

# Living radical polymerisation in heterogeneous conditions—suspension polymerisation

Adam Limer<sup>a</sup>, Alex Heming<sup>b</sup>, Ian Shirley<sup>b</sup>, David Haddleton<sup>a,\*</sup>

<sup>a</sup> *Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK*

<sup>b</sup> *Syngenta, Jealotts Hill Research Station, Bracknell RG42 6EY, UK*

Received 23 July 2004; received in revised form 29 October 2004; accepted 1 November 2004

Available online 1 January 2005

## Abstract

Transition metal mediated living radical polymerisation of butyl methacrylate has been demonstrated with a copper(I) halide *N*-alkyl-2-pyridylmethanimine ligands based catalyst. Optimum conditions were found to be with copper(I) chloride and *N*-octyl-2-pyridylmethanimine catalyst at 65 °C where conversions of 85% were achieved with polymers of  $M_n = 8900 \text{ g mol}^{-1}$  (theoretical =  $8400 \text{ g mol}^{-1}$ ) and PDI = 1.23. Both non-ionic and ionic surfactants were employed which were also made by living radical polymerisation. The non-ionic surfactant was a block copolymer of PMMA from a polyethyleneglycol macroinitiator (total  $M_n = 7600 \text{ g mol}^{-1}$ , PDI = 1.20) and the ionic surfactant PDMEAMA–PMMA (total  $M_n = 8000 \text{ g mol}^{-1}$ , PDI = 1.21) with the PDMEAMA block quaternized with MeI (13.8%, 28.4%, 47.7% and 100%). A range of ligands were employed in the suspension polymerisation by varying the alkyl group on the ligand increasing the hydrophobicity (alkyl = propyl (PrMI), pentyl (PMI), octyl (OMI), dodecyl (DMI) and octadecyl (ODMI)). The more hydrophobic ligands were found to be more effective due to lower partitioning into the aqueous phase. Block copolymers of P(EMA)–P(BMA) and P(MMA)–P(BMA) were prepared by first preparing macroinitiators via living radical polymerisation ( $M_n = 1600 \text{ g mol}^{-1}$  (PDI = 1.23) for P(EMA) and  $M_n = 1500 \text{ g mol}^{-1}$  (PDI = 1.22) for P(MMA)) and using them for initiation of BMA in suspension polymerisation. Block copolymers had  $M_n$  between 12,800 and 13,700  $\text{g mol}^{-1}$  with PDI between 1.33 and 1.54. Block copolymer growth showed excellent linear first order kinetics wrt monomer and demonstrated characteristics expected of a living radical polymerisation. Particle sizes were measured by SEM and DLS with good agreement (1.4–2.8  $\mu\text{m}$ ) and SEM showed spherical particles were formed.

© 2004 Elsevier Ltd. All rights reserved.

**Keywords:** ATRP; Living radical polymerization; Suspension polymerization; Block copolymer

## 1. Introduction

Transition metal mediated living radical polymerisation (LRP) has emerged as an effective technique for the controlled polymerisation of styrenics, methacrylates, acrylates and acrylonitrile since its inception in 1995 [1–7]. Although many hundreds of papers have been

\* Corresponding author. Tel./fax: +44 24 76523256.

E-mail address: [d.m.haddleton@warwick.ac.uk](mailto:d.m.haddleton@warwick.ac.uk) (D. Haddleton).

published in the intervening period most of these have been performed in bulk or in solution, while those in more complex heterogeneous systems have been less well studied [8,9]. Heterogeneous polymerisation is a common technique encompassing both suspension and emulsion polymerisation [10]. In addition, mini-emulsion polymerisation, leads to a similar type of final latex as emulsion polymerisation but has additional advantages concerning the mechanism and the kinetics; this has been well studied for many applications [11,12]. Recently, several reports have been published concerning emulsion, mini emulsion, suspension [13] and other aqueous dispersed transition metal mediated living radical polymerisation [14–19]. Other living radical methods are also being exploited in this way [20–22], including stable free radical polymerisation (SFRP) [23,24] and reversible addition-fragmentation chain transfer polymerisation (RAFT) [25–27]. There have also been several reports of transition metal mediated living radical polymerisation (often called ATRP) in aqueous solution and in solution in the presence of significant amounts of water [28–30].

This present work is concerned with copper(I) mediated living radical polymerisation under suspension polymerisation conditions. The first controlled radical polymerisation carried out under suspension polymerisation conditions was described by Georges et al., in 1993 [31]. Styrene was initiated with BPO in the presence of TEMPO to yield a polymer of reasonably low polydispersity ( $\sim 1.35$ ). Unfortunately this work was limited to styrenics so the scope was quite limited. In 1996 Teyssie and co-workers, [32] reported the first use of LRP in a suspension system using nickel catalysts. They reported the polymerisation of methacrylates in a controlled manner, under suspension polymerisation conditions. More recently CuCl/bpy has been reported for the ATRP of MMA in emulsion by Zhu et al. however, polydispersities were always greater than 1.5 at conversions greater than 90% [13,33] and Bicać et al. reported on the use of CuBr/HTETA for suspension polymerisation of MMA again reporting high polydispersity ( $>1.5$ ) at 90% conversion [34]. In 2001 Matyjaszewski et al., used Cu(I) mediated LRP to successfully polymerise methyl methacrylate (MMA) in suspension with good control of molecular weight and low polydispersity ( $\sim 1.2$ – $1.3$ ) [35]. Sawamoto has also demonstrated that iron catalysts can also be employed for controlled suspension polymerisation with acrylates and styrenics [36].

In all the examples discussed to date homopolymers have been reported. There seems to have been no reports of polymers with more complex architectures e.g. block or comb copolymers. Most systems reported have also employed commercially available surfactants, which has many advantages, particularly convenience. However, the use of commercial surfactants adds a limitation

to the types of polymer available and influences the quality of the final product. This results in a particle formed of a polymer which is of desired molecular weight and low polydispersity, which is prepared using a somewhat polydisperse and often only  $\sim 85\%$  pure surfactant. In this present study the copper mediated living radical polymerisation of butyl methacrylate (BMA) under suspension polymerisation conditions has been explored. It is noted that BMA has been the monomer of choice in previous reports of ATRP under heterogeneous aqueous polymerisation conditions [19,16,20]. Reactions were conducted using  $\text{Cu}^{\text{I}}\text{X}$  and a range of *N*-alkyl-2-pyridylmethanamine Schiff base ligands as catalyst [37,38]. The influence of surfactant composition has been investigated with both ionic and non-ionic surfactants studied all being prepared via  $\text{Cu}^{\text{I}}\text{X}$  mediated LRP techniques in our laboratories and reported in this paper. A range of monomers were investigated and the study extended to the preparation of block copolymers.

## 2. Experimental

### 2.1. Materials

*N*-Alkyl-2-pyridylmethanimine ligands (alkyl = propyl (PrMI), pentyl (PMI), octyl (OMI), dodecyl (DMI) and octadecyl (ODMI)) were prepared by condensation of 2-pyridine carbaldehyde with the appropriate amine, as previously reported [38]. Methyl methacrylate (Aldrich; 99%) and butyl methacrylate (Aldrich; 99%) were purified by passage through a short column of activated basic alumina before use to remove inhibitors and acidic impurities. The reaction mixture was subsequently deoxygenated by bubbling with dry nitrogen gas for 30 min and then stored at 0 °C. (Dimethylamino)ethyl methacrylate (Aldrich; 98%) was bubbled with dry nitrogen gas for 30 min prior to use. Toluene (BDH, 98%) was degassed by bubbling with nitrogen for 30 min and stored in a sealed flask under nitrogen. Copper(I) bromide (Aldrich; 99%) and copper(I) chloride (Aldrich; 98%) were purified according to the method of Keller and Wycoff [39]. The initiator, ethyl-2-bromo isobutyrate (Acros; 98%) was used as supplied. All other materials were obtained from Aldrich and were used without any further purification unless otherwise stated.

### 2.2. General polymerisation procedure

All reactions were carried out with standard Schlenk techniques under a dry nitrogen atmosphere.  $\text{Cu}(\text{I})\text{Br}$  and the initiator were placed in an oven-dried Schlenk tube. The tube was fitted with a rubber septum and pump-filled with nitrogen three times. The deoxygenated

solvent, monomer and initiator were transferred to the tube via syringe, and de-gassed ligand was added during stirring. The solution was further degassed by three freeze–pump–thaw cycles. The tube was then lowered into a thermo-statically controlled oil bath at 75 °C [38,40].

### 2.3. Synthesis of PMMA macroinitiator

A P(MMA) macroinitiator was prepared in toluene (50% v/v) at 75 °C. Purified MMA was deoxygenated by dry nitrogen bubbling through it for 30 min immediately prior to polymerisation. The reaction was stopped after approximately 20% conversion. The [MMA]/[Cu(I)Cl]/[ligand] ratio = 100/1/2 in 50% v/v toluene. MMA was polymerised with ethyl-2-bromo isobutyrate as an initiator, Cu(I)Cl and PrMI as catalyst. Typically, Cu(I)Cl (0.39 g, 0.039 mol), was added to a Schlenk tube which was fitted with a rubber septum and pump-filled with nitrogen three times. Subsequently deoxygenated and inhibitor-free MMA (42 mL, 0.4 mol), deoxygenated toluene (30 mL), PrMI (1.24 mL, 0.078 mol) and ethyl-2-bromo isobutyrate (0.586 mL, 0.039 mol) were added to the Schlenk tube under nitrogen. The solution was further degassed by three freeze–pump–thaw cycles before being heated to 75 °C. Samples were removed periodically for conversion and GPC analysis via syringe. The final polymer was purified by the passage of the solution over a basic alumina column and was isolated by precipitation in cold petroleum ether 40–60 and drying in vacuo. All macroinitiators used in this work were made under similar conditions.

### 2.4. Synthesis of PMMA–PDMAEMA block copolymers

2-(Dimethylamino)ethyl methacrylate (DMAEMA) was polymerised in the presence of the P(MMA) macroinitiator in toluene with Cu(I)Br and PMI as a catalyst. Purified DMAEMA was deoxygenated by three freeze–pump–thaw cycles just before injection into reaction vessels. Typically, Cu(I)Br (0.204 g,  $1.422 \times 10^{-3}$  mol) and P(MMA) macroinitiator (4 g,  $1.422 \times 10^{-3}$  mol) were placed in an oven-dried Schlenk tube. The tube was fitted with a rubber septum and pump-filled with nitrogen three times. Deoxygenated and inhibitor-free DMAEMA (12.7 mL, 0.071 mol), deoxygenated toluene (50 mL), and degassed PrMI (0.444 mL,  $2.84 \times 10^{-3}$  mol) were added to the Schlenk tube. The solution was degassed by three freeze–pump–thaw cycles before being heated to 100 °C for 4 h. The final block copolymer was purified by passage through a column of basic alumina and was isolated by precipitation in cold petroleum ether 40–60 and drying in vacuo. Monomer conversion was estimated by  $^1\text{H}$  NMR.

### 2.5. Quaternization

Quaternization was achieved following the method described by Baines et al. [41]. The diblock copolymer was dissolved in THF (250 mL) in a round-bottom flask. The mixture was stirred at ambient temperature and a predetermined quantity of methyl iodide was added, the solution stirred overnight. The quaternized polymer precipitated and was isolated by filtration prior to purification by Soxhlet extraction with THF for the removal of unreacted methyl iodide. The product was dried in vacuo to remove volatiles for 24 h, recovered yield = 85%.

### 2.6. Synthesis of PEG–PMMA block copolymers

Polyethylene glycol methyl ether macroinitiator was prepared via condensation of polyethylene glycol methyl ether ( $M_n = 5000$ ) with 2-bromoisobutyryl bromide [42]. A Schlenk tube was charged with Cu(I)Cl (0.0479 g,  $4.83 \times 10^{-4}$  mol) and PEG initiator (2.5 g,  $4.83 \times 10^{-4}$  mol). The tube was fitted with a rubber septum and pump-filled with nitrogen three times. Deoxygenated and inhibitor-free MMA (4.118 g, 48 mmol), toluene (10 mL), and PMI (0.1442 g,  $9.67 \times 10^{-4}$  mol) were quickly added. The solution was degassed by three freeze–pump–thaw cycles prior to heating to 80 °C for 6 h under a nitrogen atmosphere with magnetic stirring. The resulting solution was passed through a short column of alumina to remove catalyst residues and polymer isolated by precipitation into cold diethyl ether and subsequently dried in vacuo to remove volatiles. Monomer conversion was estimated by  $^1\text{H}$  NMR.

### 2.7. Synthesis of 2-bromo-2-methylpropionic acid 4-methoxyphenyl ester, **1**

4-Methoxyphenol (24.83 g, 0.2 mol), triethylamine (30.6 mL, 0.22 mol), and anhydrous THF (400 mL) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (27.2 mL, 0.22 mol) was added slowly with stirring. A white precipitate, of triethylammonium bromide, was formed, and the reaction was left for 6 h at ambient temperature with stirring. The precipitate was removed by filtration prior to removal of volatiles in vacuo to leave a yellow liquid. The product was isolated following washing with two 200 mL portions of saturated sodium carbonate solution, 0.5 M HCl(aq), and diionized water. The dichloromethane solution was dried over  $\text{MgSO}_4$  and the volatiles removed in vacuo to give a yellow oily liquid. On overnight cooling crystallization occurred, the product was recrystallized three times from ethanol at 5 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 250.13 MHz)  $\delta$  7.34 (d,  $J = 9.1$  Hz, 2H, Aro), 7.10 (d, 2H, Aro), 3.70 (s, 3H, MeO–Aro), 2.05 (s, 6H, C=O–CMe<sub>2</sub>).  $^{13}\text{C}$  NMR

(CDCl<sub>3</sub>, 298 K, 100.6 MHz)  $\delta$  170.45 (C=O), 157.38, 148.15, 124.68, 115.38 (Aro), 55.45 (C=O–CMe<sub>2</sub>), 30.54 (C=O–CMe<sub>2</sub>). IR (solid, ATR cell)  $\nu$  (cm<sup>-1</sup>) 3011, 2975, 2842, 1749, 1595, 1503, 1454, 1272, 1249, 1181, 1160, 1137, 1100, 1026, 941, 872, 816, 744. CHN analysis; calculated, C = 48.37%, H = 4.80%; Found, C = 48.38%, H = 4.79%.

### 2.8. Typical procedure for polymerisation in aqueous media

A Schlenk tube was charged with a predetermined amount of Cu(I)Cl prior to being deoxygenated by cycling between nitrogen and vacuum three times. A mixture of butyl methacrylate, ethyl-2-bromo isobutyrate, hexadecane and OMI was added to the tube. The mixture was immediately subjected to three freeze–pump–thaw cycles. A 100 mL, three-neck round-bottom flask was charged with 45 cm<sup>3</sup> degassed water which contained a predetermined amount of diblock polymer. The apparatus was fitted with an overhead stirrer, a homogenizer and purged with nitrogen. The contents of the Schlenk tube were added via syringe and the system was blended using a homogenizer for 2 min. The resultant mixture was then stirred slowly for 5 h at 65 °C. Monomer conversion was estimated using gravimetry by drying a pre-weighed aluminum pan to constant weight in a vacuum oven at 50 °C. The particle size was determined either by scanning electron microscopy (SEM) or by dynamic light scattering (DLS).

### 2.9. Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker ACF250, DPX300 and DPX400 spectrometers using deuterated solvents from Aldrich. Infra-red emission spectra were recorded on a Bruker Vector 22 FTIR spectrometer using a Golden Gate attenuated total reflection (ATR) cell. Surface tension measurements were carried out using a Nima Technology DST9005 tensiometer. Elemental analysis was conducted using a Leeman Labs CE400 elemental analyser. Dynamic light scattering measurements were carried out using a Malvern Zetasizer 3000 spectrometer equipped with a 5 mW helium neon laser operating at 633 nm and a 7132 correlator operating in 8 × 8 groups.

Size exclusion chromatography was carried out using a Polymer Laboratories system equipped with a refractive index and UV/vis detectors calibrated with linear poly(methyl methacrylate) standards ( $M_p$  = 200–1.577 × 10<sup>6</sup> g mol<sup>-1</sup>) and linear poly(styrene) standards ( $M_p$  = 540–1.640 × 10<sup>6</sup> g mol<sup>-1</sup>). The mobile phase used was 95% THF, 5% triethylamine and the elution time was standardised against that of toluene. The flow rate was set at 1.0 mL/min. The system was equipped with a PL-gel 5  $\mu$ m (50 × 7.5 mm) guard column and two

PL-gel 5  $\mu$ m (300 × 7.5 mm) mixed C columns, these were thermostated at 25 °C.

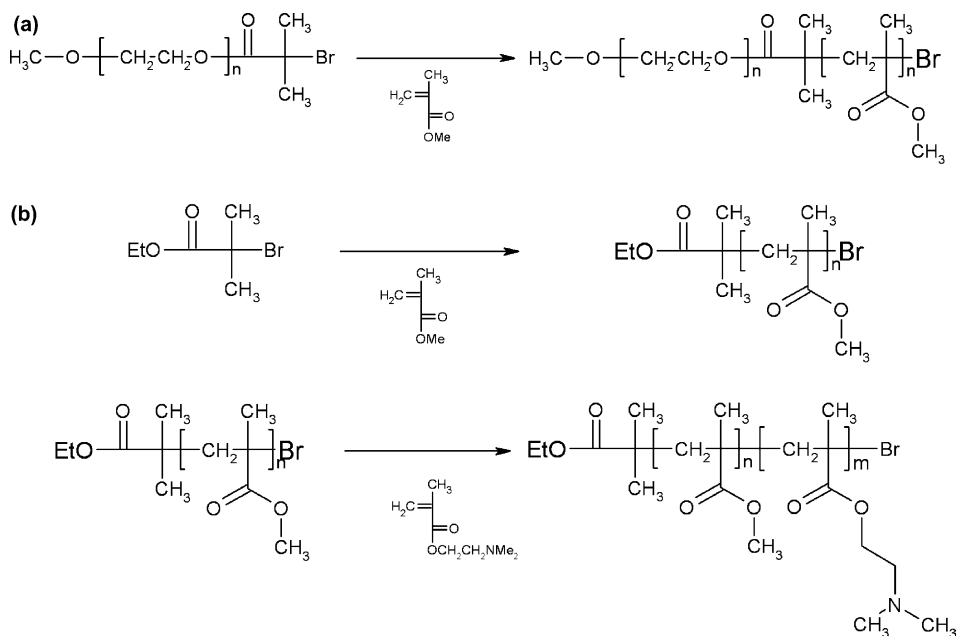
## 3. Results and discussion

### 3.1. Surfactant preparation

A range of block copolymers were prepared for use as surfactants in subsequent suspension polymerisation. Block copolymers of poly(ethylene oxide) (PEG) and PMMA were prepared for use as non-ionic surfactants. And block copolymers of poly(dimethylaminoethyl) methacrylate (PDMAEMA) and PMMA as ionic surfactants, Scheme 1. A macroinitiator based on methoxy poly(ethylene) oxide ( $D_p$  = 113) was prepared via condensation with 2-bromoisobutryl bromide with  $D_p$  = 113. This initiator was then used for the polymerisation of MMA at 80 °C in toluene (50% v/v) with Cu(I)Cl and PrMI as catalyst. The reaction carried out with a target  $D_p$  of 100 and stopped after approximately 20% conversion giving an observed  $D_p$  ~ 20 and all showed good first order kinetics, Fig. 1, Table 1. GPC indicated that molecular weight increases with conversion, polydispersity remained low, as expected for a living polymerisation, Fig. 2.

PDMAEMA–PMMA block copolymers were synthesized by first preparing a PMMA macroinitiator by copper mediated living radical polymerisation at 75 °C in toluene solution (50% v/v) with ethyl-2-bromoisobutyrate as initiator and Cu(I)Cl and PrMI as catalyst, Fig. 3. Cu(I)Cl was used as opposed to Cu(I)Br to allow the polymerisation to proceed more slowly following Br/Cl exchange [43]. Polymerisations were carried out with a target  $D_p$  of 100 and stopped after approximately 20% conversion ( $D_p$ ), ~20 maintaining termination at a minimum. The final polymer had  $M_n$  = 2600 g mol<sup>-1</sup> (PDI = 1.21) at 19.56% after 210 min. The polymer was subsequently used as a macroinitiator for the polymerisation of DMAEMA catalyzed by Cu(I)Br/PrMI at 100 °C in toluene solution (66% v/v) with a target  $D_p$  of 50. The linear first order kinetics, Fig. 4 and the GPC data, Fig. 5, are indicative of a controlled reaction. The final block copolymer had  $M_n$  = 8000 g mol<sup>-1</sup> with PDI = 1.21 ( $M_{n,Theo}$  = 8600 g mol<sup>-1</sup>) after 315 min and 77% conversion.

After purification and isolation of the product the hydrophilic block was quaternized with methyl iodide to various levels to improve the polymers water solubility and give it its ionic character. Target degrees of quaternization (10%, 25%, 50% and 100%) were achieved by adjusting the molar ratio of methyl iodide to PDMAEMA residues. <sup>1</sup>H NMR was used to determine the degree of quaternization: the integral of the trimethylammonium signal at  $\delta$  3.3 was compared to that of the oxymethylene signal at  $\delta$  4.1, as described by



Scheme 1. Reaction scheme for the preparation of ionic and non-ionic surfactants: (a) non-ionic poly(ethylene) oxide surfactant, (b) surfactant based on PDMAEMA-*b*-PMMA, ionic character will be added by the subsequent quaternization of DMAEMA with iodomethane.

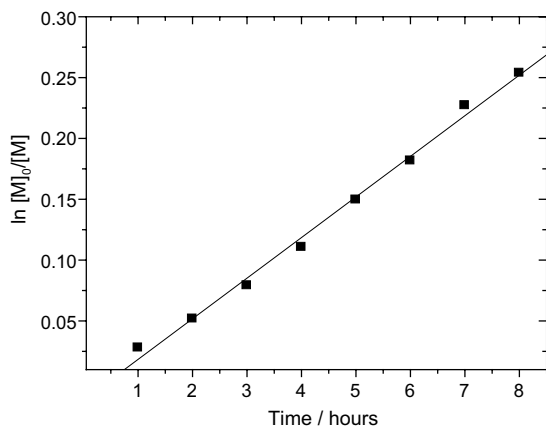


Fig. 1. First order kinetic plot for the polymerisation of MMA with a PEG initiator at 80 °C.

Table 1  
Conversion, polydispersity and molecular weight data for the polymerisation of a PEG initiator with MMA

Time/h	Conversion/%	$M_{n, GPC}/\text{g mol}^{-1}$	Polydispersity
2	4.19	5800	1.13
3	6.21	6100	1.21
4	9.01	6400	1.24
5	11.85	6700	1.24
6	15.4	7000	1.24
7	17.01	7300	1.21
8	19.99	7600	1.20

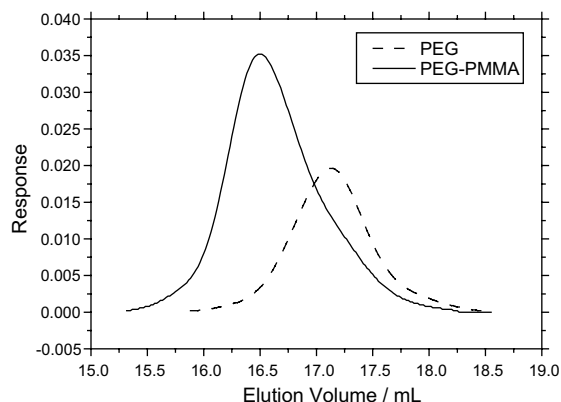


Fig. 2. GPC traces for PEG-MMA block copolymer from PEG macroinitiator.

Bütün et al. [44]. NMR analysis showed the actual degree of quaternization to be 13.8%, 28.4%, 47.7% and 100%, Fig. 6.

### 3.2. Suspension polymerisation

#### 3.2.1. Copper(I) bromide mediated polymerisations

The amphiphilic block copolymers were used as colloidal stabilisers for the suspension polymerisation of various monomers in the presence of several catalyst complexes. The catalyst used must be sufficiently



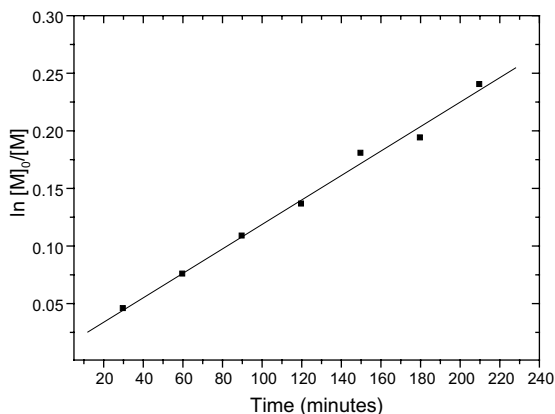


Fig. 3. First order kinetic plot for the polymerisation of MMA at 75 °C.

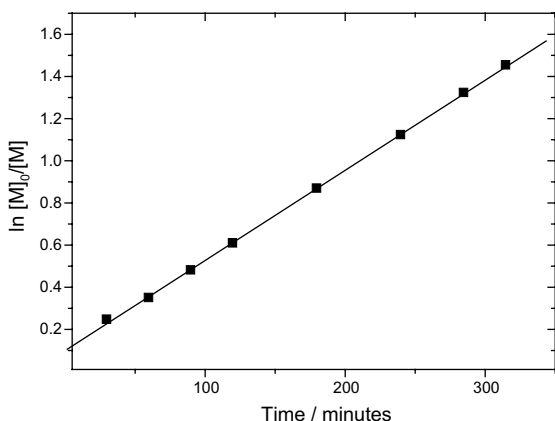


Fig. 4. First order kinetic plot for the polymerisation of DMAEMA with a PMMA macroinitiator at 100 °C.

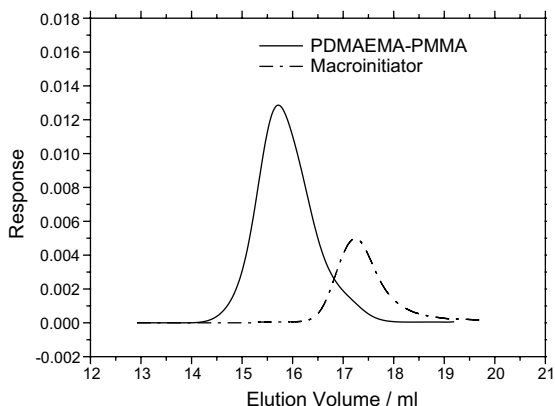


Fig. 5. GPC traces showing the PMMA-*b*-PDMAEMA product from PMMA macroinitiator.

hydrophobic to remain within the oil phase thus relatively hydrophobic ligands were used. *N*-2-Pyridylmethanimine ligands with alkyl chains of C<sub>5</sub> or longer are particularly hydrophobic with virtually no water solubility. This is important as minimizes the amount of catalyst lost by partitioning to the aqueous phase. A series of reactions were conducted to synthesize poly(BMA) suspension particles. Cu<sup>I</sup>Br was used with OMI as catalyst and ethyl-2-bromo isobutyrate as initiator. The surfactant was dispersed in the aqueous phase and after subsequent addition of the monomer, copper, ligand and initiator oil phase, the system was blended with a homogenizer before stirring at ~100 rpm. Reactions using PEG–PMMA block copolymer (PEG,  $D_p$  113 and PMMA,  $D_p$  20) based non-ionic surfactants exhibited very rapid kinetics, even at low temperatures with ~90% conversion being achieved in 1 h at 40 °C, Fig. 7. The polymerisation using the PDMAEMA–PMMA block copolymer ionic surfactant (PDMAEMA  $D_p$  50 and PMMA  $D_p$  20) reacted much more slowly, Fig. 8. In both cases the kinetic plots exhibited some upwards curvature. This is ascribed to the catalyst system changing during the course of the reaction. The  $M_n$  deviates significantly from the theoretical values at low conversion with PDI higher than expected throughout the reaction. As the reaction proceeds the molecular weight approaches the theoretical with a relatively linear increase and an associated lowering of polydispersity, Fig. 9.

### 3.2.2. Copper(I) chloride mediated polymerisations

In an attempt improve the molecular weight control in the reaction, Cu(I)Cl was used in place of Cu(I)Br. The tendency to partition to the water phase is reduced as the alkyl chain length on the ligand is increased. In addition copper chloride based complexes also exhibit higher organic solubility than their copper bromide analogues [35]. A considerable decrease in the rate of reaction by a factor of 4, Table 2. Reactions conducted at 40 °C, with ODMI and PDMAEMA–PMMA block copolymer as surfactant (PDMAEMA  $D_p$  = 50, 25% quaternized, PMMA  $D_p$  = 20) as surfactant, 2% with respect to oil phase with a target  $D_p$  = 100. Fig. 10 shows the first order kinetic plot for the suspension polymerisation of butyl methacrylate in the presence of Cu(I)Cl using a poly(ethylene) oxide based surfactant and Fig. 11 a similar reaction but using a 25% quaternized ionic surfactant. Good living polymerisation was observed, Figs. 10 and 11, with GPC analysis indicates that molecular weight increases with time, Fig. 12. Table 3 shows the molecular weight, polydispersity and conversion data for polymers prepared from both ionic and non-ionic surfactants. With Cu(I)Br as the catalyst, reactions occurred too fast due to complexation with water. In the presence of Cu(I)Cl the rate of reaction is reduced considerably and we see an excellent polymerisation.

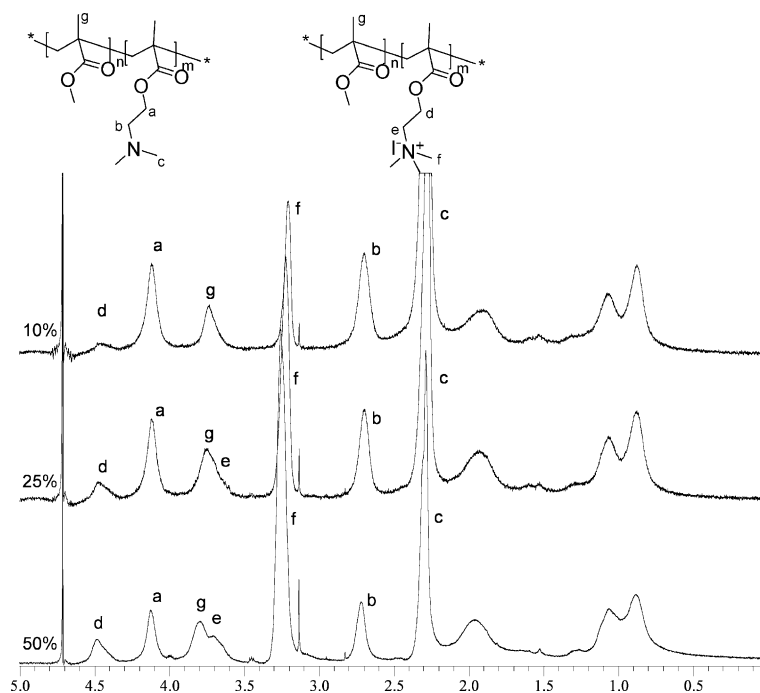


Fig. 6.  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  of 10%, 25% and 50% quaternized (MeI) PMMA–PDMAEMA diblock copolymer.

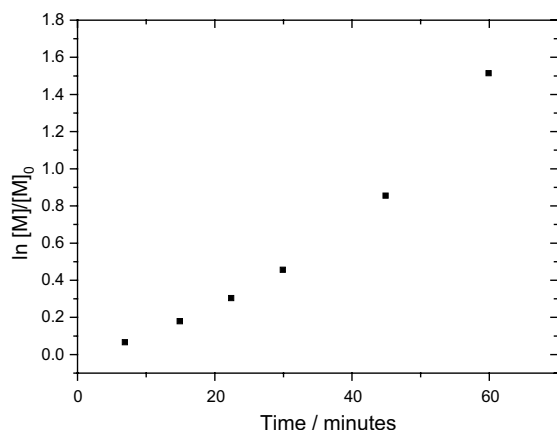


Fig. 7. First order kinetic plot for the suspension polymerisation of BMA in the presence of  $\text{Cu}(\text{I})\text{Br}$  using a non-ionic PEG–PMMA based surfactant.

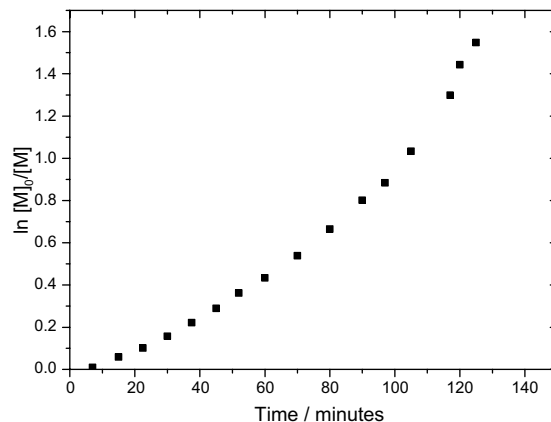


Fig. 8. First order kinetic plot for the suspension polymerisation of BMA in the presence of  $\text{Cu}(\text{I})\text{Br}$  using an ionic PDMAEMA–PMMA based surfactant.

### 3.3. Ligand effects

The *N*-alkyl-2-pyridylmethanimine Schiff base ligands employed in our laboratories are soluble in most solvents typically used for solution polymerisation. However, solubility needs to be considered carefully with certain monomer/solvent combinations. As the length of the alkyl group is increased the system becomes more hydrophobic and the ionic catalyst becomes

more soluble in non-polar solvents. For example during the bulk polymerisation of BMA using  $\text{Cu}(\text{I})\text{Cl}$  and PrMI ligand the system becomes homogeneous above  $75^\circ\text{C}$ . However, with OMI the reaction mixture is homogenous at sub ambient temperatures. During suspension polymerisation the reaction mixture is effectively a series of small bulk reactors. Preliminary solubility tests indicated that PrMI based ligands were not appropriate for the bulk polymerisation of butyl

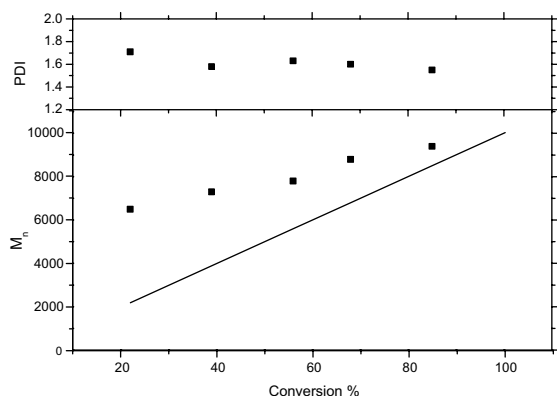


Fig. 9.  $M_n$  and PDI versus conversion for the suspension polymerisation of BMA mediated by Cu(I)Br. Using PDMAEMA–PMMA block copolymer as surfactant (PDMAEMA,  $D_p$  50, 25% quaternized, and PMMA,  $D_p$  20). Reaction conducted at 40 °C with Cu(I)Br and *n*-octyl-2-pyridylmethanimine.

Table 2

Kinetic data for the suspension polymerisation of BMA in the presence of various catalyst complexes

Ligand	Time/min	Conversion/%	$k_p/\text{min}^{-1}$
Pentyl	90	86	0.0216
Octyl	140	95	0.0168
Dodecyl	180	78	0.0072
Octadecyl	250	70	0.0051

Cu(I)Cl used in all cases at 50 °C.

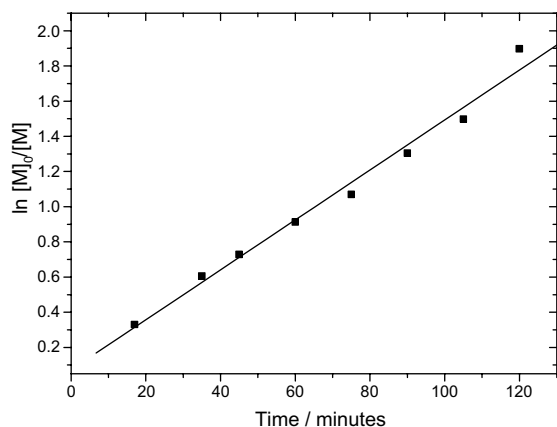


Fig. 10. First order kinetic plot for the suspension polymerisation of BMA in the presence of Cu(I)Cl using a non-ionic PEG–PMMA block copolymer based surfactant.

methacrylate as the catalyst is only soluble at elevated high temperatures. Ligands with longer alkyl chains such as pentyl, octyl and octadecyl showed much greater

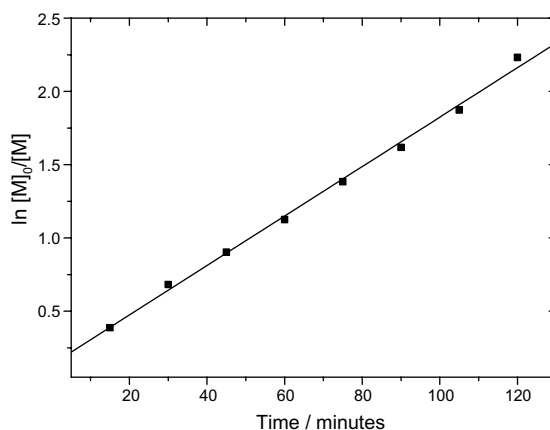


Fig. 11. First order kinetic plot for the suspension polymerisation of BMA in the presence of Cu(I)Cl using an ionic PDMAEMA–PMMA block copolymer based surfactant.

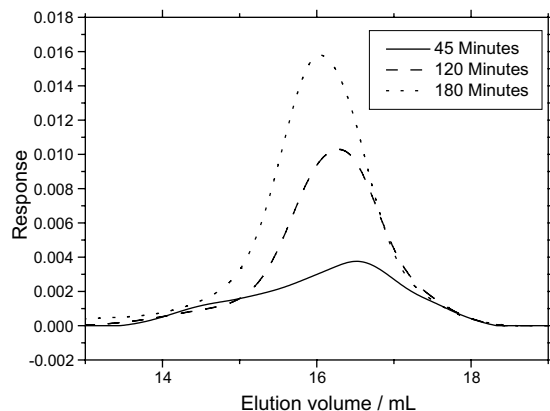


Fig. 12. GPC data for the suspension polymerisation of BMA in the presence of Cu(I)Cl and a non-ionic PEG–PMMA block copolymer surfactant.

degrees of solubility. The choice of ligand also had a substantial effect on the reaction kinetics. A series of suspension polymerisation reactions of BMA were conducted using a PDMAEMA–PMMA block copolymer (PDMAEMA  $D_p$  = 50, 25% quaternized, PMMA  $D_p$  = 20) as surfactant at a level of 2% with respect to oil phase.

A range of ligands were used including PMI, OMI, DMI and ODMI. Fig. 13 shows the first order kinetic plot for the reactions. It is evident that the reaction system using PMI based catalysts reacts much more quickly than the with an ODMI based catalyst. Table 2 shows the changes in the rate of propagation for the different catalysts. The rate of reaction for the system using the PMI is four times faster than that for ODMI. The final products of these reactions gave polymers with



Table 3

Molecular weight, polydispersity and conversion data for the suspension polymerisation of BMA in the presence of Cu(I)Cl and *n*-octyl-2-pyridylmethanimine

Surfactant	Time/min	Conversion/%	$M_{n,Theo}/g\ mol^{-1}$	$M_{n,GPC}/g\ mol^{-1}$	PDI
1	20	34	3400	3700	1.45
1	50	56	5500	5800	1.39
1	105	85	8400	8900	1.23
2	35	45	4500	5100	1.47
2	60	60	6000	6500	1.33
2	105	77	7700	8200	1.25

<sup>1</sup> PDMAEMA–PMMA (PDMAEMA,  $D_p$  50, 25% quaternized (MeI), and PMMA,  $D_p$  20).

<sup>2</sup> PEG–PMMA (PEG,  $D_p$  113 and PMMA,  $D_p$  20).

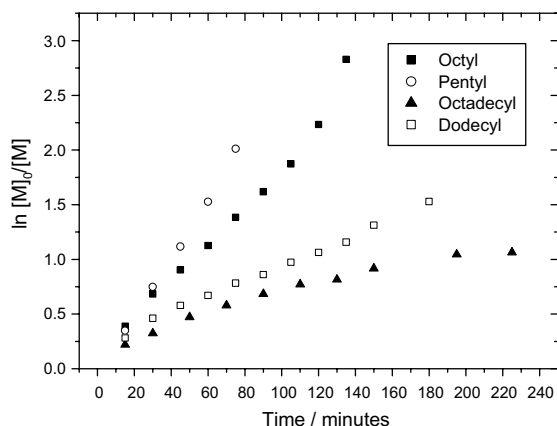


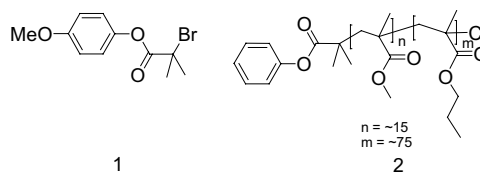
Fig. 13. Effect of ligand choice during the suspension polymerisation of BMA at 50 °C PDMAEMA–PMMA surfactant used (PDMAEMA,  $D_p$  50, 25% quaternized (MeI), and PMMA,  $D_p$  20).

$M_n$  = 12,500 (PDI = 1.39), 9400 (1.29), 9700 (1.25) and 9800 (1.23)  $g\ mol^{-1}$  for PMI, OMI, DDMI and ODMI respectively, Table 3. The target molecular weight in each case was 10,000  $g\ mol^{-1}$  and reactions were conducted at 50 °C using Cu(I)Cl. It is likely that the shorter alkyl chain ligands will be more prone to partition to the water phase. This will result in the formation of  $Cu^I X Li-gand_x:H_2O_y$  complexes which will result in an increase in the rate of propagation on returning to the oil phase. It is also likely that the shorter chain ligands will be more prone to the effects of water being present to a low degree in the oil phase. It is reasonable to expect that this would increase the rate of reaction as has been demonstrated previously in solution polymerisation reactions.

### 3.4. Block copolymer preparation

The synthesis of block copolymers by living radical suspension polymerisation has also been investigated. There are two possible approaches to the preparation of block copolymers by suspension polymerisation. Firstly, block copolymers can be formed by sequential

monomer addition. Initially one monomer is reacted and taken to high conversion (>90%), at this time a second monomer is added. This is not an ideal method as this produces somewhat of a gradient copolymer and long reaction times are necessary to achieve high conversion, which leads to low quality particles. An alternative approach is to prepare the first block by conventional LRP solution polymerisation. This is followed by subsequently isolation, characterization and purification of the polymer prior to use as a macroinitiator in a suspension polymerisation reaction, the approach chosen in the present work. In order to allow the formation of a block copolymer to be confirmed the first polymer was synthesized using an initiator that absorbs in the UV, **1** giving a polymer of structure **2**.



#### 3.4.1. Macroinitiator synthesis

Initiator **1** was employed in a conventional solution living radical polymerisation reaction of methyl methacrylate and a PrMI catalyst in toluene solution (50% v/v) at 65 °C using Cu(I)Cl. A polymer of low molecular weight was prepared so as to ensure good solubility in its subsequently use as a macroinitiator,  $M_n$  = 1500  $g\ mol^{-1}$  (target = 1600) with PDI = 1.22 which was isolated after 15% conversion. A low DP poly(ethyl methacrylate) P(EMA) polymer was also prepared in this way,  $M_n$  = 1600  $g\ mol^{-1}$  (target = 1500) with PDI = 1.23 at 15% conversion. The target molecular weight in each reaction at 100% conversion was 10,000  $g\ mol^{-1}$  and both proceeded with excellent first order kinetics.

#### 3.4.2. Block copolymer synthesis

The two low molecular weight polymers prepared above were used as macroinitiators in the suspension

polymerisation of BMA. Linear first order kinetics were observed in each case. Fig. 14 shows the first order kinetic plot for the polymerisation of a PMMA macroinitiator with BMA. GPC analysis indicates that a block copolymer has been formed, Fig. 15. A small amount of residual macroinitiator that failed to initiate can be seen in the GPC trace this is ascribed to a small amount of terminated polymer formed in the synthesis of the first block. The traces obtained indicated that block copolymers had been formed as the UV active chromophore is present in both the macroinitiator and the block copolymer. Table 4 reports the characteristics of the block copolymers produced by suspension polymerisation. It can be seen in all cases that the molecular weight of the diblock copolymer is greater than that expected although polydispersity remains low. This is caused by two factors. Firstly, a small percentage of the macroinitiator had terminated and was inactive. This reduces the concentration of active species present to below the level expected and causes the increases in molecular weight

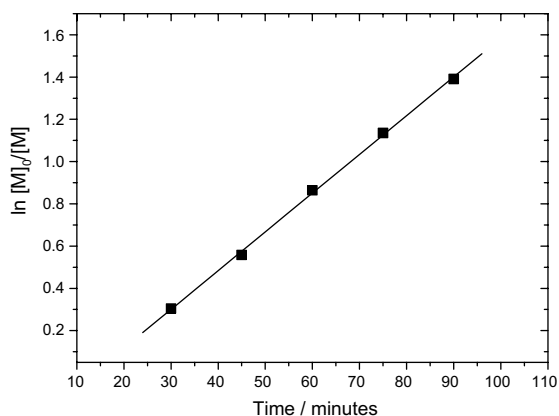


Fig. 14. First order kinetic plot for the synthesis of a PMMA–PBMA block copolymer by suspension polymerisation. PMMA macroinitiator and PDMAEMA–PMMA surfactant (PDMAEMA,  $D_p$  50, 25% quaternized, and PMMA,  $D_p$  20) used. Reaction conducted at 50 °C with Cu(I)Cl and OMI.

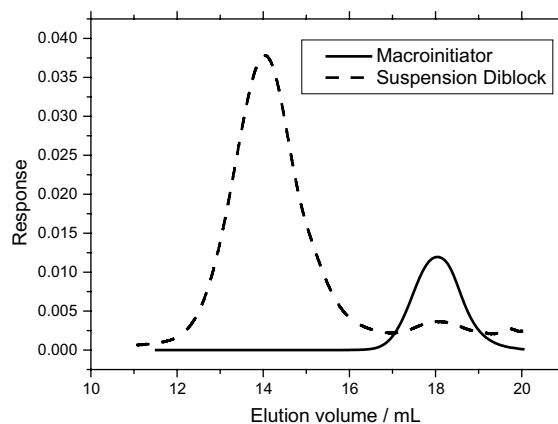


Fig. 15. GPC data for the block copolymer suspension polymerisation of a PMMA macroinitiator with BMA, UV detection at  $\lambda = 290$  nm. PDMAEMA–PMMA surfactant (PDMAEMA,  $D_p$  50, 25% quaternized (MeI), and PMMA,  $D_p$  20) used. Reaction conducted at 50 °C with Cu(I)Cl and OMI.

seen here. Secondly, the GPC is calibrated with linear PMMA standards. The polydispersity decreases as the ligand becomes more hydrophobic with both macroinitiators going from 1.55 to 1.35 (P(MMA)) and 1.54 to 1.33 (P(EMA)) with OMI and ODMI respectively. This is ascribed to a reduction of catalyst partitioning to the aqueous phase.

### 3.4.3. Particle analysis

Particles size analysis was carried out by both dynamic light scattering and scanning electron microscopy. Fig. 16 shows particles formed by the suspension polymerisation of butyl methacrylate with Cu(I)Cl in the presence of an ionic surfactant (PDMAEMA–PMMA block copolymer (PDMAEMA  $D_p$  = 50, 25% quaternized, PMMA  $D_p$  = 20) at a level of 2% with respect to oil phase). Good quality spherical particles were formed in all cases. Particle sizes of 1.4  $\mu\text{m}$ , 2.1  $\mu\text{m}$ , 2.5  $\mu\text{m}$  and 2.8  $\mu\text{m}$  for PDMAEMA–PMMA (10%, 25%, 59% and 100% quaternized) and 1.8  $\mu\text{m}$  with the PEG–PMMA

Table 4  
Molecular weight and polydispersity data of diblock copolymers prepared by suspension polymerisation

Macroinitiator	Ligand	$M_{n,\text{Theo}}/\text{g mol}^{-1}$	$M_{n,\text{GPC}}/\text{g mol}^{-1}$	PDI
P(EMA) $M_n$ 1100	OMI	11,000	13,400	1.55
P(EMA) $M_n$ 1100	DDMI	11,000	12,900	1.38
P(EMA) $M_n$ 1100	ODMI	11,000	12,800	1.35
P(MMA) $M_n$ 1200	OMI	11,500	13,700	1.54
P(MMA) $M_n$ 1200	DDMA	11,500	12,800	1.36
P(MMA) $M_n$ 1200	ODMA	11,500	12,800	1.33

PDMAEMA–PMMA surfactant (PDMAEMA,  $D_p$  50, 25% quaternized (MeI), and PMMA,  $D_p$  20) used. Reaction carried out at 50 °C with Cu(I)Cl.

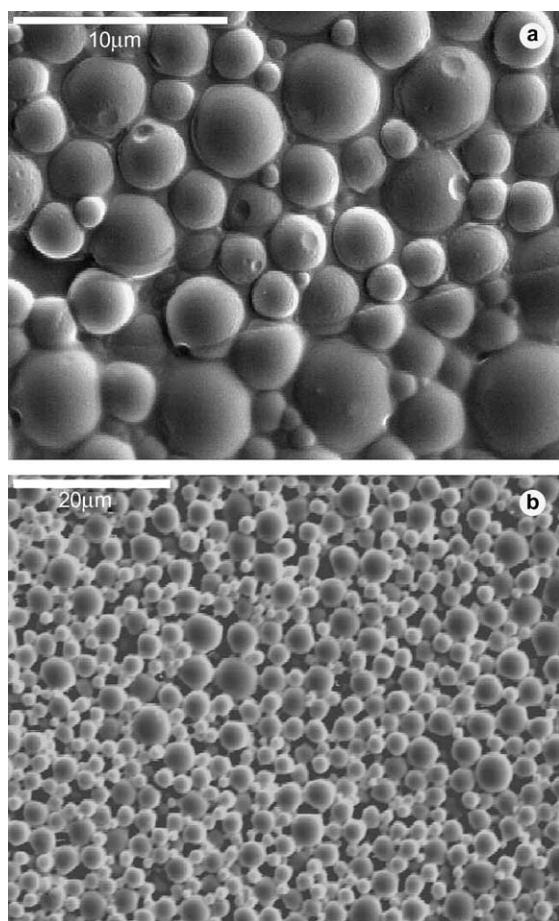


Fig. 16. SEM of particles formed by the suspension polymerisation of BMA in the presence of an ionic surfactant. Surfactant = PDMAEMA,  $D_p$  50, and PMMA,  $D_p$  20. Reactions conducted at 50 °C with Cu(I)Cl and OMI; A = 25% quaternized, B = 10% quaternized.

surfactant. There was good agreement between the particle sizes determined by DLS and SEM in all cases.

#### 4. Conclusion

Copper(I) mediated living radical polymerisation has been successfully employed for the suspension polymerisation of BMA. A range of *N*-alkyl-2-pyridylmethanimine ligands have been studied with both Cu(I)Br and Cu(I)Cl catalysts. A kinetic study of the polymerisation reactions and studies of the polymers formed yield several conclusions. Cu(I)Br catalyzed reactions are very fast and offer only limited control. Reactions using Cu(I)Cl catalysts, although slower, give a much more controlled polymerisation. The speed of reaction and hence the control over the product PDI and  $M_n$  is

dependant upon the ligand system used. More hydrophobic ligands with longer alkyl chains give more controlled reactions exhibiting slower kinetics. This is due to the increased hydrophobicity of the catalyst complex and the subsequent reduction in catalyst partitioning to the water phase. A series of block copolymers have been successfully prepared from polymeric macroinitiators. The polymers formed are of low polydispersity and GPC analysis confirms the formation of a block copolymer. The particles formed are of good quality and there is good agreement with the particle size determined by DLS.

#### Acknowledgment

We thank the EPSRC (CASE award) and Syngenta (AL) for funding this work.

#### References

- [1] Kamigaito M, Ando T, Sawamoto M. *Chem Rev* 2001; 101:3689–745.
- [2] Coessens V, Pintauer T, Matyjaszewski K. *Prog Polym Sci* 2001;26:337–77.
- [3] Matyjaszewski K, Xia JH. *Chem Rev* 2001;101:2921–90.
- [4] Kato M, Kamigaito M, Sawamoto M, Higashimura T. *Macromolecules* 1995;28:1721–3.
- [5] Matyjaszewski K, Patten TE, Xia J. *J Am Chem Soc* 1997;119:674.
- [6] Percec V, Kim H-J, Barboiu B. *Macromolecules* 1997; 30:6702.
- [7] Haddleton DM, Crossman MC, Hunt KH, Topping C, Waterson C, Suddaby KG. *Macromolecules* 1997;30: 3992–8.
- [8] Lovell PA, El-Aasser MS. *Emulsion polymerisation and emulsion polymers*. Chichester: John Wiley and Sons; 1997.
- [9] Gilbert RG. *Emulsion polymerisation. A mechanistic approach*. London: Academic Press; 1995.
- [10] Matyjaszewski K, Charleux B, Qui J. *Prog Polym Sci* 2001;26:2083–134.
- [11] Qiu J, Charleux B, Matyjaszewski K. *Prog Polym Sci* 2001;26:2083–134.
- [12] Cunningham MF. *Prog Polym Sci* 2002;27:1039–67.
- [13] Zhu CY, Sun F, Zhang M, Jin R. *Polymer* 2004;45:1141–6.
- [14] Jousset S, Qiu J, Matyjaszewski K. *Macromolecules* 2001; 34:6641–8.
- [15] Sarbu T, Pintauer T, McKenzie B, Matyjaszewski K. *J Polym Sci Polym Chem* 2002;40:3153–60.
- [16] Peng H, Cheng SY, Feng LX, Fan ZQ. *J Appl Polym Sci* 2003;89:3175–9.
- [17] Li M, Matyjaszewski K. *J Polym Sci Polym Chem* 2003;41:3606–14.
- [18] Li M, Min K, Matyjaszewski K. *Macromolecules* 2004; 37:2106–12.

- [19] Peng H, Cheng SY, Feng LX. *Polym Int* 2004;53:828–32.
- [20] Qiu J, Gaynor SG, Matyjaszewski K. *Macromolecules* 1999;32:2872–5.
- [21] Gaynor SG, Qiu J, Matyjaszewski K. *Macromolecules* 1998;31:5951–4.
- [22] Matyjaszewski K, Qiu J, Tsarevsky NV, Charleux B. *J Polym Sci Polym Chem* 2000;38:4724.
- [23] Bon SAF, Bosveld M, Klumperman B, German AL. *Macromolecules* 1997;30:324–6.
- [24] Farcet C, Belleney J, Charleux B, Pirri R. *Macromolecules* 2002;35:4912–8.
- [25] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. *Macromolecules* 1998;31:5559–62.
- [26] Shim SE, Shin Y, Lee H, Choe S. *Polym Bull* 2003; 51:209–16.
- [27] Barner-Kowollik C, Davis TP, Heuts JPA, Stenzel MH, Vana P, Whittaker M. *J Polym Sci Polym Chem* 2003;41:365–75.
- [28] Perrier S, Armes SP, Wang XS, Malet F, Haddleton DM. *J Polym Sci Polym Chem* 2001;39:1696–707.
- [29] Wang XS, Lascelles SF, Jackson RA, Armes SP. *Chem Commun* 1999:1817–8.
- [30] Ashford EJ, Naldi V, O'Dell R, Billingham NC, Armes SP. *Chem Commun* 1999;22:1285.
- [31] Georges MK, Veregin RPN, Kazmaier H, Hamer GK. *Macromolecules* 1993;26:2987.
- [32] Granel C, Teyssie P, DuBois P, Jerome P. *Macromolecules* 1996;29:8576.
- [33] Zhu CY, Zhao FK, Xia QY, Cao YR, Huang JX. *Acta Polym Sin* 2001:726–9.
- [34] Bicak N, Gazi M, Tunca U, Kucukkaya I. *J Polym Sci Polym Chem* 2004;42:1362–6.
- [35] Matyjaszewski K, Jousset S, Qui J. *Macromolecules* 2001;34:6641–8.
- [36] Fuji Y, Ando T, Kamigaito M, Sawamoto M. *Macromolecules* 2002;35:2949–54.
- [37] Even M, Haddleton DM, Kukulj D. *Eur Polym J* 2003; 39:633–9.
- [38] Haddleton DM, Crossman MC, Dana BH, Duncalf DJ, Heming AM, Kukulj D, et al. *Macromolecules* 1999; 32:2110–9.
- [39] Keller RN, Wycoff HD. *Inorg Synth* 1947;2:1.
- [40] Haddleton DM, Jasieczek CB, Hannon MJ, Shooter AJ. *Macromolecules* 1997;30:2190–3.
- [41] Baines FL, Billingham NC, Armes SP. *Macromolecules* 1996;29:3416–20.
- [42] Haddleton DM, Perrier SP, Bon SAF. *Macromolecules* 2000;33:8246–51.
- [43] Haddleton DM, Heming AM, Kukulj D, Jackson SG. *Chem Commun* 1998:1719–20.
- [44] Butun V, Armes SP, Billingham NC. *Macromolecules* 2001;34:1148–59.