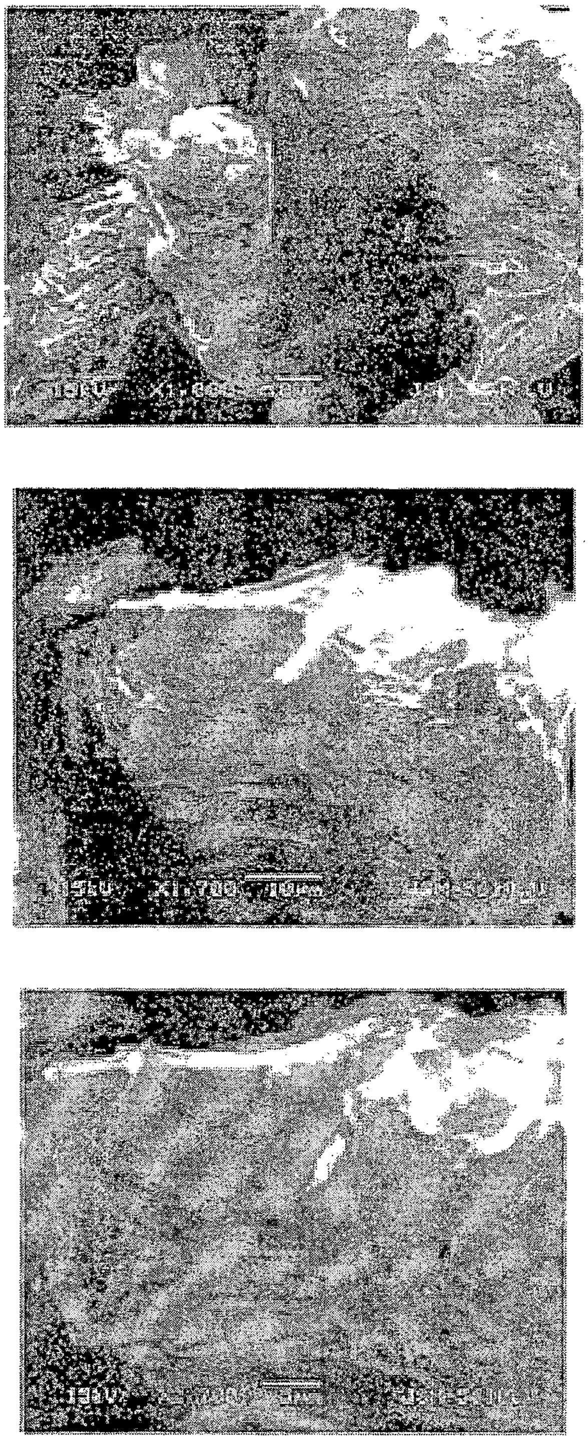

Figure 5.11 SEM images of polymer PMMA depict the foamy fibrous texture of the polymer.

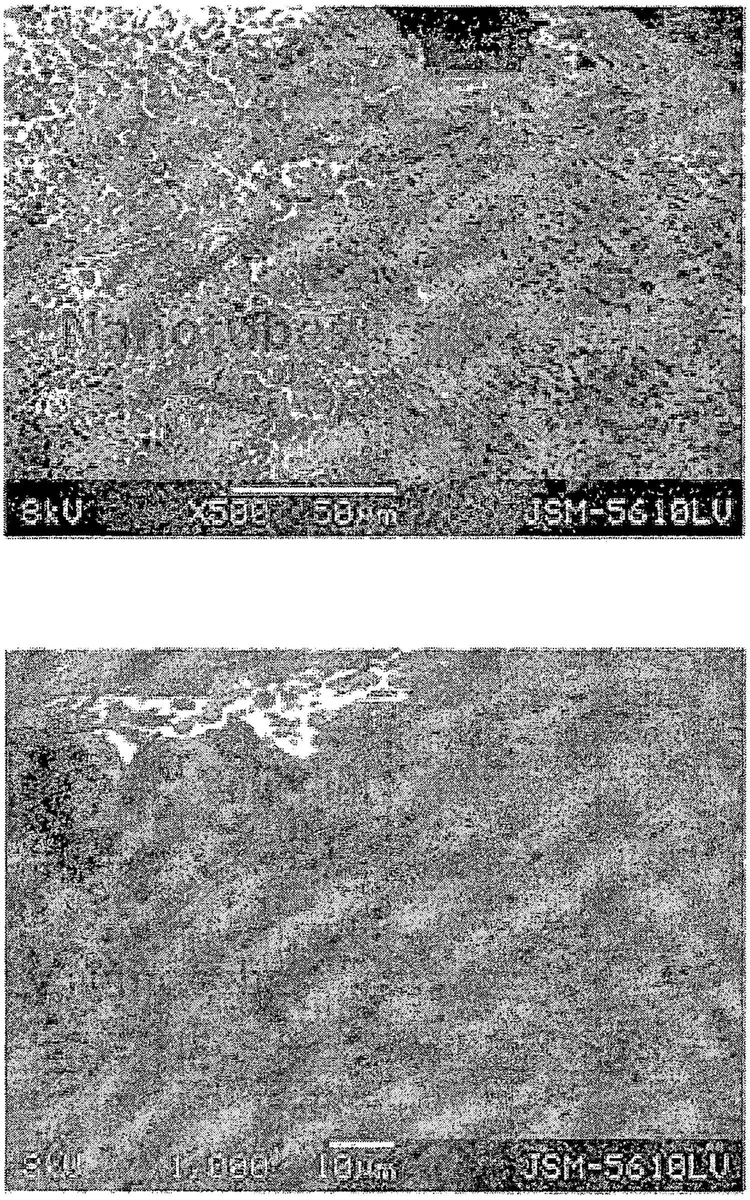

Figure 5.12 SEM images of polymer PMMA initiated by acylated CNT.

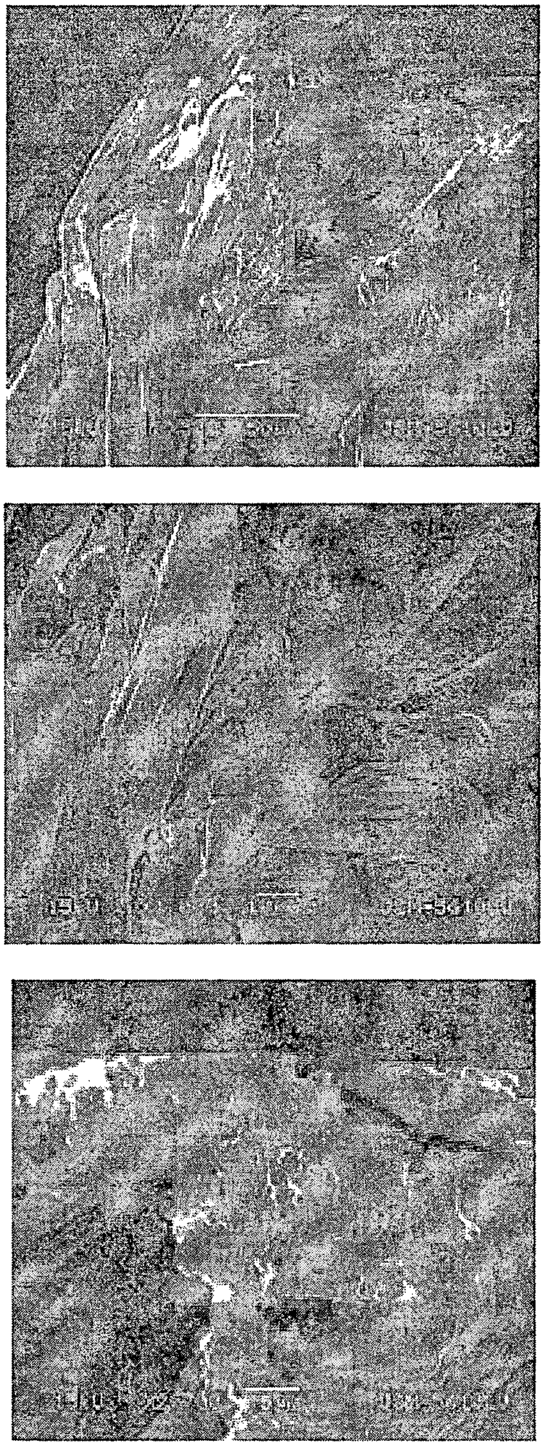

Figure 5.13 SEM images of PS (polystyrene) initiated by acylated CNT.

5.5.2.6 Size exclusion chromatography (SEC)

The number average molecular weights (Mn), weight average molecular weights(Mw) and polydispersities were determined by GPC.

The GPC results documented the formation of very high molecular weights as compared to M_{theo}

The results obtained in the different sets corresponding to different catalyst/ligand ratio, monomer/initiator ratio, solvent /surfactant ratio in polymerization of MMA by acetyl chloride are as shown in Table 5.2, Figure 5.14, Figure 5.15.

In the first set (S1) ,(catalyst : ligand :: 0.5:1) an emulsion of 4.6 gm of surfactant in 28 ml of distilled water was prepared, and used as solvent for monomer(PMMA). The number average molecular weight (Mn) and polydispersities were high as compared to that in ATRP's with other conventionally used ATRP initiators such as alkyl halides.

This can be due to number of reasons, Firstly ATRP itself may result in a broader PDI 1.2-1.7[212] depending on different reaction conditions such as catalyst system, solvent, initiator, temperature etc. Secondly, initiation by acetyl chloride would show a different character as compared to that by conventional methods. High rate of bond dissociation and radical formation tendency in acetyl chloride may disturb the rate of propagation and termination. The CH_3CO---Cl bond undergoes rapid dissociation and extraction of chloride radical under the effect of catalyst/ligand system.

In the second set (S2) catalyst :ligand ratio was changed to 1:1 ,all other conditions remaining the same. The Mn was less then ,that in set 1 but polydispersity was more.

In the sets 3,4 (S3,S4)the initiator amount was increased ,but the molecular weights were still higher, though the polydispersities were slightly close to 1.

Table 5.2 % conversions, weight average molecular weights and polydispersities for different sets.

Sets	Molar ratio M : C : L : I	Surfactant gm/10mL Solvent	Temperature (°C)	Time (h)	% Conv.	M_{theo}	Mn 1 x 10^5	Mw/Mn
S1	100:0.5:1:0.625	1.64	28	20	92	14798	4.42	1.26
S2	100:1:1:0.625	1.64	28	20	91.3	14686	1.65	1.47
S3	100:0.5:1:1.25	1.64	28	20	94	7598	5.33	1.13
S4	100:1:1:1.25	1.64	28	20	93.5	7558	2.84	1.23
ST	100:0.5:1:0.625	1.64	60	20	92	14798	2.84	1.19
PMLS	100:0.5:1:0.625	0.82	28	20	93	14958	7.22	1.05
PMVLS	100:0.5:1:0.625	0.41	28	20	93	14958	6.55	1.07
PMNS	100:0.5:1:0.625	0.00	28	20	17	2798	1.11	1.10

Monomer(M) = MMA (methyl-methacrylate), Catalyst(C) = CuCl, Ligand(L) = 2,2' bipyridyl, Initiator(I) = acetyl chloride, Surfactant= Brij 98, Solvent = water

S1--S5 : PMMA prepared in sets 1-4 at room temperature

ST : PMMA prepared at 60°C

PMLS : PMMA prepared with low surfactant concentration

PMVLS: PMMA prepared with very low surfactant concentration

PMNS: PMMA prepared with no surfactant

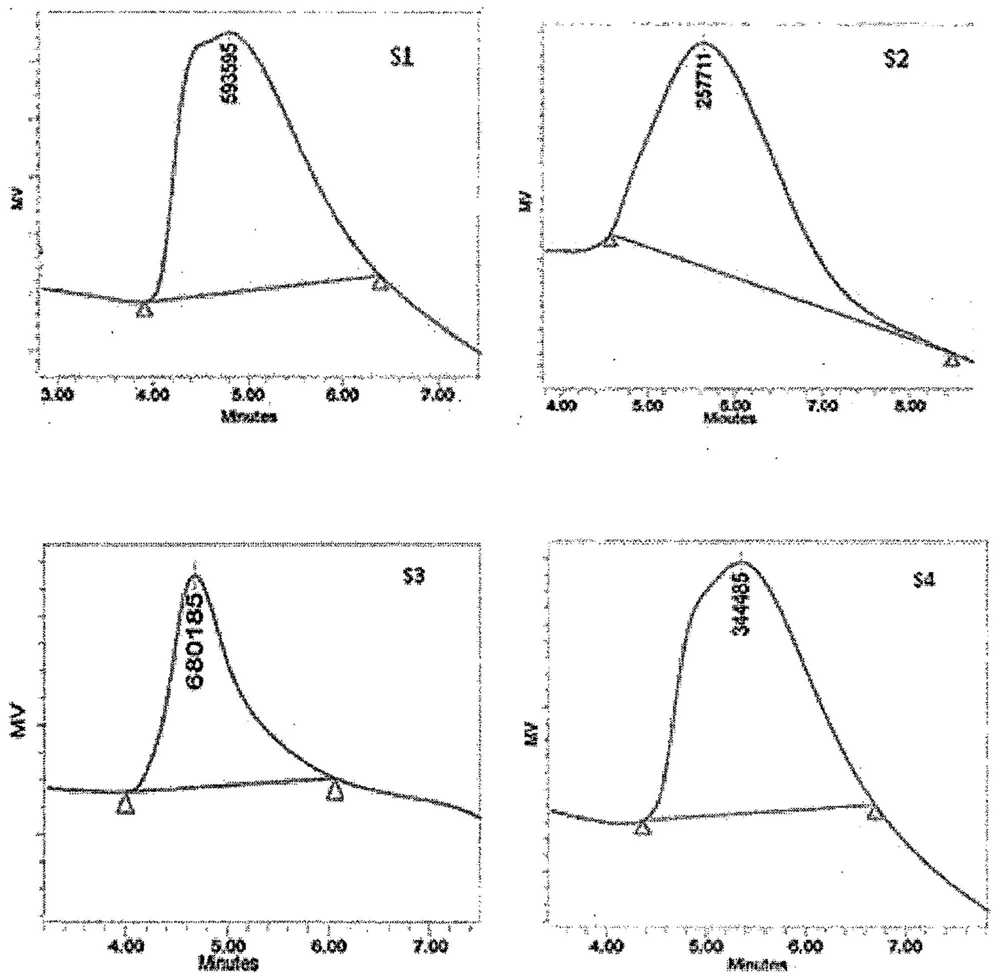

Figure 5.14 SEC curves for different sets S1, S2, S3, S4 depicting the peak apex and weight average molecular weight.

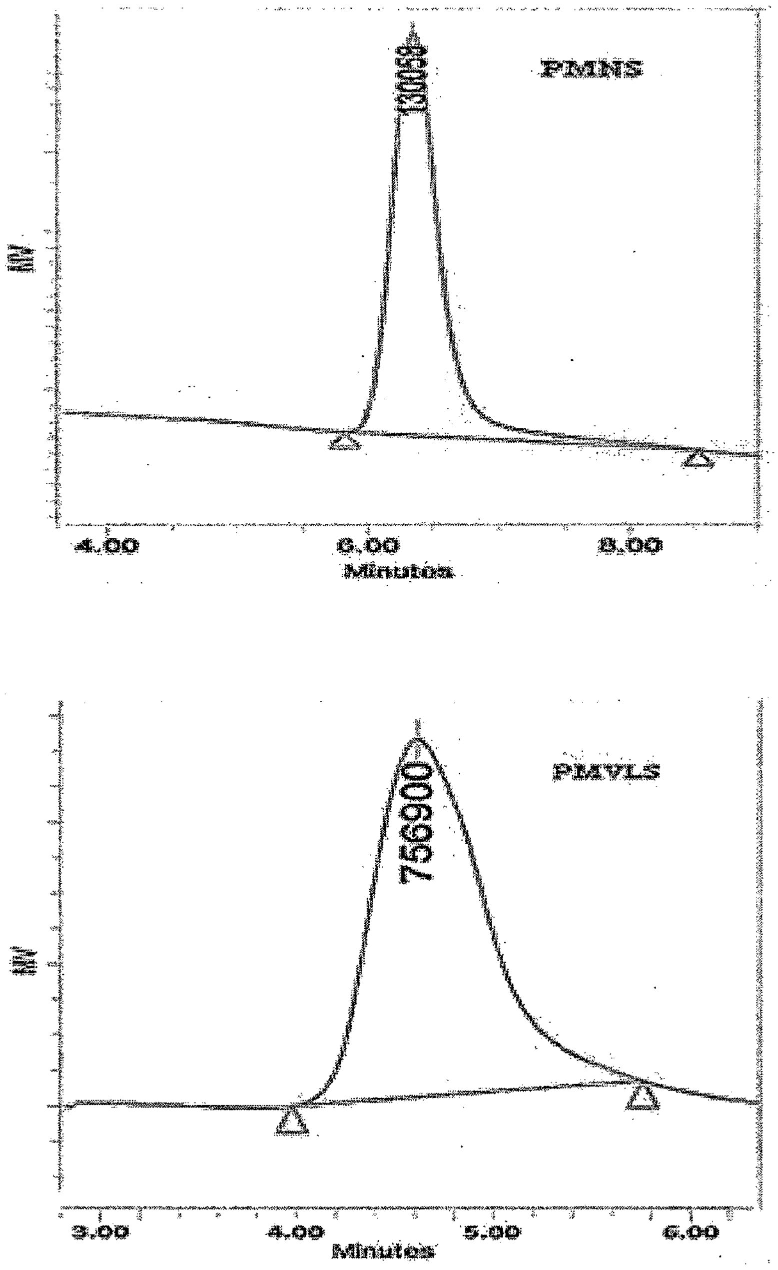

Figure 5.15 SEC curves for different sets PMNS and PMVLS depicting the peak apex and weight average molecular weight.

In the fifth set (ST) ,all conditions being same as in set 1 ,polymerization was carried out at high temperature (60°C). When the reaction proceeds at high temperature, as a result of higher activation energy for radical propagation than for radical termination, higher k_p/k_t ratios and better control is observed and thus syndiotactic polymer is dominated by isotactic species and comparatively low MW 's are obtained, but the polydispersities were still higher as compared to Sets(1-4).

When the surfactant amount was reduced, the emulsion was still stable. Set 6 (PMLS) contained 2.3g of Brij-98 where as Set 7 contained 1.15g of the surfactant. Set 8 did not contain any surfactant.

The polydispersities were found to decrease with reducing surfactant amount. The average molecular weights were found to drastically decrease to 1.11 x $10^5$when no surfactant was used in Set 8 (PMNS).

5.5.2.7 Kinectic studies

Figure 5.16(a,b) and Table 5.3 presents polydispersity (PD) and average number molecular mass (Mn) as a function of monomer conversion for ATRP of MMA 60°C. Polymer fractions were obtained at different time intervals by quenching the reaction at different times. At higher monomer conversions PD becomes very low(<1.20). A linear increase of number average molecular weight *Mn* (determined by size exclusion chromatography calibrated using polystyrene standards) versus monomer conversions up to 81% was found after 2h and up to 92% after 20h.

The graphs obtained indicate that Acetyl chloride act as efficient initiator. Initially the polydispersities are quite higher but are reduced to nearly one at higher conversions.

Table 5.3 Kinetic study of ATRP of PMMA at high temperatute using acetyl chloride as initiator (ST1-ST5)

Sets	Molar ratio M : C : L : I	Temperature (°C)	Time (h)	%Conversion	M_{theo}	Mn ($1x10^5$)	Mw/Mn
ST1	100:0.5:1:0.625	60	0.5	47	7598	1.13	1.95
ST2			1.0	60	9678	1.23	1.91
ST3			1.5	73	11758	1.35	1.79
ST4			2.0	81	13038	2.47	1.22
ST5			20	92	14798	2.84	1.19

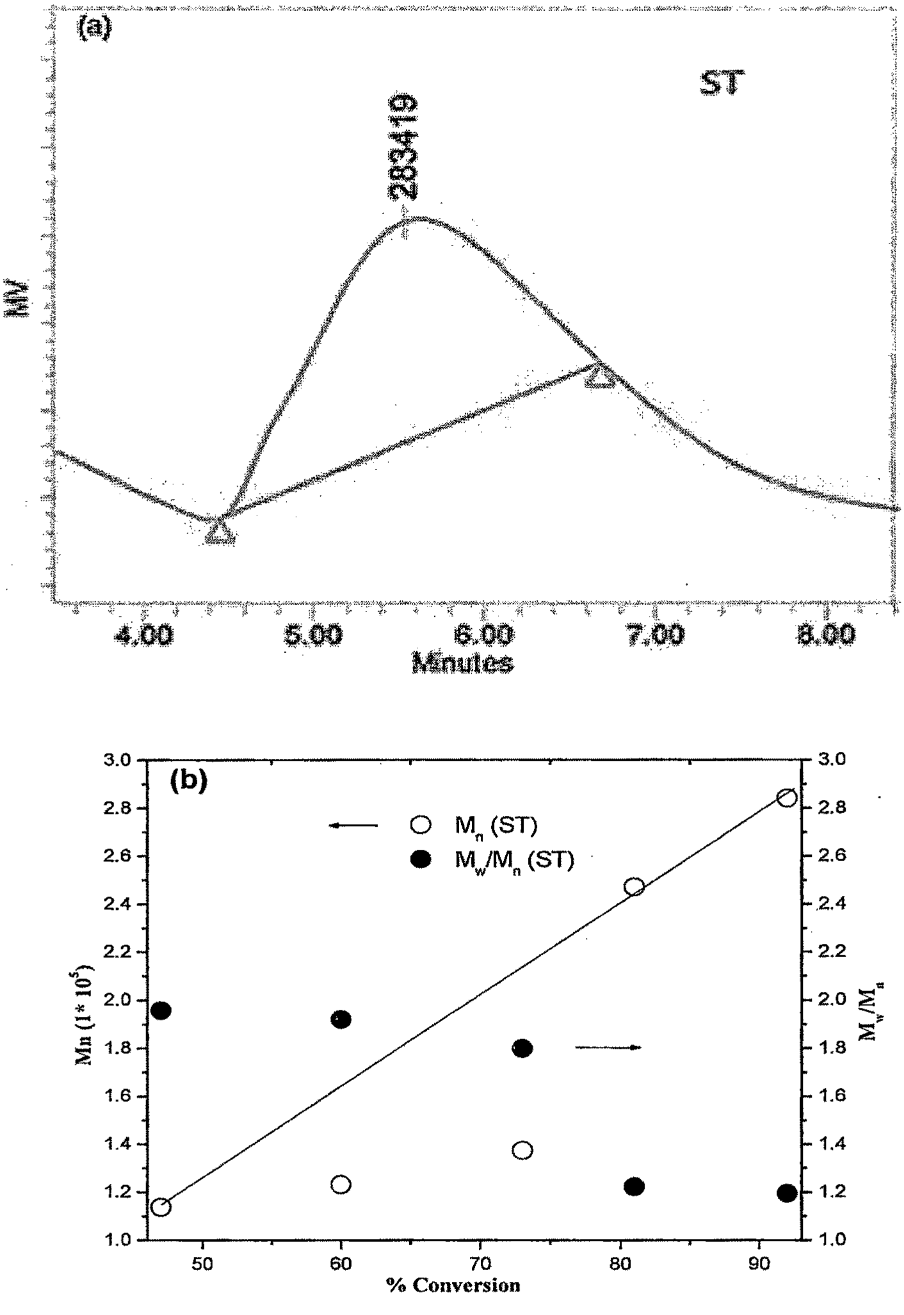

Figure 5.16 (a) SEC curve for acetyl chloride initiated ATRP of MMA depicting 2.83 x 10^5 and 2.84 x 10^5 as peak apex and weight average molecular weight respectively (b) PD and Mn as a function of monomer conversion ; reaction conditions: Temperature = 60°C and $[M]_o/[M_t^sX]_o/[L]_o/I_o$=

$[PMMA]_o/[Cu(1)Br]_o/[2,2'$ bipyridyl$]_o/[CH_3COCl]_o$=100:0.5:1:0.625 and surfactant (Brij-98)concentration =1.64gm/10 mL of distilled water.

Similar studies were also performed for set PMLS where the surfactant amount was reduced to 0.82 gm/10ml which was 1.64gm/10mL in earlier sets. Linear relationships of Mn and PD's with %conversion confirm it to be a efficient ATRP system(Table 5.4, Figure 5.17).A linear plot of $\ln([M]_o/[M])$ versus polymerization time indicate that the concentration of growing radicals remains constant, and termination is not significant. Both of these results suggest a "living" radical polymerization with negligible number of transfer and termination reactions.

The molecular weights were high as compared to those obtained in other sets, but polydispersities were very close to ideal value (i.e. 1). The reaction showed 89% completion after 2h and conversion was 93% after 20h.

Table 5.4 Kinetic study of ATRP of PMMA at low surfactant concentration (PMLS) using acetyl chloride as initiator.

Sets	Molar ratio M : C : L : I	Temperature (°C)	Time (h)	%Conversion	M_{theo}	Mn 1 x 10^5	Mw/Mn
PMLS1	100:0.5:1:0.625	28	0.5	45	7278	1.71	1.075
PMLS2			1.0	64	10318	3.96	1.068
PMLS3			1.5	76	12238	5.27	1.065
PMLS4			2.0	89	14318	6.00	1.060
PMLS5			20	93	14958	7.22	1.056

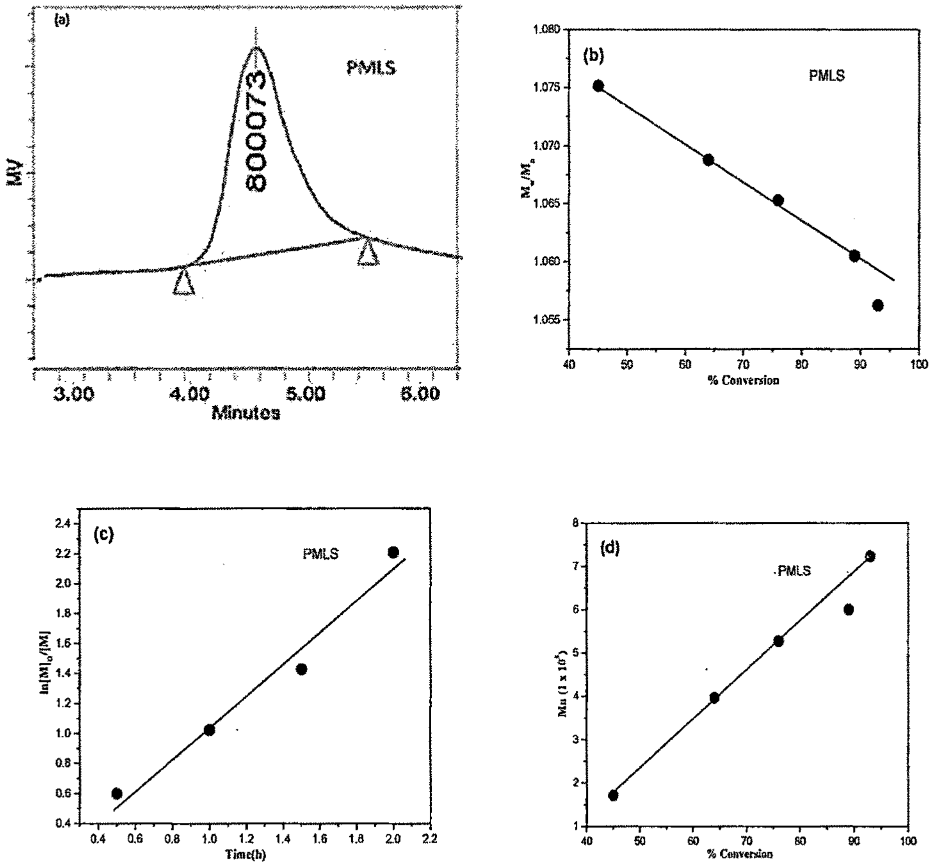

Figure 5.17 (a) SEC curve for acetyl chloride initiated ATRP of MMA depicting 8.0 x 10^5 and 7.2 x 10^5 as peak apex and weight average molecular weight respectively (b) PD as a function of %Conversion(c) ln[M]o/[M] versus time and (d)Mn as a function of %Conversion; reaction conditions: Temperature = 28°C and $[M]_o/[M_t^sX]_o/[L]_o/I_o$= $[PMMA]_o/[Cu(1)Br]_o/[2,2'\ bipyridyl]_o/[CH_3COCl]_o$= 100:0.5:1:0.625 and surfactant (Brij-98)concentration =0.82gm/10 mL of distilled water.

Similar results were obtained for Polystyrene polymer, where polymerization was carried out at room temperature as well as at high temperature of $60^{o}C$. Kinetics was performed and % conversions were evaluated. High average molecular weights were obtained as compared to theoretical values, but were less as compared to those in PMMA. Linear relationships of Mn and PD's with %conversion and a good linear plot of $\ln([M]_0/[M])$ versus polymerization time indicate a good efficient ATRP system(Figure 5.18,Table 5.5,5.6).

Table 5.5 Kinetic study of ATRP of Polystyrene at room temperature (PS1-PS5) using acetyl chloride as initiator.

Sets	Molar ratio M : C : L : I	Temperature (°C)	Time (h)	%Conversion	M_{theo}	Mn 1×10^5	Mw/Mn
PS1	100:0.5:1:0.625	28	0.5	67	11242	1.99	1.50
PS2			1.0	73	12242	2.21	1.42
PS3			1.5	81	13575	2.41	1.35
PS4			2.0	89	14908	2.46	1.34
PS5			20	94	15472	2.99	1.22

Table 5.6 Kinetic study of ATRP of Polystyrene at 60°C (PST1-PST5) using acetyl chloride.

Sets	Molar ratio M : C : L : I	Temperature (°C)	Time (h)	%Conversion	M_{theo}	Mn 1×10^5	Mw/Mn
PST1	100:0.5:1:0.625	60	0.5	67	11242	1.07	1.67
PST2			1.0	71	11909	1.09	1.56
PST3			1.5	82	13742	1.16	1.54
PST4			2.0	92	15408	1.31	1.49
PST5			20	95	15908	1.38	1.40

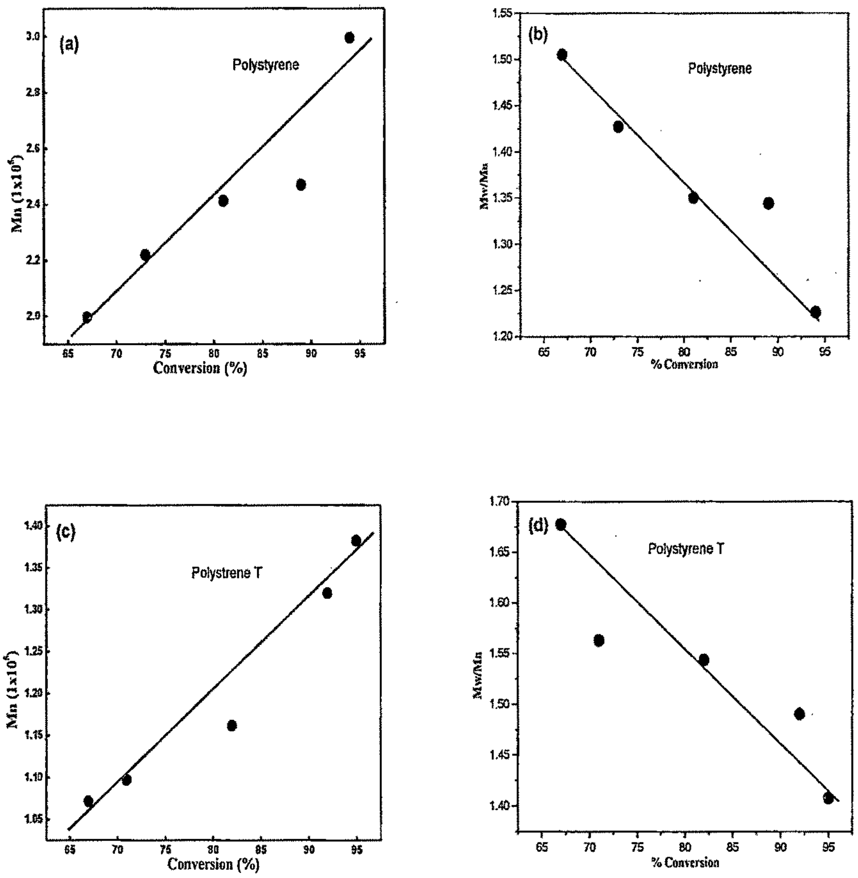

Figure 5.18 (a) Mn as a function of %Conversion (b) PD as a function of %Conversionfor polystyrene at room temperature (c) Mn as a function of %Conversion (b) PD as a function of %Conversionfor polystyrene at high temperature: $[M]_o/[M_t^sX]_o/[L]_o/I_o$= [Polystyrene]$_o$/[Cu(1)Br]$_o$/[2,2' bipyridyl]$_o$/ $[CH_3COCl]_o$=100:0.5:1:0.625 and surfactant (Brij-98)concentration =1.64gm/10 mL of distilled water.

The observed initiation by acyl radicals can be explained from the energetics of CO–X and Cu–X bonds, equilibrium and termination reactions at the initiation stage, and some side reactions for CO–Cl species. . High rate of bond dissociation and radical formation tendency in acetyl chloride may disturb the rate of propagation and termination. The formation of CH3CO· (acyl free radical) from acetyl chloride can be explained to be taking place under effect of catalyst/ ligand complex as in conventional ATRP (where the catalyst/ligand complex extracts chlorine free radical from a molecule having a readily removable halogen atom, and combines with it). Formation of acyl radical can be explained from it's stability and ability to attack a carbon-carbon double bond. It has been reported that the acyl free radicals appear to react as units below 100°C and do not decompose into alkyl radicals and carbon monoxide[213]. It has been estimated that in the gas phase, the activation energy in reaction is 16±3 Kcal (Figure 5.19). Consequently the reverse reaction, of combination of carbon monoxide and alkyl radical has little or no activation energy.

This accounts for the fact that acyl radicals have sufficient stability at room temperatures and do not show any decomposition. In contrast to this at higher temperatures, acyl radicals decompose to give alkyl radicals and carbon monoxide. At temperatures lower than 100°C, these acyl radicals have ability attack at alkene carbon. In the above study it was confirmed that in a system containing carbon monoxide, alkyl free radicals and alkene, the reaction of alkyl radicals with ethylene has greater activation energy as compared to that of reaction of acyl free radical with alkene to undergo polymerization (Figure 5.20), and thus there is a rapid attack of acyl radical on double bond which helps in polymerization of ethylene.

$CH_3CO^{\bullet} \longrightarrow CH_3{\bullet} + CO$ **Activation Energy = 16±3Kcal**

$CH_3{\bullet} + CO \longrightarrow CH_3CO^{\bullet}$ **Activation Energy = nil or very little**

Figure 5.19 Activation energies for decomposition acyl radicals and formation of acyl radical.

$RCO^{\bullet} + CH_2{=}CH_2 \longrightarrow RCOCH_2CH_2{\bullet}$ **a**

$RCOCH_2CH_2{\bullet} + CH_2{=}CH_2 \longrightarrow RCOCH_2CH_2CH_2CH_2^{\bullet}$ **b**

Figure 5.20 Action of acyl radical on double bond(a) and subsequent propagation to help in polymerization of ethene(b).

Acyl free radicals at higher temperature could be made stable at very high pressures of 600-1000 atm[214]. α-phenyl propionyl radicals have relatively less stability as compared to propionyl free radicals due to resonance stability in α-phenyl ethyl radical, but still at low temperature the former shows good stability and rapid addition to double bonds to polymerize styrene[215].

In presence of solvents such as water and methanol, there is some possibility of the reaction of complexed radical with solvent (for example, methanol) to form an acylated product and hydrogen radical, which then can attack double bond, to form polymer.

The presence of CH_3CO- as one of the terminal groups was confirmed by presence of peaks in range 177-178cm^{-1} in 13C NMR of polystyrene prepared by using acetyl chloride as initiator show that, though hydrogen radical is formed due to reaction of solvent and acyl radical in some amount, there is sufficient acyl radical available to cause polymerization. The activation energy for reaction of acyl radical with double bonds is less than the activation energy of reaction for combination of acyl radical with solvent and release of hydrogen radical. So polymerizations of MMA and Styrene with a appreciable yield was obtained using these initiator in ATRP. However this polymerization leads to a highly cross-linked structure with higher MW's as compared to the theoretical values(as confirmed by GPC). One reason for the high MW's could be that the termination reaction by combination of two acyl radicals does not interrupt the reaction, since the formation of α,α-diketones is relatively slow, and they can only add to the monomer and initiate polymerization.

5.6 Conclusions

Polymerization is fast with acetyl chloride (CH_3COCl)/CuCl as the catalytic system. The linear plots of ln[M]$_o$/[M] with time confirm the process to follow first order kinetics. The linear variation of polydispersity and average molecular weight with %conversion also account to formation of a polymer with good molecular weight distribution. But at the same time uncontrolled radical dissociation of acetyl chloride in ATRP of MMA and Styrene leads to formation of highly cross linked structures with very high molecular weights. Molecular weights do not follow the theoretical values; however, CH_3COCl/CuCl as catalysts give high conversion rates presumably due to the transfer process. Polydispersities decrease with conversion for these systems, and they are the lowest for systems with less surfactant concentration. The polydispersities follow similar trend with high surfactant concentration at high temperatures (60°C), but abnormally high polydispersities are found at low conversions, which are reduced to nearly one at the end of reaction. The phenomena observed can be explained by the energetics of CO–X and Cu–X bonds, equilibrium and termination reactions at the initiation stage, and some side reactions for CO–Cl species. Acetyl chloride is easily activated to form high concentrations of radicals. The formed acyl radicals have stability at temperatures below 100°C owing to high activation energy for decomposition reaction, and thus formed stable acyl free radicals rapidly take part in polymerization reaction. However, acetyl ($CH_3CO•$) radicals do not terminate bimolecularly, since the formation of α,α-diketones is relatively slow. Thus, they can only add to the monomer and initiate polymerization.