

The beneficial effect of small amount of water in the ambient temperature atom transfer radical homo and block co-polymerization of methacrylates

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Abstract

ATRP of several methacrylates viz. methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (*n*BMA), *t*-butyl methacrylate (*t*BMA), benzyl methacrylate (BzMA) and (*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) has been studied in neat as well as aqueous (up to 12 vol% water) acetone at 35 °C using CuCl/bipyridine (bpy) catalyst and ethyl 2-bromoisobutyrate as the initiator. Addition of water significantly enhances the rate of polymerization without losing control. Unlike CuCl/bpy the CuBr/bpy catalyst gives poor control which is attributed to the lower solubility and consequent heterogeneity in the latter case. Of the other ligands used with the CuCl catalyst viz. *o*-phenanthroline (*o*-phen), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), Me₆TREN only *o*-phen offers reasonably good control. The CuCl/bpy catalyst system has been used also in preparing some di- and tri-block copolymers with reasonably low polydispersity index (PDI) at ambient temperature (35 °C) using aqueous acetone as the solvent. The following block copolymers have been prepared PMMA-*t*BMA, PMMA-*b*-*t*BMA-*b*-MMA, PMMA-DMAEMA, by this method.

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1. Introduction

Water has a deleterious effect on the copper mediated homogeneous phase ATRP. This is caused by various factors: (i) the decrease of deactivator concentration due to the displacement of the halide ligand from the cupric complexes by water (aquation) or by hydroxyl ion (hydrolysis) [1–6] (ii) the termination of the polymer radicals by the aquo or hydroxo complexes of Cu(II) through an outer sphere electron transfer oxidation process [7,8] and (iii) the disproportionation of the Cu(I) complexes involving certain ligands [4,9]. Factor (i) can be minimized by decreasing the water concentration. Factor (ii) does not apply for polymethacrylate radicals due to steric reasons [10,11]. Factor (iii) does not exist with bipyridine (bpy) ligand [9]. On the other hand, water increases greatly the

rate of ATRP when bpy is the ligand which has been attributed to its prevention of the dimerization of Cu(I)X/bpy complexes [12]. A judicious use of a small amount of water in the ATRP of methacrylates using Cu(I)/bpy complex catalyst should therefore enable deriving the benefit of the enhancement of the rate while rendering the harmful factor (i) small.

ATRP of several hydrophilic methacrylates has been extensively performed using suitable mixtures of water with lower alcohols as polymerization media [5,13–24]. Regarding hydrophobic methacrylates the ATRP of only two of them viz. MMA in aqueous ethanol [4] and *n*BMA in aqueous isopropanol (iPA) [25] has been successfully performed. In the latter case a small amount of water not only increases the rate but also improves the control greatly. This is surprising in view of the factor (i) above. However, the alcohols, neat or aqueous, can dissolve only a few hydrophobic methacrylates. Moreover, this solubility is alcohol-polymethacrylate specific. It is therefore desirable to use a versatile solvent. Acetone is one such solvent.

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Several hydrophobic polymethacrylates are soluble in acetone and the solutions can tolerate small amount of water without causing phase separation. Some hydrophilic methacrylates such as DMAEMA are also soluble in acetone, neat or aqueous.

N,N-dimethyl formamide (DMF) also is a solvent for many polymethacrylates. In fact, mixtures of DMF with a large quantity of water have been used to polymerize and copolymerize MMA and hydrophilic monomers [26]. However, because of the considerable hydrolysis of the Cu(II) halide complexes due to the use of the large amount of water extra Cu(II) halide and ligands are to be added into the system for satisfactory control. The other plus points for acetone are its cheaper cost and lesser environmental hazard.

In this work we report the successful ATRP of four hydrophobic methacrylates viz. MMA, EMA, *n*BMA, *t*BMA and BzMA and one hydrophilic methacrylate viz. DMAEMA in aqueous acetone containing 8.6% (v/v) water using CuCl/bpy catalyst. Synthesis of di and tri-block copolymers has also been reported.

2. Experimental section

2.1. Materials

MMA (BDH) was washed with 5% NaOH solution followed by distilled water, distilled under reduced pressure and stored under nitrogen atmosphere at $-15\text{ }^{\circ}\text{C}$. Acetone (GR, E-Merck, India) was distilled and used. 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 98%), bpy (98%) and ethyl 2-bromoisobutyrate (EBib, 97%), all Aldrich products, *o*-phenanthroline (*o*-phen, GR, E-merck, India) were used as received. CuBr (98%, Aldrich) and CuCl (98%, BDH), were purified by washing with the corresponding acids (10% HX in water) followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. Me₆TREN and the difunctional initiator 1,2-bis(bromoisobutyryloxy)ethane were prepared according to a literature method [27,28].

2.2. Homo polymerization

Examples for the polymerization of MMA in aqueous acetone with the EBib/CuCl/bpy initiator/catalyst system are as follows.

2.2.1. Synthesis of a monofunctional PMMA (PMMA-Cl)

In a nitrogen purged test tube ($8\times 2.5\text{ cm}$) provided with a B-19 standard joint and a stir bar were added CuCl (0.022 g, 0.210 mmol) and bpy (0.068 g, 0.038 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. MMA (3.6 ml, 33.8 mmol),

acetone (5.3 ml), H₂O (0.5 ml), all purged separately with nitrogen were next injected into the tube with a nitrogen purged gas-tight syringe. The admixture was sonicated for 2 min. A deep brown color resulted. EBib (0.033 ml, 0.219 mmol) was then injected in. The tube was then put in an oil bath maintained at $35\text{ }^{\circ}\text{C}$. The polymerization mixture was stirred magnetically. At suitable time intervals aliquots (1 ml) of the reaction mixture were withdrawn, diluted with 1 ml THF and poured into methanol–water (50% v/v). The polymers were isolated by centrifugation, dried, redissolved in THF and reprecipitated into the water–methanol mixture. They were finally dried in a vacuum oven at $45\text{ }^{\circ}\text{C}$ for 48 h. A similar polymerization procedure was used for other methacrylates.

2.2.2. Synthesis of a di-functional PMMA (Cl-PMMA-Cl)

In a reaction vessel purged with nitrogen as described earlier in this section CuCl (0.009 g, 0.094 mmol) and bpy (0.029 g, 0.19 mmol) were taken and the reaction vessel was sealed with a rubber septum. Into the vessel were sequentially added deaerated MMA (4.70 g, 47 mmol) and the difunctional initiator 1,2-bis(bromoisobutyryloxy) ethane (0.034 g, 0.009 mmol) dissolved in 10 ml aqueous acetone (8% v/v water) using a gas tight syringe. The reaction mixture was sonicated for 2 min, placed in an oil bath at $35\text{ }^{\circ}\text{C}$ and stirred. After 30 h the conversion was 60% and the M_n and PDI were 28,100 and 1.19, respectively.

2.3. Synthesis of block copolymers

2.3.1. Synthesis of poly(MMA-*b*-*t*BMA)

For the preparation of a block copolymer with *t*BMA the purified PMMA macroinitiator (0.90 g, 0.06 mmol) prepared as given in the example ($M_n=15,500$) was dissolved in 2 ml degassed aqueous acetone (7.5% v/v water). *t*BMA (1 ml, 6.7 mmol) previously purged with nitrogen was next added into the reaction vessel under nitrogen atmosphere followed by bpy (0.018 g, 0.116 mmol) and CuCl (0.006 g, 0.058 mmol). The tube was then closed with a rubber septum which was secured with Cu wire. The reaction mixture was stirred at $35\text{ }^{\circ}\text{C}$ for the desired time. The unreacted monomer was evaporated off, the polymerized mass was dissolved in acetone (3 ml). The polymer was precipitated into water. The block copolymer thus isolated was characterized by GPC for MW and MWD as described earlier. After 40 h a 90% conversion was reached with M_n and PDI values of 31,000 and 1.23, respectively.

2.3.2. Synthesis of poly(MMA-*b*-DMAEMA)

The procedure for the preparation of the diblock copolymer is the same as above excepting the recipe which comprises PMMA-Cl (0.031 mmol, 239 mg) ($M_n=7700$, PDI=1.3), CuCl (0.031 mmol, 3 mg), bpy (0.062 mmol, 9.72 mg), DMAEMA (1 ml), acetone (0.9 ml), H₂O (0.1 ml). The block copolymer was dissolved in acetone and precipitated into petroleum ether. The

polymer was purified by column chromatography using a silica gel column and THF as eluent. After 24 h the conversion was 73%. The M_n and PDI values of the block copolymer are 30,500 and 1.24, respectively.

2.3.3. Synthesis of poly(*t*BMA-*b*-MMA-*b*-*t*BMA)

The difunctional PMMA macroinitiator (2.45 g, 0.09 mmol) ($M_n=28,100$) was dissolved in nitrogen purged aqueous acetone (7.5% v/v water) (1.9 ml) in a reaction vessel as described earlier in this section. *t*BMA (0.874 g, 6.72 mmol) was nitrogen purged and injected into the vessel. Bpy (0.027 g, 0.174 mmol) and CuCl (0.008 g, 0.087 mmol) were next added under nitrogen. The mixture was sonicated for about 2 min and the vessel was placed in an oil bath at 35 °C and the solution stirred. A conversion of 50% was reached in 12 h. The polymer with M_n and PDI values of 32,300 and 1.17, respectively was isolated as in the case of PMMA-*b*-*t*BMA.

2.4. The molecular weights (MW) and the molecular weight distributions (MWD)

These were measured by GPC at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters Ultrastaygel 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 passed through a silica gel column using THF as eluent to free them from Cu salts. They were then filtered through a prefilter-filter combination system compatible with organic solvents. Poly(methyl methacrylate) standards were used for calibration.

3. Results and discussion

Table 1 gives the results of ATRP of MMA using CuCl/bpy as the catalyst and EBib as the initiator at 35 °C in acetone–water medium of varying composition. The highest water concentration (12 vol%) is tolerated without causing

phase separation in a PMMA ($M_n=22,000$)–acetone–water ternary system at least up to a PMMA concentration of 50% w/v at 35 °C. Entries 1–3 show that the polymerization rate increases with water concentration. This is in accord with the previously reported rate enhancing effect of water which has been attributed to water promoting the more reactive monomeric form of the Cu(I)X/bpy complex catalyst [12]. Increasing the water concentration to 12 vol% the rate does not increase further (entry 4). It may be noted that these rates are much lower than that reported by us for the ATRP of MMA not only in ethanol–water but also in pure ethanol [4]. The polymerization mixtures (entries 1–4) were homogeneous to start with and brown in color which is due to the Cu(I)Cl/bpy complex. However, heterogeneity sets in after certain extents of conversion due to the precipitation of the Cu(II)Cl₂/bpy complex which is insoluble in acetone. This problem was lessened with the addition of water and eliminated in entries 3 and 4.

Fig. 1 shows the UV–visible spectra of mixtures of CuCl₂ (0.022 mmol) + bpy (0.044 mmol) in 9.4 ml of neat or aqueous acetone of varying water content. In acetone the mixture appears hazy and colorless while in the aqueous acetone (8.6–15.5 vol% water) it is clear blue in color with the intensity of the color increasing as the water content increases from 3.4 to 15.5 vol%.

The first order kinetic plots for monomer disappearance (Fig. 2) are linear which is required of a living polymerization. Fig. 3 shows that the molecular weight increases linearly with conversion. However, the agreement of the molecular weight with the theory ($M_{n(\text{theory})} = ([M]_0/[I]_0) \times \text{molecular weight of monomer} \times \text{fractional conversion}$) is best when no water is added to the system. Fig. 4 shows that the PDI is small and decreases with increase in conversion which is in qualitative agreement with theory [29–31]. Although the rate increases with the increase in water concentration, the PDI for the high conversion samples remains low. However, for the highest water concentration (12 vol%) the PDI tends to increase (entry 4). From these results we are inclined to select the solvent composition for entry 3 (8.6 vol% water) as the most favorable composition of the ATRP of MMA.

As regards the use of the CuBr/bpy vs. CuCl/bpy

Table 1
Results of ATRP of MMA in acetone–water at 35 °C using bpy as the ligand

Entry	Solvent (acetone + water)		Time (h)	% Conversion	$M_{n, \text{theo}}$	$M_{n, \text{GPC}}$	M_w/M_n
	Acetone (vol%)	Water (vol%)					
CuCl catalyst							
1	100	0	30.5	75	11,625	11,800	1.19
2	96.5	3.5	27	81	12,555	15,150	1.20
3	91.4	8.6	22.5	89	13,795	15,500	1.15
4	88	12	25	90	13,950	16,600	1.17
CuBr catalyst							
5	100	0	23	93	14,415	15,000	1.32
6	88	12	20	97	15,035	15,400	1.40

Recipe: MMA = 3.6 ml, solvent = 5.8 ml, ethyl-2-bromo isobutyrate = 0.21 mmol, CuX = 0.21 mmol and bpy = 0.42 mmol.

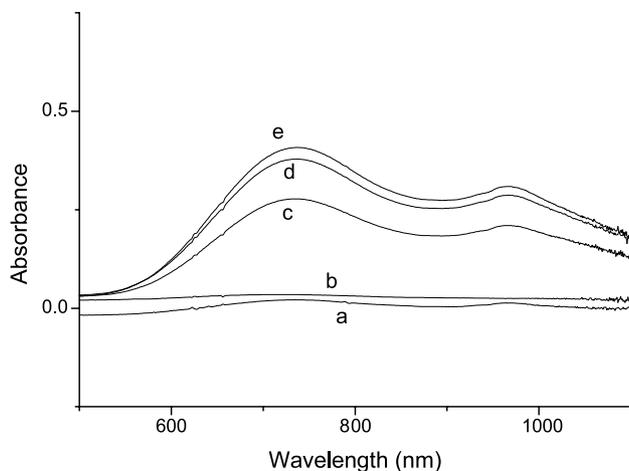


Fig. 1. Variation of absorbance of Cu(II)/bpy complex in acetone with water concentration. $[MMA]=3.6 \text{ mol/dm}^3$, $[bpy]=2 [CuCl]=0.046 \text{ mol/dm}^3$; spectra a–e are for 0, 3.4, 8.6, 12 and 15.5 vol% water in aqueous acetone, respectively.

complex as catalyst the former does not go completely into solution in acetone. On the other hand, although it is soluble in acetone/water=13/1 (v/v), the polymerization system becomes heterogeneous when only 30% conversion is reached. The heterogeneity could be the reason why PDI is significantly higher (entries 5 and 6) when CuCl is replaced by CuBr. Were the complexes soluble, one would have expected an opposite result in as much as the extent of aqution (replacement of the halide ligand by water) of the CuX_2/bpy complexes would be more (hence lesser rate of deactivation) when $X=Cl$ than when $X=Br$ [4]. It is noteworthy that CuX/bpy catalysts were reported to be unsuitable for ATRP in aprotic solvents due principally to their insolubility. In order to overcome this problem bpy is derivatized e.g. 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNBpy) to form a soluble catalyst complex with CuX . However,

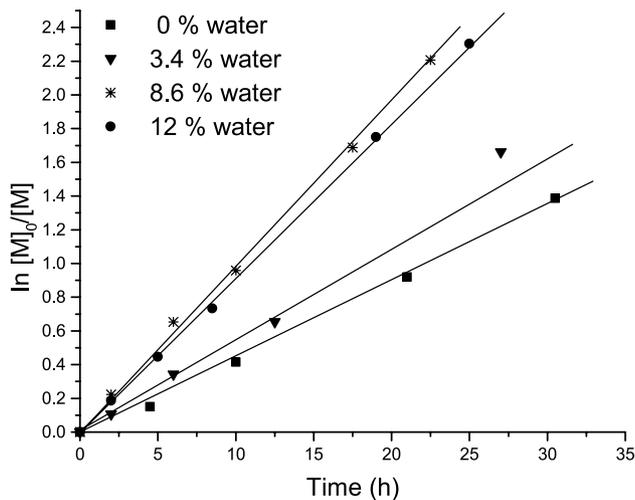


Fig. 2. Kinetic plots for monomer disappearance in the ATRP of methyl methacrylate in neat and aqueous acetone at 35 °C. $[MMA]=3.6 \text{ mol/dm}^3$, $[CuCl]=\frac{1}{2}[bpy]=[EBiB]=0.023 \text{ mol/dm}^3$.

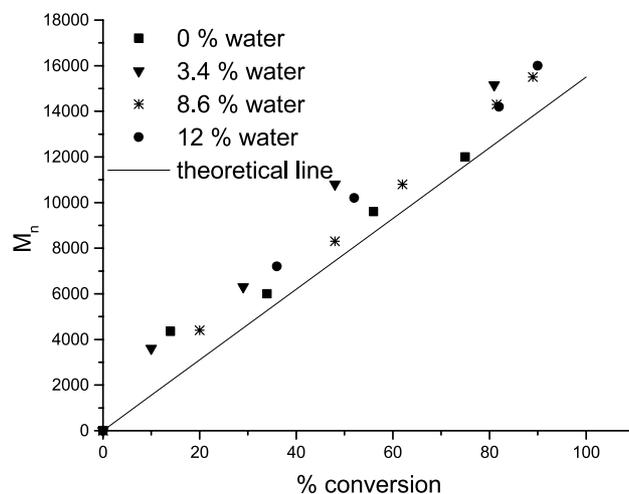


Fig. 3. M_n vs. % conversion for ATRP of MMA in neat and aqueous acetone. $[MMA]=3.6 \text{ mol/dm}^3$, $[CuCl]=\frac{1}{2}[bpy]=[EBiB]=0.023 \text{ mol/dm}^3$.

satisfactorily controlled ATRP with the latter catalyst was reported only at elevated temperature ca. 90 °C [32].

Ligands other than bpy were also examined using aqueous acetone (12% v/v water) as the medium. The results are given in Table 2. With *o*-phenanthroline (*o*-phen) ligand the catalyst complex does not go completely into solution but the control is reasonably good. With Me_6TREN the yield is low. With PMDETA and HMTETA ligands disproportionation occurred as was evident from the development of blue color on mixing CuCl with these ligands due to the Cu(II) formed as a result. Also, the catalyst is oxidized rapidly to Cu(II) on the addition of the initiator. Occurrence of such a situation was reported and explained earlier by us in the homogeneous ATRP of MMA in ethanol–water [4]. In contrast, in bulk or in polar organic solvents e.g. anisole, diphenyl ether, etc. ATRP is

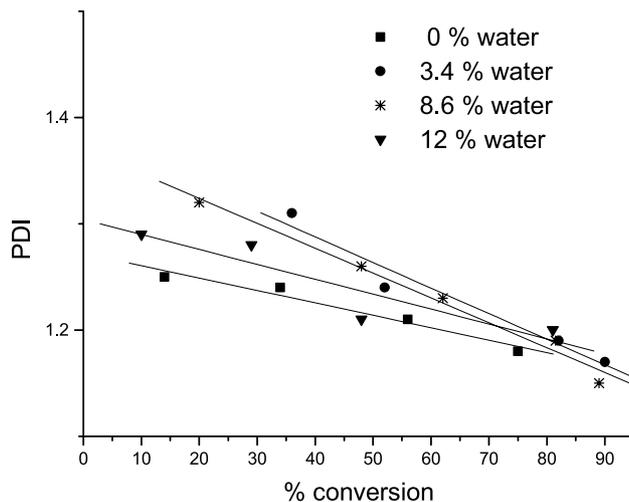


Fig. 4. PDI vs. % conversion for ATRP of MMA in neat and aqueous acetone. $[MMA]=3.6 \text{ mol/dm}^3$, $[CuCl]=\frac{1}{2}[bpy]=[EBiB]=0.023 \text{ mol/dm}^3$.

Table 2
Results of ATRP of MMA in acetone–water (12 vol% water) at 35 °C using various ligands

Entry	Ligand	Time (h)	% Conversion	$M_{n, \text{theo}}$	$M_{n, \text{GPC}}$	M_w/M_n
1	<i>o</i> -phen	21	95	14,725	18,900	1.22
2	PMDETA	21	56	8680	20,500	1.40
3	HMTETA	10	78	12,090	17,200	1.69
4	Me ₆ TREN	21.5	10	1550	8000	1.26

Recipe: MMA = 3.6 ml, solvent = 5.8 ml, ethyl-2-bromo isobutyrate = 0.21 mmol, CuCl = PMDETA = HMTETA = Me₆TREN = 0.21 mmol, *o*-phen = 0.42 mmol.

reportedly successful using these ligands [33,34]. With anisole as the solvent control is reported to be better at ambient temperature than at elevated temperatures [35]. As regards the kinetics the first order kinetic plots for monomer disappearance are linear only for the *o*-phen ligand but nonlinear for the HMTETA, PMDETA and Me₆TRN ligands as has been shown in Fig. 5. This result confirms that except with *o*-phen the control is poor using these latter ligands.

Results of ATRP of five other hydrophobic methacrylates viz. EMA, *n*BMA, *t*BMA, BzMA in neat or aqueous (8.6 vol% water) acetone are shown in Table 3. Expectedly, higher yields in lesser time are obtained in aqueous acetone. The PDI is low indicating good control. McDonald and Rannard earlier reported significant improvement of both rate and control in the ATRP of *n*BMA when water added (7.5 vol%) to iPA was used as the solvent for homogeneous polymerization [25]. The simultaneous increase of the rate and lowering of the PDI in the latter system is rather surprising. In neat iPA the PDI was very high (ca. 3.25) at lower conversions (10%) and decreased to a low value (1.25) at about 50% conversion, while in aqueous iPA (7.5 vol% water) the PDI remained almost unchanged at ~1.2 as the conversion increased from ca. 20 to 90%. In contrast, this work shows that for the ATRP of *n*BMA the

control in neat acetone is not as poor as in neat iPA at low conversions as would be evident from the PDI values shown in Fig. 6. It is interesting to note that the line showing the variation of PDI with conversion in neat acetone has a steeper slope than in aqueous acetone (Fig. 6). This is opposite to that observed for the ATRP of MMA (Fig. 4). Such differences with monomer reflect the complexity of the systems. The high PDI at low conversion in iPA for the ATRP of *n*BMA was attributed to significant termination [25] which may not be the case since the PDI became low at high conversion. Instead, a slow initiation may be the cause.

Table 3 also includes the ATRP result for the hydrophilic monomer DMAEMA. This system also gives controlled polymerization in both neat and aqueous acetone as would be evident from the low PDI and closeness of the molecular weight to that predicted by theory. As expected, the rate is much faster in the aqueous acetone (8.6 vol% water).

Fig. 7 shows that the first order kinetic plots for monomer disappearance for the ATRP of these methacrylates in aqueous (8.6 vol% water) acetone are linear which fulfills one of the criteria for living polymerization. Linear plots were also obtained for the ATRP in neat acetone (not shown). Fig. 8 shows that the molecular weights for all the systems increase with conversion as would be expected for a living polymerization. The molecular weights are close to the theoretical. Part of the disagreement between the

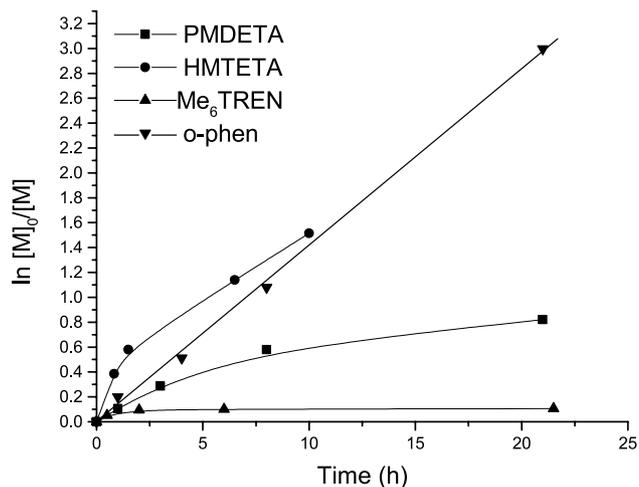


Fig. 5. Kinetic plots for monomer disappearance in the ATRP of methyl methacrylate in aqueous acetone using various ligands at 35 °C. [MMA] = 3.6 mol/dm³, [H₂O] = 12% (v/v), [CuCl] = [PMDETA] = [HMTETA] = [Me₆TREN] = ½[*o*-phen] = [EBiB] = 0.023 mol/dm³.

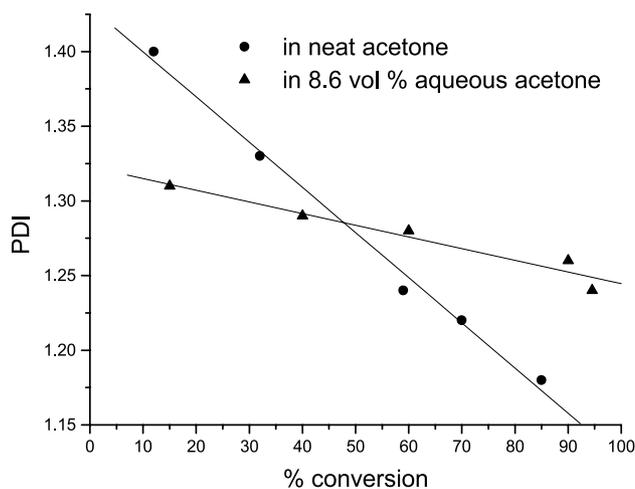


Fig. 6. PDI vs. % conversion for ATRP of *n*BMA in neat and aqueous acetone at 35 °C using [*n*BMA] = 2.45 mol/dm³, [H₂O] = 8.6% (v/v), [CuCl] = ½[bpy] = [EBiB] = 0.022 mol/dm³.

Table 3
Results of ATRP of various methacrylates in neat or aqueous acetone (8.6 vol% water) at 35 °C using CuCl-bpy catalyst

Entry	Solvent (acetone + water)		Monomer	Time (h)	% Conversion	$M_{n, \text{theo}}$	$M_{n, \text{GPC}}$	M_w/M_n
	Acetone (vol%)	Water (vol%)						
1	100	0	EMA	57	81	12,555	13,000	1.19
2	91.4	8.6	EMA	42	98	15,190	17,000	1.18
3	100	0.0	<i>t</i> BMA	82	61	9455	9500	1.24
4	91.4	8.6	<i>t</i> BMA	48.5	82	12,700	12,200	1.24
5	100	0	<i>n</i> BMA	58	85	13,175	14,000	1.18
6	91.4	8.6	<i>n</i> BMA	33	95	14,725	16,200	1.24
7	100	0	BzMA	42	88	13,640	13,800	1.15
8	91.4	8.6	BzMA	20	91	14,100	14,400	1.17
9	100	0	DMAEMA	74.5	80	12,400	12,000	1.20
10	91.4	8.6	DMAEMA	20.5	97	14,260	14,400	1.19

Recipe: Monomer=3.6 ml, Solvent=5.8 ml, ethyl-2-bromo isobutyrate=0.21 mmol, CuCl=0.21 mmol and bpy=0.42 mmol.

experimental and the theoretical molecular weights must arise from the difference in hydrodynamic volume of the PMMA calibration standard and the polymethacrylate analyte. Fig. 9 shows that the PDI decreases with conversion and is reasonably low which is suggestive of good control on the polymerization.

3.1. Block copolymerization

Some di and tri-block copolymethacrylates have been synthesized using the present method.

3.1.1. Poly(MMA-*b*-*t*BMA) and poly(*t*BMA-*b*-MMA-*b*-*t*BMA)

Fig. 10(a) shows the GPC traces of the PMMA-Cl

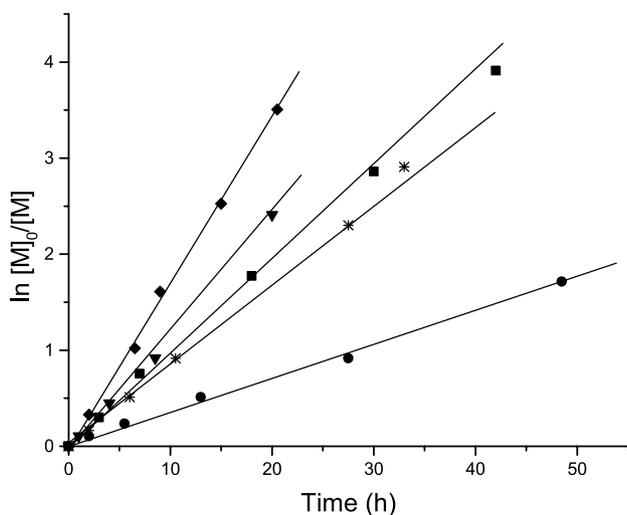


Fig. 7. Kinetic plots for monomer disappearance in the ATRP of different methacrylates in aqueous (8.6 vol% water) acetone at 35 °C using [EMA]=3.06 mol/dm³, [CuCl]=½[bpy]=[EBiB]=0.022 mol/dm³; [BzMA]=2.26 mol/dm³, [CuCl]=½[bpy]=[EBiB]=0.026 mol/dm³; [*n*BMA]=2.45 mol/dm³, [CuCl]=½[bpy]=[EBiB]=0.022 mol/dm³; [*t*BMA]=2.36 mol/dm³, [CuCl]=½[bpy]=[EBiB]=0.021 mol/dm³; [DMAEMA]=2.29 mol/dm³, [CuCl]=½[bpy]=[EBiB]=0.023 mol/dm³. ■, EMA; ●, *t*BMA; **n*BMA; ▼, BzMA and ◆, DMAEMA.

macroinitiator and of the block copolymer. The polydispersity of the block copolymer is reasonably low. The PDI of the di-block is lower than that of the macroinitiator which is indicative of efficient initiation by the macroinitiator. The difunctional macroinitiator (Fig. 10(b)) has a PDI lower than that of the monofunctional macroinitiator. During the synthesis of the former more Cu(II) is formed as was discerned visually. This is suggestive of greater termination in the initial stage when most of the Cu(II) is formed. The biradicals formed in this case is subject to more termination than the monoradicals because of a higher local concentration of the radicals in the former system. The triblock copolymer (Fig. 10(b)) prepared using the difunctional macroinitiator also has a low PDI. Previously, such block copolymers were prepared by Lemstra et al. using ATRP [28,36]. They used CuX/PMDETA or CuX/HMTETA catalysts and a polymerization temperature of 90 °C. The PDI of their diblocks was about the same as that of ours, while for the triblock the PDI of our sample is decidedly lower. These block copolymers are of interest because

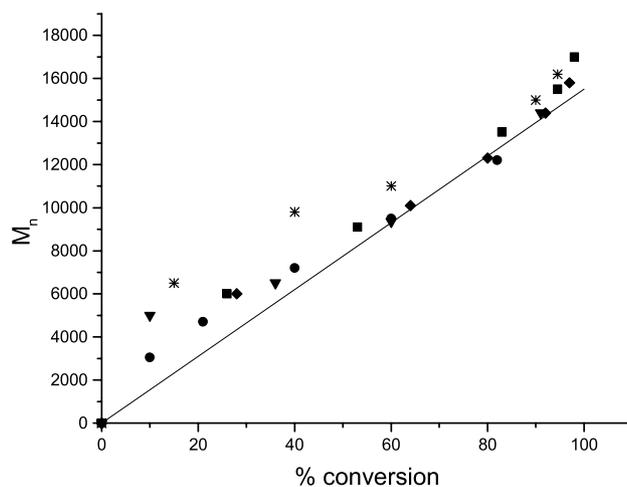


Fig. 8. M_n vs. % conversion for ATRP of various methacrylates in aqueous (8.6 vol% water) acetone using the same recipe as in Fig. 7. ■, EMA; ●, *t*BMA; **n*BMA; ▼, BzMA and ◆, DMAEMA.

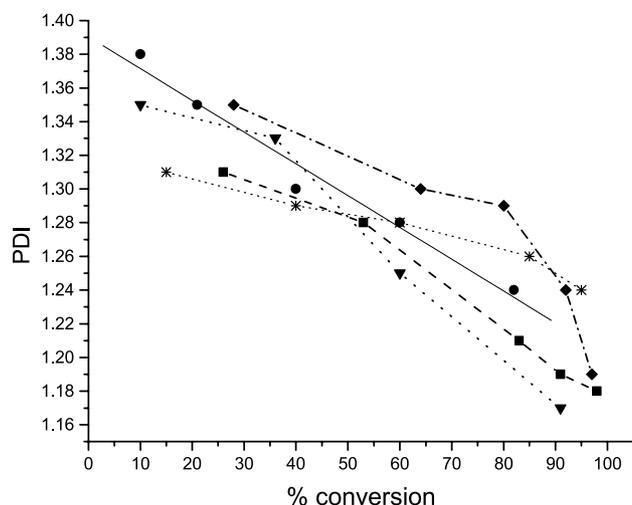


Fig. 9. PDI vs. % conversion for ATRP of various methacrylates in aqueous (8.6 vol% water) acetone using the same recipe as in Fig. 7. ■, EMA; ●, *t*BMA; **n*BMA; ▼, BzMA and ◆, DMAEMA.

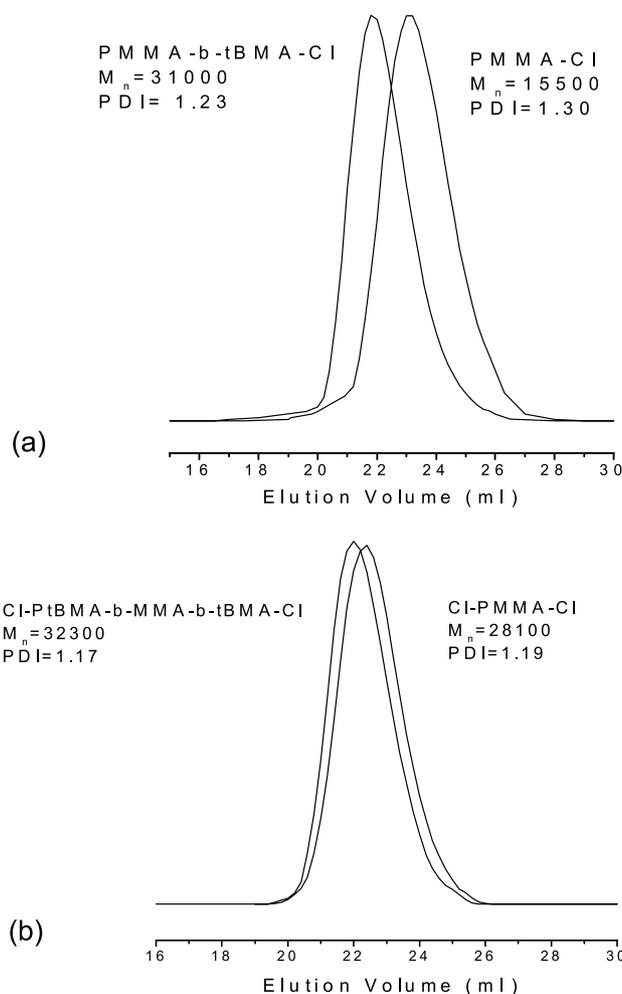


Fig. 10. (a) GPC traces of the MMA-Cl macroinitiator and MMA-*b*-*t*BMA diblock copolymer and (b) GPC traces of the difunctional macroinitiator Cl-MMA-Cl and *t*BMA-*b*-MMA-*b*-*t*BMA tri-block copolymer.

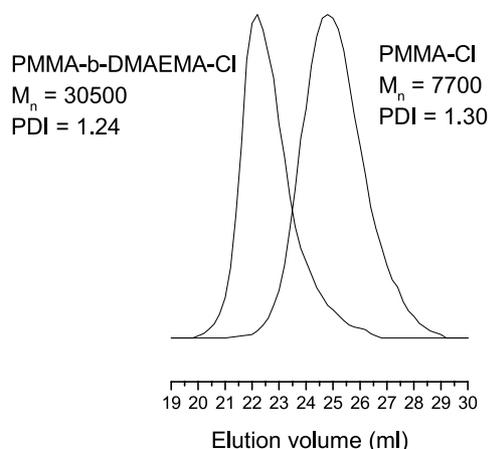


Fig. 11. GPC traces of the MMA-Cl macroinitiator and MMA-*b*-DMAEMA diblock copolymer.

amphiphilic polymers or block ionomers may be derived from them on deprotection of the poly *t*BMA blocks [37,38]. The ionic block lengths are kept low in order to reduce the processing difficulty arising out of the strong ionic interaction [32,33]. For this reason the *t*BMA block lengths in the tri block copolymer, in particular, has been kept low.

3.1.2. Poly(MMA-*b*-DMAEMA)

This amphiphilic diblock copolymer was first prepared by Baines et al. using the group transfer polymerization technique. The properties of the polymers were studied as functions of the block lengths [39]. The polymer was subsequently prepared by the ATRP method at 90 °C using a PMMA-Cl of PDI=1.07 as macroinitiator, CuCl/HMTETA as the catalyst and 1,2-dichlorobenzene as the solvent [40]. The PDI of the block copolymer ranged between 1.12 and 1.18 depending on the PDMAEMA block length. The present method produces the block co-polymer at much milder condition (35 °C) and using an environmentally less hazardous solvent viz. aqueous acetone (Fig. 11).

4. Conclusion

ATRP of several hydrophobic and hydrophilic methacrylates can be carried out at ambient temperature in acetone mixed with a small volume of water with as good control as in neat acetone but at a much faster rate. The method is useful also for the synthesis of block copolymermethacrylates.

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