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Living Radical Polymerization of Styrene Mediated by Copper(I)/ *N*-*n*-Alkyl-2-pyridylmethanimine Catalysts

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ABSTRACT: The polymerization of styrene mediated by copper/*N*-*n*-alkyl-2-pyridylmethanimine is reported. Two different types of initiator were employed, viz., 1-phenylethyl bromide, chosen for its similar structure to the final end group of the polymer, and alkyl-2-bromisobutyrates, as models for the synthesis of diblock copolymers via macroinitiators. The copper catalyst structure was varied by changing the alkyl group on the *N*-*n*-alkyl-2-pyridylmethanimine ligand where alkyl = propyl (**3**), pentyl (**4**), and octyl (**5**) and used over a temperature range of 90−130 °C. At 90 °C, polymerization reactions were relatively slow with polymerization taking approximately 7 days to reach 100% conversion, 12 h to reach 36% conversion at 110 °C, and 7 h to reach 90% conversion at 130 °C. The PDI of the polymer broadens on increasing the temperature, reaching 1.15, 1.17, and 1.32 at 90, 110, and 130 °C, respectively, when the reaction was stopped. Thus, 110 °C is the optimal temperature for the polymerization of styrene with this type of ligand. The catalyst prepared with *N*-*n*-propyl-2-pyridylmethanimine is not completely soluble over all temperatures, and the catalyst solubility affects both the rate and the control of the polymerization. As the length of the alkyl chain increases, the solubility in nonpolar solvent also increases. Hence, *N*-*n*-pentyl-2-pyridylmethanimine is the best ligand for copper bromide to ensure homogeneity of the reaction and achieve good control over the polymerization. The effect of the solvent polarity was also investigated to elaborate the optimal polymerization conditions using xylene, anisole, and ethylene glycol diethyl ether. Based on these results, the synthesis of di- and triblock copolymers was undertaken using respectively poly(ethylene glycol) methyl ether and poly(propylene glycol) derived initiators. The latter led to an amphiphilic block copolymer with a low PDI = 1.27 and a molecular weight close to the theoretical value ($M_n^{SEC} = 10\,900$ mol g^{-1}). A large batch (40 g) of block copolymer was synthesized with a block of PS = 5000 g mol^{-1} by stopping the reaction at 50% conversion, which had [St]/[I] = 100.

Introduction

Styrene is probably the most important monomer encountered in the literature when developing new processes for radical polymerization. A wide range of publications have recently described its polymerization via various new radical polymerization techniques, e.g., iniferter mediated,[1] nitroxide mediated,[2] transition metal mediated,[3,4] and reversible addition−fragmentation chain-transfer polymerizations.[5] Styrene is not only an important monomer from an academic viewpoint, but it is also one of the most industrially important monomers and is used to produce homopolymer, statistical copolymers, and block copolymers. Commercial products are made by a whole range of processes from solution, suspension, emulsion, and anionic polymerization. Thus, it is important to be able to demonstrate the applicability of any new process for styrene.

Transition-metal-mediated living radical polymerization has been a major step forward in controlled polymerization since its inception in 1995 by both Sawamoto[4,6] and Matyjaszewski.[3,7,8] The initial polymerization studies using copper(I) in conjunction with bipyridine ligands were reported to be effective for styrene and acrylates in nonpolar solvents and in the bulk using 1-phenylethyl bromide initiators.[7] Rather broader polydispersities were achieved for MMA with ethyl acetate as solvent. Subsequent studies reported optimized conditions for styrene in bulk, in diphenyl ether solution, and in the presence of a range of additives.[9] Addition of polar additives such as water, methanol, and acetonitrile had little effect and if anything retarded the rate of reaction. Alkyl-substituted bipyridine ligands gave the narrowest polydispersities in anisole and diphenyl ether solvents, and "rules" were established for the nature of the initiator for methacrylates.[10] However, little conclusions were drawn from the choice of solvent in this work. Polymerization using copper(I)-based catalyst has generally followed this example, and the universal initiators reported by Percec also used diphenyl ether as solvent at temperatures up to 165 °C. Percec's[11,12] early work again focused on the polymerization of styrene.[13] Acrylates have subsequently been be polymerized effectively using commercially available aliphatic amine ligands in conjunction with copper(I).[14]

We have been using Schiff base *N*-*n*-alkyl-2-pyridylmethanimine ligands in association with copper(I) bromide, which has been effective for the living radical polymerization of methacrylates.[15] These catalysts work most effectively in nonpolar solvents such as toluene and xylene at between 70 and 90 °C. In contrast to the polymerization of styrene, the polymerization rate in this system is accelerated with the addition of phenols,[16] water,[17] acids,[18] and essentially just about anything that contains a N- or O-donor atom. This concurs with results published by Matyjaszewski reporting that ethylene carbonate has a "remarkable" accelerating effect on the polymerization of *n*-butyl acrylate.[19] This was ascribed to changes in solubility of the copper(I) and copper(II) species. It is noted that the color of the reaction solutions for MMA polymerization can vary considerably with copper(I) N-donor ligand complexes being bright green

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with bipyridine/copper(I) bromide and dark brown for the *N*-*n*-alkyl-2-pyridylmethanimine/copper(I) bromide systems. Fraser has reported the use of quadridentate amine ligands with a range of metals for MMA polymerization.[20] Picolylamine ligands gave relatively narrow polydispersity polymers with faster polymerization rates in anisole relative to toluene.[20] There are whole ranges of effects that are apparent from the experimental observations that have been rationalized by relatively simple explanations.

In our early work,[15,21] we reported that the *N*-*n*-alkyl-2-pyridylmethanimine ligands gave very broad polydispersities for styrene under the conditions chosen. In our original work with styrene we assumed the accepted mechanism, and this led us to accept that the results we obtained were typical for the *N*-*n*-alkyl-2-pyridylmethanimine ligands.[15,21] We concentrated on methacrylates which in themselves are a rich source of functionality and give polymers with many different applications. However, the mechanism of the reaction is far from being simple and understood. Our original experiments used similar conditions to those used for MMA with 30−50 wt % in nonpolar solvents at 90 °C. One of the most useful aspects of the *N*-*n*-alkyl-2-pyridylmethanimines is that the solubility of the complexes can be readily tuned by modification of the alkyl group. Indeed, for MMA the ligand of choice is *N*-(*n*-propyl)-2-pyridylmethanimine in toluene which gives catalysts that are soluble at reaction temperature but insoluble at ambient temperature aiding separation of product from catalyst. In thinking about the optimum conditions for styrene, we realized that the shorter alkyl chain ligands will not be completely soluble in nonpolar solvents at ambient temperature, and longer chain alkyl ligands might be more suited for styrene. Perhaps the reason for our disappointing early results can be ascribed to solubility problems and not to the redox potential of the copper complexes or the relative reactivity of the styryl radical. For these reasons, we reinvestigated styrene. This paper reports the results from this study and finds good reaction conditions for styrene.

Experimental Section

General Procedures. Reactions were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. NMR spectra were recorded on Bruker AC400 and DPX300 spectrometers. Molar mass distributions were measured using size exclusion chromatography (SEC) at ambient temperature, on a system equipped with a guard column and one 3 μm mixed E column (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran as eluent, at a flow rate of 1 mL min^{-1} at ambient temperature. Poly(styrene) standards in the range 28 500−100 g mol^{-1} were used for specific calibration.

Reagents. *N*-(*n*-Alkyl)-2-pyridylmethanimines were synthesized as previously reported[15] and stored under anhydrous conditions prior to use. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[22] Phenyl 2-bromoisobutyrate,[23] poly(ethylene glycol), and poly(propylene glycol) initiators[24] were synthesized as previously reported. Styrene was obtained from Aldrich and was filtered before utilization through a basic alumina column to remove the radical inhibitor. Xylene (98%, Aldrich), anisole (99.7%, Aldrich), ethylene glycol diethyl ether ($(EtO)_2EG$, 98%, Aldrich), ethyl 2-bromoisobutyrate (E2IBr, 98%, Aldrich), and 1-phenylethyl bromide (98%, Aldrich) were used as received. All other reagents and solvents were obtained from Aldrich at the highest purity available and used without further purification.

General Polymerization Procedure. All polymerizations were carried out using a Schlenk tube. Cu(I)Br (1 equiv, 0.131 g, 9.1 × 10^{-4} mol) was placed in a oven-dried Schlenk tube. The tube was fitted with a rubber septum and then evacuated and flushed with dry nitrogen three times so as to remove oxygen. Ethyl 2-bromoisobutyrate (1 equiv, 0.13 mL, 9.1 × 10^{-4} mol) was added. Styrene (96 equiv, 10 mL, 87 × 10^{-3} mol) and xylene (20 mL; 66% v/v) were transferred to the tube via degassed syringe. The resulting solution was degassed by three freeze−pump−thaw cycles. The mixture was stirred rapidly under nitrogen, and *N*-*n*-propyl-2-pyridylmethanimine (2 equiv, 0.28 mL, 1.8 × 10^{-3} mol) was added, which imparted a deep brown color to the solution. The resulting mixture was brought to reaction temperature (90−130 °C) in a stirred, thermostatically controlled oil bath. Samples for kinetic data were taken periodically using degassed syringes for conversion and molecular weight analysis. Conversion was measured by gravimetry: a sample was accurately weighed into a preweighed aluminum pan, and then volatile solvents and monomers were removed under vacuum in an oven at 60 °C until constant sample weight was achieved. The catalyst was removed from the samples by passing through a column of activated basic alumina prior to molecular weight analysis.

For small-scale reactions with other initiators, 1-phenylethyl bromide (**1**), phenyl 2-bromoisobutyrate (**2a**), poly(ethylene glycol), and poly(propylene glycol) initiators, the procedure was as above with the ethyl 2-bromoisobutyrate (**2b**) being replaced by either **1**, **2a**, or macroinitiator. In each case the [monomer]/[initiator] is taken as the ratio of [styrene]/[*C*−Br] groups and was 96 in each case. The calculated (theoretical) M_n = [styrene]/[initiator] × $RMM_{styrene}$ (104.15) × conversion. In each case [ligand]:[CuBr] = 2.

General Procedure for the Polymerization with MeOPEG-Based Macroinitiators: Large Batch Polymerizations. For a targeted degree of polymerization, DP_{Theo} = 100 CuBr (0.36 × 10^{-2} mol, 1.37 g) was placed in a round-bottom flask and placed under a nitrogen atmosphere. Deoxygenated Sty (0.96 mol, 100.00 g), xylene (33 vol %), and poly(ethylene glycol) methyl ether 2-methyl-2-bromopropionate (0.96 × 10^{-2} mol, 5.95 g (DP = 12), 19.90 g (DP = 45), 48.60 g (DP = 113)) were added at room temperature. The mixture was deoxygenated by bubbling N_2 over 30 min, after which the *N*-(*n*-propyl)-2-pyridylmethanimine ligand was added (2 mol equiv to CuBr, 1.92 × 10^{-2} mol, 2.9 mL). Subsequently, the round-bottom flask was immersed in a thermostated oil bath at the reaction temperature (time = 0 s). The reaction conversion was measured by ^{1}H NMR by integration of the vinylic protons signals (5.5 and 6.0 ppm) and the backbone CH and CH_2 (1.0−1.5 ppm).

Isolation and Purification of Polymers. Polymers used in synthetic experiments were prepared by reactions mediated by copper bromide complexed with *N*-*n*-pentyl-2-pyridylmethanimine ligands. This complex was soluble in a monomer/xylene mixture at reaction temperature but relatively insoluble at room temperature. After the polymerization was complete, the solution was cooled to room temperature, and the polymer was purified by passing the solution over basic alumina column and subsequent precipitation into methanol.

Results and Discussion

Styrene was polymerized by living radical polymerization in the presence of copper bromide complexed with selected *N*-*n*-alkyl-2-pyridylmethanimine ligands in xylene solution. 1-Phenylethyl bromide (**1**) was used as the initiator, due to its similar structure to the dormant terminal unit of polystyrene, in addition to phenyl 2-bromoisobutyrate (**2a**), which is similar to the initiators previously reported for the polymerization of methacrylates using these catalysts (Figure 1).[15] Initial experiments were carried out using a catalyst based on the *N*-*n*-pentyl-2-pyridylmethanimine (**4**)/Cu(I)Br complex at 110 °C in xylene (50% v/v) with both **1** and **2a**. In both cases, good first-order kinetics were observed (Figure 2a), with the rate of polymerization 4 times faster for **1** relative to **2a** (k_p[Pol*] = 0.0053 and 0.0013

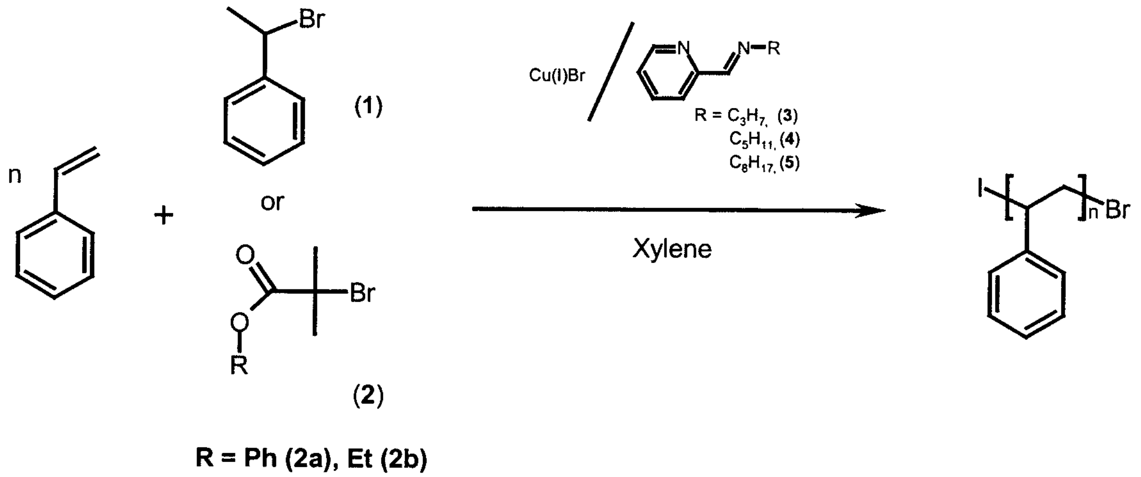

Figure 1. Polymerization of styrene mediated by *N*-*n*-alkyl-2-pyridylmethanimine/Cu(I)Br, initiated with 1-phenylethyl bromide (**1**) or phenyl-2-bromoisobutyrate (**2a**), in xylene solution.

mol dm^{-3} for **1** and **2a**, respectively), with some curvature for **1** at the start of the reaction. This results in 90% conversion obtained for **1** over 7 h and 45% conversion for **2a** over the same time period. The number-average molecular weight increases linearly with conversion (Figure 2b), following the theoretical line, while the polydispersity stays approximately constant with conversion. The PDI is relatively high when compared to that of methacrylate polymerization (1.2 < PDI < 1.5). This is extenuated with **1**, which should to be a slower initiator than **2a**. However, slow initiation is not seen in either the first-order rate plot which has no “induction period” or the evolution of M_n. Faster initiation with **2a** results in increased small radical–radical coupling at the start of the reaction, giving a quick buildup of copper(II), *the persistent radical*. Copper(II) acts as an inhibitor for the polymerization, reducing the rate of termination throughout the propagation, “the persistent radical effect” as described by the seminal work of Fischer.[25] Thus, the slower initiation from **1** actually results in a faster propagation and poorer control, as a direct consequence of this effect. Hence, slow initiation results in poor control over the polymerization. The effect of concentration of the monomer was investigated with **2a** in xylene using concentrations of monomer of 50% v/v and 33% v/v. Surprisingly, there is little difference in the rate of reaction (Figure 3a). This is ascribed to a reduced rate of initiation at 33% v/v seen as an induction period that is balancing the persistent radical effect. The plots of molecular weight and PDI vs concentration are similar in both cases with relatively narrow PDI in each case (Figure 3b).

These results suggest that initiators based on isobutyrates are more efficient in the control of the polymerization of styrene due to a faster rate of initiation leading to an acceleration in increasing the persistent radical which is necessary for controlled M_n and narrow PDI polymers. We have previously reported the facile synthesis of macroinitiators by esterification reaction, resulting in an initiator of structure ***R***-2-isobutyrate with ***R*** being the first block of a copolymer.[24] These types of initiator and macroinitiator are easily prepared and are very versatile. Thus, ethyl 2-bromoisobutyrate, **2b**, and macroinitiators with similar structures were chosen as the initiators for the remainder of this study. When macroinitiators were employed, the solvent was generally used at a concentration of 66% v/v to monomer

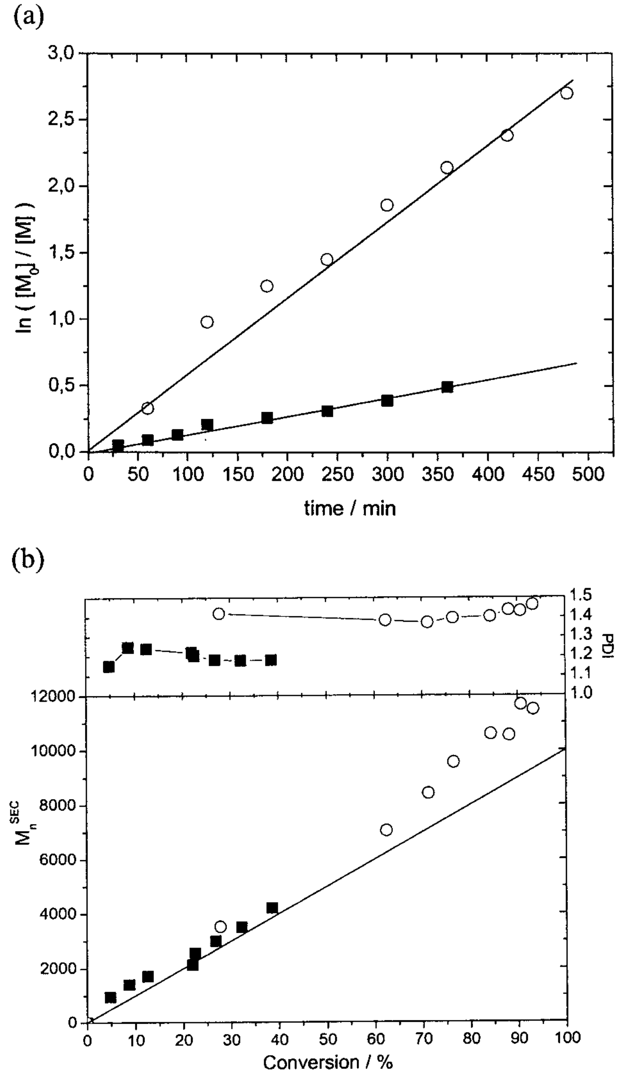

Figure 2. Polymerization of styrene with *N*-*n*-pentyl-2-pyridylmethanimine (**4**)/Cu(I)Br, initiated with 1-phenylethyl bromide (**1**) (○) or phenyl 2-bromoisobutyrate (**2**) (■), in xylene (50% v/v) at 110 °C, [Sty]:[initiator] = 96. (a) First-order kinetic plot; lines are regression fit through data points. (b) Evolution of the molecular weight with conversion; line is theoretical M_n, where $M_{n(theo)}$ = RMM$_{monomer}$ × [monomer]/[initiator] × % conversion.

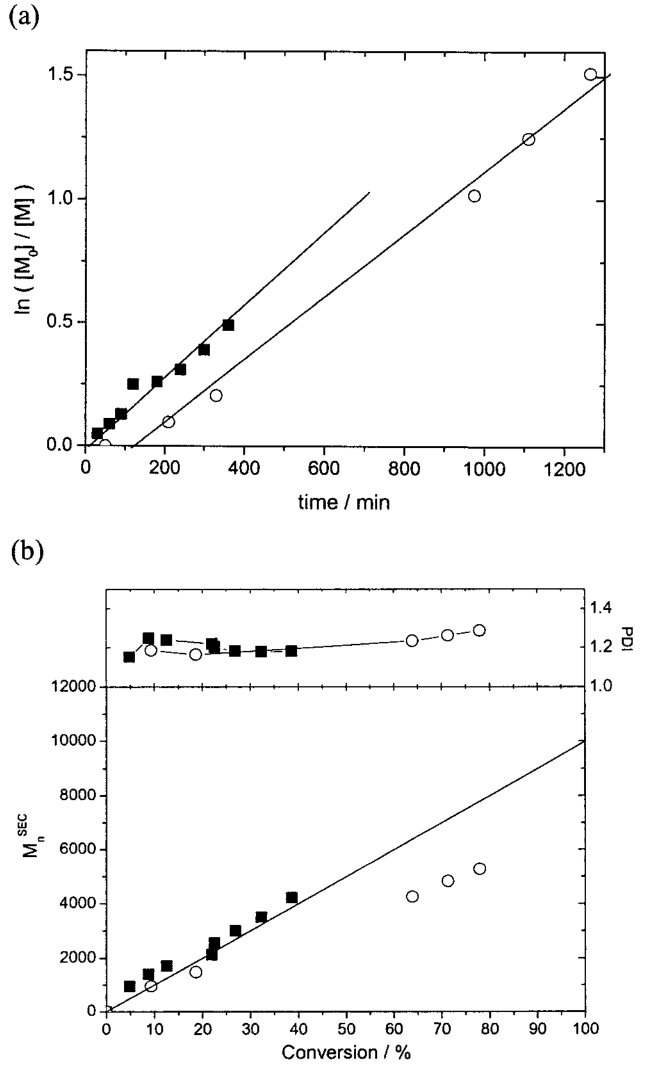

Figure 3. Polymerization of styrene mediated by *N*-*n*-pentyl-2-pyridylmethanimine (**4**)/Cu(I)Br, initiated with phenyl 2-bromoisobutyrate (**2**) in xylene 33% v/v (○) and 50% v/v (■) at 110 °C, [Sty]:[initiator] = 96. (a) First-order kinetic plot; lines are regression fit through data points. (b) Evolution of the molecular weight with conversion; line is theoretical M_n, where $M_{n(theo)} = \mathrm{RMM}_{monomer} \times [\mathrm{monomer}]/[\mathrm{initiator}] \times \%$ conversion.

to ensure the full solubility of the macroinitiator. As the concentration of the solvent does not seem to greatly influence the polymerization (see above), these conditions were also used for the remainder of this study.

Influence of the Ligand on the Polymerization of Styrene. *N*-Alkyl-2-pyridylmethanimine ligands have a high degree of π conjugation and are good electron acceptor ligands for copper(I). These ligands are easily prepared via the condensation of pyridine-2-carboxaldehyde and virtually any primary amine[15] (Figure 4). The structure of the primary amine used determines many of the physical properties of the resultant imine ligand and its transition-metal complexes, such as its affinity for different solvents, monomers, etc. Solubility in both hydrophilic and hydrophobic solvents may be controlled by the nature of the alkyl chain. The copper catalyst is an ionic salt; thus, short chain alkyl groups prefer hydrophilic solvents/monomers, and longer chain alkyl groups impart solubility in hydrophobic reaction mixtures. We have previously reported that the optimum ratio of ligand to copper for MMA is approximately 2:1.[15] A similar finding was made by Matyjaszewski et al. for styrene.[26] All polymerizations were carried out using this ratio of reagents.

To determine the importance of the catalyst structure over the control of polymer architecture and rate of polymerization, a series of *N*-*n*-alkyl-2-pyridylmethanimine ligands were investigated (R = propyl, **3**, pentyl, **4**, and octyl, **5**). Ethyl 2-bromoisobutyrate was used as the initiator in each case. The first-order rate plots (Figure 5a) show that polymerization occurs with all *N*-*n*-alkyl-2-pyridylmethanimines ligands for copper(I)-mediated polymerization of styrene at 90 °C. In the case of **3**, slow initiation followed by an increase in the concentration of the active species resulted in an increase of the rate of polymerization ($R_p = k_p[\mathrm{Pol}^*]$, where Pol* is the active propagating species as yet undefined). This is due to the partial solubility of the various complexes involved in the reaction, as yet unidentified copper(I) and copper(II) species. The increase in rate is probably due to the copper(II) species formed during the reaction, which act as deactivators, being less soluble than the activating copper(I) species. This is similar to that observed in going from the propyl to ethyl ligand in MMA polymerization, which shows a similar increase in rate due to precipitation of copper(II) species in a more polar medium than in the present case. In each case the M_n increases fairly linearly with conversion. Reactions with **3** showed residual nondissolved amounts of catalyst complex in the Schlenk tube while **4** and **5** were fully homogeneous at the beginning of the reaction (Figure 6). Both **4** and **5** show first-order kinetics consistent with a living system. In the case of such a low temperature (90 °C), the polymerizations are slow with 100% conversion achieved after approximately 7 days. When the reaction is monitored over these long time periods, a linear increase in M_n with conversion is observed, and PDI remains approximately = 1.20 (Figure 5b, Table 1). At 90 °C the observed value is approximately 50% of the theoretical value. This cannot be due to autopolymerization as it occurs at the lowest temperature used, and no high molecular weight peak is observed in the SEC. We have no explanation for these observations at the present time. Polymerizations of methacrylates are generally homogeneous with **3**, **4**, or **5** as ligands. This is due to the lower polarity of the reaction medium in the case of styrene, which is insufficient to solubilize the ionic catalyst.

Polymerizations at higher reaction temperatures were investigated to increase the rate of polymerization while achieving polymers with narrow PDI and maintaining

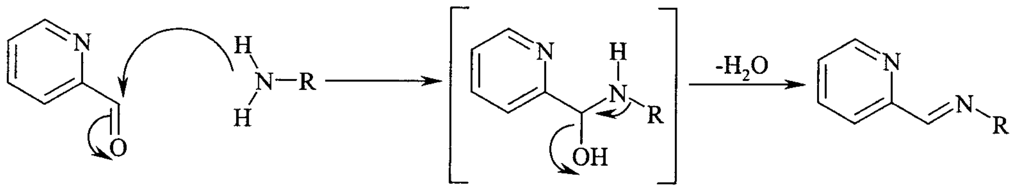

Figure 4. Schiff base condensation reaction.

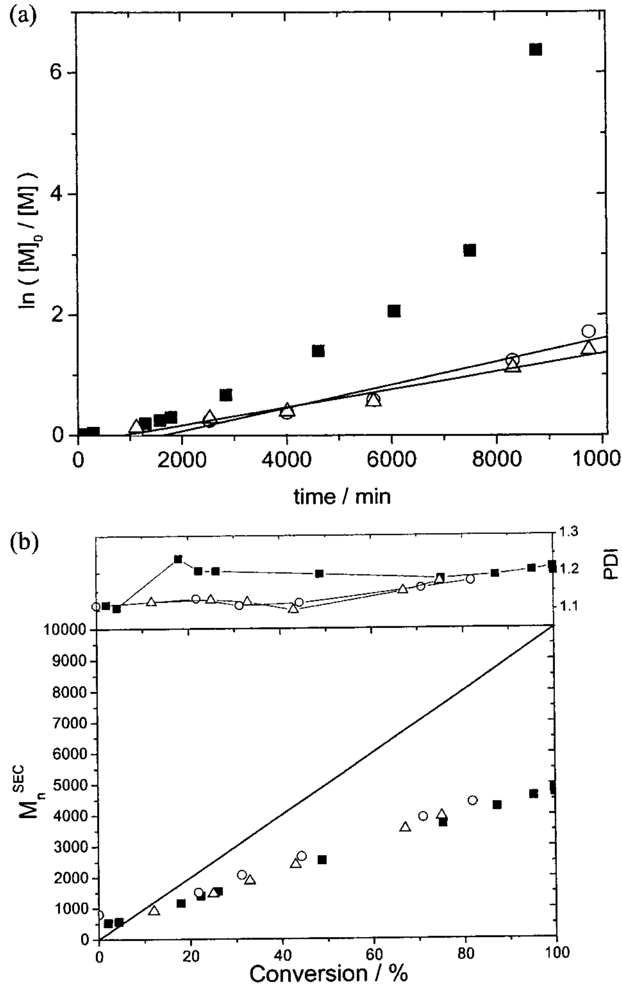

Figure 5. Polymerization of styrene mediated by *N*-*n*-alkyl-2-pyridylmethanimine/Cu(I)Br, initiated with ethyl 2-bromoisobutyrate in xylene at 33% v/v at 90 °C, propyl (■), pentyl (○), and octyl (△) ligands; [Sty]:[initiator] = 96. (a) First-order kinetic plot; lines are regression fit through (○) and (△) data points. (b) Evolution of the molecular weight with conversion; line is theoretical M_n, where $M_{n(theo)} = RMM_{monomer} \times [monomer]/[initiator] \times \%$ conversion.

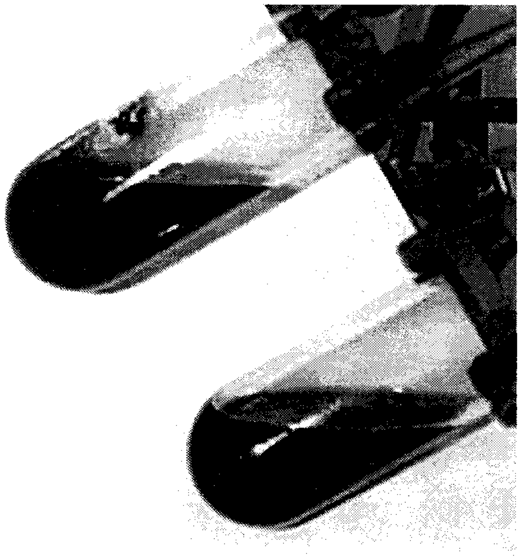

Figure 6. Reaction media in Schlenk tubes using *N*-*n*-propyl-2-pyridylmethanimine (**3**) as ligand (upper) and of *N*-*n*-octyl-2-pyridylmethanimine (**5**) (lower).

Table 1. Summary of the Final Properties of Polystyrene Obtained by Copper Mediated Living Radical Polymerization; [Styrene]/[Ethyl 2-Bromoisobutyrate] = 96, [Ligand]/[CuBr] = 2, 33% v/v in Xylene Solution

ligand	temp (°C)	time (min)	conv (%)	M_n SEC	PDI
3	90	10080	100	5700	1.15
4	90	9755	82	5300	1.10
5	90	9755	75	4800	1.08
3	110	700	36	4600	1.17
4	110	1265	78	5400	1.07
5	110	1265	60	3800	1.15
3	130	650	89	12700	1.32
4	130	640	94	8600	1.30
5	130	645	78	12900	1.40

a concentration of 33 v/v % with [M]/[I] = 96. At 110 °C (Figure 7, Table 1) the propyl ligand derived catalyst, **3**, is still partially soluble at this temperature, resulting in a less controlled polymerization. However, in the case of **4** and **5**, a more controlled polymerization is obtained, leading to final products with narrow PDI (Table 1). The first-order rate plots for both **4** and **5** increase linearly with time, indicating little termination. The slight deviation from passing through the origin can be attributed to slow initiation with respect to propagation. The molecular weights increase linearly with conversion but deviate from the theoretical values (Figure 7b). As the polymerizations were still much slower than for MMA at 90 °C (80% conversion after 21 h), the temperature was further increased to 130 °C (Figure 8, Table 1). The lower rate of polymerization of styrene with respect to MMA is usually explained by the production of a secondary radical stabilized by the aromatic ring. However, an alternative explanation can be considered. Methyl methacrylate is significantly more polar than styrene due to its ester functionality, making it a better solvent/coordinator copper(I). Indeed, it is envisaged that methacrylates coordinate to copper(I) via oxygen donor interactions. Thus, we might expect a change in medium polarity to influence control in the polymerization of styrene when using *N*-*n*-alkyl-2-pyridylmethanimine ligands. At 130 °C the reactions were fast, exhibiting good kinetic behavior (Figure 8a), but the PDI broadens significantly throughout the polymerization (Figure 8b, Table 1). This effect is ascribed to increased of termination reactions from radical−radical reactions due to the higher reaction temperature. Polymerizations with the longer chain ligand **5** show a slower rate of polymerization as compared to the cases of **3** and **4**. This could be due to the steric hindrance of the long aliphatic chain, which will affect the approach of polymer chains, leading to a lower rate of activation and slow down the complex rate of diffusion through the reaction solution. The molecular weight of polystyrene produced increases linearly with conversion for all three reactions, with a slight deviation for **3** (Figure 8b). The molecular weights of the final products are close to the theoretical, with a broader polydispersity than at 110 °C (Table 1).

For all temperatures, the product obtained using **3** is easily purified, as on cooling, the catalyst precipitates, and a filtration through basic alumina leaves the products essentially metal free. As the alkyl chain length is increased, the solubility of the catalyst increases at ambient temperature, which results in less precipitation prior to filtration. *N*-*n*-Alkyl-2-pyridylmethanimines are effective in conjunction with copper(I) bromide for the living polymerization of styrene to polymers with a linear increase in M_n and narrow PDI over acceptable time scales. In all cases an increase in

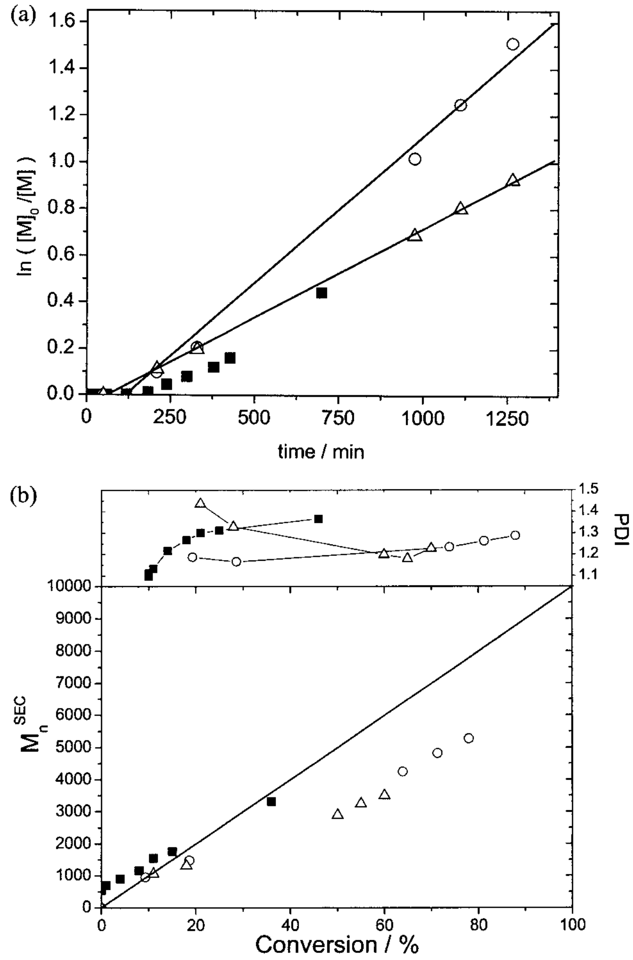

Figure 7. Polymerization of styrene mediated by *N*-*n*-alkyl-2-pyridylmethanimine/Cu(I)Br, initiated with ethyl 2-bromoisobutyrate in xylene at 33% v/v at 110 °C, propyl (■), pentyl (○), and octyl (△) ligands; [Sty]:[initiator] = 96. (a) First-order kinetic plot; lines are regression fit through data points. (b) Evolution of the molecular weight with conversion; line is theoretical M_n, where $M_{n(theo)}$ = $RMM_{monomer}$ × [monomer]/[initiator] × % conversion.

termination is observed at higher temperatures. At 90 °C, polymerization reactions are too slow, and thus 110 °C is the optimal temperature under these conditions for styrene. *N*-*n*-Propyl-2-pyridylmethanimine is not completely soluble over all temperatures, and catalyst solubility affects both the rate and the control of the polymerization. Hence, *N*-*n*-pentyl-2-pyridylmethanimine is the best ligand for copper bromide to ensure homogeneity of the reaction and achieve good control over the polymerization. The control achievable is illustrated by copper/*N*-*n*-pentyl-2-pyridylmethanimine-mediated polymerization of styrene at 110 °C, with a targeted degree of polymerization of 50 and 200 (Table 2).

Influence of the Solvent on the Copper-Mediated LRP of Styrene. The nature of the solvent can have a dramatic effect on the rate of polymerization for methacrylates[19] and a less pronounced effect for styrene.[9] We have previously reported on an increase in the rate of methacrylate polymerization when introducing oxyethylene groups in the reaction medium.[16] Experiments were carried out to examine the solvent influence in the polymerization of styrene with the copper(I) bromide/**4** complex at 110 °C. Polymerizations were carried out in diethyl ether ethylene glycol ((EtO)$_2$EG) and anisole as solvent. The kinetic plots (Figure 9) show the opposite effect than that for MMA. An increase in the polarity of the solvent results in a decrease in the rate of reaction with a more pronounced effect with anisole than with (EtO)$_2$EG. This confirms the previous observation of Percec et al.[11] on the effect of the polar solvent on the solubility of the catalyst. However, an alternative explanation can be considered. Previous studies by Zammit et al.[27] showed that solvent has an effect on the conventional free radical polymerization of styrene. This influences both the activation energy and preexponential factors in the propagation

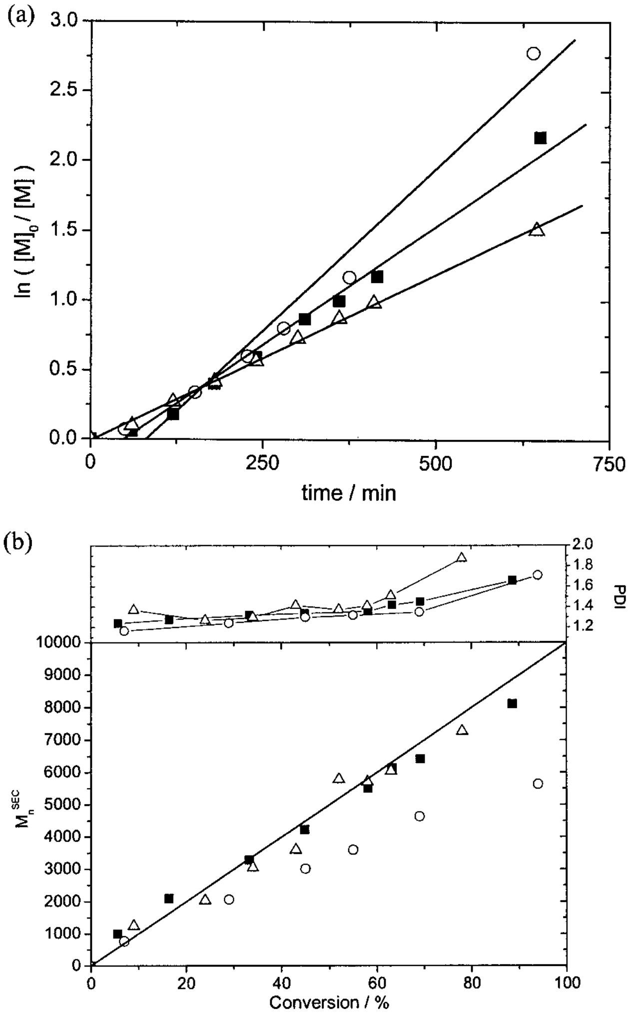

Figure 8. Polymerization of styrene mediated by *N*-*n*-alkyl-2-pyridylmethanimine/Cu(I)Br, initiated with ethyl 2-bromoisobutyrate in xylene at 33% v/v at 130 °C, propyl (■), pentyl (○), and octyl (△) ligands; [Sty]:[initiator] = 96. (a) First-order kinetic plot; lines are regression fit through data points. (b) Evolution of the molecular weight with conversion; line is theoretical M_n, where $M_{n(theo)}$ = $RMM_{monomer}$ × [monomer]/[initiator] × % conversion.

Table 2. Summary of the Final Properties of Polystyrene for Various Degrees of Polymerization in Various Solvents; [Styrene]/[Ethyl 2-Bromoisobutyrate] = 96, [4]/[CuBr] = 2, 33% v/vin Xylene Solution at 110 °C

DP	solvent	time (min)	conv (%)	M_n	PDI
50	xylene	1423	81	4200	1.38
100	xylene	1265	78	5400	1.07
200	xylene	1423	76	12900	1.40
100	xylene	1265	78	5400	1.07
100	anisole	3180	68	6200	1.33
100	(EtO)$_2$EG	3180	84	8100	1.51

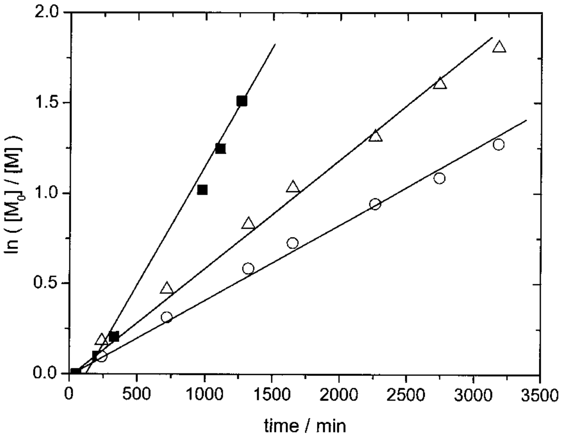

Figure 9. Kinetic plots for the polymerization of styrene mediated by **4**/Cu(I)Br, initiated with ethyl 2-bromoisobutyrate in xylene (33% v/v) (■), anisole (33% v/v) (○), and (EtO)$_2$EG (33% v/v) (△) at 110 °C; [Sty]:[initiator] = 96 lines are regression fit through data points.

reaction, which supports a solvent–radical complexation that can result in stabilization of the radical. Chambard et al. have reported on the effect of solvent polarity on the activation process during the copper-mediated living radical polymerization process.[28] Experiments carried out in xylene, dioxane, butyl acetate, 1-butanol, and dimethylformamide (DMF) as solvent showed that the activation rate parameter decreases when increasing the polarity of the solvent or when the solvent is able to act as ligand on the copper catalyst (dioxane and DMF). These observations also offer an explanation for the decrease in the polymerization rate. The difference between anisole and (EtO)$_2$EG is however not well understood. Table 2 summarizes the final properties of the various products obtained by polymerization in the different solvents.

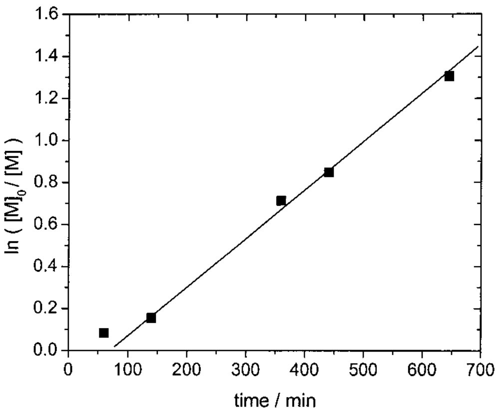

Figure 10. First-order kinetic plot for the polymerization of triblock copolymer of styrene with poly(propylene glycol) macro-diinitiator mediated by **4**/Cu(I)Br, in xylene 33% v/v at 110 °C.

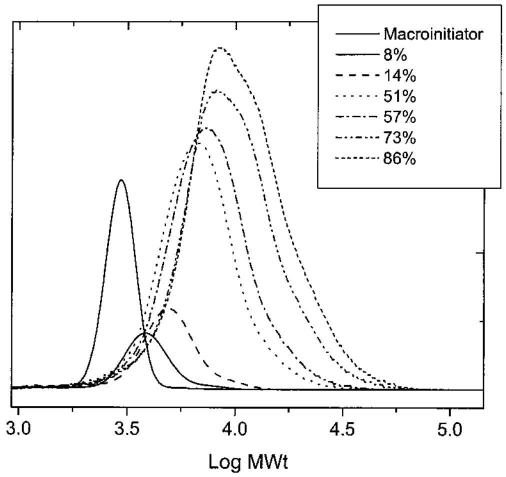

Figure 11. Evolution of the molecular weight distribution for the polymerization of triblock copolymer of styrene with poly(propylene glycol) macro-diinitiator mediated by **3**/Cu(I)Br, in xylene 33% v/v at 110 °C.

Table 3. Summary of the Final Product Properties of the Polymerization of Styrene with MeOPEG Initiators; [Styrene]/[Initiator] = 96, [4]/[CuBr] = 2, 33% v/v in Xylene Solution at 110 °C

polymer	M_n(MeOPEG) (g mol^{-1})	M_n(PS) NMR (g mol^{-1})	M_n SEC (g mol^{-1})	PDI
MeOPEG$_{113}$-*b*-PS	5060	19000	23250	1.27
MeOPEG$_{113}$-*b*-PS	5060	12000	12700	1.17
MeOPEG$_{45}$-*b*-PS	2070	9000	12800	1.16
MeOPEG$_{12}$-*b*-PS	620	3500	4640	1.22

Synthesis of Poly(styrene) Containing Block Copolymers. Living polymerization is the method of choice for the synthesis of acrylic block copolymers. To demonstrate the ease of poly(styryl) containing block copolymers via *N*-*n*-alkyl-2-pyridylmethanimine ligands, triblock copolymers with poly(propylene glycol) (PPG; 2000 g mol^{-1}) midblocks and diblock copolymers with poly(ethylene glycol) methyl ether (MeOPEG; 500, 2000, and 5000 g mol^{-1}) were synthesized. Block copolymers were synthesized via the macroinitiator approach to give block copolymers with interesting amphiphilic properties. The optimal conditions for the polymerization of styrene, as above, were employed at 110 °C with ligand **4**. Both macroinitiators were prepared via an esterification reaction using 2-bromoisobutyryl bromide and the (di)hydroxy group of MeOPEG or PPG, as reported previously.[24,23] The kinetic plot for the polymerization of styrene initiated by PPG in xylene is shown in Figure 10. This polymerization was also carried out in anisole, (EtO)$_2$EG, and xylene to different length A blocks; see Supporting Information for full data sets. The linear relationship between ln([M]$_0$/[M]) and time shows a constant concentration of active species and illustrates the living character of the system. The rate of polymerization is slower in the first few hours of the reaction, due to slow initiation by the macroinitiator. Figure 11 shows the evolution of the molecular weight distribution with conversion. The molecular weight increases with time, keeping a low PDI. At high conversion (80%) a bimodal distribution is observed. This can be explained by bimolecular termination by combination, leading to polymer chains showing molecular weight twice bigger than the growing species; this is not observed for MMA where termination by combination is less prevalent. The final product has a relatively low PDI = 1.27 with a molecular weight close to the theoretical value (M_n^{SEC} = 10 900 mol g^{-1}). This is good evidence of the synthesis for an ABA copolymer, with A = PSty and B = PPG.

The same polymerization conditions were used with MeOPEG-derived initiators. To demonstrate the viability of this process, a large batch of product was targeted with approximately 40 g of product obtained in each case (Table 3). When a DP < 100 was targeted, polymerizations were stopped at lower conversions equivalent to the molecular weight aimed for; e.g., PSt = 5000 g mol^{-1} was obtained by stopping the reaction at 50% conversion, which had [St]/[I] = 96.

Conclusions

Copper(I) bromide mediated living radical polymerization is efficient in the polymerization of styrene in xylene solution in conjunction with *N*-*n*-alkyl-2-pyridylmethanimines. Alkyl 2-bromoisobutyrate initiators with various catalyst complexes were utilized by varying the *N*-alkyl-2-pyridylmethanimine ligand used at different temperatures. The optimal conditions were obtained with *N*-pentyl-2-pyridylmethanimine (**4**) copper complexes in a ratio ligand/Cu(I) = 2/1 at 110 °C. The influence of the solvent was examined, and an increase in the solvent polarity decreases the polymerization rate, in contrast to that previously observed for MMA. These conditions were applied in the synthesis of a amphiphilic diblock and triblock styrene containing copolymers, using poly(ethylene glycol) methyl ether and poly(propylene glycol) macroinitiators. Products exhibiting narrow polydispersity and a molecular weight close to the theoretical at quantities up to 40 g were obtained.

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Supporting Information Available: Full data sets for polymerization reactions reported. This material is available free of charge via the Internet at http://acs.pubs.org.

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