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Polymer 45 (2004) 3149–3155

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# Efficiency of ligands in atom transfer radical polymerization of lauryl methacrylate and block copolymerization with methyl methacrylate

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Received 6 January 2004; received in revised form 11 March 2004; accepted 15 March 2004

**Abstract**

Atom transfer radical polymerization of lauryl methacrylate (LMA) was carried out in the presence of various ligands using ethyl-2-bromoisobutyrate as initiator and CuBr as catalyst in toluene at 95 °C. The ligands used were 2,2′-bipyridyl,4,4′-dimethyl-2,2′-bipyridyl, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and *N*-(*n*-propyl)-2-pyridylmethanimine (PPMI). Controlled polymerization was observed with PMDETA and PPMI ligands and poly(LMA)s with narrow molecular weight distribution (MWD) ($M_w/M_n \leq 1.2$) were obtained. The first-order time-conversion plot showed the presence of termination in the presence of PMDETA. A linear first-order time-conversion plot with a small induction period (~10 min) was observed in the presence of PPMI ligand. Di-block copolymers of LMA and methylmethacrylate with controlled molecular weight and narrow MWDs were synthesized via sequential monomer addition.

*Keywords:* Atom transfer radical polymerization; Block copolymer; Poly(lauryl methacrylate)

## 1. Introduction

The polymers of higher (alkyl)methacrylate draw significant importance in material science due to their low glass transition temperature [1]. One of the problems associated with higher (alkyl)methacrylate is their low solubility in common solvents at low temperature. Lauryl methacrylate (LMA) and stearyl methacrylate (SMS) are industrially very important monomers, which are soluble in polar and non-polar solvents at ≥ −45 °C. Hence, it is difficult to polymerize them using living anionic polymerization technique, which generally works well at < −60 °C. Nevertheless, attempts have been made in the past to polymerize LMA using anionic polymerization at low temperature [2–4]. Anderson and coworkers attempted to synthesis block copolymer of methyl methacrylate (MMA) and LMA using anionic polymerization at −78 °C [2]. They obtained polymers with broad molecular weight distribution (MWD) ($M_w/M_n = 1.72$). Group transfer polymerization has been employed for the polymerization of LMA at room temperature and low molecular weight polymers with moderate control were obtained [5,6].

During the last decade, atom transfer radical polymerization (ATRP) has emerged as a best method for the synthesis of acrylic and methacrylic homo and block copolymers [7–15]. ATRP of various (alkyl)methacrylates proceeds in a controlled manner under an appropriate condition. However, application of ATRP for the polymerization of higher (alkyl)methacrylate has not been widely studied. Haddleton and coworkers [11] examined the ATRP of *n*-butyl, *n*-hexyl and *n*-octyl methacrylates using ethyl-2-bromoisobutyrate as initiator, CuBr as catalyst, and *N*-(*n*-butyl)-2-pyridylmethanimine as ligand in xylene at 90 °C. Polymers with controlled molecular weight and moderately narrow MWD of ≤1.27 were obtained.

Poly(lauryl methacrylate) (PLMA) possesses a low $T_g$ and can be used as a rubbery block in the synthesis of acrylic thermoplastic elastomers. The hydrophobic nature of PLMA can also be used in constructing various amphiphilic block copolymers [16]. An ability to polymerize LMA in a controlled manner could offer a new opportunity for the synthesis of well-defined homo and block copolymers. Recently, Xu et al. [17] reported ATRP polymerization of LMA using ethyl 2-bromobutyrate/CuCl/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) initiating-system

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doi:10.1016/j.polymer.2004.03.042

in the presence of a small amount of solvent ($[M]_0 = 11.4$ mol/l). They obtained PLMAs with broad MWD ($1.25 < M_w/M_n < 1.50$) that increased with increasing conversion.

In this paper, we examine the efficiency of various ligands in ATRP of LMA using CuBr as catalyst in toluene at 90 °C. The polymerization kinetics are performed in the presence of *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and *N*-(*n*-propyl)-2-pyridylmethanimine (PPMI) ligands. The synthesis of block copolymers with methyl methacrylate (MMA) is also accomplished using sequential monomer addition method.

## 2. Experimental part

### *2.1. Materials*

All the manipulations were carried out in a pure nitrogen atmosphere and transfer of reagents was done using syringe and capillary techniques. Nitrogen gas (Industrial oxygen, Pune) was purified by passing through a series of columns (5 × 1 m) containing Cu catalyst at 200 °C, activated 4A molecular sieves, and $CaH_2$ granules ($20 \times 1$ in.$^2$) (Aldrich, USA) and finally bubbled through a toluene solution of oligostyryllithium.

LMA (Aldrich, USA) was purified by fractional distillation (104 °C at 0.007 mbar) after stirring over $CaH_2$ for 12 h at 25 °C. MMA (Aldrich, USA) was purified over $CaH_2$ for 6 h followed by distillation. Copper bromide (CuBr) (Aldrich, USA) was purified by stirring in glacial acetic acid under nitrogen followed by filtration, washing with dry ethanol and dried at 100 °C [18]. The ligands, 2,2′-bipyridine (BP), 4,4′-dimethyl-2,2′-bipyridine (DMBP), and pyridine-2-carboxaldehyde, were used as received from Aldrich, USA. Ethyl-2-bromoisobutyrate (EBI) (Aldrich, USA) and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) (Aldrich, USA) were distilled over $CaH_2$. Sodium and potassium metals, sodium sulfate, activated alumina (neutral) and *n*-propyl amine (S.D. Fine Chemicals, Mumbai) were used as received. Toluene (S.D. Fine Chemicals, Mumbai) was refluxed over potassium metal and stored over Na–K alloy on a vacuum line.

*N*-(*n*-propyl)-2-pyridylmethanimine (PPMI) was synthesized as reported in the literature [11] by reacting pyridine-2-carboxaldehyde, 14.5 ml (0.152 mol) and *n*-propylamine, 15 ml (0.183 mol) in diethyl ether at room temperature for 5 h. It was purified by distillation under reduced pressure (31–35 °C at ~0.1 mbar). Yield: 85%. $^1$H NMR ($CDCl_3$): $\delta$ 0.85 (t, 3H), 1.62 (m, 2H), 3.53 (t, 2H), 7.18 (m, 1H), 7.61 (m, 1H), 7.86 (m, 1H), 8.27 (s, 1H), 8.54 (m, 1H). Elemental analysis: calculated for $C_9H_{12}N_2$: C: 72.97; H: 8.10; N: 18.92. Found: C: 72.31; H: 8.60; N: 19.33.

### *2.2. Polymerization*

Polymerization reactions were carried out in a single necked round bottom flask equipped with a magnetic stirring bar and a 3-way septum adapter. In a typical reaction (Table 1, run 1), 0.109 g of CuBr (0.76 mmol), 0.324 g of BP (2.97 mmol), 5 ml of LMA (17.05 mmol) and 20 ml of toluene were transferred under nitrogen. The contents were degassed using three freeze–thaw cycles and finally evacuated and backfilled with nitrogen. The reaction mixture was heated to the polymerization temperature, and then the initiator, EBI, 0.1 ml (0.68 mmol) was added via a syringe. After 5 h, the polymerization was quenched by freezing the reaction mixture in a liquid nitrogen bath. The mixture was diluted with tetrahydrofuran (THF) and passed through a short column of activated alumina to remove the catalyst. The polymer was precipitated in a water–methanol (20/80, v/v) mixture. Then, the polymer was dried under dynamic vacuum for 8 h and the yield was determined gravimetrically.

Kinetic experiments were carried out in the presence diphenylmethane as internal standard, and small portions of reaction mixture were withdrawn at different times for the analysis of monomer concentration and polymer molecular weight.

Synthesis of block copolymers was carried out by sequential addition of monomers in a similar manner as described for the homopolymerization. After 6 h of homopolymerization, a small portion of the reaction mixture was withdrawn for characterization and the second monomer (LMA or MMA) was added and stirred for another 6 h. Poly(MMA-*b*-LMA)s were recovered and dried in a similar way as described for the homopolymer.

### *2.3. Characterization*

Molecular weight and MWD of PLMAs were determined by size exclusion chromatography (SEC) equipped with UV, RI detectors and two 60 cm PSS SDV-gel columns, 1 × 100 Å and 1 × linear ($10^2$–$10^5$ Å). PMMA standards (Polymer Laboratories) were used for the calibration. THF was used as an eluent at 1 ml/min flow rate at room temperature. Monomer conversion was determined from GC (Perkin–Elmer Auto System XL) and diphenylmethane was used as internal standard. $^1$H NMR (Bruker-200 MHz) was used for determining the block copolymer composition.

## 3. Results and discussion

### *3.1. ATRP of LMA in presence of various ligands*

The ATRP of LMA was performed in toluene at 95 °C using EBI as initiator and CuBr as catalyst in conjunction with various ligands (Fig. 1). The ligands examined are 2,2′-bipyridine (BP), 4,4′-dimethyl-2,2′-bipyridine (DMBP),

Table 1
ATRP of LMA using EBI (I) as initiator and CuBr (C) catalyst in the presence of various ligands (L) in toluene at 95 °C for 5 h

| Run. no. | [LMA] (mol/l) | [C] : [I] : [L] | Yield[a] (%) | $M_{n,cal}$[b] ($\times 10^{-3}$) | $M_{n,SEC}$[c] ($\times 10^{-3}$) | $M_w/M_n$ | $M_{n,SEC}/M_{n,cal}$ |
|---|---|---|---|---|---|---|---|
| *Ligand: 2,2′-Bipyridine (BP)* | | | | | | | |
| 1 | 0.68 | 1:1:3 | 43 | 2.8 | 11.9 | 1.31 | 4.25 |
| *Ligand: 4,4′-Dimethyl-2,2′-bipyridine (DMBP)* | | | | | | | |
| 2 | 0.68 | 1:1:3 | 44 | 2.8 | 13.6 | 1.33 | 4.86 |
| *Ligand: N,N,N′,N′,N″-Pentamethyldiethylenetriamine (PMDETA)* | | | | | | | |
| 3 | 1.14 | 1:1:3 | 93 | 6.0 | 15.6 | 1.45[d] | 2.60 |
| 4 | 1.14 | 1:1:1 | 65 | 4.2 | 7.8 | 1.29 | 1.86 |
| 5 | 1.14 | 1:1:0.5 | 33 | 2.1 | 9.0 | 1.20 | 4.29 |
| *Ligand: N-(n-Propyl)-2-pyridylmethanimine (PPMI)* | | | | | | | |
| 6 | 0.68 | 1:1:3 | 70 | 4.5 | 10.8 | 1.19 | 2.40 |
| 7 | 1.14 | 1:1:3 | 69 | 4.4 | 9.4 | 1.29 | 2.14 |
| 8 | 0.68 | 1:1:2 | 65 | 4.2 | 8.3 | 1.24 | 1.98 |
| 9 | 0.49 | 1:1:3 | 58 | 3.7 | 8.2 | 1.18 | 2.22 |
| 10 | 0.26 | 1:1:3 | 22 | 1.4 | 3.7 | 1.16 | 2.64 |

[a] Yield was determined gravimetrically.

[b] $M_{n,cal} = [([M]_0/[I]_0) \times \text{mol.wt.of monomer} \times \text{conversion}]$.

[c] PMMA standards were used for calibration.

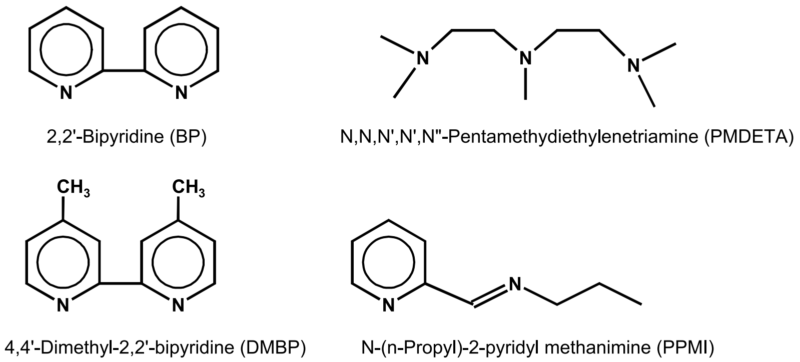
[d] Bi-modal molecular weight distribution.

*N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) and *N*-(*n*-propyl)-2-pyridylmethanimine (PPMI). The polymerization was carried out in the presence of 3-mol excess of ligand with respect to initiator and catalyst ($[C]_0 : [I]_0 : [L]_0 = 1 : 1 : 3$). The results of ATRP of LMA in the presence of these ligands are given in Table 1. The polymerization in the presence of commercially available bipyridine based ligands, such as BP and DMBP, was heterogeneous at 95 °C and the PLMAs obtained with these ligands exhibited broad MWD ($M_w/M_n \leq 1.33$, Fig. 2(a) and (b)). These results indicate that BP and DMBP ligands do not efficiently coordinate with catalyst, and promote faster equilibrium dynamics between $Cu^I$ and $Cu^{II}$ species during propagation in LMA polymerization.

Matyjaszewski and coworkers [7,8] have successfully used triamine ligand such as PMDETA for ATRP of several acrylates. When PMDETA was used as ligand for the polymerization of LMA, the reaction mixture was homogenous, which indicates an efficient coordination between the ligand and CuBr. It was noticed that the conversion of LMA was almost quantitative after 5 h. The polymerization becomes difficult to control due to higher rate in the presence of a 3-mol excess of PMDETA as PLMA with broad and bimodal MWD was obtained (Fig. 2(c)). However, the polymerization proceeds at a slower rate in the presence of low concentration of PMDETA ($[L] \leq 1$) (Table 1, runs 4 and 5). The control of polymerization was also improved as evidenced from the obtained PLMAs, which exhibited narrow MWD (Table 1, runs 4 and 5).

It was observed that the solubility of the catalyst complex is low at low ligand concentration at room temperature. However, the reaction mixture was homogenous at 95 °C. Further decrease in the ratio of ligand with respect to initiator resulted in an insufficient complexation leading to a partial precipitation of CuBr. These results indicate that it is necessary to have at least an equimolar amount of PMDETA with respect to CuBr for an efficient polymerization.

The molecular weight of PLMAs obtained from SEC ($M_{n,SEC}$) is higher than the theoretically calculated ones using the feed ratio of monomer and initiator. The reason for



2,2'-Bipyridine (BP)

N,N,N',N',N"-Pentamethydiethylenetriamine (PMDETA)

4,4'-Dimethyl-2,2'-bipyridine (DMBP)

N-(n-Propyl)-2-pyridyl methanimine (PPMI)

Fig. 1. Various ligands used in ATRP of LMA.

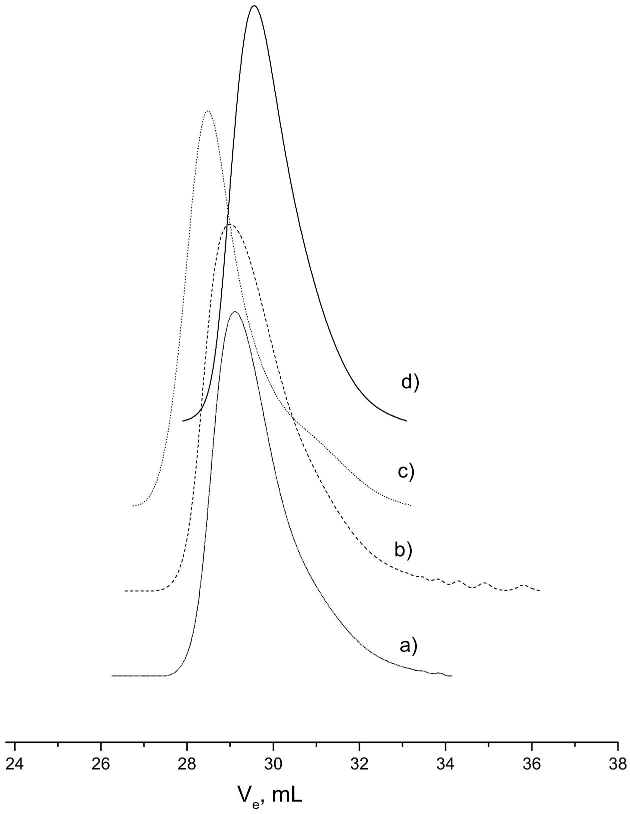


Fig. 2. GPC traces of PLMA synthesized using ATRP in toluene at 95 °C ($[C]_0$:$[I]_0$:$[L]_0 = 1$:1:3) in the presence of (a) BD, (b) DMBP, (c) PMDETA (Table 1, run 3), and (d) PPMI (Table 1, run 7).

the higher molecular weights ($M_{n,SEC}$) is a large hydrodynamic volume of PLMA as compared with PMMA standards used for SEC calibration. Hence, the efficiency of catalyst/ligand system for the ATRP of LMA cannot be determined from $M_{n,SEC}$. However, the ratio of $M_{n,SEC}/M_{n,cal}$ can be used as a measure of molecular weight control in the presence of various ligands used in this study.

Recently, Haddleton and coworkers [11] have reported the use of substituted pyridinemethanimines as ligands in the ATRP of MMA. They obtained polymers with relatively narrow MWD (≤1.2) with good initiator efficiency. We examined the efficiency of CuBr/PPMI catalyst system for the ATRP of LMA. It was observed that PPMI forms a heterogenous complex with CuBr at room temperature. However, the reaction mixture becomes homogenous during the polymerization at 95 °C. The PLMAs exhibited narrow MWD ($M_w/M_n \leq 1.20$, Fig. 2(d)) with high initiator efficiency on the basis of $M_{n,SEC}/M_{n,cal}$. The ratio of $M_{n,SEC}/M_{n,cal}$ for PPMI/CuBr system is around a constant value (~2). This suggests that the actual molecular weight of PLMA is approximately half the $M_{n,SEC}$ obtained from PMMA calibration. The active center concentration of the polymerization remains constant, while changing the monomer concentration as a constant $M_{n,SEC}/M_{n,cal}$ value (~2) was obtained indicating a controlled polymerization (Table 1, runs 6–9). These results suggest that the PPMI ligand is an efficient one compared to the other ligands used in producing controlled molecular weight PLMAs with narrow MWD.

### *3.2. Kinetic studies of ATRP of LMA in the presence of PMDETA and PPMI ligands*

The kinetics of ATRP of LMA in the presence of PMDETA and PPMI ligands were performed in toluene at 95 °C. First order time-conversion plot in the presence of PMDETA shows a downward curvature indicating the presence of termination reaction (Fig. 3). However, a linear semilogarithmic time-conversion plot was obtained in the presence of PPMI indicating the absence of termination reaction. The rate expression for the dependence of monomer concentration with time for a polymerization in the presence of termination is given by the following equation [19]

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]_\mathrm{t}} = \frac{k_\mathrm{app}}{k_\mathrm{t}}(1 - \mathrm{e}^{-k_\mathrm{t}t})$$

where $k_t$ is the rate constant of termination and $k_{app}$ is the apparent rate constant of propagation. Using non-linear curve fit, the rate constants, $k_{app}$ and $k_t$ were determined. The rate constants, $k_{app}$ and $k_t$, were found to be 0.01266 and 0.00511 $\text{min}^{-1}$, respectively, in the case of PMDETA and a lower $k_{app}$ was observed in the presence of PPMI (0.00888 $\text{min}^{-1}$) (Fig. 3). A small induction period (~10 min) was observed in the presence of PPMI ligand in toluene at 95 °C. Such an induction period was not observed in the presence of PMDETA ligand.

Recently, Xu et al. [17] reported kinetics of ATRP of LMA in the presence of PMDETA ligand at higher monomer concentration ($[M]_0 = 11.4$ mol/l) in toluene at 110 °C and observed induction periods ≥30 min. The

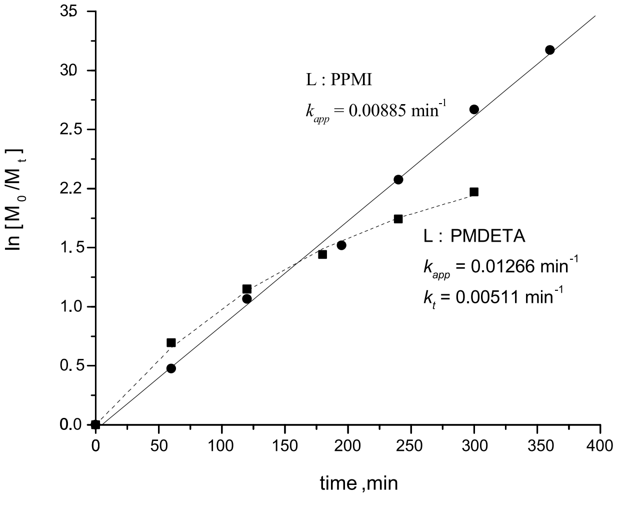


Fig. 3. First-order time conversion plots of LMA polymerization in toluene at 95 °C in the presence of PMDETA ($[C]_0$:$[I]_0$:$[L]_0 = 1$:1:1, $[LMA]_0 = 1.7$ mol/l) and PPMI ligands ($[C]_0$:$[I]_0$:$[L]_0 = 1$:1:2, $[LMA]_0 = 0.85$ mol/l). $[I]_0 = 0.067$ mol/l.

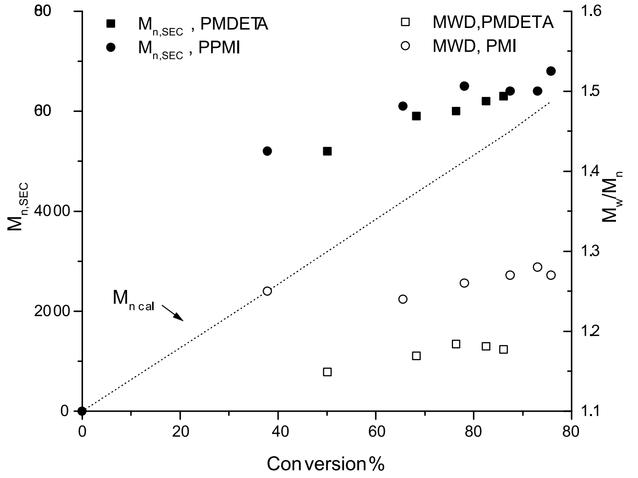


Fig. 4. Dependence of apparent molecular weight and polydispersity index, $M_w/M_n$, versus conversion in the LMA polymerization in toluene at 95 °C in the presence of PMDETA and PPMI ligands ($[C]_0$:$[I]_0$:$[L]_0 = 1$:1:3).

absence of induction period observed in our experiment for the same ligand (PMDETA) could be attributed to a low monomer concentration ($[M]_0 = 1.7$ mol/l) or a higher polarity of the medium, due to the presence of excess solvent. The presence of a large amount of solvent enhances the solubility of CuBr/PMDETA ligand complex that increases the $k_{app}$ without any observable induction period.

The plots of $M_{n,SEC}$ vs. conversion show a very slight upward curvature at higher conversion indicating some transfer reactions in the presence of these ligands (Fig. 4). The deviation of data points from theoretical $M_{n,cal}$ line is largely due to the $M_{n,SEC}$ determination using PMMA calibration. Although the MWDs of PLMAs obtained are moderately narrow throughout the polymerization, a slight increase is noticeable at higher conversion. However, the presence of a small amount of transfer reaction is not significant as PLMAs with narrow MWDs ($M_w/M_n \leq 1.20$) are obtained in batch polymerization.

A comparison of both the kinetic and the batch polymerization experiments clearly indicates that the polymerization is more controllable and polymers with predictable molecular weight with narrow MWD can be obtained in the presence of PPMI ligand. On the contrary, the polymerization proceeds with termination in the presence PMDETA and the course of the polymerization depends significantly on the concentration of the PMDETA ligand. The polymerization is uncontrollable at higher concentration of the ligand ($\geq 3 \times [C]_0$) due to a fast equilibrium dynamics between propagating chain ends and the catalyst and at lower concentration of the ligand ($\leq 1 \times [C]_0$) due to inefficient coordination with the catalyst.

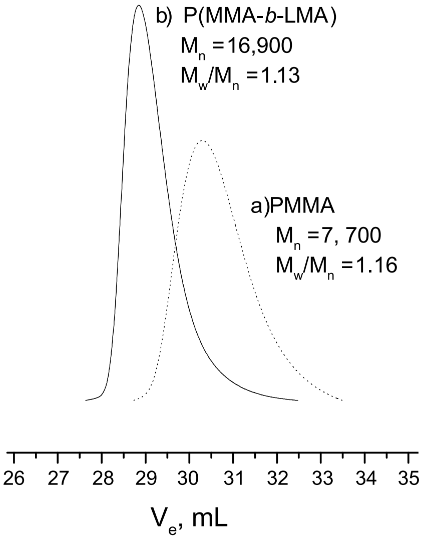


Fig. 5. GPC trace of poly(MMA-*b*-PLMA) copolymer in the presence of PPMI ligand synthesized via sequential monomer addition method in toluene at 95 °C (Table 2, run 4). (a) PMMA block before LMA addition and (b) the dibock copolymer after LMA addition.

### 3.3. Synthesis of poly(MMA-b-LMA) copolymers using sequential monomer addition

Synthesis of block copolymers by ATRP is generally done using a two-step process involving the use of isolated

Table 2
Synthesis of poly(LMA-*b*-MMA) copolymers by ATRP using CuBr as catalyst, EBI as initiator in toluene at 95 °C

| Run. No. | [MMA] (mol/l) $[M]_0$ | [LMA] (mol/l) $[L]_0$ | Ligand | Homopolymer | | | Block copolymer | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $M_{n,cal}$[a] ($\times 10^{-3}$) | $M_{n,SEC}$[b] ($\times 10 - {}^3$) | MWD | $M_{n,cal}$ ($\times 10^{-3}$) | $M_{n,SEC}$ ($\times 10^{-3}$) | MWD | $[MMA]_0$:$[LMA]_0$ [c] ($^1$H NMR) |
| 1[d] | 1.86 | 0.55 | PMDETA[e] | 5.1 | 9.1 | 1.25 | 14.9 | 42.1 | 1.14 | 76:24 |
| 2 | 1.86 | 0.55 | PMDETA | 5.1 | 12.5 | 1.46 | 14.2 | 40.3 | 1.37 | 76:24 |
| 3[d] | 1.86 | 0.55 | PPMI[f] | 5.1 | 8.5 | 1.22 | 14.9 | 16.7 | 1.28 | 70:30 |
| 4 | 1.86 | 0.55 | PPMI | 5.0 | 7.7 | 1.16 | 14.2 | 16.9 | 1.13 | 80:20 |

Polymerizations were carried out with $[C]_0 : [I]_0 : [L]_0 = 1 : 1 : 3$.

[a] $M_{n,cal} = [([M]_0/[I]_0) \times$ mol.wt.of monomer $\times$ conversion].

[b] Number of average molecular weights were determined using PMMA caibration.

[c] The monomer feed ratio in all the polymerizations, $[MMA]_0$:$[LMA]_0 = 77$:23.

[d] LMA was polymerized first.

[e] $[c]_0 : [I]_0 : [L]_0 = 1 : 1 : 0.5$.

[f] $[c]_0 : [I]_0 : [L]_0 = 1 : 1 : 2$.

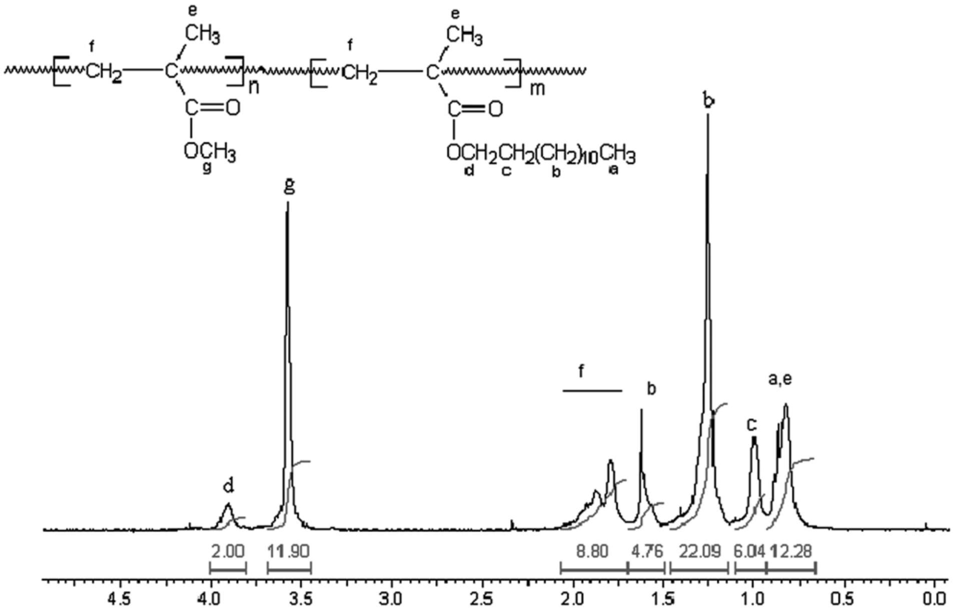


Fig. 6. $^1$H NMR spectrum of poly(MMA-*b*-PLMA) in $CDCl_3$ synthesized by ATRP in the presence of PPMI ligand (Table 2, run 4).

first block homopolymer as macro-initiator for the block copolymerization of a second monomer [10,20,21]. The kinetics of LMA polymerization in the presence of PPMI ligand showed that the polymerization proceeds without termination. Hence, we attempted to synthesize diblock copolymers from LMA and MMA by a sequential monomer addition method in the presence of PPMI and PMDETA ligands. First PMMA (or PLMA) macro-initiator was synthesized and a small fraction was withdrawn for analysis after 6 h and a second monomer LMA (or MMA) was added. After continuing the reaction for another 6 h, the reaction was quenched and the diblock copolymer was isolated. The results are shown in Table 2.

In the presence of PMDETA ligand at low concentration ($[C]_0 : [I]_0 : [L]_0 = 1 : 1 : 0.5$) the polymerization of LMA proceeds in a controlled manner with good control over molecular weight and MWD. Viscosity of the reaction mixture increased considerably after MMA addition. The obtained poly(LMA-*b*-MMA) diblock copolymer exhibited narrow MWD (Table 2, run 1). However, in reverse monomer addition with a higher concentration of PMDETA ($[C]_0 : [I]_0 : [L]_0 = 1 : 1 : 3$), both the PMMA and the final poly(MMA-*b*-LMA) diblock copolymer exhibited broad MWD (Table 2, run 2). When the block copolymerization was carried out in the presence of PPMI ligand ($[C]_0:[I]_0:[L]_0 = 1:1:3$), the diblock copolymers with moderate control of molecular weight and narrow MWD were obtained irrespective of the sequence of monomer addition (Table 2, runs 3 and 4). This suggests that the PPMI ligand is more advantageous over PMDETA.

The SEC of the block copolymers showed the absence of oligomer or homopolymer contamination and exhibited narrow MWD with good initiator efficiency (Fig. 5). The monomer content in the block copolymers was calculated from $^1$H NMR from the integration ratios corresponding to $-OCH_2$ protons of PLMA (3.9 $\delta$) and $-OCH_3$ protons of PMMA (3.6 $\delta$) (Fig. 6). The calculated monomer composition is in agreement (with ±5% error) with the feed ratio of the monomers (Table 2).

## 4. Conclusions

ATRP of lauryl methacrylate (LMA) was carried out in the presence of various ligands using ethyl-2-bromoisobutyrate as initiator and CuBr as catalyst in toluene at 95 °C. Bipyridine type ligands did not give adequate control over the polymerization. PLMAs with moderately narrow MWD ($<1.29$) were obtained in the presence of triamine (PMDETA) and methanimine (PPMI) type ligands. The first order time-conversion plot in the presence of PEDETA shows a downward curvature indicating the presence of termination reaction. However, a linear semilogarithmic time-conversion plot was obtained in the presence of PPMI indicating the absence of termination reaction. Poly(MMA-*b*-LMA) copolymer with moderate control of molecular weight and narrow MWD without homopolymer contamination was synthesized in the presence of PPMI ligand by sequential addition of monomers.

**Acknowledgements**

V.R. thanks CSIR for the award of a senior research fellowship.

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