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SYNTHESIS OF STAR LIKE POLYMERS VIA ATRP USING FOUR ARMS ORGANIC INITIATOR

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Abstract: Four arm star- shaped poly (lauryl methacrylate) and polystyrene were synthesized by atom transfer radical polymerization with “core-first” technique. Four arm organic initiator pentaerythritol tetrakis(2-chloropropionate) was synthesized and used in the CuBr catalyzed atom transfer radical polymerization of LMA with N-(n-octyl)-2-pyridinemethanimine (OPMI) as ligand and styrene with N,N,N’,N’’,N’’-pentamethyldiethylenetriamine (PMDETA) as ligand. Polymers were characterized by GPC which shows that in both cases molecular weight increases with increasing conversion that indicate the living nature of polymerization. The star- shaped polymers were characterized by FT-IR and thermo-gravimetric analysis which shows that four arm star initiator was successfully used for the preparation of star-shaped polymer.

Keywords: Atom transfer radical polymerization (ATRP), “core-first” technology, *N*-(-n-octyl)-2-pyridinemethanimine, star shaped polymers, Gel permeation chromatography (GPC)

INTRODUCTION

Star polymers have been a consistent area of exploration in the ongoing pursuit of structure property relationships in macromolecular science[1]. These polymers have drawn increasing interest because their viscosity is lower than that of the corresponding linear polymers[2].Star polymers also have lower melting points and solution viscosities, superior mechanical properties and higher degree of chain end functionality compared to the corresponding linear polymers of similar molecular weight. Therefore, star polymers are used as rheological modifiers [3-10].

There are two broad approaches used for making star polymers e.g. “arm- first” and “core-first” approach. In the “arm-first” approach mono-functional, living linear macromolecules are initially synthesized then star formation occurs either of the two ways: a di-functional co-monomer is used to provide cross-linking through propagation or a multifunctional terminating agent is added connecting a precise number of arms to a central core molecule[11]. The former, micro gel, technique produces macromolecule with a large often heterogeneous number of arms while in the latter case, separation technique is used to isolate star from uncoupled linear polymers. In the “core- first” method, multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structure in both arm number and length. Advantage of this method is that the reaction consists solely of stars in the absence of linear polymers [12-15]. To synthesize well- defined stars, the use of initiator with precise functionality is essential. Furthermore, regular star- shaped polymers can not be successfully synthesized by means of conventional free-radical polymerization, as it would inevitably result in cross linked materials owing to uncontrolled termination reactions. Among the variety of methods reported, living polymerization seems to be the most suitable for the synthesis of branched polymers with controlled structure. Living ionic [16, 17], metathesis [18] and group transfer polymerization [19, 20] were adequate for the application, but all required strenuous methods of reagent purification. However controlled /living free radical polymerization was found to be good technique for the synthesis of polymer with controlled architecture [21]. Specifically atom transfer radical polymerization (ATRP) provides control over chain length and functionality by equilibrium between a dormant alkyl halide and a free radical mediated by an interchange between copper (I) /copper (II) salts and the organic polymeric chain ends [22-34].

A variety of transition metal complexes have been utilized for this role, but N-alkyl-2-pyridinemethanimines appears to be the most interesting, as they are known to be more effective at stabilizing metals on low oxidation states than either of the other alternatives [35-38]. Controlled polymerization of higher alkyl methacrylates by ATRP method is difficult due to the insolubility of catalyst. Since both monomer and the polymer formed are hydrophobic in nature however Cu (I) Br/ Cu (II) Br catalysts are polar in nature therefore catalyst gets precipitated. In most cases the ATRP of higher methacrylates was done in the presence of solvent. Haddelton et al. examined the ATRP of n-butyl, n-hexyl & n-nonyl methacrylate using EBiB as initiator, CuBr as catalyst & N-(-n butyl-)-2-pyridinemethanimine as ligand in xylene at 95°C [39]. Raghunadh et al. also reported the ATRP of LMA in the presence of EBiB/ CuBr/N-(-n propyl-2pyridinemethanimine) (PPMI) with controlled way but they used the very dilute solution of monomer (15% by volume) [40]. Bulk polymerization of stearyl acrylate (ODA) by ATRP (CuBr/PPMI) at 95°C reported by Street et al. was poorly controlled. It is well reported in the literature that the solubility of catalyst system can be enhanced by introduction of groups similar to monomer [41]. For example in case of long alkyl methacrylate, solubility can be enhanced by increasing the length of alkyl group in the catalyst, initiator or both. The catalytic amounts of quaternary ammonium halide Aliquet336, ® a phase transfer catalyst shows better control on polymerization of higher alkyl methacrylate at ambient temperature by using CuCl/PMDETA as the catalyst system [42]. Bulk and solution polymerization of LMA was carried out in our lab by ATRP method using EBiB as initiator, CuBr as catalyst and N-(-n propyl[PPMI] / n-hexyl[HPMI]/n- octyl -2-pyridinemethanimine)[OPMI] as ligands. In those cases better control was observed when OPMI was used as ligand. OPMI was found to be very efficient ligand for homogeneous bulk and solution polymerization of higher alkyl methacrylate[43].

Poly (lauryl methacrylate) (PLMA) is a well known polymer for their bulk and solution properties. The presence of long side chain groups in the polymer extends the use of such polymers as pour-point depressants, rheological modifier and additives in petroleum based products [44]. Therefore, the synthesis of star- shaped PLMA is task of prime importance. Qui et al. also synthesized star polymers of LMA via ATRP using "arm-first" method [45]. He used linear poly (lauryl methacrylate) as macroinitiator and ethylene glycol dimethacrylate (EGDMA) as cross linker. Better result was observed when star polymers formed from shortest arms had larger molecular weight and narrow MWD. However, when the length of the arms reaches to a relatively high level, the cross-linking reaction cannot go on. The lower ratio of EGDMA to PLMA (2:1) cannot initiate the cross-linking reaction, but excess high ratio of EGDMA to PLMA (7:1) results in the gelation. Therefore, it was considered of interest to investigate systematically the properties of star- shaped polymers using "core-first" approach.

The paper describes the synthesis and characterization of four arm star polymer of LMA and styrene with narrow molecular weight distribution using four arm initiator i.e. pentaerythritol tetra- kis(2- chloro propionate), CuBr as catalyst and OPMI as ligand in the presence of toluene. Although initiator prepared by reacting pentaerythritol with 2- bromo propionyl bromide/ 2- bromo isobutyryl bromide have been used in the past to prepare star shaped homo polymers / copolymers using different monomers [46]. However no reports are available of pentaerythritol tetrakis (2- chloro propionate) as initiator for the synthesis of four arm star polymers. Therefore we thought of evaluating the homopolymers of LMA using of pentaerythritol tetrakis(2- chloro propionate) as initiator. At first, four arm star initiator [pentaerythritol tetrakis(2- chloropropionate) obtained by reacting pentaerythritol with 2-chloropropionyl chloride in the presence of triethylamine. Similarly styrene was also polymerized using pentaerythritol tetrakis(2-chloropropionate) as initiator, CuBr as catalyst and pentamethyldiethylenetriamine (PMDETA) as ligand.

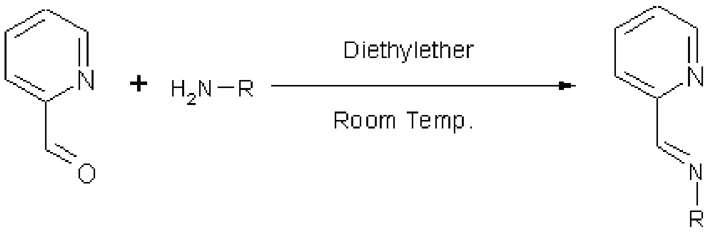
EXPERIMENTAL

Materials

Lauryl methacrylte, LMA (Aldrich, USA, 96%) was purified by washing with 5% aqueous NaOH solution, followed by washing with water till neutral and then dried over anhydrous $CaCl_2$. Finally it was distilled under vacuum and stored in refrigerator below 5°C. Copper bromide (Aldrich USA, 98%) was purified by stirring in glacial acetic acid under nitrogen followed by filtration, washing with dry ethanol and dried at 100°C as reported in literature [47]. Pentaerythritol 99%, ethyl-2-bromo isobutyrate (EBiB) 98%, pyridine-2-carboxaldehyde 99%, n-octylamine 99% (Aldrich, USA), were used as received. 2-Chloropropionyl chloride 99% (Merck, Germany), triethylamine (Qualigens, India) was stirred over night with anhydrous sodium sulphate under nitrogen and filtered before the reaction. Tetrahydrofuran and toluene (Merck) was dried by refluxing with sodium and benzophenone under nitrogen.

Synthesis of *N*-(n-octyl)-2-pyridinemethanimine (OPMI)

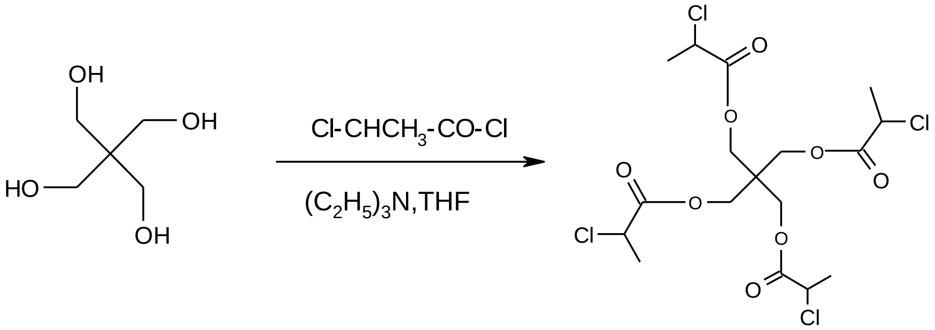
OPMI was synthesised by reacting n-octylamine and pyridine-2-carboxaldehyde according to the procedure represented.



R = octyl [OPMI]
Scheme 1 *Synthesis of N-(n-octyl)-2-pyridinemethanimine*

The detailed procedure for the synthesis of N-(n-octyl)-2-pyridinemethanimine was reported elsewhere[39].
Yield: 92%, boiling point 101°C/0.2 Torr
^{1}H-NMR ($CDCl_3$ δ ppm): 8.63(m,1H), 8.37(s,1H), 7.97(m,1H), 7.70(m,1H), 7.27(m,1H), 3.65(t,2H), 1.70(m,2H), 1.27(m,10H), 0.85(t,3H)
^{13}C-NMR ($CDCl_3$ δ ppm): 161.6, 154.6, 149.3, 136.4, 124.5, 121.1, 61.5, 31.8, 30.6, 29.3, 29.2, 27.3, 22.6,14.0
IR:1649cm^{-1}(νC=N)

Synthesis of pentaerythritol tetrakis(2-chloropropionate) (Star initiator)
It was prepared by reacting pentaerythritol with 2-chloro propionoyl chloride according to following scheme.



***Scheme 2**: Synthesis of pentaerythritol tetrakis(2- chloropropionate)*

Procedure:
Pentaerythritol (3.4g, 0.025mole) was placed into a 500 ml round bottom flask with 75 ml of THF and 15 ml (0.215 mole) triethylamine and cooled to 0°C by placing it in an ice cooled water bath. A solution of 2-chloropropionoyl chloride (10.42 ml, 0.215 mole) and 25 ml THF was added to a 50 ml pressure equalizing addition funnel fitted to the flask under nitrogen. The reaction mixture was added drop wise to the pentaerythritol solution. The reaction was stirred overnight and allowed to warm to room temperature. The mixture was transferred to a 1 liter separating funnel with 300ml of diethyl ether and extracted consecutively with H_2O, washed with aqueous solution of $NaHCO_3$ till neutral followed by washing with water. The organic phase was dried over anhydrous Na_2SO_4 and filtered and the solvent removed using rotary vacuum evaporator. The product, a white solid, was re-crystallized directly from the diethyl ether.
The initiator synthesized was characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR spectra.

Pentaerythritol tetrakis(2-chloropropionate)
Yield: 75%, Melting point:88.25°C
^{1}H-NMR ($CDCl_3$ δ ppm): 1.7(d,3H),4.2(s,2H),4.7(m,1H)
^{13}C-NMR ($CDCl_3$ δ ppm):168.80,62.50,52.70,46.03,21.50
FTIR: 1748 cm^{-1}(νC=O)

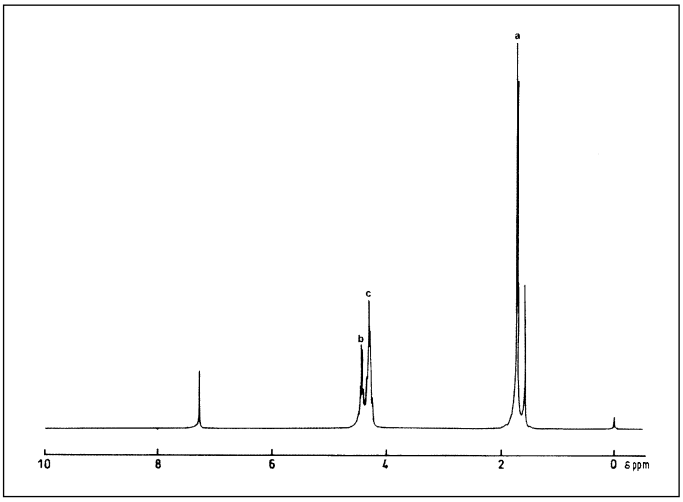


Figure 1: ^{1}H-NMR spectrum of pentaerythritol tetrakis(2-chloropropionate).

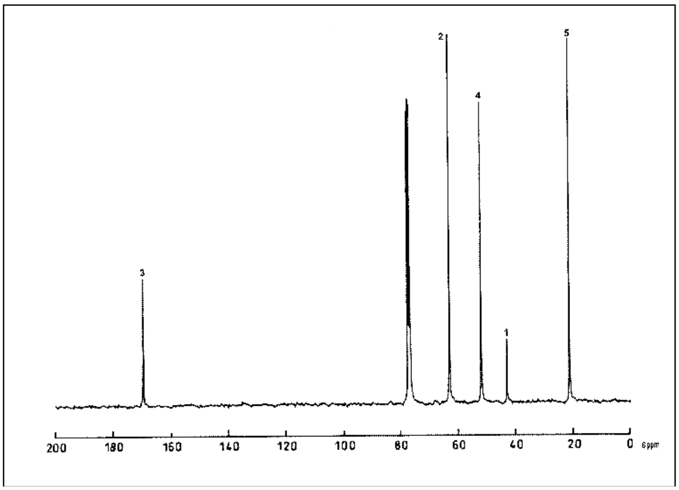


Figure 2: ^{13}C-NMR spectrum of pentaerythritol tetrakis(2-chloropropionate)

Synthesis of star polymers

Star poly (lauryl methacrylate) (SPLMA):

A dry schlenk tube was filled with CuBr (0.0390g, 0.272 mmole), OPMI (0.1484g, 0.68 mmole), LMA (9.9ml, 0.034 mole), initiator [0.1354g, 0.272 mmole pentaerythritol tetra- kis(2-chloropropionate)] and toluene (2.0 ml) was added in that order. The reaction mixture was purged with nitrogen to remove traces of oxygen. The tube was degassed three times by repeated freeze/ vacuum/ thaw cycles and finally evacuated and back filled with nitrogen. The reaction mixture was placed in preheated oil bath at 95°C. The polymerization was stopped at a desired time by cooling the tube in ice water. The reaction mixture was diluted with THF and passed through a short neutral alumina column to remove the catalyst. The polymer was precipitated using methanol as non-solvent. Then, the polymer was separated by filtration dried under vacuum for 24h at 60°C and yield was determined gravimetrically.

Star polystyrene (SPS):

A dry schlenk tube filled with CuBr (0.0390g, 0.272 mmole), PMDETA (0.1ml, 0.54 mmole) and styrene (4.7ml, 40.8 mmol), initiator [(0.1354g, 0.272 mmol; pentaerythritol tetrakis(2-chloropropionate)] and was added in that order. The nitrogen was purged in the reaction mixture to remove traces of oxygen. The tube was degassed three times by repeated freeze/ vacuum/ thaw cycles and finally evacuated and back filled with nitrogen. The reaction mixture was placed in preheated oil bath at 110ºC. The polymerization was stopped at a desired time by cooling the tube in ice water. The reaction mixture was diluted with THF and passed through a short neutral alumina column to remove the catalyst. The polymer was precipitated with methanol. Then, the polymer was dried under vacuum for 24h at 60°C.

Hydrolysis of star- shaped polymers:

Star-PS (Mn=13900,PDI=1.19)(0.16g) was dissolved in 50ml of THF, 3g of KOH and 50ml of ethanol were added, and the mixture was refluxed for 20h. The solvent was evaporated and the dry residue was suspended in water. The polymer was filtered off, dried and reprecipitated from THF/methanol.

CHARACTERIZATION

Structural characterization: FT-IR spectra were recorded as thin films using a Nicolet FTIR spectrophotometer (Walthan,MA). NMR spectra were recorded on a Bruker spectrospin DPX 300 spectro-meter (Fallenden, Switzerland) using $CDCl_3$ as a solvent and tetramethyl silane as an internal standard.

Molecular Characterization: Waters (1525) gel permeation chromatograph (Milford, MA) equipped with styragel (HR-3 and HR-4, 7.8x 300 mm) columns along with Evaporating Light Scattering Detector (ELSD-2420) was used to determine the molecular weight and molecular weight distribution in polymers. For calibration, polystyrene standards (Shodex Standards SL-105, Japan) having molecular weight of 197,000, 51,000, 13,900 and 2100 were used. THF was used as solvent at a flow rate of 1 ml/min.

Inherent viscosity (η_{inh}) of polymer in toluene was determined using Ubbelhode viscometer at 25ºC at 0.5% w/v solution.

Thermal characterization: Thermal characterization was done using thermogravimetry and differential scanning calorimetry. TA 2100 thermal analyzer was used for recording TG/DTG traces in nitrogen atmosphere over the temperature range of 20-800ºC. A heating rate of 20ºC/ min and a sample size of 10 ± 5mg were used in each experiment. A perkin Elmer Pyris 6 differential scanning calorimeter (Walthan, MA) was used for the thermal characterization of polymers. DSC scans were recorded in a static air atmosphere at a heating rate of 10ºC /min with 5±1 mg of samples.

RESULTS AND DISCUSSION

Synthesis of four arm star initiator:

As we know "core- first" method is very suitable method for the synthesis of star-polymers. Therefore, pentaerythritol and 2-chloropropionoyl chloride were used as the starting materials for the synthesis of the four-arm pentaerythritol tetrakis(2-chloropropionate) initiator.

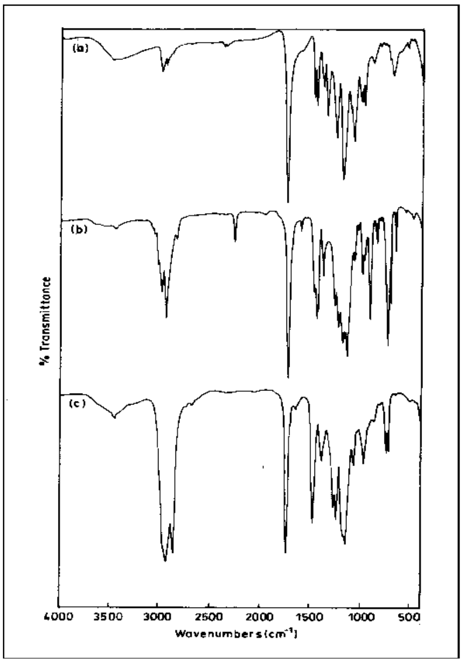


Figure 3: FTIR spectra of (a) star- initiator; (b) star- shaped polystyrene and (c) star- shaped poly(lauryl methacrylate)

Figure 3 shows the FT-IR spectrum of star initiator. The absorption band at 1748cm^{-1} ascribed to the presence of ester bond. The absence of absorption band of hydroxyl group of pentaerythritol at 3456 cm^{-1} in the star initiator indicates the conversion of all hydroxyl groups to ester. The ^{1}H-NMR spectrum of star initiator is shown in Figure.2. The presence of multiplet for Cl-$\underline{CH}$ (4.2 ppm), singlet for O-$\underline{CH_2}$ (4.7 ppm) and multiplet for $\underline{CH_3}$ observed at 1.7ppm.This shows that star initiator has a structural formula as shown in scheme 2. This was also confirmed by the ^{13}C-NMR spectrum which clearly indicates the five set of carbon of star initiators (Figure 3). DSC of the star initiator indicates the melting point at 88.25ºC.

Synthesis of star- shaped polystyrene and poly (lauryl methacrylate): The four-arm star initiator having terminal chlorine group was capable of initiating atom transfer living radical polymerization. In the synthesis of star-shaped polystyrene and PLMA, CuBr was used as catalyst and PMDETA and OPMI were used as ligands respectively. The polymerization of styrene monomer and LMA monomer were carried out at 110ºC and at 95ºC respectively. The use of OPMI as ligand for the polymerization of LMA facilitates the solubility of CuBr in reaction medium due to the presence of octyl group. The molecular weight of polymer [PS/or PLMA] increased with increasing percent conversion (Figure 4 and 5) without much change in polydispersity. Figure 6 and 7 shows the plot of $\ln[M]_0/[M]$ Vs polymerization time for the ATRP of lauryl methacrylate and styrene. In case of LMA polymerization, a sigmoidal plot was observed whereas in case of styrene, a linear relationship was observed. The first-order kinetic plots indicate that the living radical concentration was constant during the polymerization.

Figure 3 shows the FT-IR spectra of star- shaped polystyrene and star shaped poly (lauryl methacrylate). The presence of absorption band at 1748 cm^{-1} (ester bond) confirmed the incorporation of star initiator in the polystyrene. However, in case of PLMA, the ester stretching of initiator over laps with that of the PLMA ester stretching hence we cannot confirm the presence of initiator.

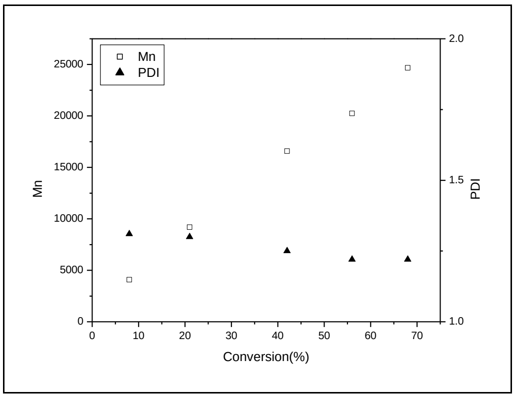


Figure 4: Plot of number average molecular weight (Mn GPC) and PDI vs. conversion(%) for homopolymer of LMA using four arm initiator [molar ratio of LMA: initiator: CuBr: OPMI: 125:1:1:2.5].in toluene at 95ºC.

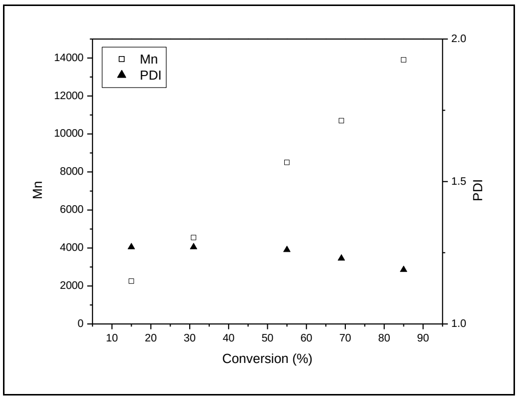


Figure 5: Plot of number average molecular weight (Mn GPC) and PDI vs. conversion (%) for hom-polymer of styrene in toluene at 110ºC [molar ratio of styrene: initiator: CuBr : PMDETA 150:1:1:2].

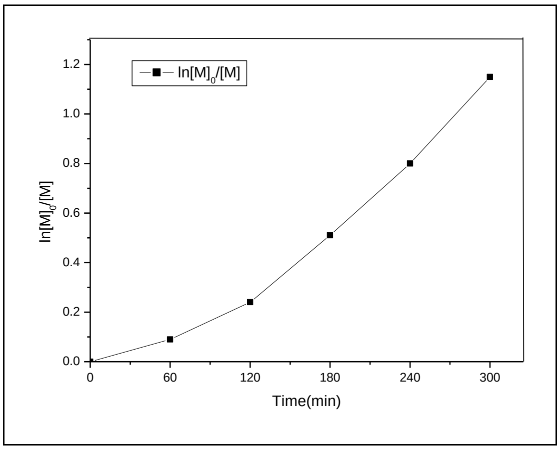


Figure 6 Plot of ln[M]0/[M] vs time for ATRP of LMA in toluene at 95ºC [mol ratio of LMA: Initiator: CuBr: OPMI 125:1:1:2.5]

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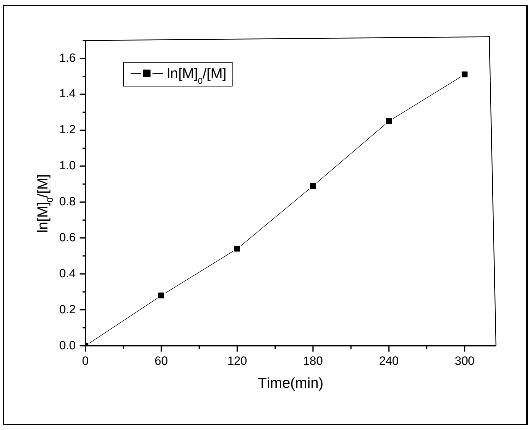

Figure 7: Plot of ln [M]0/ [M] vs time for ATRP of styrene at 110ºC [mol ratio of styrene: Initiator: CuBr: PMDETA. 150:1:1:2]

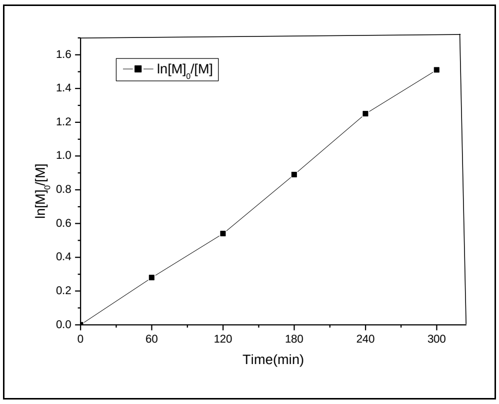

Figure 8: ^{1}H-NMR spectrum of "star-shaped" poly(lauryl methacrylate) (Mn,GPC=8.1 x 103g/mol) in CDCl$_3$

The chemical structure of the obtained star-shaped PLMA/ or PS were characterized by ^{1}H NMR and ^{13}CNMR as shown in figure 9 and 10.

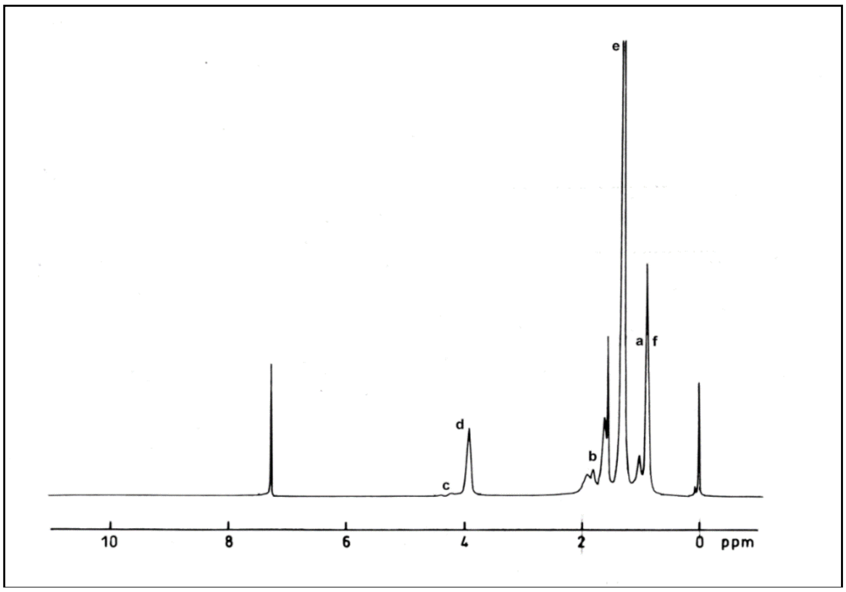

Figure 9: ^{1}H-NMR spectrum of "star-shaped" poly(lauryl methacrylate) (Mn,GPC=8.1 x 103g/mol) in CDCl$_3$

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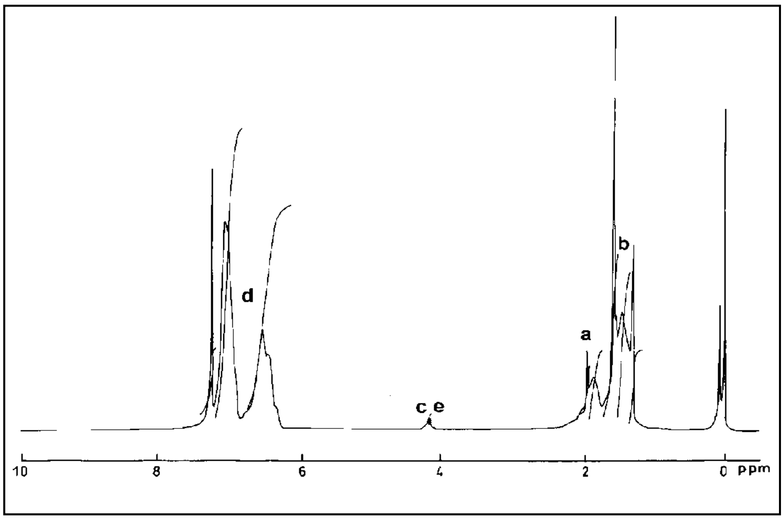

Figure 10: ^{1}H-NMR spectrum of “star-shaped” polystyrene (Mn,GPC = 2.2 x 103g/mol) in $CDCl_3$

GPC analysis and Molecular weight calculation:

From table 1 the GPC result shows that star- shaped polystyrene and star- shaped PLMA were successfully synthesized. By using ATRP product with narrow MWD were obtained. The theoretical molecular weights for star-shaped PS and star- shaped PLMA can be calculated from the following equation:

$$Mn_{,theo} = \text{Molecular weight(Monomer)} \times [M]_0/[I]_0 \times \text{Conversion}$$

Where $[M]_0$ is the initial concentration of monomer and $[I]_0$ is the initial concentration of the initiator. From the above equation the theoretical number average molecular weights Mn_{the} for star- shaped PS and star- shaped PLMA are 13900 and 23500 $gmol^{-1}$ respectively. The initiator efficiency ($Mn_{,the}$ / $Mn_{,GPC}$) in the case of star- shaped polystyrene was close to 1.0. However in the case of star shaped PLMA the calculated molecular weight is lower than the molecular weight of PLMA obtained from SEC ($Mn_{,SEC}$). The reason for the higher molecular weight ($Mn_{,SEC}$) is a larger hydrodynamic volume of PLMA as compared with PS standards used for SEC calibration[40]. Hence, the efficiency of catalyst/ ligand system for the ATRP of LMA can not be determined from Mn_{SEC}.

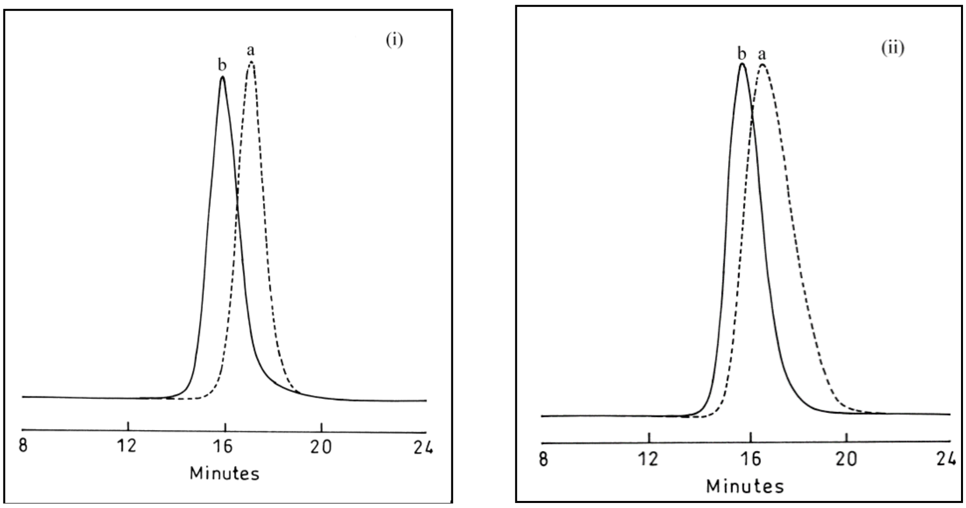

Figure 11: GPC traces of (i) poly(lauryl methacrylate) (a) macoinitiator and chain extended polymer and (ii) polystyrene (a) macoinitiator and (b) chain extended polymer.

Molecular weight Mn of both the star-shaped poly (lauryl methacrylate) and polystyrene polymer were calculated from ^{1}H NMR [Figure 8 and 9]. In the case of star- shaped polystyrene, a signal observed at 4.19 ppm is due to the hydrogen atom -CH_2-**CH** (Ph)-Cl of end group and CO-**CH**-CH_3 of initiator. However in case of star-shaped poly (lauryl methacrylate) there is a signal at 3.92 ppm due to –O-$\mathbf{CH_2}$- of alkyl side chain of LMA that can be used in the calculation of molecular weight of the both the star- shaped polymers. The Mn (NMR) was calculated according to equation 1 and 2 for star-shaped poly (lauryl methacrylate) and polystyrene respectively.

$$M_{n.(NMR)} = 4(\boldsymbol{I}d/2\boldsymbol{I}c)\ x256 + 496 \qquad (1)$$

$$M_{n\ (NMR)} = 4(2\boldsymbol{I}d/5\boldsymbol{I}c,e)\ x105 + 496 \qquad (2)$$

Where 4 define the branch value of the star-shaped polymer, the values 496, 256 and 105 are molar masses of star- shaped initiator, lauryl methacrylate and styrene monomer.

The molecular weight calculated from NMR (Mn=6.6 x10^3 g/mole) for star- shaped poly (lauryl methacrylate) is lower than the Mn$_{GPC}$. However it is equal to the theoretically calculated molecular weight. The reason is similar as reported[40].On the other hand, in the case of star-shaped polystyrene the molecular weight calculated by the NMR (Mn=2.1 x 10^3 g/mole) is equal to the theoretically calculated molecular weight and Mn$_{GPC..}$ Chain extension polymerization was carried out using star shaped PLMA/ or PS as macroinitiator and polymerization was done using LMA/ or styrene monomer. It was observed that molecular weight increased from 6428 to 10,369 in the case of poly (lauryl methacrylate) (figure10) and from 4452 to 10,696 in case of polystyrene (figure11).That confirm the living nature of the terminal Cl end group.

Viscosity measurement:

For comparison, linear polymers with similar molecular weights were also prepared by ATRP. As seem from the table 1 it is apparent that star- shaped polymers have much lower viscosities than the corresponding linear polymers. This can be attributed to smaller hydrodynamic radii in toluene for star-shaped polymers, indicating more compact forms of this type of material The molecular weight of hydrolyzed polymer (2100gmol^{-1} and PDI 1.23) was the approximately1/4th of the star polystyrene that confirm the equal length of the each arm. However, the hydrolysis experiment in the case of PLMA could not be performed because the side chain in the LMA linked to the main chain by the ester bond

Table 1 Molecular characterization of star shaped polymers

Sample	$M_{n\mathit{Theo}}$ gmol-1	$M_{n(GPC)}$ gmol-1	PDI (M_w/M_n)	η_{inh} (mL/g)	Yield [%]
SPLMA	19810	23500	1.22	13	62
PLMA	18340	24900	1.31	19	65
SPS	13260	13900	1.19	9	88
PS	13884	13700	1.25	15	89

Mn Theo = Molecular Weight (monomer) X [M]0/[I]× Conversion (%)
ηinh= Inherent viscosity at 25°C in toluene[at 0.5 %]

Table 2 Hydrolysis data of star-polystyrene polymers

	Mn x 10-3 [g/mol -1] for star polystyrene	
Sample	Before hydrolysis	After hydrolysis
1	[6.65] (1.23)	[1.53] (1.24)
2	[8.10] (1.20)	[1.88] (1.21)
3	[13.90] (1.19)	[2.40] (1.23)

Thermal analysis:

Figure 12 show TG traces for initiator, star PS, star PLMA, linear PS and linear PLMA. Single step degradation was observed for the star initiator whereas star PS and PLMA showed two steps and three steps degradation respectively. Linear PS and PLMA showed single and two step degradation respectively. In case of polystyrene [star- shaped], first step mass loss in the temperature range of 230-240°C could be due to degradation of core followed by chain scission.

Mass loss in this temperature range was also observed in star initiator. Second step degradation was similar to what we observed in linear polymers.

In case of star PLMA, first step degradation observed in the temperature range of 230-240ºC could be due to the degradation of core followed by side chain elimination of PLMA observed in the temperature range of 290-310ºC. The third step could be due to the random scission leaving behind no char.

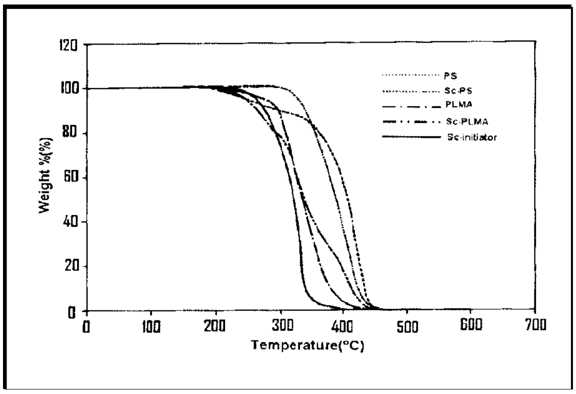

Figure 12: TG traces of star initiator, linear and star shaped polymers under N2 atmosphere [heating rate 200C/min]

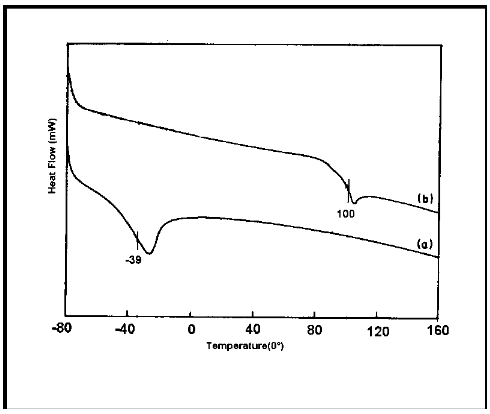

Figure 13: DSC scans of star shaped polymers (a) poly(laurylmethacrylate)) and (b) polystyrene.

Figure 13 show the DSC scans of star- shaped homo-polymer of PLMA and polystyrene. An endothermic shift in base line corresponding to the glass transition temperature was observed. Tg was noted as a midpoint inflexion and it was observed at -39ºC [PLMA] and 100ºC [PS]. Star- shaped polymers and linear polymers had similar Tg.

CONCLUSION

The four arms organic initiator was synthesized successfully and was used successfully in the atom transfer radical polymerization of lauryl methacrylate and styrene. Viscosity measurement shows that star- shaped polymers had lower solution viscosity as compared to the linear polymer of similar molecular weight. The molecular weight increased with increasing percentage conversion without any affect in the polydispersity index. Incorporation of star initiator was confirmed by FTIR and NMR. This was further supported by ester hydrolysis. The molecular weight of polystyrene after hydrolysis was found to be one fourth of the original molecular weight this supporting the formation of four arm polymers. Livingness of polymerization was confirmed by the chain extension polymerization.

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