Copper(I)-Mediated Living Radical Polymerization in the Presence of Oxyethylene Groups: Online ^{1}H NMR Spectroscopy To Investigate Solvent Effects

David M. Haddleton,* Sébastien Perrier, and Stefan A. F. Bon

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom

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ABSTRACT: The use of oxyethylene methacrylate monomers, initiators, and 1,2-diethoxyethane as a cosolvent in the living radical polymerization mediated by copper(I) pyridylmethanimine complexes has been studied. Online ^{1}H NMR monitoring of the reaction has been used to investigate the living radical polymerizations. Polymerization of poly(ethylene glycol) methyl ether methacrylate macromonomer (MeO-(PEG)MA; $M_n = 480$) was carried out in toluene mediated by a copper(I) bromide/*N*-(*n*-propyl)-2-pyridylmethanimine catalyst, using phenyl α-bromoisobutyrate (**1**) as initiator. The measured number-average molar mass, M_n, of the product increases linearly with monomer conversion in close agreement to the theoretical M_n, with low polydispersity products (PDI < 1.2) achieved in all cases, as expected for a living polymerization. The overall rate of polymerization was very fast (ca. 90% conversion after 1 h at 90 °C) when compared to polymerization of benzyl methacrylate (BzMA) under similar conditions, indicating high values for $k_p[R^*]$, where $R^* =$ active propagating species. The origin of this dramatic rate enhancement was investigated by carrying out the polymerization of MeO(PEG)MA over a range of temperatures and by the polymerization of alkyl methacrylates with a MeO(PEG)-derived macroinitiator. Polymerization of BzMA was carried out in 1,2-diethoxyethane as solvent, which showed an enhanced rate when compared to polymerization in nonpolar/noncoordinating solvents. The high value of $k_p[R^*]$ is ascribed to complexation of the oxyethylene groups at the copper in a dynamic state with the pyridylmethanime ligand complexation, which results in a more active catalyst.

Introduction

An important recent innovation in addition polymerization is the emergence of living radical polymerization.[1,2] In particular, transition-metal-mediated living radical polymerization has proven to be robust for the precise design of polymers of complex architecture and predetermined molar mass. Transition-metal-mediated living radical polymerization is inert to many functional groups present in monomers and/or solvents as well as polar and protic impurities present in solvents and monomers. This allows for the facile synthesis of many functional polymers of novel structure and topology.

Transition-metal-mediated living radical polymerization proceeds via the homolytic cleavage of an activated carbon−halogen bond.[3] The overall rate of polymerization is reportedly solvent-dependent and enhanced by the presence of numerous polar/coordinating additives.[4,5] Previously this has been ascribed to different solubilities of copper(I) and copper(II) species, for the case of copper bipyridyl complexes.[4] However, pyridylmethanimine ligand-derived copper(I) catalysts can be solubilized by judicious choice of alkyl group within the ligand.[6] In addition, chain transfer in ordinary radical polymerizations using halogen compounds as chain transfer agents show profound solvent effects.[7] These observations pose interesting questions regarding the exact nature of the active catalyst and for the mechanism of the reaction. Also, the question remains whether the propagating species is truly a free radical or if it is constrained within the vicinity of the catalyst, causing "*in-cage*" propagation.[8]

A variety of poly(ethylene oxide) (PEO) containing polymers[9,10] are used in many diverse applications, including surfactants, e.g., poly(styrene)-*block*-poly(ethylene oxide),[11] poly(methyl methacrylate)-*block*-poly(ethylene oxide),[12] and poly(soaps).[13] An interesting utilization of poly(ethylene oxide)s is in *so-called* polymer brushes,[9] which are characterized by a high branch density along a 'backbone', e.g., solid surfaces via covalent bonding or physisorption, or a polymer chain. The conventional route toward homogeneous polymer brushes is homopolymerization of macromonomers to give poly(macromonomers). Such poly(macromonomers) are of increasing interest and are commonly synthesized via free-radical polymerization.[14] This type of polymer brush is distinct from the more widely demonstrated graft copolymers, which have a lower branch density, obtained via copolymerization of macromonomers commonly based on acrylic esters or styrene, with more conventional vinylic monomers.[15] Formation of poly(macromonomers) is complicated by the intrinsic low concentration of polymerizable groups in the system and a possible reduction in the rate of monomer addition as a result of steric hindrance. Thus, low degrees of polymerization (DP) are generally obtained. Tsukhara et al.[16] have reported high DP polymer brushes. Polymers incorporating oxyethylene units have been previously prepared using nitroxide-mediated living radical polymerization[17] and transition-metal-mediated polymerization to produce dendrimer-like star block and amphiphilic copolymers.[18] Homopolymerization of vinyl ether-based PEO derived macroinitiators have also been used to prepare block copolymers.[19,20]

Herein, we report an explorative kinetic study on the polymerization of α-methoxy ω-methacryloyl poly(ethyleneoxy) macromonomers using copper(I)-mediated

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* Corresponding author. Tel +44 (0)24 7652 3256/8438; fax +44 (0)24 7652 4112; E-mail D.M.Haddleton@warwick.ac.uk.

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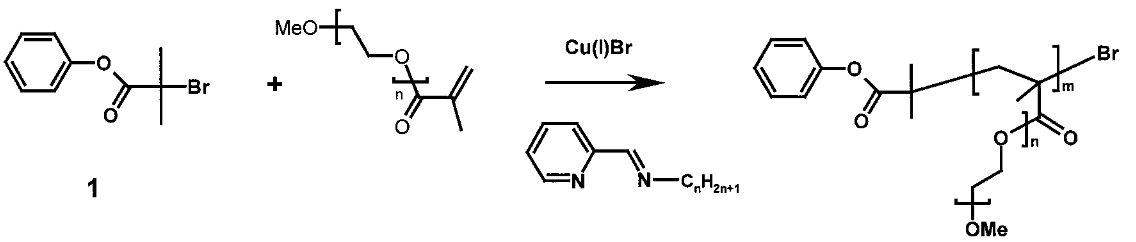
Scheme 1



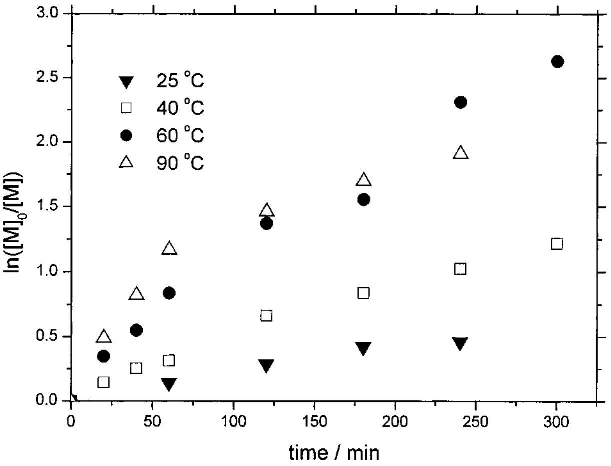


Figure 1. Kinetic data for the polymerization of MeO(PEG)-MA, $[M]_0/[I]_0/[Cu(I)Br]_0/[n\text{-Pr-L}]_0 = 10/1/1/2$ in toluene at various temperatures, reaction sampled with time.

living radical polymerization. This has been carried out to prepare comb polymers with hydrophilic teeth. The dramatic rate increase observed with these monomers led to the synthesis of several α-methoxy poly(ethylene oxide) initiators which have been used for the polymerization of benzyl methacrylate (BzMA) to give poly(ethylene oxide)-*block*-poly(BzMA). Finally, the polymerization of BzMA has been carried out in 1,2-diethoxyethane as a solvent, so as to investigate the observed unusually fast rates of polymerization.

Results and Discussion

Polymerization of MeO(PEG)MA. Polymerization of MeO(PEG)MA was mediated by copper(I) bromide/*N*-(*n*-propyl)-2-pyridylmethanimine (*n*-Pr-L) using phenyl α-bromoisobutyrate (**1**) as initiator (Scheme 1) in toluene solution over a range of temperatures. Compound **1** was chosen as initiator so as to enable the number-average molar mass, M_n, of the final polymer product to be determined using ^{1}H NMR. Integration of the oxyethylene proton resonances, 3.5−4.5 ppm, and the aromatic resonances, 6.9−7.5 ppm, were used for the calculation of M_n. Polymerizations were carried out at various temperatures using typical living radical polymerization conditions, as used for alkyl methacrylates with these catalysts, at the initial molar ratios of $[M]_0/[I]_0/[Cu(I)Br]_0/[n\text{-Pr-L}]_0 = 10/1/1/2$. The rates of polymerization were unusually high; see Supporting Information and Figure 1. Polymerization at 90 °C resulted in a conversion of greater than 70% within 1 h (conversion measured with size exclusion chromatography, SEC, using DRI detection). The final properties of the products from these reactions are summarized in Table 1; for full data sets see Supporting Information. The M_n from NMR was in excellent agreement with the theoretical M_n, and the polydispersity remained below 1.20 in all cases. Indeed, polymerization proceeded to 81% conversion after 15 h even at 25 °C. It is apparent from Figure 1 that at higher temperatures, 60 and 90 °C, the first-order plots show significant curvature, which prompted us to investigate these reactions in more detail. Moreover, experiments were carried out where the [monomer]/[initiator] ratio was varied at 60 °C (see Table 2, E−G). Overall, these results show that the experimental values of the number-average molar mass, $M_{n,exp}$, are in reasonable agreement with the theoretical values, $M_{n,th}$, as would be expected for living polymerization, and low polydispersity, <1.2, was achieved in each case. Lowering the amount of catalyst with respect to the initiator (E, H, and I, Table 2) reduced the rate of polymerization. However, even at reduced levels of catalyst efficient polymerizations ensued, and narrow polydispersity polymers with M_n close to the theoretical values were obtained.

Table 1. Final Conversion and MMD Data for the Polymerization of MeO(PEG)MA at Various Temperatures

	T/°C	*t*/min	conv/%	$M_{n,th}$[a]	$M_{n,exp}$[b]	$M_{n,exp}$[c]	PDI[c]
A	25	910	81	3900	4600	6000	1.16
B	40	430	91	4400	5200	7530	1.12
C	60	595	99	4800	5400	7500	1.12
D	90	175	95	4600	5100	7000	1.14

[a] $M_{n,th} = ([M]_0/[I]_0 \times \text{MW of monomer} \times \text{conv})/100$. [b] Determined by the ^{1}H NMR peak intensity ratio. [c] Estimated by PMMA-calibrated SEC.

Table 2. Final Conversion and MMD Data for the Polymerization of MeO(PEG)MA at 60 °C for Different Targeted Degrees of Polymerization

	$[M]_0/[I]_0/[Cu(I)]_0$	*t*/min	conv/%	$M_{n,th}$[a]	$M_{n,exp}$[b]	PDI[c]
E	10/1/1	360	93	4500	4200	1.11
F	10/0.5/1	360	89	8600	9600	1.10
G	10/0.25/1	360	80	15600	16000	1.09
H	10/1/0.5	360	68	6600	7000	1.11
I	10/1/0.25	360	44	8500	9200	1.13

[a] $M_{n,th} = ([M]_0/[I]_0 \times \text{MW of monomer} \times \text{conv})/100$. [b] Determined by the ^{1}H NMR peak intensity ratio. [c] Estimated by PMMA-calibrated SEC.

Monitoring Polymerization Using Online ^{1}H NMR Spectroscopy. To investigate the polymerization of MeO(PEG)MA in more detail, reactions were followed in situ by ^{1}H NMR. Polymerizations were carried out over a range of temperatures, 25, 40, 60, and 90 °C, in NMR tubes fitted with Young's taps, so as to maintain an inert atmosphere. To ensure a homogeneous polymerization with both soluble copper(I) and copper(II) species, *N*-(*n*-octyl)-2-pyridylmethanimine (*n*-Oct-L) was used as a ligand with a ratio of $[n\text{-Oct-L}]_0/[CuBr]_0 = 3$. Monomer conversion was measured by ^{1}H NMR, by integration of the vinyl resonances (6−5 ppm) relative to the combined values of the CH_2 α to OC=O from the monomer and polymer (4.1 ppm). Figure 2 shows a

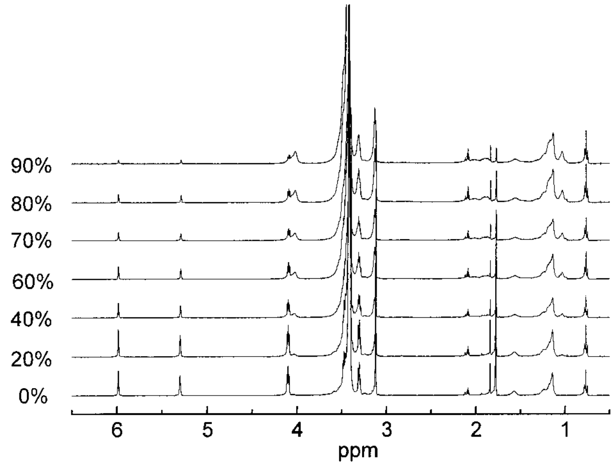


Figure 2. Partial ^{1}H NMR spectra at different stages of monomer conversion for the polymerization of MeO(PEG)MA at 40 °C.

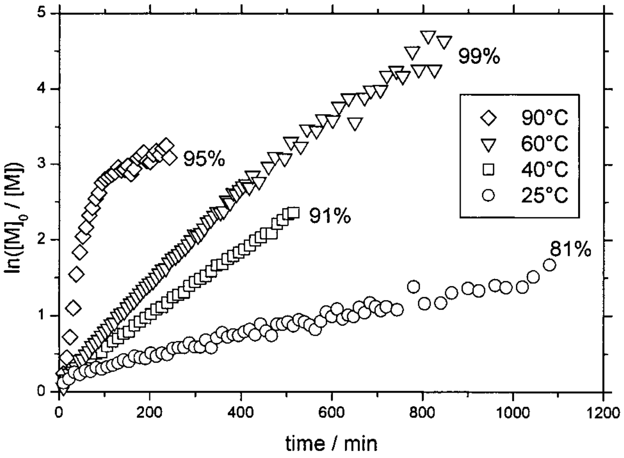


Figure 3. First-order kinetic plots for the polymerization of MeO(PEG)MA in toluene over a range of temperatures as monitored by ^{1}H NMR.

selection of the spectra obtained from the reaction carried out at 40 °C. Analysis of the data results in ln([M]$_0$/[M]) vs time plots with many more data points than from a *sampled* reaction (Figure 3) as above and also avoids the possibility of introducing impurities/oxygen during sampling.

Fischer et al. have derived that, in the absence of external radical generation with no Cu(II) species present at time = 0 s, ln([M]$_0$/[M]) vs time should show a $^{2}/_{3}$-order dependence on time, as a direct result of the persistent radical effect.[21] All our experiments were carried out using purified Cu(I)Br, so as to match the boundary conditions for the model which predicts a $^{2}/_{3}$-order dependence. Fitting the experimental data, shown in Figures 3 and 4, using a nonlinear least-squares (NLLS) method of analysis, using the two empirical functions $\ln([M]_0/[M]) = a + bt^{2/3}$ and $\ln([M]_0/[M]) = a + bt$ shows an overall better fit with a linear dependence on time, the second expression. The empirical constant is used as it accounts for deviation from ideal conditions at the start of the reaction arising from normal experimental errors. Only the polymerization of benzyl methacrylate with 1,2-diethoxyethane as a cosolvent at 25 °C showed a better agreement with a $^{2}/_{3}$-order time dependence. The fit parameters, *a* and *b*, together with r^2 and the standard fit error are listed in the Supporting Information.

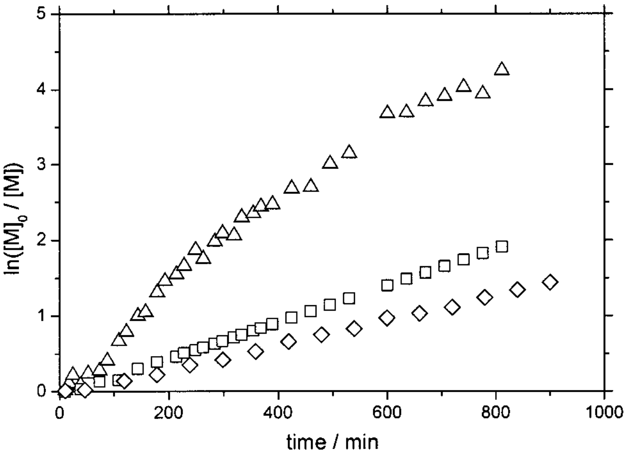


Figure 4. First-order kinetic plots for the polymerization of benzyl methacrylate (BzMA) in d_8-toluene at 50 °C (◇), in toluene using an oxyethylene macroinitiator, MeO(PEG)I (M_n = 5000; □), and in d_8-toluene/1,2-diethoxyethane (4/1 g/g; △). Conversion monitored by ^{1}H NMR.

One of the restrictions of the current models is that they do not take into account a chain length dependence for the rate coefficients. Other points of criticism are that the nature of catalyst is only divided into two structures, a Cu(I) and Cu(II) compound, and that chain growth is assumed to occur via conventional free-radical propagation. The current models are too oversimplified to describe transition-metal-mediated living radical polymerization, and the kinetics are more complex and not well understood. It is also noted that even small deviations in starting materials, e.g., a small amount of Cu(II) present at the start of the reaction, will cause deviation from ideal kinetics. Thus, it is difficult to make precise statements concerning the mechanism of the reaction from kinetic data alone.

A clear deviation from the expected monomer conversion profile is seen in Figure 3 at high conversion (>90%) and high temperature. There are a number of possible explanations for this behavior. First, the enhanced viscosity of the reaction medium results in the rate of macromonomer diffusion becoming important in the overall rate coefficient of polymerization, k_p. This results in a suppression of values of $k_p[R^*]$. It has previously been reported that propagation in the metal-mediated living radical polymerization of isobutyl vinyl ether methacrylate (MA-PIBVE) becomes diffusion-controlled[19] and also in conventional radical polymerization systems with macromonomers of a variety of chemical structures.[22,23] This effect would be more likely to happen at elevated temperatures as a direct result of a higher activation energy for propagation for methacrylates (typically 20−28 kJ mol^{-1}) than for monomer diffusion (7−15 kJ mol^{-1}). An alternative explanation is the occurrence of certain chain-transfer events, e.g., from monomer to polymer, which would generate secondary and primary carbon-centered radicals and thus logically the corresponding brominated dormant analogues. This would result in a reduction of the concentration of activated species due to a lower rate coefficient of activation and thus to a reduction in $k_p[R^*]$. An accurate estimation of the extent and relative contribution of these two explanations for the observed deviation in monomer conversion is, however, not known from the present data.

Polymerization in the Presence of Added Oxyethylene Groups. A striking observation from the

Table 3. λ_{max} and E_{NR} for Nile Red in Different Media

	λ/nm	E_{NR}[a]
water	593.2	201.7
benzyl methacrylate (BzMA)	535.1	223.6
MeO(PEG)MA/toluene (50/50)	533.6	224.2
1,2-diethoxyethane/BzMA (50/50)	532.0	224.9
BzMA/toluene (50/50) + 0.9 M MeO(PEG)I	531.0	225.3
BzMA/toluene (50/50)	530.4	225.5
P(BzMA)/toluene (50/50)	530.2	225.6
1,2-diethoxyethane	522.3	229.0
toluene	521.5	229.4
n-hexane	484.4	247.0

[a] $E_{NR} = (hcNa/\lambda) \times 10^6$ kJ mol^{-1}.

polymerization reactions discussed above is that the overall rate of polymerization is very fast compared to that of *n*-alkyl methacrylate monomers under similar experimental conditions. For example, 90% conversion is reached after ca. 1 h at 90 °C for MeO(PEG)MA whereas only about 35% conversion is achieved for methyl methacrylate under similar conditions.[2] This unusually fast rate of polymerization stimulated us to investigate these effects further. Kinetic data available for the rate coefficients of propagation for *n*-alkyl methacrylates under conventional free-radical polymerization do not show such large effects due to a change in monomer structure or due to solvent effects.[23] To determine whether alkyl ether groups affect the rate of polymerization, living radical polymerizations of benzyl methacrylate (BzMA) were carried out in a d_8-toluene solution with (a) a poly(ethylene oxide)-based macroinitiator, MeO(PEG)I (**2**), and (b) 1,2-diethoxyethane as cosolvent. Poly(ethylene glycol) dimethyl ether with M_n = 500, 750, 2000, and 5000 g mol^{-1} were transformed into initiators by condensation with 2-methyl-2-bromopropionate and used as initiators for polymerization of BzMA via copper(I)-mediated living radical polymerization. The use of oxyethylene-containing macroinitiators increased the overall rate of polymerization markedly in comparison to a similar living radical polymerization with ethyl 2-bromoisobutyrate as initiator (Figure 4). The addition of 1,2-diethoxyethane as cosolvent in the polymerization of BzMA also showed a large rate enhancement, in comparison to reactions carried out in neat d_8-toluene (Figure 4).

It seems that the increase in the rate of polymerization with an ethylene oxide-based monomer, initiator and solvent, is due to the influence of the polarity of the reaction medium, which increases with the presence of ethylene oxide units. To investigate this a solvatochromic dye, Nile Red, was employed which increases λ_{max} in the UV spectrum with an increase in the polarity of the medium.[24] The UV spectrum of Nile Red was measured in a range of different media including the polymerization medium (Table 3). There is a relationship between the overall rate of polymerization and the polarity of the medium with an increase in polarity resulting in an increase in the polymerization rate. A similar observation has been made by Armes where polymerizations were carried out in water.[25] Polymerization of MeO(PEG)MA in water at 25 °C with propyl ligand occurs so fast that online ^{1}H NMR analysis was not possible under the same experimental conditions. High conversions (>90%) were obtained in less than 10 min.

The influence of the nature of the reaction on the rate of polymerization is ascribed to a change in the nature of the copper catalyst by competitive coordination of oxyethylene groups at the metal. This was probed by measuring the ^{1}H NMR spectra of the catalyst under different conditions. Figure 5 shows the partial ^{1}H NMR spectra of *N*-(*n*-octyl)-2-pyridylmethanimine in d_8-toluene, (1) in the absence of additive and (2) in the presence of 1,2-diethoxyethane, (3) bis(*n*-Oct-L)copper in the absence of additive, (4) bis(*n*-Oct-L)copper with 1,2-diethoxyethane (1:1), and (5) bis(*n*-Oct-L)copper with 1,2-diethoxyethane (1:5). 1,2-Diethoxyethane does not influence the spectrum of *N*-(*n*-octyl)-2-pyridylmethanimine but does alter the spectrum of the copper complex. As the amount of 1,2-diethoxyethane is increased, the spectrum shifts toward that of the free ligand. The ligand is in fast dynamic equilibrium with copper on the NMR time scale. The observed NMR spectrum is an average of complexed and uncomplexed ligand. An increase of polarity favors a more "loose" catalyst structure. This is excellent evidence that the ethylene oxide groups coordinate to the copper in competition with the diimine, thus changing the nature of the active species.

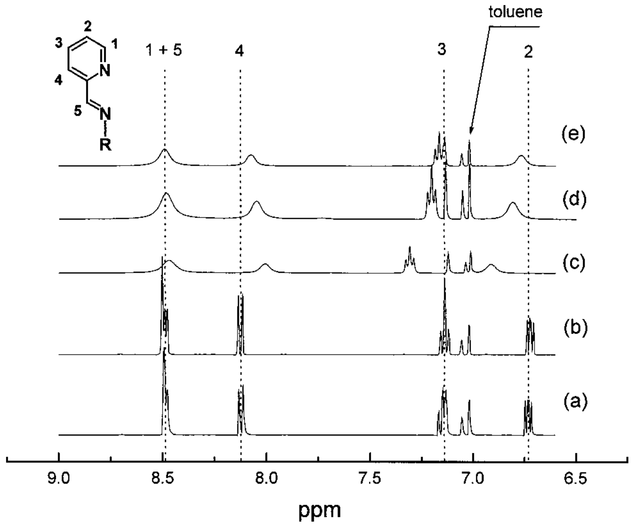


Figure 5. Partial ^{1}H NMR spectra, aromatic region, of (a) *N*-(*n*-octyl)-2-pyridylmethanimine in d_8-toluene, (b) *N*-(*n*-octyl)-2-pyridylmethanimine with the addition of 2 equiv of ethylene glycol diethyl ether, (c) bis(*N*-(*n*-octyl)-2-pyridylmethanimine)copper(I) (2:1, ligand to CuBr), (d) bis(*N*-(*n*-octyl)-2-pyridylmethanimine)copper(I) (2:1, ligand to CuBr) with 2 equiv of ethylene glycol diethyl ether, and (e) bis(*N*-(*n*-octyl)-2-pyridylmethanimine)copper(I) (2:1, ligand to CuBr) with 5 equiv of 1,2-diethoxyethane.

Experiments designed to follow the kinetics of the polymerization in situ by NMR allow monitoring of the complex throughout the reaction (Figure 6). First it is noted only one set of resonances is observed for the ligand even though it is present in excess, demonstrating rapid exchange between complexed and noncomplexed ligand. A continuous broadening of the aromatic peaks is observed upon increasing polymerization conversion. This can be ascribed to a decrease in mobility of the complex, as the viscosity increases. Broadening due to the accumulation of paramagnetic Cu(II) species in the medium can be ruled out as explanation as the other peaks (e.g., toluene) do not alter in this way.

An increase in polarity of the medium might have a marked influence on the stability of the reactants/intermediates involved in the events typical of the transition-metal-mediated living radical polymerization process, e.g., the activation/deactivation process. Charge separation in the transition state would be stabilized

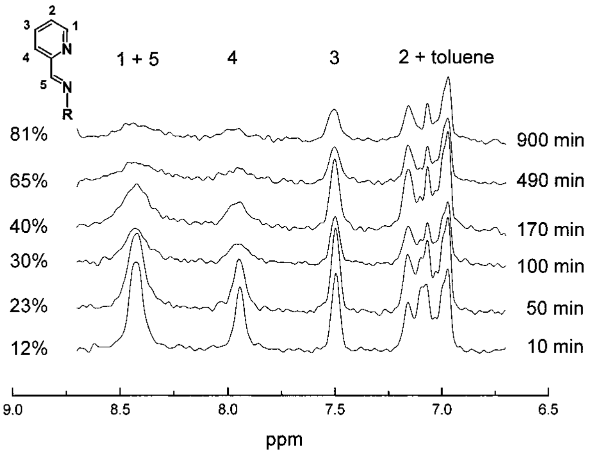


Figure 6. Partial ^{1}H NMR spectra of *N*-(*n*-octyl)-2-pyridylmethanimine ligand during the polymerization of MeO(PEG)MA in d_8-toluene at 25 °C using 3 equiv of ligand to CuBr.

by an increase in polarity of the medium. In the present case higher rate coefficients for activation and lower rate coefficients for deactivation would explain the observed increase in the overall rate of polymerization. Enhanced rate coefficients of activation upon increase of solvent polarity have been found by Chambard et al.[26] for poly(butyl acrylate) macroinitiators using 4,4′-di-*n*-heptyl-2,2′-bipyridine, which can be explained by a change in catalyst structure and/or the above elucidated change in energy levels. Contradictory results, however, were found for poly(styrene) macroinitiators.[26]

Conclusions

Online NMR has been extremely valuable in studying living radical polymerizations mediated by copper(I) catalysts. The presence of oxyethylene groups within solvent, monomer, and initiator lead to an enhanced rate of polymerization. ^{1}H NMR shows a change in the catalyst structure upon variation of the polarity of the reaction medium which mirrors the overall increase in the rate of polymerization using *N*-(*n*-alkyl)-2-pyridylmethanimine ligands. The increase in rate is ascribed to coordination of the ether groups to copper, solvating the metal displacing a diimine ligand. The dramatic increase in rate is not due to solubility effects of Cu(I) and Cu(II) species as the reactions with *N*-(*n*-alkyl)-2-pyridylmethanimine ligands are homogeneous reactions under the conditions used. These results confirm that in these systems the active catalyst is produced by displacement of a diimine ligand creating coordination sites at the metal, and it seems unlikely that a pentacoordinate square-based pyramidal copper(II) intermediate is required with this type of ligand. Thus, the mechanism of copper(I)-mediated living radical polymerization is certainly more complicated than has been previously postulated. The only other possible explanation we have for our observations is that the transition state involves a large amount of charge separation. This would also lead to an increase in the rate with increasing polarity of the solution. However, even in this case we expect the nature of the catalyst to be very different to that proposed in the case of bipyridyl. The increase in rate is not necessarily desirable as an increase in termination is also observed; this can be circumvented by reducing the levels of catalyst required or lowering the reaction temperature—an overall beneficial effect. Thus, the presence of coordinating ether groups necessitates a change in reaction conditions in order to obtain living polymerization.

Experimental Section

General Procedures. Experiments were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. NMR spectra were recorded on a Bruker AC400 spectrometer. Online ^{1}H NMR measurements to monitor polymerizations as a function of time were carried out under a nitrogen atmosphere using Young's tap NMR tubes with d_8-toluene as a locking agent. Long relaxation delays (5 s) and low spin angles (<15°) were applied to give quantitative results. FTIR spectra were recorded on a Bruker Vector 22 spectrometer equipped with an attenuated total reflection (ATR) cell. Mass spectra were measured on a Kratos MS80 spectrometer. Molar mass distributions were measured using size exclusion chromatography (SEC) at ambient temperature using a system equipped with a guard column and one mixed E column (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran as eluent, at a flow rate of 1 mL min^{-1}. Poly(MMA) standards in the range (6×10^4 to 200 g mol^{-1}) were used for calibration.

Reagents. Phenyl α-bromoisobutyrate (**1**) was synthesized from the condensation of phenol and 2-bromoisopropionyl bromide.[27] Poly(ethylene glycol) methyl ether-2-methyl-2-bromopropionate (MeO(PEG)I) was synthesized from poly(ethylene glycol) methyl ether (M_n ca. 500, 750, 2000, 5000, Aldrich) following a modified literature procedure.[28] *N*-(*n*-Propyl)-2-pyridylmethanimine and *N*-(*n*-octyl)-2-pyridylmethanimine were synthesized as previously reported[2] and stored under anhydrous conditions under nitrogen. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[29] Benzyl methacrylate (BzMA) (Aldrich, 99%) was filtered through a column of basic alumina to remove polymerization inhibitors prior to use. All other chemicals were used as purchased.

Typical Polymerization Procedure for MeO(PEG)MA. Poly[poly(ethylene glycol) methyl ether methacrylate] (targeted degree of polymerization, $DP_{Theo} = 10$) and CuBr (0.442 g, 3.1 mmol) were placed in a Schlenk tube and placed under a nitrogen atmosphere. Deoxygenated MeO(PEG)MA (10 mL, 0.031 mol), toluene, and phenyl α-bromoisobutyrate (**1**) (0.751 g, 3.1 mmol) were added at room temperature. The mixture was deoxygenated by three freeze−pump−thaw cycles after which the *N*-(*n*-propyl)-2-pyridylmethanimine ligand was added (2 mol equiv to CuBr, 6.2 mmol, 0.97 mL). Next the Schlenk tube was immersed in a thermostated oil bath at the reaction temperature (time = 0 s). Samples for analysis of the molar mass distribution (MMD) and monomer conversion were taken at different intervals throughout the reaction. Catalyst residues were removed by passing the samples through a short column of basic alumina prior to SEC and NMR analysis.

Typical Polymerization Followed by Online ^{1}H NMR. For the reactions followed in situ by ^{1}H NMR, *N*-(*n*-octyl)-2-pyridylmethanimine was used as ligand, with a molar ratio of 3:1, with respect to CuBr so to ensure that the complex was fully soluble, for all temperatures. For a $DP_{th} = 10$, the procedure was as above. MeO(PEG)MA (10.3 mmol, 5.00 g), copper (1.03 mmol, 0.147 g), *N*-(*n*-octyl)-2-pyridylmethanimine (3.09 mmol, 0.675 g), ethyl-2-bromoisobutyrate (1.03 mmol, 0.250 g), and d_8-toluene (5.00 g). An aliquot of 2 mL of this solution was transferred to a Young's tap NMR tube and with time = 0 s taken once the tube was at reaction temperature within the NMR spectrometer.

Polymerization of BzMA Using Poly(ethylene glycol) Methyl Ether 2-Methyl-2-bromopropionate (MeO(PEG)I) as Macroinitiator. A degree of polymerization of 100 was targeted. CuBr (1.13×10^{-4} mol, 0.0162 g), BzMA (11.3 mmol, 2.00 g), poly(ethylene glycol) methyl ether 2-methyl-2-bromopropionate (1.135×10^{-4} mol, 0.5855 g), and *N*-(*n*-octyl)-2-pyridylmethanimine ligand (3.40×10^{-4} mol, 0.0743 g). The polymerization was carried out as described above at 50 °C.

Polymerization of BzMA in Various Solvents. A degree of polymerization of 100 was targeted. CuBr (1.13×10^{-4} mol, 0.0162 g), BzMA (11.3 mmol, 2.00 g), solvent (2.0 mL of d_8-toluene or 1.6 g of d_8-toluene + 0.4 g of 1,2-diethoxyethane), ethyl 2-bromoisobutyrate (1.13×10^{-4} mol, 0.0221 g), *N*-(*n*-propyl)-2-pyridylmethanimine ligand (1.13×10^{-4} mol, 0.0743 g). The polymerization was carried out as described above at 50 °C.

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Supporting Information Available: Full data set for the polymerization of MeO(PEG)MA and fitting results for the data set for the polymerization of MeO(PEG)MA and BzMA in d_8-toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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