

N-(*n*-alkyl)-2-Pyridinemethanimine Mediated Atom Transfer Radical Polymerization of Lauryl Methacrylate: Effect of Length of Alkyl Group

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ABSTRACT: The article describes the polymerization of lauryl methacrylate (LMA) using Cu(I)Br as catalyst for atom transfer radical polymerization in conjunction with *N*-(*n*-propyl) [PPMI]/(*n*-hexyl) [HPMI]/(*n*-octyl) [OPMI]-2-pyridinemethanimine as complex ligands. The polymerization of LMA was investigated in bulk and solution (toluene as solvent) using Cu(I)Br as catalyst, *N*-(*n*-alkyl)-2-pyridinemethanimine as ligands and ethyl-2-bromo isobutyrate (EBiB) as initiator. The ratio of LMA : CuBr : Ligand : EBiB was kept constant in all the polymerizations. In bulk polymerization, the solubility of the catalyst complex increased with increasing the length of alkyl chain on the ligand from propyl to octyl and also gave

polymers with narrow molecular weight distribution. The PDI was further narrowed by using OPMI as ligand and toluene was used as solvent. The kinetics of polymerization was also analyzed and it clearly shows that % conversion increased with time. Increase in molecular weight with % conversion without affecting PDI clearly show that the system is living and living nature can be controlled by increasing the length of alkyl group. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 31–37, 2012

Key words: atom transfer radical polymerization (ATRP); molecular weight distribution; gel permeation chromatography; metal-organic catalysts; kinetics

INTRODUCTION

The synthesis of polymers with controlled architectures, molecular weight, and narrow polydispersity is the most significant accomplishments in polymer chemistry achieved by the development of living radical polymerization. Of all the advances in living radical polymerization, atom transfer radical polymerization (ATRP)^{1–5} has proved to have the potential for the direct application in the industrial production of polymers with controlled molecular weight distribution besides other controlled radical polymerization techniques such as reversible addition-fragmentation termination (RAFT)⁶ and nitroxide mediated polymerization (NMP).⁷

The success of ATRP depends not only on fast initiation step but also on deactivation step so that free radical is not available for the chain transfer and termination step. A variety of transition metal complexes have been utilized for this role, but Cu(I) halides complexed by a diimine ligand seem to be

extremely effective and the most widely studied. Three distinct classes of α -diimine ligand have been reported: 2,2'-bipyridines,^{1,2,8} 1,10-phenanthrolines⁹ and *N*-(*n*-alkyl)-2-pyridinemethanimine.^{10–14} Of these, *N*-alkyl-2-pyridinemethanimines appear to be the most interesting, as they are known to be more effective in stabilizing metals in the low oxidation states than either of the other alternatives.¹⁵ Therefore, the use of *N*-alkyl-2-pyridinemethanimine derivatives in ATRP should result in an enhanced deactivation step, compared to bipyridyl and phenanthroline, imparting the potential to afford a higher degree of control over polymerization, and was chosen in the present study.

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, ATRP of higher methacrylates was done in the presence of solvent. Haddleton et al. examined the ATRP of *n*-butyl, *n*-hexyl, and *n*-nonyl methacrylate using EBiB as initiator, CuBr as catalyst, and *N*-(*n*-butyl)-2-pyridinemethanimine as ligand in xylene at 95°C.¹⁶ Raghunadh et al. also reported the ATRP of LMA in the presence of EBiB/CuBr/*N*-(*n*-propyl)-2-pyridinemethanimine (PPMI) in controlled way using a very

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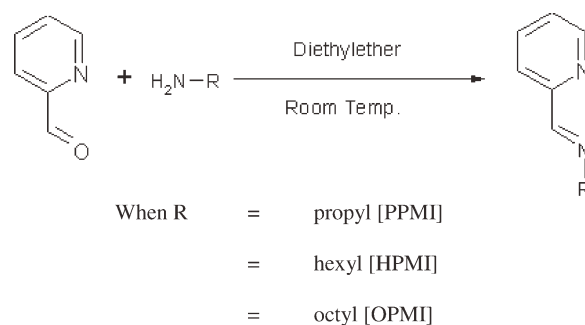
dilute solution of monomer (15% by volume).¹⁷ Bulk polymerization of stearyl acrylate (ODA) by ATRP (CuBr/PPMI) at 95°C was reported by Street et al. which was poorly controlled. It is well reported in the literature that the solubility of catalyst system can be enhanced by introduction of groups similar to monomer. 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.¹⁸ The catalytic amounts of quaternary ammonium halides Aliquet 336[®] a phase transfer catalyst shows better control on polymerization of higher alkyl methacrylate at ambient temperature by using CuCl/PMDETA as the catalyst system.^{19,20} The bulk and solution properties of poly(lauryl methacrylate) (PLMA) are interesting due to the presence of long side chain groups in the polymer which find application as pour-point depressants, rheological modifier, and as additives in petroleum-based products.²¹

Although polymerization of LMA using EBiB/CuBr/*N*-(*n*-propyl)-2-pyridinemethanimine (PPMI) has been reported in the literature,¹⁷ however no reports are available investigating systematically the effect of length of alkyl group in the ligand on the bulk and solution polymerization of LMA. It was therefore considered of interest to investigate systematically the effect of the length of alkyl group in the ligand on the polymerization of LMA in the presence of CuBr as catalyst and EBiB as initiator. For this purpose, *N*-(*n*-propyl/hexyl/octyl)-2-pyridinemethanimines as ligands were used for the polymerization of LMA [bulk and solution] using CuBr as catalyst and EBiB as initiator. The effect of alkyl chain length on the kinetics, molecular weight, and molecular weight distribution was also investigated.

EXPERIMENTAL

Materials

Lauryl methacrylate, 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 CaCl₂. 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.²² Ethyl-2-bromoisobutyrate (EBiB) 98%, pyridine-2-carboxaldehyde 99%, *n*-octyl amine 99%, *n*-hexyl amine 99% (all from Aldrich, USA), *n*-propyl amine, (S.D. Fine chemicals, Mumbai, India, 99%) were used as received. Toluene (Merck) was dried by refluxing with sodium and benzophenone under nitrogen.



Scheme 1 Synthesis of *N*-(*n*-alkyl)-2-pyridinemethanimine.

Synthesis of *N*-(*n*-alkyl)-2-pyridinemethanimine

N-(*n*-alkyl)-2-pyridinemethanimines were synthesized according to the Scheme 1 by reacting the corresponding amine i.e., *n*-propyl/*n*-hexyl/or *n*-octyl amine with pyridine-2-carboxaldehyde using the procedure reported in literature.¹⁶

A typical procedure used for the preparation of *N*-(*n*-octyl)-2-pyridinemethanimine [OPMI] is as follows:

An excess of *n*-octyl amine (0.25 mol, 10.5 mL) was added to a stirred solution of pyridine-2-carboxaldehyde (0.21 mol, 5 mL) in 5 mL diethyl ether cooled in an ice bath. After the complete addition of amine, 2.5g of anhydrous sodium sulfate was added and the slurry stirred for 2–4 h at room temperature. The solution was filtered and the solvent was removed by vacuum stripping. The product was purified by distillation under reduced pressure to give golden yellow oil.

Similarly PPMI and HPMI were synthesized by reacting propyl amine or hexyl amine with pyridine-2-carboxaldehyde respectively. *N*-(*n*-alkyl)-2-pyridinemethanimine thus prepared were characterized by ¹H NMR, ¹³C NMR, FTIR, and elemental analysis.

N-(*n*-propyl)-2-pyridinemethanimine (PPMI)

Yield: 90%, boiling point 60°C/0.4 Torr.

¹H NMR (CDCl₃ δ ppm): 8.63(m,1H), 8.37(s,1H), 7.97(m,1H), 7.70(m,1H), 7.28(m,1H), 3.62(t,2H), 1.69(m,2H), 0.93(t,3H)

¹³C NMR (CDCl₃ δ ppm): 160.7, 154.3, 149.3, 136.4, 124.5, 121.1, 63.3, 23.8, 11.8

IR: 1650 cm⁻¹ (νC=N)

Elemental analysis: Calculated: C = 72.97; H = 8.10; N = 18.92. Found: C = 72.31; H = 8.60; N = 19.32.

N-(*n*-hexyl)-2-pyridinemethanimine (HPMI)

Yield: 94%, boiling point 65°C/0.2 Torr.

¹H NMR (CDCl₃ δ ppm): 8.63(m,1H), 8.37 (s,1H), 7.97 (m,1H), 7.71 (m,1H), 7.28(m,1H), 3.64(t,2H), 1.67(m,2H), 1.33 (m,6H), 0.80(t, 3H)

^{13}C NMR (CDCl_3 δ ppm): 161.6, 154.6, 149.3, 136.4, 124.5, 121.5, 61.6, 31.6, 30.6, 27.0, 22.6, 14.0

IR: 1649cm^{-1} ($\nu\text{C}=\text{N}$)

Elemental analysis: Calculated: C = 75.7; H = 9.5; N = 14.7. Found: C = 75.3; H = 9.5; N = 14.7.

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

Yield: 92%, boiling point $101^\circ\text{C}/0.2$ Torr

^1H 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} ($\nu\text{C}=\text{N}$)

Elemental analysis: Calculated: C = 77.0; H = 10.2; N = 12.8. Found: C = 76.8; H = 10.2; N = 13.1.

Copper solubility

The amount of soluble CuBr in the monomer is directly proportional to the copper concentration in the monomer and this was determined. The ratio of CuBr : ligand : LMA i.e., 1 : 2 : 50 was same both in bulk and solution. However in solution, we used 0.33 mL of toluene as solvent. The mixture was heated at 95°C [polymerization temperature] for 3 h with stirring. It was then left undisturbed for 1 h. From supernatant liquid, 0.5 mL was taken and evaporated to dryness. The residue was dissolved in a mixture of 1 mL nitric acid and 3 mL hydrochloric acid followed by dilution with double deionized water. The copper concentration was then measured using atomic absorption spectroscopy.

Polymerization

Bulk polymerization

In the bulk polymerization, a dry schlenk tube was filled with CuBr (0.0585 g, 0.408 mmol), OPMI (0.2227 g, 1.02 mmol) and LMA (5.97 mL, 20.4 mmol) in that order. The reaction mixture was purged with nitrogen for 15 min 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 schlenk tube was placed in the preheated oil bath at 95°C followed by the addition of initiator i.e., ethyl-2-bromoisobutyrate (0.0585 mL, 0.408 mmol). The polymerization was stopped at a desired time by cooling the tube in ice water. The reaction mixture was diluted with toluene and passed through a short neutral alumina column to remove the catalyst. The polymer was precipitated using methanol as nonsolvent. The polymer was then dried under vacuum for 24 h at 60°C and yield was determined gravimetrically.

Solution polymerization

A dry schlenk tube was filled with CuBr (0.0585g, 0.408 mmol), OPMI (0.2227g, 1.02 mmol), LMA (5.97 mL, 20.4 mmol) and 2 mL of toluene in that order. The reaction mixture was purged with nitrogen for 15 min 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 initiator ethyl-2-bromoisobutyrate (0.0585 mL, 0.408 mmol) was added to the reaction mixture in the schlenk tube. The polymerization was stopped at a desired time by cooling the tube in ice water. The reaction mixture was diluted with toluene and passed through a short neutral alumina column to remove the catalyst. The polymer was precipitated with methanol. The polymer was then dried under vacuum for 24 h at 60°C and yield was determined gravimetrically.

Similarly the polymerization of LMA in bulk and solution was done using PPMI and HPMI as ligands to investigate the effect of the length of alkyl chain in ligands on the polymerization of LMA.

Studies on the kinetics of atom transfer radical polymerization of LMA

For kinetic studies, polymerization of LMA was carried out using the same procedure as reported above and 1 mL of reaction mixture was withdrawn at definite time for the analysis of conversion and out of this sample small portion was injected directly in the GPC instrument after dilution with THF. The solution was filtered using 0.2μ PTFE filter before injection for the analysis of molecular weight and molecular weight distribution.

Characterization

Copper concentrations were recorded on a Varian AA 240 Z Zeeman atomic absorption spectroscopy.

FTIR spectra were recorded as thin films using a Nicolet FTIR spectrophotometer.

NMR spectra were recorded on a Bruker spectropin DPX 300 spectrometer using CDCl_3 as solvent and tetramethyl silane as an internal standard.

Waters (1525) gel permeation chromatograph (Milford, MA) equipped with styragel (HR-3 and HR-4, $7.8 \times 300\text{ mm}^2$) 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^{-1} .

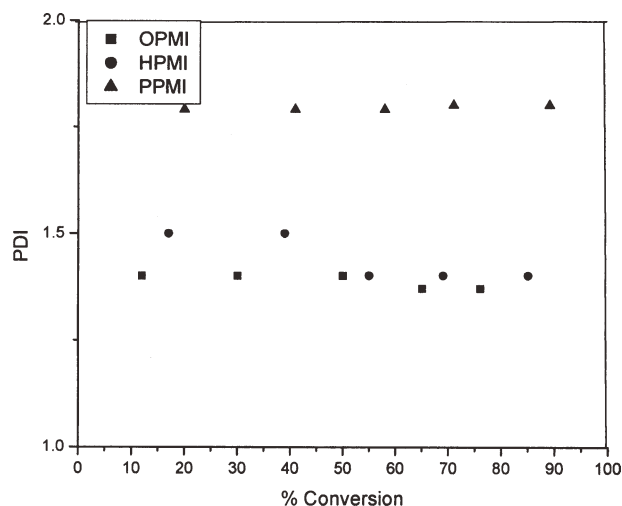


Figure 1 Plot of polydispersity index (PDI) versus percent conversion for polymerization of LMA by ATRP at 95°C using different ligands [mol ratio of LMA : EBiB : CuBr : Ligand 50 : 1 : 1 : 2.5].

RESULTS AND DISCUSSION

Bulk polymerization

In the bulk polymerization of LMA using CuBr : EBiB and *N*-(*n*-alkyl)-2-pyridinemethanimine system, the solubility of catalyst changes significantly as the length of alkyl group in ligand was increased from C₃ to C₈.

In case of CuBr/PPMI system, a heterogeneous complex was obtained with CuBr at room temperature which remains heterogeneous even at polymerization temperature i.e., 95°C, whereas in case of CuBr/HPMI system, HPMI forms a heterogeneous complex with CuBr at room temperature, which became homogeneous at polymerization temperature (95°C) initially. However after ~ 55% conversion, the system became heterogeneous. This could be due to the increased viscosity of the system (with increasing conversion) or due to the increased hydrophobicity which results in the precipitation of CuBr/HPMI complex. As the length of alkyl group

was increased to C₈ i.e., in CuBr/OPMI system, a homogeneous complex was obtained at room temperature and it remained homogeneous throughout the polymerization, irrespective of % conversion.

The polymers after purification were analyzed for the molecular weight and molecular weight distribution using GPC. The length of alkyl group showed a significant effect on the molecular weight and molecular weight distribution. The use of PPMI or HPMI as ligands, gave polymers with higher PDI values whereas the use of OPMI as ligand gave polymers with controlled molecular weight and PDI (1.37) (Fig. 1). These results clearly show that as the length of the alkyl chain increases, the solubility of catalyst increases and polymer with predetermined molecular weight and narrow PDI could be obtained (Table I).

The bulk polymerization of LMA using CuBr/PPMI catalyst system gave polydisperse products with molecular weights well below the theoretical values. The reason for poor control of polymerization using this catalyst system may be due to: (i) a relatively slow rate of deactivation compared to the rate of propagation and/or (ii) low rates of initiation compared to propagation. In such cases, ATRP resembles a normal free-radical polymerization and gave polymer with poor polydispersity index.²³ This is due to the poor solubility of Cu catalyst, leading to slow deactivation rates and/or poor initiation rates. Beers and Matyjaszewski also observed a similar behavior during the polymerization of lauryl acrylate that was improved by changing from poorly soluble tridentate amine ligands to the more soluble 4,4'-di-(5-nonyl)-2,2'-bipyridine ligand which improves both molecular weight and polydispersity.²⁴ Xu et al. also reported ATRP of LMA using ethyl-2-bromoisobutyrate/CuCl/PMDETA initiating system and showed better control in the presence of solvent.²⁵ Raghunadh et al. used the same initiator and the CuBr/PPMI catalyst system that gave polymer which has good correlation between molecular weight and PDI but they used very dilute solution of monomer (15% by volume).¹⁷ In the present work,

TABLE I
Polymerization of LMA Using Different Ligands at 95°C

Reaction	Ligand	Solvent ^a	M_n theory ^b ($\times 10^{-3}$)	M_n^c ($\times 10^{-3}$)	M_w/M_n	Time (in min)	% Conversion ^d
1	PPMI	None	11.3	9.0	1.82	300	89
2	PPMI	Toluene	10.4	8.7	1.78	300	82
3	HPMI	None	10.7	9.5	1.40	300	85
4	HPMI	Toluene	9.5	8.6	1.31	300	75
5	OPMI	None	9.6	12.6	1.37	300	76
6	OPMI	Toluene	8.8	10.5	1.27	300	70

^a 2 mL toluene added.

^b Molecular weight (monomer) $\times [M_0]/[I] \times \% \text{ conversion}$ (theoretical molecular weight).

^c By SEC in THF using polystyrene standards (experimental values).

^d By gravimetric analysis.

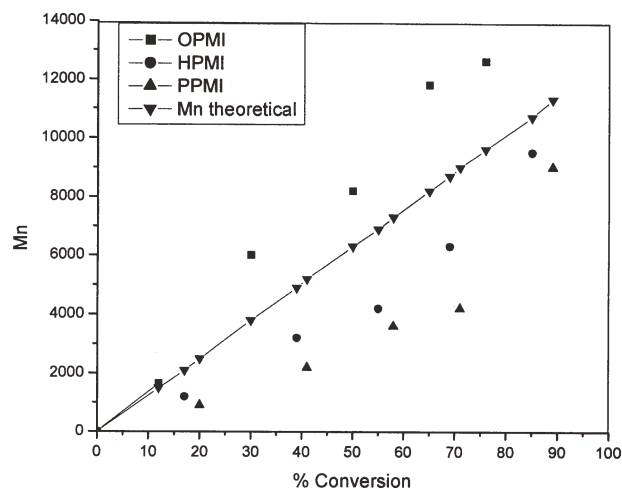


Figure 2 Plot of number average molecular weight (M_n GPC) versus percent conversion for bulk polymerization of LMA by ATRP at 95°C using different ligands [mol ratio of LMA : EBiB : CuBr : Ligand 50 : 1 : 1 : 2.5].

when we used PPMI and HPMI as ligands, M_n SEC molecular weight was lower than the calculated molecular weight with broad PDI ($M_w/M_n = 1.82$ – 1.40). In the case of HPMI ligand the M_n SEC increases with increasing % conversion but below the calculated molecular weight and polydispersities ranges from 1.55 to 1.40 (Table I). The reason of lower M_n SEC molecular weight than the calculated molecular weight and higher PDI in the case of polymer prepared using PPMI and HPMI ligands was that during the polymerization of higher methacrylates as the conversion increases reaction mixture becomes viscous and solubility of catalyst becomes difficult which result in the precipitation of Cu (II) (Fig. 2). With the precipitation of Cu (II) the deactivation step would not occur properly and polymer with poor control of molecular weight and polydispersity index were obtained. Therefore, in the polymerization of LMA by ATRP method, a suitable Cu ligand is important to ensure the chemical compatibility of monomer, polymer and catalyst

From Table II, it is observed that in the absence of ligand, the solubility of copper was very low which increased in the presence of ligands. The solubility of copper was found to be dependent on the type of ligand and it increased with increasing length of alkyl group in the ligand. Hutchinson et al. also reported that the solubility of CuBr in the monomer increased in the presence of ligand.²⁶ Thus ligand increases the chemical compatibility of catalyst with monomer. It was also observed that when toluene was used as a solvent, the solubility of CuBr in the monomer increased in all the cases (Table II). In case of CuBr/OPMI catalyst system, the longer alkyl chain in ligand increased the compatibility between catalyst and monomer. The visual appearance of the system indi-

cated that OPMI forms a homogeneous complex with CuBr at room temperature or at 95°C and remained homogeneous throughout the polymerization irrespective of % conversion. In this case, the molecular weight obtained from GPC is higher than the theoretically calculated molecular weight with narrow PDI (Table I). The reason for the higher molecular weight (M_n , SEC) observed than calculated could be due to the difference in hydrodynamic volume of PLMA and PS which has been used as calibration standards.

Solution polymerization

The solution polymerization was performed using toluene as solvent to investigate the effect of length of alkyl substituent in ligands on the polymerization of LMA. All other conditions were kept constant. Figure 3 indicate that in case of PPMI/CuBr catalyst system, there was no marked improvement in the observed molecular weight and PDI, whereas with HPMI/CuBr system, polymer having PDI of 1.31 was obtained at higher conversion in the presence of solvent. In presence of OPMI/CuBr system, observed molecular weight was higher than the calculated molecular weight but there was marked improvement in the PDI ($M_w/M_n = 1.27$) which did not change with % conversion.

When we examined the polymerization of LMA in presence of CuBr/OPMI with toluene as solvent, the system was homogeneous during the course of polymerization and polymer of LMA exhibited little higher PDI at very low conversion which decreased significantly at higher conversion ($M_w/M_n = 1.27$). The plot of % conversion versus time is shown in Figures 4 and 5 shows the plot of % conversion versus molecular weight. Increase in molecular weight with % conversion showed that the system is living.

Kinetics of polymerization

Three ligands which differ in the length of alkyl chain were used for both bulk and solution polymerization

TABLE II
Solubility of Copper in the Absence/Presence of Ligand at 95°C

S. no.	Ligand	Copper concentration ^a (ppm)	Copper concentration ^b (ppm)
1	No ligand	0.986	1.210
2	PPMI	2.512	2.813
3	HPMI	3.456	3.739
4	OPMI	3.924	4.394

^a CuBr : Ligand : Monomer = 1 : 2 : 50.

^b CuBr : Ligand : Monomer = 1 : 2 : 50 in 0.33 mL toluene.

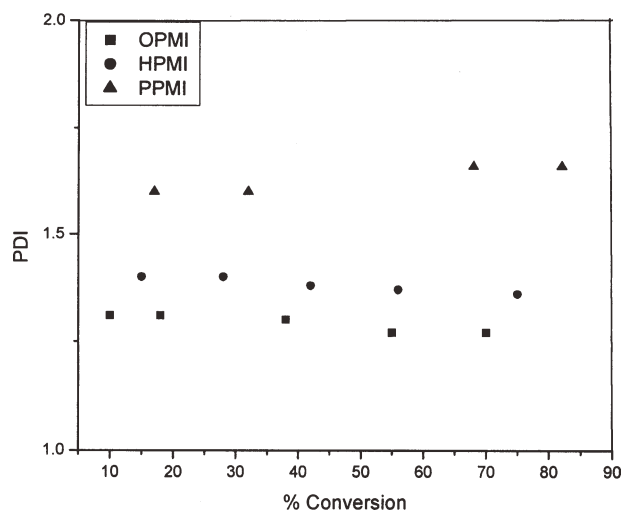


Figure 3 Plot of polydispersity index (PDI) versus percent conversion for solution polymerization of LMA by ATRP in toluene at 95°C using different ligands [mol ratio of LMA : EBiB : CuBr : Ligand 50 : 1 : 1 : 2.5].

of LMA. Table I indicates that use of solvent improves the PDI in every case; however the final yield decreases due to dilution of reactive species. Figure 6 shows the sigmoidal nature of the kinetic plots for the reaction. It is evident that the reaction system using PPMI- and HPMI-based catalyst reacts much more quickly than with an OPMI-based catalyst. It also shows that the rate of reaction for the system using PPMI and HPMI are faster than that of OPMI. The reason for this is likely that when PPMI and HPMI catalyst were used they formed heterogeneous system with monomer and polymer so Cu (II) precipitates out and backward reaction does not occur properly and polymer formed rapidly following normal free radical

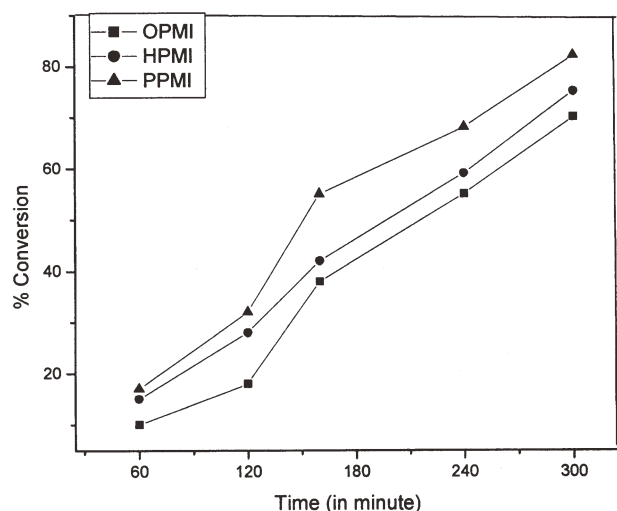


Figure 4 Plot of % conversion versus time for the ATRP of LMA in toluene at 95°C [mol ratio of LMA : EBiB : CuBr : Ligand 50 : 1 : 1 : 2.5].

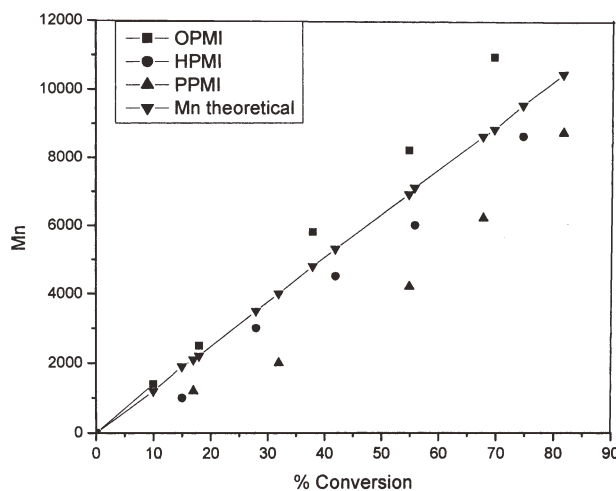


Figure 5 Plot of number average molecular weight (M_n , GPC) versus percent conversion for solution polymerization of LMA by ATRP in toluene at 95°C using different ligands [mol ratio of LMA : EBiB : CuBr : ligand 50 : 1 : 1 : 2.5].

polymerization. However the lower rate of polymerization observed when OPMI was used as ligand could be due to the enhanced solubility and a higher active concentration of deactivating Cu (II) Br₂/ligand species, which in turn would lead to a more efficient deactivation process and a lower steady state concentration of propagating species.

CONCLUSIONS

A range of *N*(*n*-alkyl)-2-pyridinemethanimine ligands have been studied for the copper (I)-mediated living radical polymerization of LMA. These results clearly show that in bulk polymerization of LMA, increasing the length of alkyl chain in the ligand from

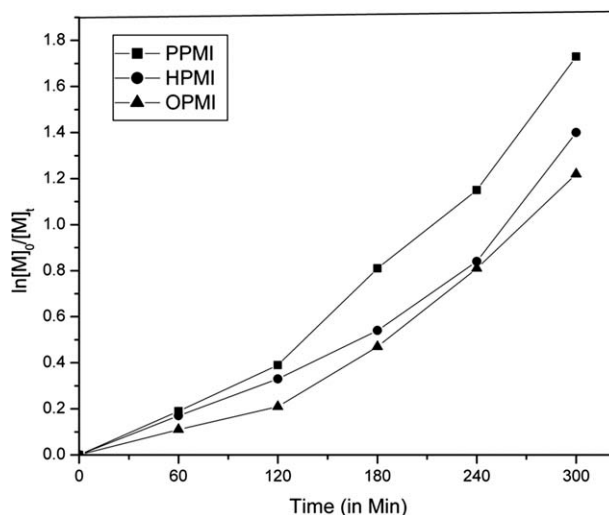


Figure 6 Plot of $\ln [M]_0/[M]_t$ versus time for ATRP of LMA in toluene at 95°C [mol ratio of LMA : EBiB : CuBr : Ligand 50 : 1 : 1 : 2.5].

propyl to octyl enhanced the solubility of catalyst and gave polymers with controlled molecular weight and narrow polydispersity-index. This can be further improved by using small amount of toluene as solvent.

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