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Facile atom transfer radical homo and block copolymerization of higher alkyl methacrylates at ambient temperature using CuCl/PMDETA/quaternaryammonium halide catalyst system

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Abstract

Controlled polymerization of higher alkyl methacrylates, e.g. lauryl methacrylate (LMA) and stearyl methacrylate (SMA) has been successfully achieved by atom transfer radical polymerization (ATRP) at ambient temperature using CuCl/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA)/tricaprylylmethylammonium chloride (Aliquat®336) as the catalyst system and ethyl 2-bromoisobutyrate or 2,2,2-trichloroethanol as the initiator. Although the bulk polymerization gives satisfactory control, the latter becomes better when anisole or THF is added into the system. Without AQCl the control was lost. A large deviation of molecular weight from theory has been observed which has been attributed to the very high-molecular weight of the dead polymers formed during the building-up of the persistent radical. The controlled polymers have been used as macroinitiators for block (di, tri and penta) ATR copolymerization with several methacrylates.
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Keywords: Atom transfer radical polymerization; Living radical polymerization; Block copolymers

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1. Introduction

The ATRP is a robust as well as a versatile living radical polymerization process for the controlled synthesis of polymers [1–3]. The copper mediated ATRP (CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) catalyst) of alkyl (meth)acrylates with large alkyl groups ($R=C_{12}$,C_{18}) has been shown to require specially the addition of the deactivator (ca. 5 mol% of catalyst) to start with, in order to achieve satisfactory control [4–6]. This has been attributed to the very low-termination rate constants of polymer radicals with large α substituents [7,8] and consequently a weak build-up of the deactivator towards the equilibrium regime in the unaided system [9].

As regards the choice of ligands for the Cu-based catalyst, Matyjaszewski and co-workers tested PMDETA as a ligand for the ATRP of lauryl acrylate and found it to be unsuitable for solubility reasons even when solvents like anisole or acetone which serve well in the ATRP of MMA were used [4]. Although the systems were homogeneous to start with, the heterogeneity sets in through the precipitation of the Cu(II) complex and the polymer [4]. However, the use of the CuBr/dNbpy catalyst eliminates the heterogeneity problem from Cu(II) complex precipitation at an elevated temperature (90 °C) even without the use of a solvent [4]. This latter catalyst was successfully used also for the ATRP of stearyl methacrylate (SMA) and stearyl acrylate (SA) in xylene at 90 °C [5,6].

On the other hand, Xu et al. claimed satisfactory control in the ATRP of lauryl methacrylate (LMA) using the CuCl/PMDETA catalyst but without any added Cu(II) complex in various solvents which were added to keep the copper complexes in solution at 110 °C. However, the chain extension experiment showed bimodality and larger PDI in the chain extended polymer [10]. Raghunadh et al. also did not use any extraneously added deactivator and found that the CuBr/PMDETA catalyst does not provide satisfactory control, while the CuBr/N(*n*-propyl)2-pyridylmethanimine (PPMI) catalyst does [11]. But for the latter system they had to use a dilute solution of LMA (15% by volume) in toluene at 95 °C. Also, very recently, Street et al. reported that the CuBr/PPMI catalysed bulk ATRP of ODA at 95 °C is poorly controlled. However, the control improves significantly on increasing the alkyl group size in the methanimine catalyst from *n*-propyl to

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n-octyl which increases the compatibility of the catalyst with such a highly non-polar monomer. Further improvement in control occurs on using an initiator having a large alkyl group which has been supposed to be more compatible with the monomer. Best control (PDI = 1.15) was reported when the non-polar character of the initiator was further increased by replacing the alkyl group with its perfluoro derivative, e.g. using zonyl-2-bromo-2-methyl propionate initiator [12].

Recently, we showed that cuprous halide/linear alkylamine catalysts are solubilized in MMA at ambient temperature by catalytic amounts of quaternaryammonium halides. The chloride-based catalyst CuCl/PMDETA/AQCl (AQCl = Aliquat®336 = tricaprylylmethylammonium chloride) used with ethyl 2-bromoisobutyrate (EBiB) initiator provides excellent control and that too at ambient temperature which is attractive due to lower side reactions (hence better product) and cost advantage [13].

We show here the efficacy of this catalyst system as well in the ATRP of LMA and SMA at ambient temperature without requiring any extraneous addition of the deactivator, or any special initiator. Moreover, the ATRP of LMA can be successfully performed without using any solvent. The facility of the method is demonstrated through the synthesis at ambient temperature of some block copolymers.

2. Experimental section

2.1. Materials

LMA (Aldrich, 96%), MMA (BDH) and *n*-butyl methacrylate (*n*BMA) (Acros Organics, 99%) were washed with 5% aqueous NaOH solution, dried over anhydrous $CaCl_2$, then vacuum distilled and stored under nitrogen at −15 °C. SMA (Aldrich) was dissolved in hexane and the solution passed through a basic alumina column in order to remove the inhibitor. The solvent was removed under reduced pressure. *t*-Butyl methacrylate (*t*BMA) (Aldrich, 98%) was passed through a neutral alumina column and then vacuum distilled and stored at −15 °C. PMDETA (99%), Aliquat®336, EBiB (97%), 2,2,2-trichloroethanol (TCE, 99+%) all Aldrich products were used as received. Tetrahydrofuran (THF) (GR, E. Merck, India) was dried over CaH_2 and distilled. Anisole (GR, E. Merck, India) was distilled and used. CuCl (98%, BDH) was purified by washing with 10% HCl in water followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. The difunctional initiator 1,2-bis(bromoisobutyryloxy)ethane (BiBE) was prepared according to a literature method [14].

2.2. Synthesis of a ω-chloro PLMA (PLMA–Cl)

In a nitrogen purged test tube (8×2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.035 g, 0.086 mmol) and CuCl (0.0043 g, 0.043 mmol). Nitrogen purging was continued for 10 min following which the tube was closed with a rubber septum which was secured by a Cu wire. LMA (0.868 g, 3.42 mmol) previously purged with nitrogen was next introduced into the tube with a nitrogen purged gas-tight syringe. The mixture was stirred magnetically for 30 min to prepare a homogeneous solution. PMDETA (0.008 g, 0.043 mmol) followed by EBiB (0.008 g, 0.043 mmol) were then injected in. The polymerization was conducted at 35 °C with stirring. For kinetic studies, separate runs were performed for different times. After the desired time period, the contents of the tube were diluted with 1 ml THF and poured into 300 ml methanol. The separated polymer was isolated, redissolved in THF and reprecipitated into excess methanol. It was finally dried in a vacuum oven at 45 °C for 48 h, and weighed. The $M_{n(gpc)}$ and PDI of the polymer were 25,000 and 1.25, respectively, at 98% conversion.

2.3. Synthesis of a α,ω-dichloro PLMA (Cl–PLMA–Cl)

The procedure was similar to the above. The following recipe was used: AQCl = 0.028 g (0.068 mmol), CuCl (0.0034 g, 0.034 mmol), PMDETA (0.006 g, 0.034 mmol), LMA (1.736 g, 6.83 mmol), BiBE (0.0125 g, 0.034 mmol). After 8 h the conversion was 98% and the $M_{n(gpc)}$ and PDI were 41,000 and 1.24, respectively.

2.4. Synthesis of the triblock copolymer poly(MMA-b-LMA-b-MMA)

A one pot procedure was followed. In the pot containing the Cl–PLMA–Cl (macroinitiator) synthesized as above for 8 h was added by a gas-tight syringe MMA (0.752 g, 7.52 mmol) which was separately purged with N_2. The mixing was done using a vortex mixer. The mixture was then allowed to stand unstirred at 35 °C. After 20 h the polymer was isolated, purified and dried as described in the case of PLMA. The conversion of MMA was 81% and the $M_{n(gpc)}$ and PDI of the triblock copolymer were 56,000 and 1.17, respectively.

2.5. Synthesis of the pentablock copolymer poly(nBMA-b-MMA-b-LMA-b-MMA-b-nBMA)

The pentablock copolymer was prepared using the purified triblock Cl–PMMA-*b*-PLMA-*b*-PMMA–Cl as the macroinitiator (0.52 g, 0.009 mmol) in the polymerization of *n*BMA (0.53 g, 3.76 mmol). The mole ratios of the macroinitiator:CuCl:AQCl was 1:1:2. *n*BMA was previously purged with nitrogen before addition into a nitrogen purged septum sealed reaction vessel containing the macroinitiator, CuCl and AQCl. The macroinitiator was allowed to dissolve in *n*BMA for 24 h. PMDETA (0.0016 g, 0.009 mmol) was then injected into the tube and mixed with the solution with a vortex mixer. The polymerization was conducted at 35 °C unstirred. After 22 h the polymer was isolated, purified and dried as described in the case of PLMA. Conversion was 35%. The $M_{n(gpc)}$ and PDI values were 69,000 and 1.13, respectively.

2.6. Synthesis of a ω-chloro poly(stearyl methacrylate) (PSMA–Cl)

In a nitrogen purged test tube (8×2.5 cm) provided with a B-19 standard joint and a stir bar were added AQCl (0.035 g, 0.086 mmol) and CuCl (0.0043 g, 0.043 mmol). Nitrogen purging was continued for 10 min following which the tube was closed with a rubber septum which was secured by a Cu wire. SMA (0.864 g, 2.55 mmol) and anisole (1 ml) both previously purged with nitrogen were next introduced into the tube with nitrogen purged gas-tight syringes. The mixture was stirred magnetically to prepare a homogeneous solution following which PMDETA (0.008 g, 0.043 mmol) was added and stirring continued for a few minutes to make a clear solution. EBiB (0.008 g, 0.043 mmol) was then injected in. The polymerization was conducted at 35 °C with stirring. For kinetic studies, separate runs were performed for different times. After the desired time period, the contents of the tube were diluted with 1 ml THF and poured into 300 ml cold (10 °C) methanol. The separated polymer was isolated, redissolved in THF and reprecipitated into excess cold methanol and finally washed with a large volume of acetone. It was finally dried in a vacuum oven at 45 °C for 48 h, and weighed. The $M_{n(gpc)}$ and PDI of the polymer were 20,200 and 1.15, respectively, at 88% conversion.

2.7. Synthesis of the diblock copolymer (PSMA-b-PtBMA)

The diblock copolymer was synthesized using the purified PSMA–Cl macroinitiator (0.3 g, 0.015 mmol, $M_{n(gpc)}=20{,}200$, PDI = 1.15) in the polymerization of *t*BMA (0.7 g, 4.9 mmol). In a nitrogen purged septum sealed reaction vessel containing CuCl (0.0015 g, 0.015 mmol), AQCl (0.013 g, 0.03 mmol) and the macroinitiator was added the monomer and anisole (0.2 ml), both previously purged with nitrogen. The macroinitiator was allowed to dissolve in the monomer for 24 h. PMDETA (0.0026 g, 0.015 mmol) was then injected into the tube and mixed with the solution with a vortex mixer. The polymerization was conducted at 35 °C unstirred. After 36 h the polymer was isolated, purified and dried as described in the case of PLMA. Conversion was 85%. The $M_{n(gpc)}$ and PDI values were 70,000 and 1.2, respectively.

3. Characterization

The molecular weights and polydispersity index (PDI) were measured by gpc at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters Ultrastyragel columns of 10,000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF (Spectrochem, India) was used as the eluent at a flow rate of 1 ml/min. Before injection into the gpc system the polymer solutions were filtered through a prefilter–filter combination system compatible with organic solvents. PMMA standards were used for calibration.

Molecular weights of a few samples were also checked by viscometry in *n*-amyl alcohol which is a θ solvent at 29.5 °C. The intrinsic viscosity was determined by the single point method using Eq. (1) [15]

$$[\eta] = \frac{\sqrt{2\eta_{sp} - 2\ln\eta_{rel}}}{C} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, η_{rel} is the relative viscosity at concentration C in g/dl unit and η_{sp} is the specific viscosity. The viscosity average molecular weight (M_v) was calculated using the following Mark–Houwink relation [16] with $[\eta]$ in dl/g units.

$$[\eta] = 3.48\times10^{-4} M_w^{0.5} \tag{2}$$

As because the polymers are of low polydispersity, $M_v \approx M_w$. The number average molecular weight M_n was therefore calculated from M_w using the PDI values of the samples which were determined by gpc.

3.1. Dynamic mechanical analysis

Dynamic mechanical properties were measured with a (DMA Q800, TA instruments) dynamic mechanical analyzer. The temperature sweep experiments were carried out at 1 Hz (ramp mode, heating rate of 2 °C/min) using a film tension clamp for sample mounting.

4. Results and discussion

4.1. ATRP of LMA

The first-order kinetic plots for monomer disappearance in the polymerization of LMA (plots of $\ln [M]_0/[M]$ vs. *t*, where $[M]_0$ and $[M]$ are, respectively, the monomer concentration at time (t) = 0 and t, respectively) using CuCl/PMDETA with or without added AQCl as the catalyst and EBiB as the initiator at 35 °C (which is close to room temperature) under various reaction conditions are shown in Fig. 1. The polymerization

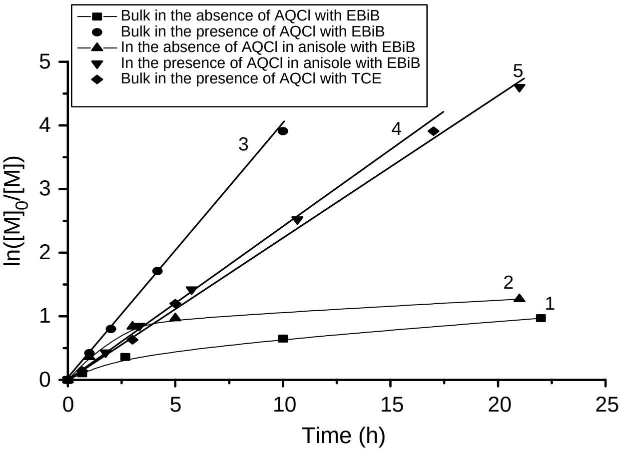

Fig. 1. ln $[M]_0/[M]$ vs. time plots for the ATRP of LMA in bulk and in presence of anisole at 35 °C with AQCl. ■, ●, $[CuCl]_0=[PMDETA]_0=[EBiB]_0=0.043$ mol/dm^3; ▲,▼ $[CuCl]_0=[PMDETA]_0=[EBiB]_0=0.036$ mol/dm^3; ◆, $[CuCl]_0=[PMDETA]_0=[TCE]_0=0.043$ mol/dm^3. Anisole where used is 20% of monomer (v/v); $[AQCl]=2[CuCl]_0$ where used.

gives low yield and a non-linear kinetic plot when the ATRP was conducted in bulk in the absence of AQCl (curve 1). This was due to the insolubility of both the Cu(I) and Cu(II) complexes in bulk LMA in the absence of AQCl. In contrast, the CuCl/PMDETA complex dissolves in bulk LMA in the presence of a catalytic amount of AQCl (two times [CuCl]) and the kinetic plot becomes linear (line 3) even though a translucent dispersion of the Cu(II) complex appeared after the polymerization progressed awhile. On the other hand, the CuCl/PMDETA complex dissolves in a mixture of LMA and anisole (20 vol% of LMA) without the aid of AQCl. The beneficial effect of anisole in solubilizing the CuCl/PMDETA catalyst complex in MMA was reported earlier [17]. However, unlike in the ATRP of MMA the Cu(II) complex precipitates out due presumably to the more non-polar character of LMA. This caused limited conversion and non-living polymerization which is evident from the non-linear kinetic plot (curve 2). However, the best reaction condition is obtained when both anisole (20 vol% of LMA) and AQCl (2 times [CuCl]) were added as additives. In such a medium not only the kinetic plot is linear (line 5) but the PDI is the lowest also (see below).

Fig. 2 shows that the gpc determined M_n values lie significantly above the theoretical M_n line ($M_{n,theo}$ = amount of monomer (g) consumed/mole of initiator) even for the systems for which the kinetic plots discussed in the above paragraph are linear. Fig. 2 also includes for one system the M_n values determined by the viscometric method. It is evident that the M_ns determined by the two methods differ by only about 10%. It thus follows that the PMMA standards used for gpc calibration give fair estimates of M_ns for PLMA. The difference between $M_{n(theo)}$ and $M_{n(exp)}$ as shown in Fig. 2 is therefore real. The M_n values increase with conversion, but they are not proportional to it which is uncharacteristic of a living polymerization. However, a closer look at the data points reveals that the percentage of positive deviation of the $M_{n(exp)}$ from $M_{n(theo)}$ becomes smaller with increase in the conversion. Thus, for the bulk ATRP using EBiB initiator the $M_{n(exp)}$ is 135% greater than $M_{n(theo)}$ at 34% conversion and only 35% greater at 98% conversion. This is a consequence of the dead polymer formed at the early stages of ATRP before the persistent radical (the cupric complex) concentration becomes sufficiently large to take control [9]. In ATRP the dead polymer molecules constitute about 5% of the total polymer molecule population [18,19].

The deviation is much greater than that seen in the ATRP of a monomer of smaller molecular weight, e.g. MMA which was carried out using this same initiator/catalyst complex system reported in our earlier work [13], the results of which are included in Fig. 3. The difference in the M_n deviation for the two monomers may be explained as follows. Assuming steady-state kinetics to be applicable at the early stages of ATRP, the P_n of the dead polymers can be expressed as

$$P_n = k_p[M]/(R_i k_t)^{0.5} \qquad (3)$$

where k_p and k_t are the rate constants of propagation and termination, respectively, $[M]$ is the monomer concentration and R_i is the rate of initiation. For the same initiator and catalyst concentrations R_i would be about the same for both systems. Then with the following literature values of k_t and k_p ($k_t = 0.6 \pm 0.2 \times 10^6$ l/(mol/s) for LMA [20] and $30.9 \pm 3.7 \times 10^6$ l/(mol/s) for MMA [21], $k_p = 427 \pm 38$ l/(mol/s) for MMA [21] and 460 ± 140 l/(mol/s) for LMA [20]) we calculate that the P_n of the dead PLMAs would be 2.8 times and the M_n 7.1 times as great as those of the dead PMMA chains. Making use of the first data points in Fig. 3 for PMMA and PLMA prepared using the EBiB initiator we calculate the M_ns of the dead chains assuming their population to be 5% of all chains and using the following relation

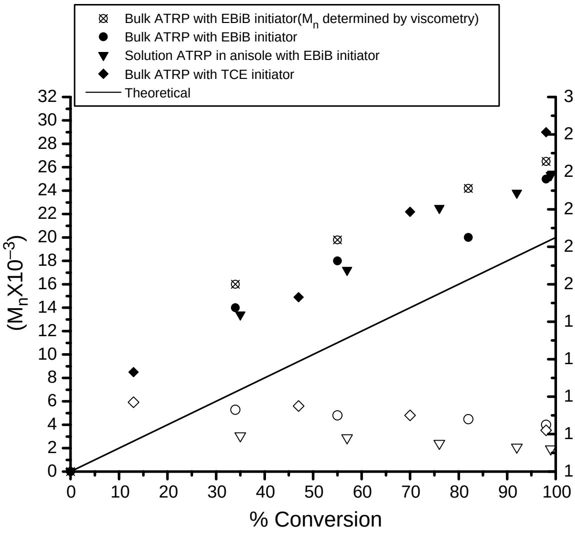

Fig. 2. $M_{n(gpc)}$ and PDI vs. conversion for the ATRP of LMA at 35 °C with the mole ratios of LMA:EBiB:CuCl:PMDETA:AQCl = 78.7:1:1:1:2. Anisole where used is 20% of LMA (v/v). The solid symbols represent M_n and the open ones the PDI.

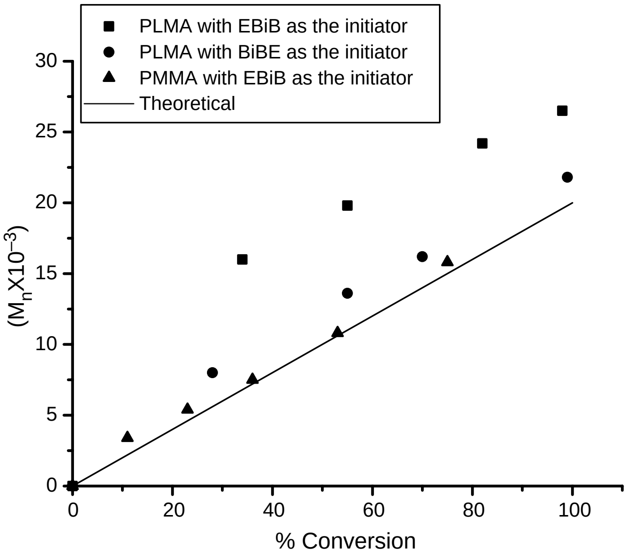

Fig. 3. A comparison of the deviation of the $M_{n(exp)}$ from $M_{n(theo)}$ for various systems ■, this work; ●, data taken from Ref. [22]; ▲, data taken from Ref. [13]. The target M_n = 20,000 at 100% conversion for all systems.

Table 1
ATRP of stearyl methacrylate at 35 °C, monomer:EBiB:CuCl:PMDETA:Aliquat®336 = 60:1:1:1:2

Entry	Solvent (% of SMA, v/v)	Time (h)	Conversion (%)	M_n (theoretical)	M_n (gpc)	PDI
1	None	2	30	6000	14,000	1.53
2	Anisole (30%)	5	65	13,000	26,000	1.21
3	Anisole (100%)	2	20	4000	5800	1.22
4	Anisole (100%)	8	60	12,000	14,000	1.2
5	Anisole (100%)	12	74	14,800	17,800	1.18
6	THF (100%)	8	82	16,400	19,200	1.19

Recipe, SMA = 1 ml, CuCl, PMDETA; EBiB = 1/2 AQCl = 0.043 mmol, solvent as shown in column 2.

$$M_{n(\text{exp})} = 0.95M_{n(\text{theo})} + 0.05M_{n(\text{dead chains})} \quad (4)$$

The M_ns of the dead chains are thus calculated to be 187,000 for PLMA and 26,200 for PMMA. The former is 7.1 times greater than the latter. This value fortuitously agrees 100% with that estimated using Eq. (3) as given above. The disagreement between $M_{n(\text{theo})}$ and $M_{n(\text{exp})}$ should not therefore be considered as indicative of uncontrolled polymerization.

It is also of interest to discuss the difference between monofunctional and the bifunctional initiator in regard to M_n deviation. Elsewhere, we reported the kinetics of ATRP of LMA using the difunctional initiator BiBE [22]. The positive deviation of $M_{n(\text{exp})}$ from $M_{n(\text{theo})}$ found in that system is much less than that seen here with the monofunctional initiator EBiB. A comparison of the two systems is also available from Fig. 3. The difference is indicative of lower molecular weight dead polymer formed in the bifunctional system. In the latter case, there exists a finite probability of simultaneous activation of both ends of the molecules. The biradicals so generated from the initiator as well as from the oligomers would be prone to termination due to a high-local concentration of the radicals and accordingly the dead polymers will be of lower molecular weight.

A further proof of the controlled polymerization is that the PDI is small and it decreases with conversion as is required by the theory [1,9,23]. The lowest PDI is obtained in the anisole diluted system in which case the PDI decreases from a value of 1.19 at 35% conversion to 1.12 at 99% conversion. The control is therefore best for this system which is in conformity with the best solubility situation visually observed in here for the Cu(II) complex.

Regarding other initiators our previous work showed that *p*-toluenesulfonyl chloride (*p*-TsCl) which is an efficient initiator for the ATRP of MMA with CuBr/dNbpy or CuBr/PMDETA catalyst [17,24] was unsatisfactory with the present catalyst [13] and so not used here. However, another initiator, viz. trichloroethanol, which is effective in the ATRP of methacrylates with other catalysts [14,25] works well as would be evident from the linear kinetic plot in Fig. 1 (line 4) and a reasonably low PDI (Fig. 2).

4.2. ATRP of SMA

The ATRP of stearyl methacrylate was also studied using CuCl:PMDETA:AQCl = 1:1:2 as the catalyst. The complex is soluble in the bulk monomer but turbidity followed by precipitation of the Cu(II) complex occurs soon after polymerization starts in the initially homogeneous system. In order to improve upon the solubility of the Cu(II) complex anisole or THF was added into the system. Table 1 shows the results. Entries 1 and 3 show that the PDI decreases substantially on the addition of anisole. Also, M_n becomes closer to the theoretical value. The PDI for the systems using anisole as the solvent remains almost independent of anisole concentration in the range of 30–100 vol% of SMA, although, the M_n deviates from the theoretical value to a greater extent for the lower solvent concentration. Replacement of anisole by THF gives almost as good control.

The kinetic plots for monomer disappearance for the polymerization of SMA in equal volume of anisole with or without the addition of AQCl are shown in Fig. 4. It is evident from the figure that the polymerization in the absence of AQCl is not controlled. Fig. 5 shows the evolution of molecular weight and PDI with conversion. The variation of M_n with conversion for the controlled system (AQCl present) may be explained in the same way as has been done earlier in this paper in the case of the polymerization of LMA. On the other hand, for the system without AQCl, although M_n increases with conversion, the deviation from the theoretical value increases with conversion which is uncharacteristic of controlled

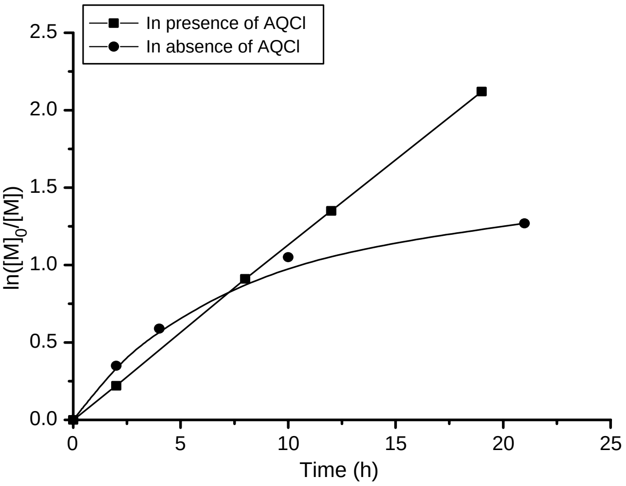

Fig. 4. ln [M]$_0$/[M] vs. time plots for the ATRP of SMA in equal volume of anisole at 35 °C with or without AQCl. $[SMA]_0 = 1.28$ mol/dm^3, $[CuCl]_0 = [PMDETA]_0 = [EBiB]_0 = 0.022$ mol/dm^3 , $[AQCl] = 0.044$ mol/dm^3 where applicable.

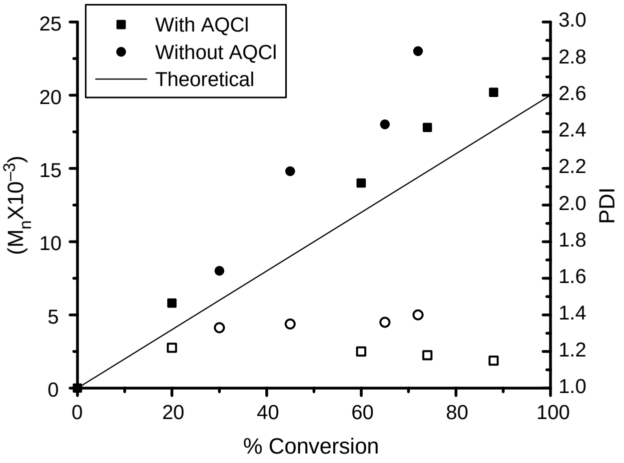

Fig. 5. M_n and PDI vs. conversion for the ATRP of SMA using the same recipe as in Fig. 4. The solid symbols represent M_n and the open ones the PDI.

polymerization. As regards, the PDI, it is lower for the system with AQCl than for that without AQCl. Also, for the former system it decreases with increase in conversion as is predicted by the theory [1,9,23].

4.3. Block copolymerization

The effectiveness of the present catalyst system is demonstrated with the convenient synthesis of a diblock copolymer PSMA-*b*-P*t*BMA, a triblock copolymer PMMA-*b*-PLMA-*b*-PMMA and a pentablock copolymer P*n*BMA-*b*-PMMA-*b*-PLMA-*b*-PMMA-*b*-P*n*BMA at 35 °C. For the first one a chlorine ended monofunctional PSMA was first prepared. This was used as the macroinitiator for the polymerization of *t*BMA. The gpc trace of the diblock copolymer (Fig. 6) shows monomodal distribution. The result demonstrates that the catalyst system is efficient as well for the ATRP of the sterically hindered monomer *t*BMA. There is some tailing of course, in the low-molecular weight region. Low-molecular weight tail in the gpc trace of P*t*BMA synthesized by ATRP using EBiB initiator and CuX/PMDETA catalyst has been previously observed [14]. This was traced to low-initiation rate since the tailing decreased with the use of the mixed halide system, bromide initiator and chloride catalyst, i.e. EBiB and CuCl which gives faster initiation than the system comprising of EBiB and CuBr [26]. In the present case, both the macroinitiator and the catalyst have been used in the chloride form which should give slower initiation than the above-mentioned mixed halide system inasmuch as the C–Cl bond is stronger than the C–Br bond. Nevertheless, the block copolymer is of interest since on hydrolysis it will give novel ionomers.

For the synthesis of the triblock copolymer with PLMA as the middle block Cl–PLMA–Cl was used as the macroinitiator in a bulk polymerization of MMA. AQCl was added to the extent of 4 times [CuCl] [13]. The system remained homogeneous all through. The gpc traces for the macroinitiator and the triblock copolymer are shown in Fig. 7. The curves shifted to higher molecular weights and the PDI became smaller following block copolymerization which suggests that initiation is fast. The pentablock copolymer was prepared using the Cl ended difunctional PMMA-*b*-PLMA-*b*-PMMA triblock copolymer so prepared as the macroinitiator for the bulk polymerization of *n*-BMA. The pentablock formation is indicated from the gpc traces in Fig. 7. The syntheses of the triblock and pentablock copolymers were confirmed from the dynamic mechanical measurements. Fig. 8 shows the temperature dependence of the storage modulus (G') of the polymers from −75 to 150 °C. The triblock copolymer exhibits the behavior of a thermoplastic elastomer with two glass transitions (peak positions of tan δ), a rubbery plateau

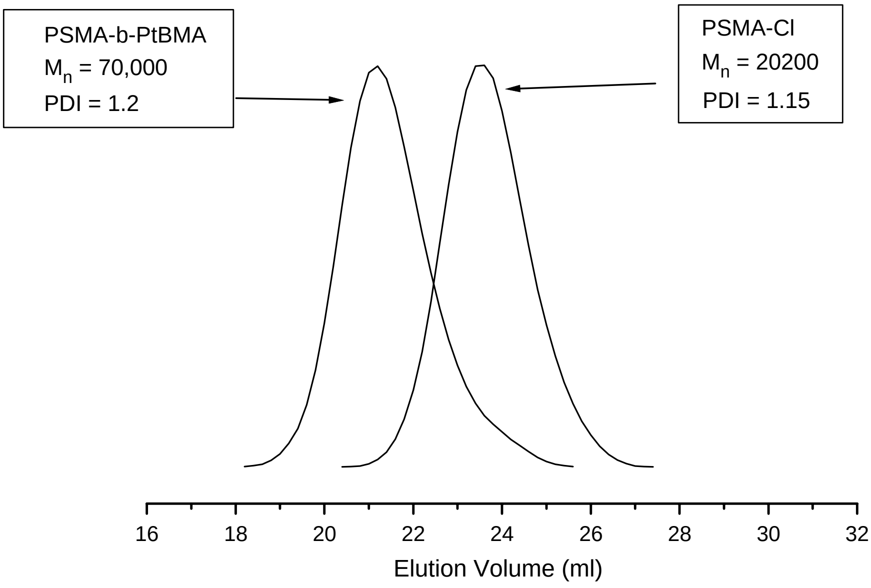

Fig. 6. GPC traces of the PSMA–Cl macroinitiator and the PSMA-*b*-PtBMA diblock copolymer.

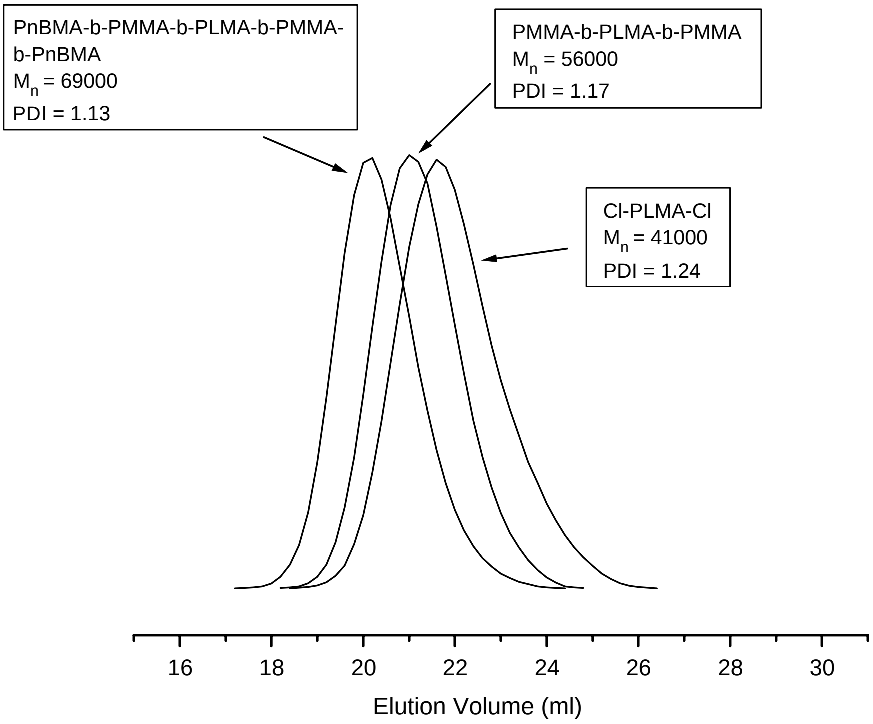

Fig. 7. GPC traces of the Cl–PMMA–Cl macroinitiator, the PMMA-*b*-PLMA-*b*-PMMA triblock copolymer and the PnBMA-*b*-PMMA-*b*-PLMA-*b*-PMMA-*b*-PnBMA pentablock copolymer.

between them and a terminal zone after the high-T_g. The pentablock copolymer shows three glass transitions, one for the rubbery PLMA domain at −13.63 °C and two others for the two glassy domains one at 59.2 °C for the P*n*BMA domain and the other at 128.9 °C for the PMMA domain. Detailed studies on these block copolymers will be published elsewhere.

This study thus shows that the CuCl/PMDETA/AQCl works well for the ambient temperature ATRP of higher alkyl methacrylates as it does for the lower members of the homologous alkyl methacrylate series [13]. Regarding the role of AQCl in increasing the solubility of the catalyst, it was suggested from phenomenological consideration in our earlier work [13] that more than one halide ion gets involved as ligands in the formation of the catalyst complex which in the absence of the extra halide ions has the composition [Cu(PMDETA)X] [27]. The resultant new complex would require PMDETA to act either as a bidentate or as a monodentate ligand due to the maximum co-ordination number of Cu^+ being 4. Also, the complex would be negatively charged which would be counter balanced by the AQ^+ ion. The latter being highly hydrophobic helps to take the complex into solution. In fact, such involvement of halide ions in complex formation with Cu^+ ion in aqueous medium in the presence of halide ions and PMDETA has been suggested from UV–visible spectroscopic studies in an earlier work from this laboratory [28].

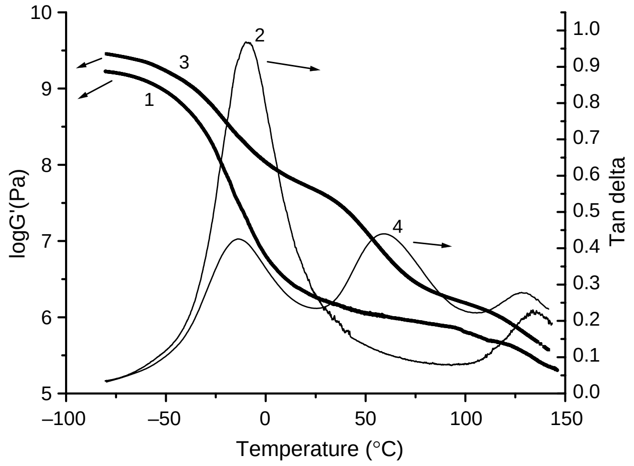

Fig. 8. Plots of log storage modulus (1 Hz, 2 °C/min) and tan δ vs. temperature of a PMMA-*b*-PLMA-*b*-PMMA triblock (curves 1 and 2) and a P*n*BMA-*b*-PMMA-*b*-PLMA-*b*-PMMA-*b*-P*n*BMA pentablock copolymer (curves 3 and 4).

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