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Copper-Mediated ATRP of Methyl Methacrylate in Polar Solvents Using a Bifunctional Pyridinal Diimine Ligand

*Mihaela Iovu, Norah Maithufi, Selwyn Mapolie**

Chemistry Department, University of the Western Cape, Private Bag x17
Bellville, 7535, South Africa
E-mail: smapolie@uwc.ac.za

SUMMARY: The bifunctional pyridinal diimine ligand, *bis*(2-pyridinal)ethylenediimine, was employed in copper-mediated ATRP of methylmethacrylate using solvents such as acetonitrile, *N,N*-dimethyl formamide and dimethylsulfoxide. Solvent polarity was found to play a crucial role in determining the extent of control in the ATRP process. Acetonitrile showed the best control when used at a level of 33 vol.-%.

Introduction

Of the various controlled radical polymerization (CRP) processes, atom transfer radical polymerization (ATRP) has proven to be extremely popular and has been applied to a wide range of vinylic monomers. The first successful ATRP processes were reported almost simultaneously by two independent research groups *viz.* that of Matyjaszewski [1] and Sawamoto. [2] The process is mediated by a range of transition metal catalysts. Recently several reports have appeared describing the use of different metal complexes as ATRP catalysts; Cu [1,3-6] and Ru [7-8] have been the metals most frequently used. There have also been reports on the use of Fe [9-13], Pd [14], Rh [15] and Re [16], but these have not been as effective. The efficiency of the ATRP process is largely dependent on the establishment of a rapid equilibrium between an active radical species and a dormant polymer chain. This process is mediated by a metal complex which is capable of undergoing a reversible one-electron redox process. [17] The ATRP process is mechanistically illustrated in Scheme 1. ATRP, like all controlled radical polymerization processes, produces polymers with

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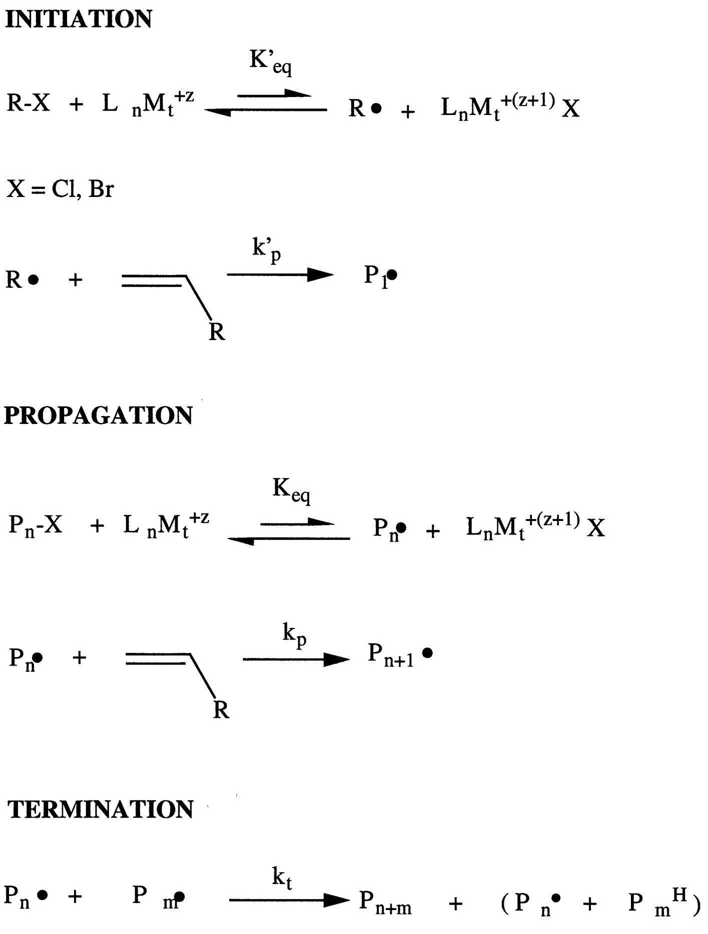
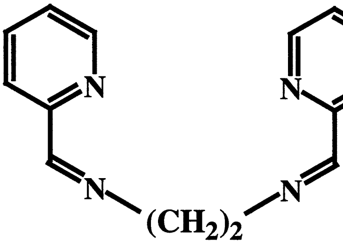
predictable molecular weights and molecular weight distributions (M_w / M_n) lower than 1.5.

As alluded to earlier, copper has been the most effective catalyst for the ATRP of vinylic monomers such as styrene, methacrylates and acrylates[18]. Cu(I) salts have traditionally been employed in conjunction with nitrogen-donor ligands such as 2,2'-bypryridine and substituted bipyridines.[19] Linear amines of a multidentate nature have also found use in copper-mediated ATRP. In addition to the above, ligands such as picolylamines[20], terpyridyl derivatives,[21] tetradentate, [22] and tridentate [23] N-donor ligands have also been employed as ligands for copper-based ATRP catalysts, albeit less frequently. Haddleton and co-workers have also found that Schiff bases can be effective ligands for the copper-mediated ATRP of methacrylates in non-polar media.[24]



Scheme 1

Even though a substantial amount of work has been done on a range of nitrogen-containing ligands, there have been no reports on bifunctional diimine systems. These are systems in which the ligand can potentially bind to two metal centres simultaneously. We now report on some results in which the bifunctional ligand/*bis*(2-pyridinal)ethylenediimine (**L**) (Figure 1), was used in the copper-mediated ATRP of methyl methacrylate in solution, using polar solvents. The effect of solvent polarity on the ATRP process was also evaluated. The results are described here.



L

Fig. 1 Structure of *bis*(2-pyridinal)ethylenediimine.

Experimental

General: NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200 MHz for ^{1}H-NMR and 50.3 MHz for ^{13}C-NMR, using tetramethylsilane as an internal standard. Microanalyses were performed on a Carlo Erba NA 1500 Analyzer. Gel Permeation Chromatography (GPC) measurements in THF were carried out using a Waters 610 liquid chromatograph pump equipped with four Phenogel columns (100 Å, 10^3 Å, 10^4 Å and 10^5 Å) in series, with a Waters 410 differential refractometer. The molecular weight values were determined using Millenium software with calibrations based on the molecular weights of methyl methacrylate standards with low polydispersities.

Cyclic voltammetry (CV) experiments were performed under ambient conditions employing a BAS CV50W electrochemical analyzer (Bioanalytical Systems, Lafayette, IN). The CV measurements were conducted using acetonitrile or DMF solutions under a blanket of argon, in a three-electrode cell. The counter electrode consisted of a platinum wire, while non-aqueous Ag/AgCl was employed as a reference electrode. A platinum electrode (0.5 mm diameter) was used as working electrode. A scan rate of 100 mV/s was used in all the experiments. Tetrabutylammonium tetrafluoroborate was used as supporting electrolyte in a concentration of 0.1 M (acetonitrile or DMF solution). The concentration of the copper complexes was maintained at 0.01 M in all experiments.

Materials: 1,2-diaminoethane, pyridine-2-carboxaldehyde, ethyl 2-bromoisobutyrate, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (all from Aldrich), magnesium sulphate (Univar), diethyl ether and tetrahydrofuran (Kimix), were used as received. Dimethylformamide (DMF) (Merck, 99.5%), dimethylsulfoxide (DMSO) (Merck, 99.5%) and acetonitrile (Riedel de Haen, 99.8 %) were stored over molecular sieve and deoxygenated prior to use. Methyl methacrylate (Aldrich, 99 %) was purified by passing through a column of activated basic alumina, to remove any inhibitor, followed by vacuum distillation from CaH_2. Copper (I) bromide (Aldrich, 98%) was purified by stirring in glacial acetic acid for 12 h., filtering and washing with absolute ethanol under an argon blanket, followed by drying under vacuum.

***bis*(2-Pyridinal)ethylenediimine:** This was prepared using a modification of the method previously reported.[25] Pyridine-2-carboxaldehyde (8 mL, 84 mmol) was dissolved in diethyl ether (20 mL) at room temperature. To this was added 1,2-diamino ethane (2.7 mL, 40 mmol) in a drop-wise fashion, with rapid stirring. Anhydrous magnesium sulphate (2 g) was then added and the reaction continued for 3.5 h at room temperature. The mixture was filtered and the solvent evaporated from the filtrate. The residue was dissolved in methylene chloride and washed with water (3x30mL). The organic phase was dried over magnesium sulphate, which was filtered off. The filtrate was taken to dryness, yielding a light yellow oil which solidified on standing at room temperature. The solid product was purified by recrystallization from diethyl ether-hexane at low temperature, to give a white solid. Yield: 7.2 g (75 %). ^{1}H-NMR ($CDCl_3$): δ 8.61 (m, 2H), 8.41 (s, 2H), 7.95 (m, 2H), 7.72 (m, 2H), 7.26 (m, 2H), 4.06 (s, 4H). ^{13}C-NMR ($CDCl_3$): δ 163.4, 154.4, 149.4, 136.5, 124.7, 121.3, 61.3. GC-MS (EI) : $m/z+1$ = 239. Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.566; H, 5.922; N, 23.512. Found: C, 70.18; H, 6.02 ; N, 23.55.

Procedure of polymerization: An oven-dried 50 mL Schlenk flask was charged with the appropriate amount of CuBr (catalyst), followed by the appropriate volume of solvent, under an argon blanket. The required amount of argon-purged methyl methacrylate was added at room temperature and the reaction mixture degassed with argon for at least 20 minutes. The flask was then immersed in a silicon oil bath, which had previously been allowed to equilibrate at 90°C for all reactions except those carried out in acetonitrile (the latter were performed at 70°C). The initiator (I) was added as soon as the reaction mixture reached the required temperature. The conversion was determined gravimetrically by periodically removing a small sample, using an argon-purged syringe. The sample was syringed into a pre-weighed vial and the mass of the reaction mixture determined. Upon addition of hexane to the vial the polymer precipitated from the reaction mixture. The precipitated polymer was dried under vacuum at 55°C until a constant mass was obtained. The conversion was calculated by comparing the mass of polymer obtained with that of the initial mass of the monomer employed.

Results and Discussion

One of the major problems associated with copper-mediated ATRP is that many of the ligand systems employed lead to complexes which have limited solubility in the pure monomer. Thus, many ATRP reactions take place in heterogeneous media and this often results in the loss of control. We observed a similar behaviour with our ligand system i.e. a substantial amount of undissolved material remained on the walls of the polymerization flask when reactions were attempted in the pure monomer. In addition, none of the polymerizations showed any control. It was, thus, envisaged that the introduction of a solvent that could solubilize the copper complex would lead to an improvement in the polymerization behaviour and ensure that the prerequisites for controlled radical polymerization be met.

The effects of polar solvents on ATRP have previously been investigated by Matyjaszewski *et al.*[23] who concluded that the introduction of a polar solvent to a heterogeneous ATRP reaction resulted in increased solubility of both Cu(I) and Cu(II) species in the reaction mixture. Initial evaluation of the solubility of the complex obtained when CuBr combined with our ligand **L**, in the presence of a range of solvents, revealed dimethyl formamide, acetonitrile and dimethylsulfoxide to be the best solvents.

These solvents were thus employed for the solution polymerization of methyl methacrylate.

MMA Polymerization in Acetonitrile

Polymerizations of methyl methacrylate were carried out using acetonitrile levels of 16.5 vol.-% and 33 vol.-%, at molar ratios [MMA] : [I] : [CuBr] = 100 : 1 : 0.5 and [CuBr] : [L] = 1 : 1. Both reactions were performed at 75^0C. The CuBr-**L** complex was found to be soluble in acetonitrile, however, on addition of the monomer, in the case of the reaction performed in the presence of 16.5 vol.% acetonitrile, which means some precipitation was noted that the reaction occurred in a heterogeneous medium. The reaction carried out in the presence of 33 vol.% acetonitrile was initially homogeneous but some precipitate was observed as the reaction proceeded. This could be due to the low solubility of the $CuBr_2$-**L** complex in acetonitrile. This hypothesis was verified by testing the solubility of the $CuBr_2$-**L** complex in acetonitrile; it was found to be only partially soluble.

First order kinetic plots were observed for both reactions i.e. the reaction performed in the presence of 16.5% as well as in the presence of 33 vol % acetonitrile. This is indicative of the conservation of active species during the reaction (Figure 2).

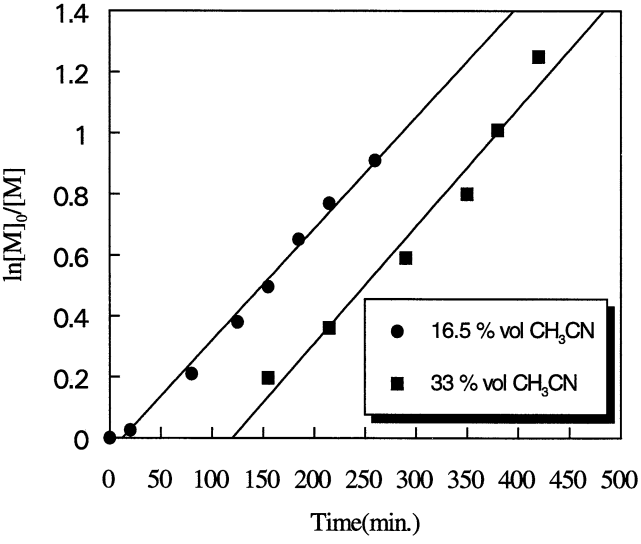


Fig. 2 First-order kinetic plots for polymerization of MMA in presence of acetonitrile with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, [CuBr] : [L] = 1 : 1, 75^0C.

However, both reactions gave induction times; 30 minutes for the reaction in the presence of 16.5 vol. % acetonitrile and 120 minutes for the reaction in the presence of 33 vol.% acetonitrile. Induction times are usually a consequence of the presence of trace amounts of air in the reaction mixture, which leads to the consumption of some of the Cu(I). They also occur as a result of there being a slow activation process. Despite carefully performing several thaw-freeze cycles before the initiation of the polymerization process, we still observed these induction periods. Thus it would appear that slow activation is the most likely cause of the induction times.

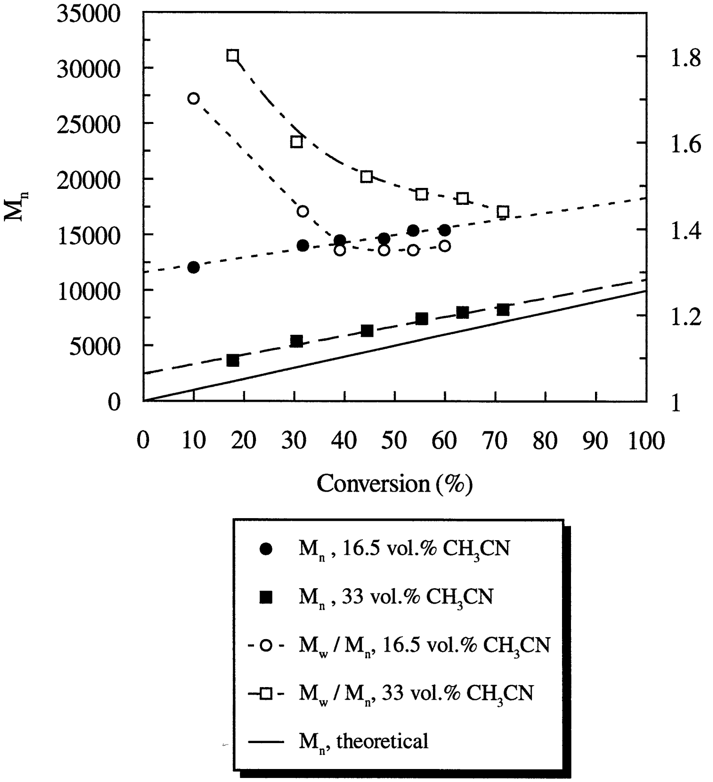


Fig. 3 Molecular weight *vs.* conversion and polydispersity index *vs* conversion plots for polymerization of MMA in presence of acetonitrile with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, [CuBr] : [L] = 1 : 1, 75^{0}C.

The reaction conducted using an acetonitrile concentration of 16.5 vol% yielded polymers with molecular weights higher than predicted (Figure 3). In addition, relatively high polydispersity indices were obtained, although these were still within the accepted limits for ATRP. In the case of the reaction performed at 33 vol% acetonitrile a fairly good agreement between calculated and observed molecular weights was obtained. However, slightly higher values for the polydispersity indices were observed.

MMA Polymerization in N,N-Dimethylformamide (DMF)

MMA polymerizations were conducted in the presence of 16.5 and 33 vol % DMF at molar ratios of [CuBr] : [L] = 1 : 1 and 1 : 2 and [MMA] : [I] : [CuBr] = 100 : 1 : 0.5. The motivation for using this particular ratio of [I] : [CuBr] was to reduce the amount of copper salt used in ATRP. In addition, our initial investigations using a [I]:[CuBr] ratio of 1:1 yielded polymerizations with no control. It was also observed that during polymerizations using this ratio of [I] : [CuBr] most of the copper salt remained undissolved, and stuck to the walls of the polymerization vessel.

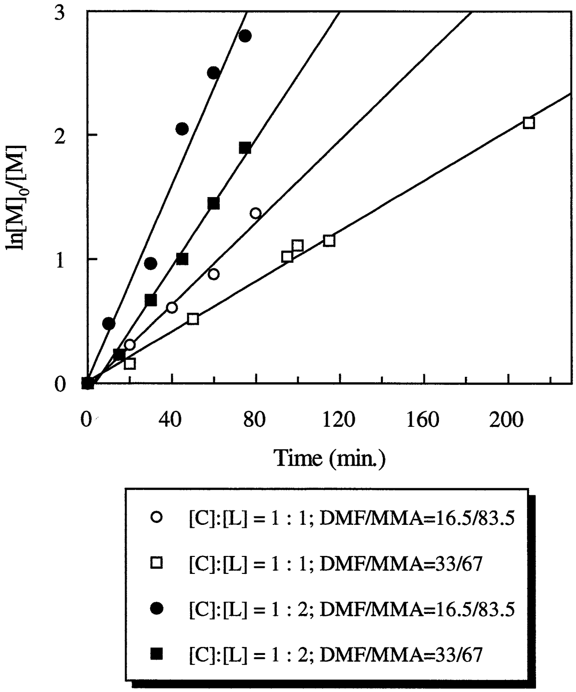


Fig. 4 Kinetic plots for the polymerization of MMA in the presence of DMF with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, temperature = 90^{0}C.

The CuBr-**L** complex is soluble in neat DMF but a precipitate formed when the monomer was added for the reactions performed in the presence of 16.5 vol.% DMF. Thus the reaction carried out using 16.5 vol% DMF still occurred in a heterogeneous medium, while the polymerization performed in 33 vol.% DMF took place in a completely homogeneous medium.

All the reactions performed in the presence of DMF exhibited first-order kinetics (Figure 4). This indicates that the concentration of active species remained relatively constant throughout the reaction and that the contribution of termination reactions was rather restricted.

The effect of ligand concentration was also examined and it was found that the rate of reaction increased at the higher level of ligand.

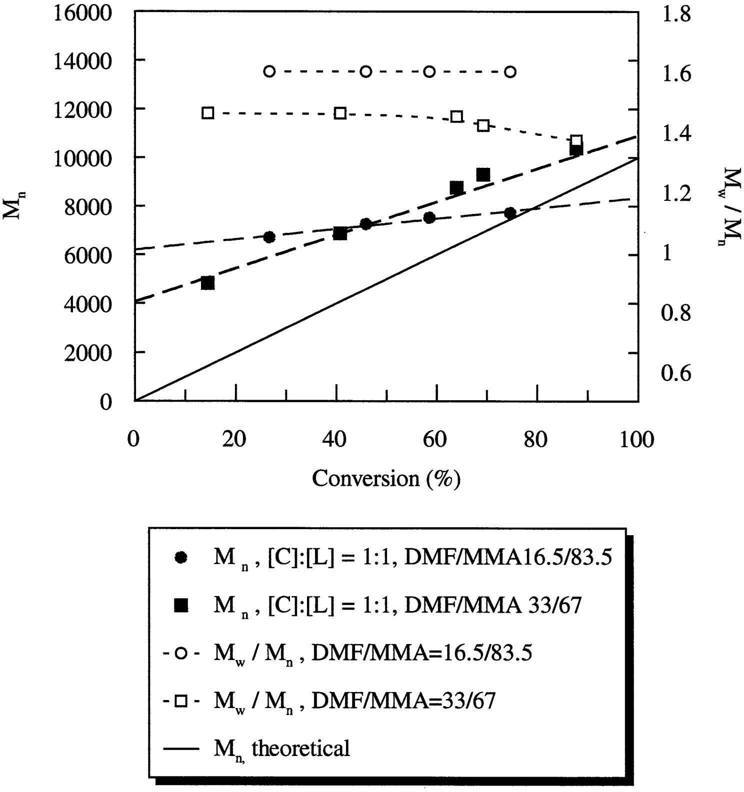


Fig. 5. Molecular weight *vs.* conversion and polydispersity index *vs.* conversion plots for polymerization of MMA in presence of DMF with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, and [CuBr]: [L] =1:1, temperature = 90°C.

Molecular weight versus conversion and polydispersity index versus conversion plots for the reactions at 16.5vol % and 33 vol% DMF are shown in Figures 5 and 6, respectively. For both the reactions performed at 16.5 vol % DMF, but at different ligand concentrations, the molecular weights of the polymers obtained showed only a slight variation from the start to the end of the process. Polymers with relatively broad molecular weight distributions were also obtained (PDI = 1.6 for [CuBr] : [L] = 1 : 1 and PDI= 1.56 for [CuBr] : [L] = 1 : 2). This behaviour resembles that normally observed in classical radical polymerization. The influence of ligand concentration on the control of the polymerization process was found to be insignificant.

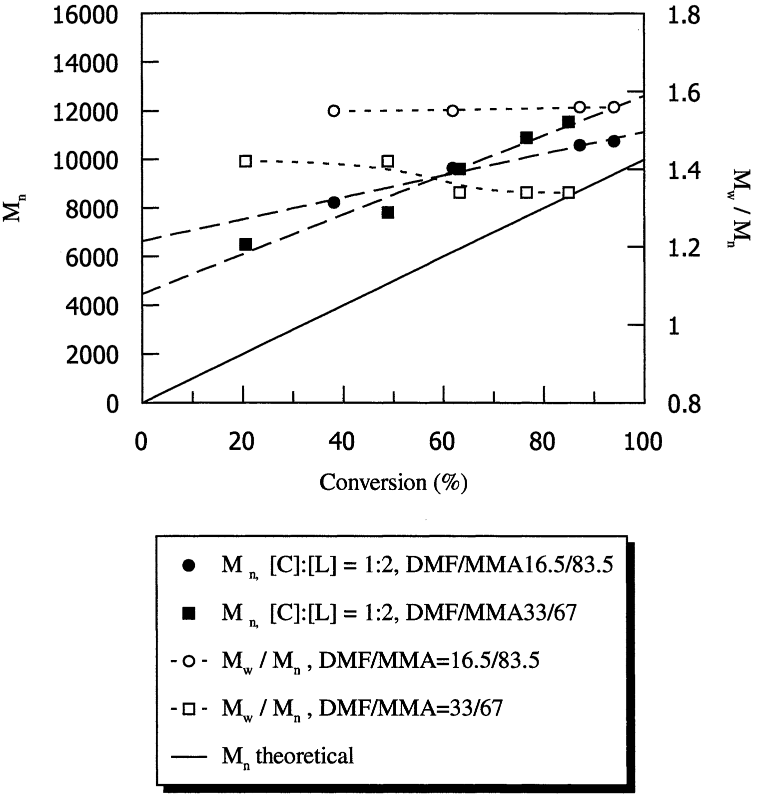


Fig. 6 Molecular weight *vs.* conversion and polydispersity index *vs.* conversion plots for polymerization of MMA in presence of DMF with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, [CuBr]:[L] = 1:2, temperature = 90^{0}C.

For the polymerizations performed using 33 vol % DMF it was found that the molecular weight increased linearly with conversion for reactions carried out at both concentrations of ligand i.e. [CuBr] **:** [L] = 1 **:** 1 and 1 **:** 2. However, molecular weights higher than predicted were obtained in both cases. For example, (M_n(GPC)=11547 at 85 % conversion, M_n(calcd.)=8469 for the reaction with [CuBr] : [L] = 1 : 2 and M_n(GPC)=11291 at 87.8 % conversion, M_n(calcd.)=8748 for the reaction with CuBr] : [L] = 1 **:** 1. Polymers with fairly acceptable PDI values were obtained for these reactions performed at 33% vol.% DMF. This was found to be 1.37 for PMMA synthesized with [CuBr] : [L] = 1 : 1 and 1.34 for PMMA synthesized with [CuBr] : [L] = 1 : 2).

Figure 6 shows that the reactions performed at the higher concentration (33%) of DMF showed better control over molecular weights and polydispersities of the polymers synthesized. This is most likely due to the fact that reactions took place in a homogeneous medium. Under such conditions it is assumed that both Cu(I) and Cu(II) species are totally soluble. Solubilizing the Cu(II) species would result in better control over the ATRP process. It was previously shown that the Cu(II) species is responsible for maintaining a low polydispersity index. Again it was found that the ligand concentration had no real effect on the molecular weight and molecular weight distribution.

Higher concentrations (>33%) of DMF were not evaluated as it was envisioned that an excess of polar solvent could result in loss of control over the polydispersity index. Preliminary experiments performed in neat DMF i.e. in the absence of any ligand, gave extremely poor control over the polymerization process. It has also previously been reported by other workers that a coordinating solvent such as DMF has the potential to displace ligands from the complex, resulting in saturation of the coordination sphere around the Cu(I) and Cu(II) species.[27] In addition, Vairon and co-workers found that ATRP of styrene in a solution of DMF but in the absence of ligand was extremely slow and showed no control whatsoever.[28]

MMA Polymerization in Dimethylsulfoxide (DMSO)

Polymerization of methyl methacrylate was also performed in the presence of 16.5 vol % dimethylsulfoxide (DMSO) at 90^{0}C. The CuBr - **L** complex is soluble in DMSO but a precipitate formed when the monomer was added, as was found when using DMF as solvent.

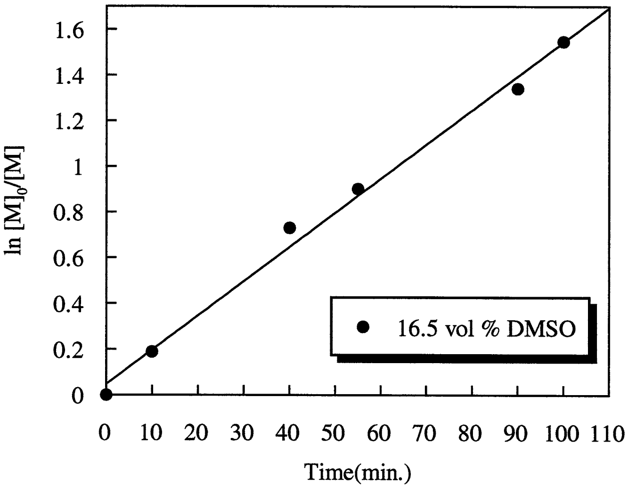


Fig. 7 Kinetic plot for the polymerization of MMA in the presence of DMSO with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, temperature = 90^0C.

Again, linear kinetic plots were obtained, indicating the conservation of radicals throughout the reaction (Figure 7). Polymers with higher molecular weights than theoretically expected and with relatively high polydispersity indices (PDI = 1.56) were obtained (Figure 8).

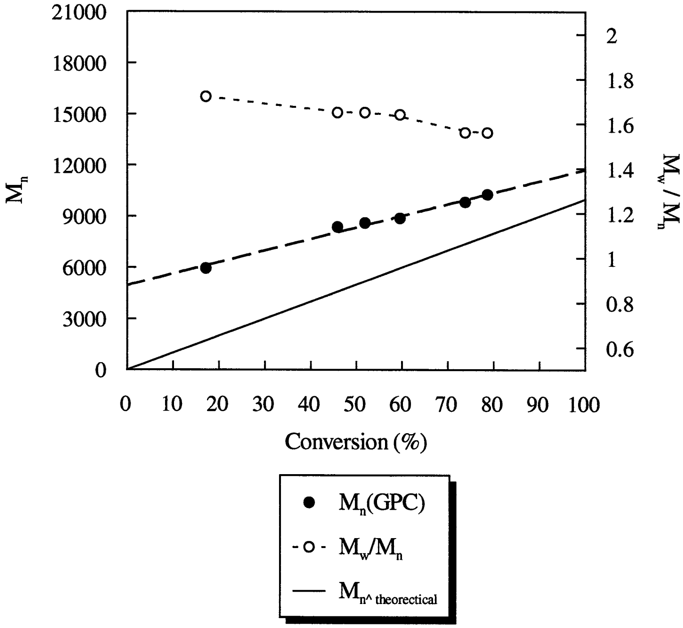


Fig. 8 Molecular weight *vs.* conversion and polydispersity index *vs* conversion plots for polymerization of MMA in presence of DMSO with [MMA] : [I] : [CuBr] = 100 : 1 : 0.5, [CuBr] : [L] = 1 : 1, 90^0C.

Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were performed on the copper complexes with the aim of obtaining some insight into the behaviour of these metal complexes in solution. The CV experiments were carried out in both acetonitrile and DMF. The results are summarized in Table 1. Molar ratios of [Cu Salt] : [Ligand] = 1 : 1 and 1 : 2 were used for all the experiments. Cyclic voltamogramms for CuBr-**L** complexes (molar ratio 1 : 1 and 1 : 2) in acetonitrile are presented in Figure 9. From Table 1 it can be seen that the anodic-cathodic peak potential separations (ΔE = 264 mV for CuBr-L and ΔE = 316 mV for CuBr-2L) exceed the value (~60 mV), theoretically expected for a one-electron redox process. In addition, in both cases, the forward-to-backward peak ratio does not show the expected value of 1 (Table 1, entries 1 and 2). Thus it can be considered that both Cu(I)-**L** and Cu(I)-2**L** complexes in acetonitrile gave quasi-reversible redox couples.

Table 1 Cyclic voltammetry data obtained in acetonitrile and DMF for the CuBr-L complexes.

Entry	**Solvent**	**[CuBr]:[L]**	**$E_{p,a}$[i] (V)**	**$E_{p,c}$[i] (V)**	**$E_{1/2}$ (V)**	**ΔE (mV)**	**i_b/i_f[ii]**
1	CH_3CN	1 : 1	0.327	0.063	0.226	264	0.88
2	CH_3CN	1 : 2	0.356	0.040	0.198	316	0.72
3	DMF	1 : 1	0.248	-0.042	0.103	290	0.88
4	DMF	1 : 2	0.288	-0.049	0.119	337	1.35

Potentials refer to Ag/AgCl electrode at scan rate of 100 mV/s for the measurements performed under the conditions mentioned in the experimental section.

[i] $E_{p,a}$ and $E_{p,c}$ - peak potentials of the oxidation and reduction waves, respectively

$E_{1/2} = 1/2\ (E_{p,a} + E_{p,c})$

[ii] i_b/i_f – ratio of backward-to-forward peak current

From the cyclic voltammetry data obtained in acetonitrile (entry 1 in Table 1) it can be seen that the Cu(I)-L complex is relatively difficult to oxidize ($E_{p,a}$ = 0.327 V) but the reduction of Cu(II)-L to Cu (I)-L takes place easily ($E_{p,c}$ = 0.063 V). The difficulty in the oxidation of Cu(I)-L complex can be explained taking into account the fact that nitriles are able to stabilize the Cu (I) oxidation state.[29 ,30] Furthermore, the stabilization of Cu(I) is greater than that of Cu(II) due to the fact that the former is capable of forming a more extended system of Cu(I)-N π interactions. [31-32] It has also previously been shown that ligands containing unsaturated nitrogen atoms assist with the reduction of Cu(II) to Cu(I).[33] This consistent with what was observed in our electrochemical studies of the copper-ligand complex in acetonitrile.

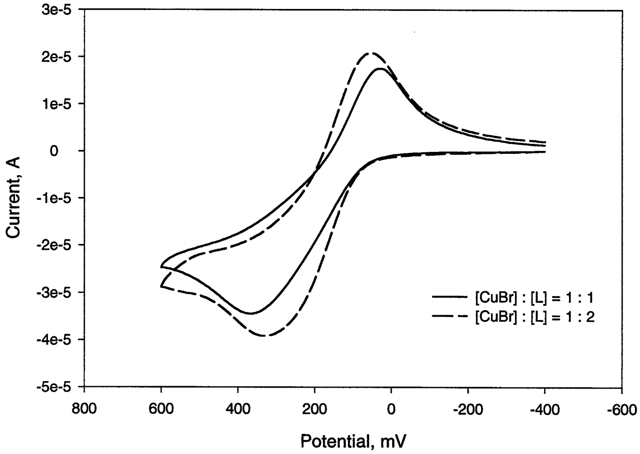


Fig. 9 Cyclic voltamogramms of CuBr/L in acetonitrile ([CuBr]: [L] = 1 : 1 and 1 : 2); [CuBr] = 0.01 M.

A comparison with previously reported [34] cyclic voltammetry data showed that negative values for $E_{p,c}$ were also obtained in that particular case. It was also found in these studies that copper complexes which are effective in ATRP gave low oxidation (-30 to –100 mV) and reduction potentials (-340 to –110 mV).[23, 35]

From the observed electrochemical behaviour of the Cu(I)-L complex we would expect the activation rate to be lower than the deactivation rate for the polymerization performed in acetonitrile, resulting in a relatively slow polymerization. As far as the polydispersity index is concerned, we could still obtain polymers with small PDI values if the rate of deactivation exceeded the rate of propagation. However, in our case we observed that polymers with relatively broad molecular weight distribution were obtained. This is possibly due to the low solubility of the Cu(II)-ligand species in the reaction medium. The Cu(II)-ligand species is the deactivator in the process and if its concentration is low then the rate of deactivation will also be low.

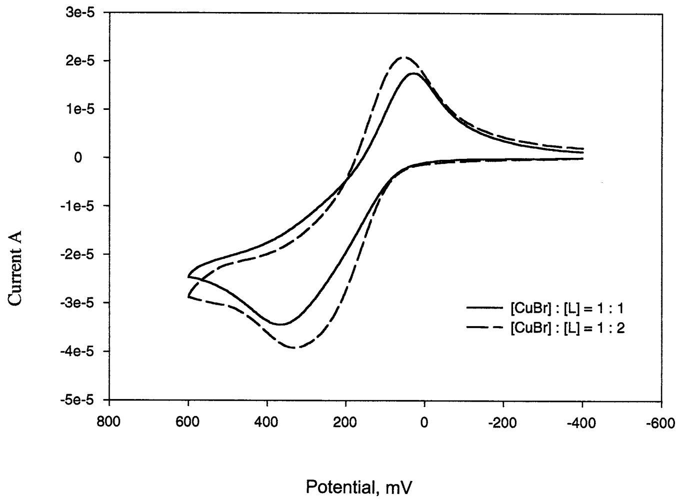


Fig. 10. Cyclic voltammograms of CuBr/L complexes (molar ratio 1 : 1 and 1 : 2) [CuBr]: [L] = 1 : 1 and 1 : in DMF; [CuBr] = 0.01 M.

Quasi-reversible redox couples were also obtained for both Cu(I)-**L** complexes (molar ratio 1 : 1 and 1 : 2) in DMF (entries 3 and 4 in Table 1 and Figure 10).

From the cyclic voltammetry data obtained for the CuBr-**L** complex (molar ratio 1 : 1) in DMF (entry 3 in Table 1) it can be seen that the Cu(I)-**L** complex is more easily oxidized ($E_{p,a}$ = 0.248 V) when compared with the corresponding data obtained in acetonitrile (entry 1 in Table 1). The peak potential of the reduction wave is shifted towards negative values ($E_{p,c}$ = -0.042 V), indicating a more stable Cu(II)-L complex in DMF. The latter is more difficult to reduce than the Cu(II)-**L** complex in acetonitrile. Such behaviour indicates a higher rate of activation for the polymerizations performed in DMF, which will result in a higher reaction rate. This was confirmed during the polymerization studies.

Changing the molar ratio [CuBr] : [L] to 1 : 2 did not lead to a significant change in both cases (cyclic voltammograms obtained in DMF or acetonitrile) as can be seen in Figures 9 and 10 (entries 2 and 4 in Table 1).

Conclusion

Solution polymerization of methylmethacrylate in polar solvents such as acetonitrile, dimethylfomamide and dimethylsulfoxide affords ATRP with various degrees of control. In all cases, except for reactions in 16.5% DMF, an increase in molecular weight with conversion was observed. However, control over molecular weight was not as good as expected since in some cases molecular weights higher than those predicted were obtained. This was more obvious for polymerizations performed at higher monomer concentrations. Control improves with increasing amounts of solvent used. The nature of the solvent also played a crucial role in determining the rates of polymerization. Reactions in DMF were the fastest reactions while the slowest were obtained in acetonitrile. This is most likely a result of the fact that the copper-ligand complex appears to be more soluble in DMF than in the other solvents. Induction periods were also observed in the case of the reaction carried out in acetonitrile. This solvent clearly induces slow initiation. It is thought that acetonitrile could possible stabilize the copper (I)-ligand complex as well as facilitate the reduction of Cu(II) to Cu(I). Both of these scenarios would lead to a high level of deactivator species being present and hence the low rate of initiation.

Initial results of cyclic voltammetry studies also confirmed our initial results, namely that the reactions in DMF proceeded much faster than reactions in acetonitrile and DMSO. Here it was found that the oxidation of Cu(I) was much more facile in DMF.

It is clear from the results obtained that careful choice of solvent could enhance the control over the ATRP process using a bifunctional ligand such as the one evaluated in this study. We are currently investigating the use of other bifunctional ligand systems and will report on these in due course.

Acknowledgements

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