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Low-Temperature Living “Radical” Polymerization (Atom Transfer Polymerization) of Methyl Methacrylate Mediated by Copper(I) *N*-Alkyl-2-Pyridylmethanimine Complexes

David M. Haddleton,* Dax Kukulj, David J. Duncalf, Alex M. Heming, and Andrew J. Shooter

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

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ABSTRACT: This paper demonstrates that atom transfer polymerization of methyl methacrylate mediated by CuBr/*N*-alkyl-2-pyridylmethanimine complexes in toluene proceeds effectively at temperatures as low as 15 °C, while maintaining control over molecular weights and yielding narrow polydispersity indexes. The reaction can even be performed at −15 °C with a number average molecular weight, M_n, of 6980 and a polydispersity, PDI, of 1.28 being achieved in 116 h; however, the molecular weight control is less effective. The polymerizations were performed at 90, 60, 40, and 15 °C with the first-order rate plots, molecular weight vs conversion plots, and final polydispersity indexes consistent with little or no termination—*living/controlled* polymerization. Methyl hydroquinone (MeHQ) has been demonstrated to accelerate the polymerization by a factor of 3−4 at temperatures below 40 °C. An activation energy, E_a, for polymerization in the absence of phenol was determined to be 60.3 kJ·mol^{-1} and is significantly reduced to 44.9 kJ·mol^{-1} in the presence of MeHQ. These results suggest that coordinating phenols modify the active polymerization center. The stereochemistry of the polymers produced are consistent with that observed for conventional free-radical polymerization in that the fraction of syndiotactic arrangements increases as the reaction temperature is lowered. At 90 °C, 59.1% *rr* triads are obtained with a persistence ratio of 0.924 and at −15 °C, 71.5% *rr* triads are obtained.

Introduction

Living/controlled polymerization of vinyl monomers is a route to a wide range of well-defined polymers. It allows the design, and subsequent synthesis, of macromolecules with narrow molecular weight distribution, targeted number average molecular mass (M_n), specific end groups, and unusual geometry/topology.[1,2] Traditionally this has been accomplished by living ionic polymerization techniques. One of the major limitations of ionic polymerization is difficulty in polymerizing monomers containing polar and/or functional groups, e.g., hydroxyethyl methacrylate, methacrylic acid, and glycidyl methacrylate, as they can complicate reaction pathways. Functional monomers, such as these, can be readily polymerized via free-radical routes, and as such, the development of living free-radical processes has been the focus of much activity in recent years.

The nitroxide-mediated free-radical polymerization of styrene has been shown to be successful; however, it is somewhat limited in its monomer set and often requires temperatures greater than 130 °C with reaction times of days, even under bulk polymerization conditions.[3−9] The most recent development in controlled free-radical polymerization has been transition-metal-mediated living free-radical polymerization. Transition-metal-mediated living free-radical polymerization offers a more versatile route, being effective for a range of monomers, and has been achieved with a range of transition metal systems including Cu^IX/bipyridines (X = Cl, Br),[10−15] Cu^IX/Schiff base complexes,[16−19] $RuCl_2(PPh_3)_3$,[20−22] and $[Ni\{o,o'\text{-}CH_2NMe_2)_2C_6H_3\}Br]$.[23]

To date transition-metal-mediated living free-radical polymerization has been reported to be effective at temperatures between 60 and 130 °C and is usually carried out at above 80 °C so as to obtain acceptable rates of polymerization. Percec *et al.* has studied the rate of initiation of arenesulfonyl halides, utilizing a copper(I)/dinonylbipyridene catalyst, with methyl methacrylate (MMA) and styrene at 23 °C and stated that polymerization did not occur under the reactions conditions used.[24,25] There has been an example of palladium-catalyzed polymerization MMA at 20 °C;[26] however, the polydispersity was high (≈1.8) and the control over M_n poor.

Atom transfer polymerization has been developed from the Kharash transition-metal-mediated radical addition and cyclizations used extensively in organic synthesis.[27,28] In organic synthesis, elevated temperatures have often been employed to achieve acceptable rates of reaction, e.g., the intramolecular cyclization of (trichloromethyl)alkenes with a range of Ru(II), Fe(II), and Mo(I) compounds at 155 °C[29] and the cyclization of *N*-allyltrichloroacetamides catalyzed by $RuCl_2(PPh_3)_3$ in hydrocarbon solvent at 140 °C.[30] This latter reaction also proceeds at 80−110 °C catalyzed by Cu^ICl in acetonitrile solvent.[30] However, similar reactions have been demonstrated at much lower temperatures. For example, N-protected allyltrichloroacetamides cyclize readily at room temperature when the N atom is substituted with an electron-withdrawing group such as tosyl with both Cu^ICl/acetonitrile and $RuCl_2(PPh_3)_3$ catalysts.[31] When CuCl/bipyridine has been used, the corresponding lactams were produced in good yield at temperatures as low as −78 °C.[31] Thus it is apparent that with the appropriate transition metal catalyst,

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* Author for correspondence. Telephone: +44 1203 523256. Fax: +44 1203 524112. E-mail: msrgs@snow.csv.warwick.ac.uk.

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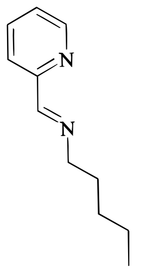
coordinated to electron-withdrawing ligands, atom transfer chemistry can proceed at ambient or subambient temperatures.

We have recently reported the use of copper(I) bromide complexes of **1** or **2** in conjunction with initiator ethyl 2-bromoisobutyrate, **3**, as an efficacious atom transfer polymerization system for the controlled polymerization of methacrylates.[16−19] In our studies, we have fortuitously observed that this system will lead to effective polymerization at ambient temperatures. Our initial observation was that polymerization of methyl methacrylate (MMA) initiated by **3** in the presence of CuBr and 3 equiv of **2** went to high conversion at ambient temperature on leaving overnight. Leading from this, we have investigated the reaction over a range of temperatures, from −15 to +90 °C. In addition the effect of 4-methoxyphenol (methylhydroquinone, MeHQ) and phenol at various temperatures was studied.



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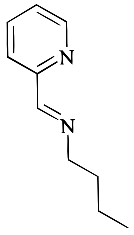

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Experimental Section

General Information. All reactions were carried out using standard Schlenk line techniques under a nitrogen atmosphere. Methyl methacrylate (Aldrich, 99%) was purified by passing through a column of activated basic alumina to remove inhibitor. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[32] *N*-(*n*-butyl)-pyridylmethanimine (**2**) was synthesized as described previously.[17] Toluene (Fisons, 99.8%) was dried over sodium. Ethyl 2-bromoisobutyrate (**3**) (Aldrich, 98%), phenol (May & Baker, 99%), and 4-methoxyphenol (Aldrich, 98%) were used as received.

Preparation of *N*-(*n*-Pentyl)-2-pyridylmethanimine (1). *n*-Pentylamine (24.4 mL, 0.21 mol, Aldrich, 99%) was added dropwise to pyridine-2-carboxaldehyde (20.0 mL, 0.21 mol, Aldrich, 99%) with stirring in an ice bath. After complete addition of the amine, approximately 5 g of dried magnesium sulfate was added and the reaction left for a further 2 h. The solution was filtered and distilled under reduced pressure. The product was collected at 60 °C, 0.4 mbar. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.60$ (d, 1H), 8.33 (s, 1H), 7.94 (d, 1H), 7.69 (t, 1H), 7.27 (t, 1H), 3.63 (t, 2H), 1.69 (sex, 2H), 1.31 (overlapping quintets, 2H each), 0.87 (t, 3H).

Typical Polymerization Procedure. A stock solution of MMA (25.0 g, 0.25 mol), toluene (75.0 g), *N*-(*n*-pentyl)-pyridylmethanimine (**1**) (1.32 g, 7.46×10^{-3} mol), and ethyl 2-bromoisobutyrate (0.487 g, 2.50×10^{-3} mol) was prepared and degassed by three freeze−pump−thaw cycles. The fraction of MMA in toluene was 25% w/w. Appropriate amounts of Cu^IBr (0.0949 g, 6.61×10^{-4} mol), 4-methoxyphenol (methyl hydroquinone, MeHQ) (0.822 g, 6.61×10^{-3} mol), and phenol (0.623 g, 6.61×10^{-3} mol) were respectively added to three Schlenk flasks, which were purged with nitrogen. A 30 mL (27.1 g) portion of the stock solution was added to each Schlenk flask, and then they were placed in an oil bath at the appropriate temperature. Samples were taken periodically for conversion and molecular weight analysis.

Analysis Methods. Conversion was measured by gravimetry by drying to constant weight in a vacuum oven at 70 °C. The catalyst was removed from the samples for molecular weight analysis by passing through a column of activated basic alumina. Molecular weight distributions were measured using size exclusion chromatography (SEC), on a system equipped with a guard column and one mixed E column (Polymer Laboratories) with differential refractive index detection, using tetrahydrofuran at 1 mL·min^{-1} as an eluent. Poly(MMA) standards in the range (6×10^4 to 200 g·mol^{-1}) were used to calibrate the SEC. The polymer microstructure was analyzed using ^{13}C NMR on a Bruker AC400 spectrometer operating at 100.63 MHz with over 20 000 scans and a relaxation delay of 1 s.

Results and Discussion

Before the discussion of specific observations, it needs to be shown that at all the temperatures studied the atom transfer polymerization reaction is operating effectively, i.e., *living/controlled* polymerization. This is established by three primary features. (i) The first-order rate plot (ln $[M]_0/[M]$ vs time) should be linear, indicating that the concentration of active species is constant throughout the reaction (i.e., effects from termination are small). The gradient of this plot is equal to the pseudo first-order rate coefficient, k^{app}, which gives an indication of the rate of reaction. k^{app} is defined by

$$\ln\frac{[M]_0}{[M]} = k_p[Pol^*]t = k^{app}t \qquad (1)$$

where [M] is the monomer concentration, $[M]_0$ is the initial monomer concentration, k_p is the propagation rate coefficient, [Pol*] is the concentration of active propagating species, and t is time. (ii) The polydispersity index (PDI) should be below 1.5. (iii) An increase in the number average molecular weight of the polymer as conversion proceeds, indicating that all the chains are growing, described by eq 2,

$$M_n^{theo} = \frac{\%\ \text{conversion}}{100}\frac{[M]_0}{[In]_0}MW_M + MW_{In} \qquad (2)$$

where $[M]_0$ and $[In]_0$ are the initial concentrations of monomer and initiator respectively, and MW_M and MW_{In} are the molecular weights of monomer and initiator, respectively.

For the experiments performed at 90, 60, 40, and 15 °C the first-order rate plots and molecular weight vs conversion plot (for 40 °C) are shown in Figures 1−5 and the final polydispersity indexes and k^{app}s for each series are shown in Table 1. In each case, the first-order rate plots are linear, M_n follows conversion (close to the theoretical line) and the polydispersity indexes are less than about 1.3; indicating that the atom transfer polymerization reaction is operating successfully in all cases.

Effect of MeHQ at Different Temperatures. The reaction at 90 °C was used as a reference point as this is a commonly used temperature for these systems. The first-order rate plot, Figure 1, shows no significant difference in the rate of reaction without and with the addition MeHQ. It is noted that MeHQ is often used as an inhibitor for MMA by commercial suppliers; however, MeHQ is clearly not acting as an inhibitor to this reaction under these conditions. We have previously reported that the addition of phenols and phenol

Table 1. Final Results for the Polymerization of MMA at Various Temperatures[a]

T/°C	additive[b]	time/h	conv/%	M_n^{theo} [c]	M_n^{SEC}	PDI	k^{app}/s^{-1}
90	none	9.10	94.6	9670	8620	1.31	8.59×10^{-5}
90	MeHQ	9.10	87.9	9000	8770	1.29	7.86×10^{-5}
60	none	25.7	85.9	8800	8940	1.17	1.92×10^{-5}
60	MeHQ	25.7	95.7	9780	8910	1.18	2.70×10^{-5}
40	none	68.0	48.5	5050	4460	1.28	2.67×10^{-6}
40	MeHQ	45.1	87.0	8910	7960	1.26	1.15×10^{-5}
40	phenol	45.1	80.3	8235	7640	1.30	9.33×10^{-6}
15	none	207	31.1	3310	4990	1.17	5.06×10^{-7}
15	MeHQ	207	73.8	7580	8530	1.18	1.58×10^{-6}

[a] 25 wt % in toluene; [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3. [b] [additive]:[CuBr] = 10:1. [c] Calculated using eq 1.

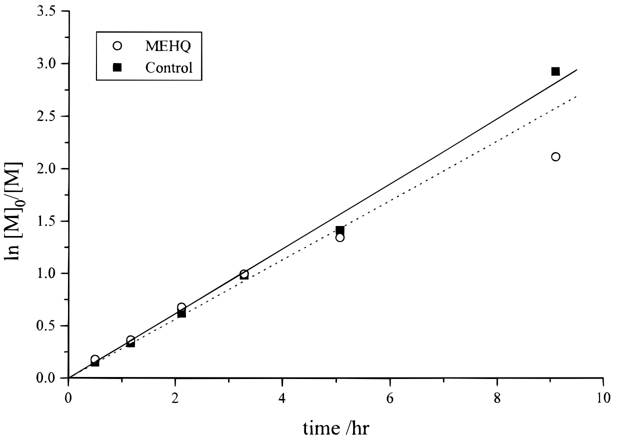

Figure 1. First-order rate plot for the polymerization of MMA at 90 °C (25 wt % in toluene, [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3, [MeHQ]:[CuBr] = 10:1).

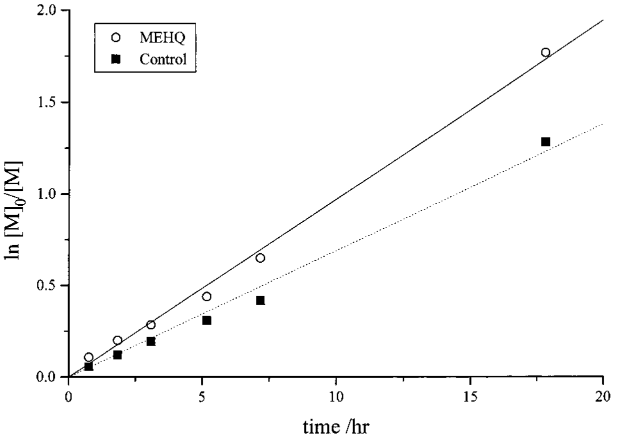

Figure 2. First-order rate plot for the polymerization of MMA at 60 °C (25 wt % in toluene, [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3, [MeHQ]:[CuBr] = 10:1).

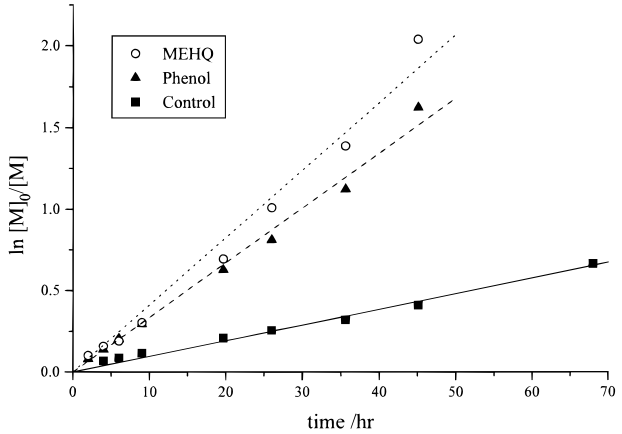

Figure 3. First-order rate plot for the polymerization of MMA at 40 °C (25 wt % in toluene, [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3, [MeHQ]:[CuBr] = 10:1, [phenol]:[CuBr] = 10:1).

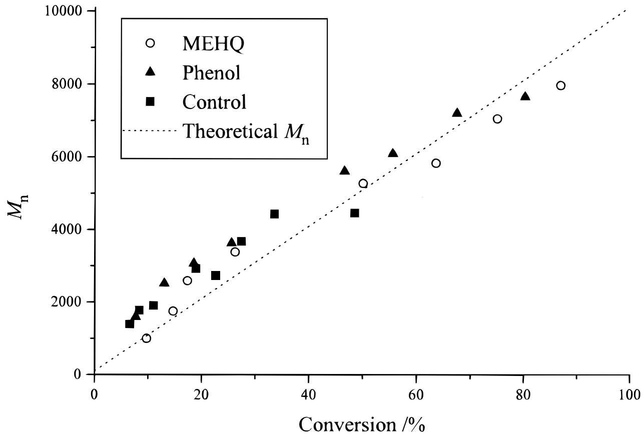

Figure 4. Dependence of M_n on conversion for the polymerization of MMA at 40 °C (25 wt % in toluene, [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3, [MeHQ]:[CuBr] = 10:1, [phenol]:[CuBr] = 10:1).

derivatives to atom transfer polymerization using these types of ligands can result in the reduction of an apparent induction period which has been observed in some cases.[33] There is no significant effect of MeHQ on the either M_n vs conversion or PDI, Table 1. The PDIs are typically ≤1.3, indicating that good molecular weight control is being achieved in the reaction.

At 60 °C the addition of MeHQ slightly increases the rate over the control reaction, Figure 2. At 40 °C the addition of MeHQ significantly increases the rate of reaction compared to the control, Figure 3. The addition of phenol has a similar effect as MeHQ on the rate of reaction. In comparing the rates of reaction k^{app}, Table 1, it can be seen that the control at 40 °C is approximately a factor of 30 slower than at 90 °C and the addition of MeHQ resulted in a 4-fold increase in the rate of reaction. Although the addition of MeHQ and phenol increases the rate of reaction, they have no apparent effect on M_n vs conversion, Figure 4, or the polydispersity index, Table 1, as compared to the control reaction, and so the increase in rate has not been at the expense of molecular weight control.

The reactions at 15 °C also show that the addition of MeHQ has a significant effect on the rate of the polymerization, Figure 5. From Table 1 it can be seen that rate at 15 °C is 170 times slower than at 90 °C and the addition of MeHQ increases the rate by a factor of 3. Again, there is no apparent difference in the polydispersities and the dependence of M_n on conversion with the addition of MeHQ. This is surprising, since it

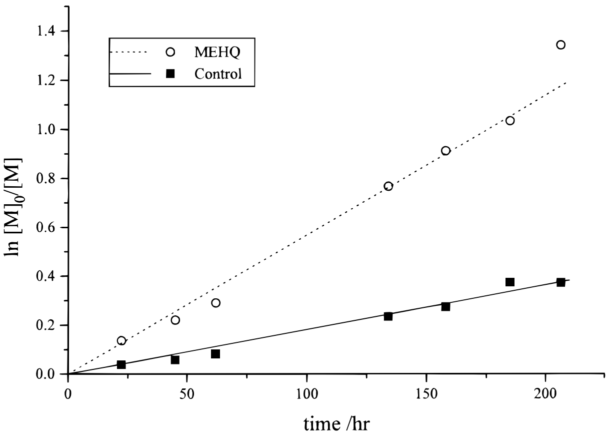

Figure 5. First-order rate plot for the polymerization of MMA at 15 °C (25 wt % in toluene, [MMA]:[**3**]:[CuBr]:[**1**] = 100:1:1:3, [MeHQ]:[CuBr] = 10:1).

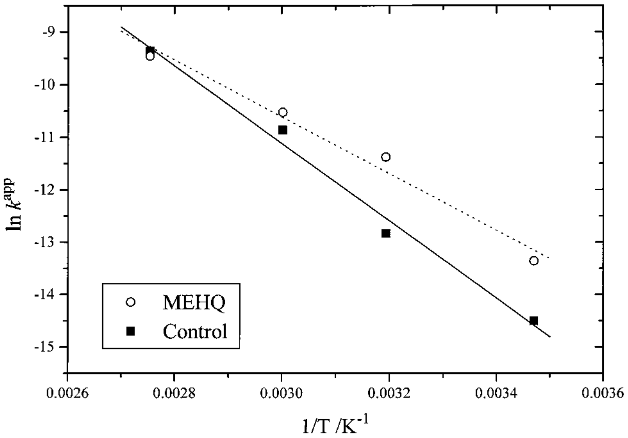

Figure 6. Effect of MeHQ on the Arrhenius plot of the pseudo first-order rate coefficient, k^{app}, for the polymerization of methyl methacrylate in toluene over the temperature range 15−90 °C.

Table 2. Arrhenius Parameters for the Apparent First-Order Rate Coefficient (k^{app})

series	E_a/kJ·mol^{-1}	log(A/s^{-1})
control	61.3 ± 4.5[a]	4.78 ± 0.75[a]
MeHQ	44.9 ± 4.5[a]	2.43 ± 0.75[a]

[a] Calculated from the standard deviations of the linear regression fits in Figure 6.

would be expected that as the rate of polymerization is increased, control over the molecular weight distribution (M_n and PDI) would be reduced. There is no observed systematic dependence of the polydispersity index of the polymers produced over the temperature range studied, Table 1.

Temperature Dependence on the Rate of Reaction. To asses the temperature dependence of the reaction, the Arrhenius parameters for the apparent first-order rate constant, k^{app}, were determined, Figure 6 and Table 2. The activation energy, E_a, for the control systems is 60.3 kJ·mol^{-1} which compares well to value of 62.9 kJ·mol^{-1} reported by Matyjaszewski *et al.*[34] for the related Cu^{I}Cl−dinonylbipyridene system in diphenyl ether. The agreement in these two values may be coincidental since the work of Matyjaszewski *et al.*[34] was performed in diphenyl ether with CuCl−dinonylbipyridene catalyst and chloro functional initiator with added Cu^{II}Cl. More recently, Percec et al.[24] has reported a significantly different value of 106 kJ·mol^{-1} for E_a for the polymerization of MMA in *p*-xylene with CuCl−dinonylbipyridene catalyst and chloro functional initiator.

The addition of MeHQ to the reaction significantly reduces the E_a to 44.9 kJ·mol^{-1}. It is difficult to ascribe a direct meaning to these activation energies as they do not reflect an elementary reaction; however, it suggests that MeHQ affects the position of the Cu(I)/Cu(II) equilibrium. MeHQ may act as a coordinating ligand for the copper catalyst, displacing one of the diimine ligands. Such coordination has been previously reported where we observed the oxidation of Cu(I) complexes similar to the ones used in these studies by phenol.[35] The removal of a chelating diimine ligand from the metal creates a coordination site(s) and may facilitate propagation. A similar effect is observed when benzoic acid is added to the polymerization.[36] The exact nature of these reactions is beyond the scope of the present work but is actively being pursued in our laboratory.

Other Conditions. Table 3 provides a summary of reactions which have been performed to explore atom transfer polymerization at low temperatures. In each case the polydispersity is narrow and M_n close to the theoretical value. It is especially noteworthy that it is possible to produce polymer at temperatures even as low as −15 °C using standard atom transfer polymerization reaction conditions. Normal free-radical polymerization at temperatures this low typically requires UV initiators which limits its application. Molecular weight control suffers at this temperature as can be seen by comparing M_n^{SEC} with M_n^{theo}. The polydispersity index, however, still remains narrow (<1.3).

Polymer Stereochemistry. The microstructure of the poly(MMA) was investigated by ^{13}C NMR. The fraction of triads was measured by integration of the 44 to 46 ppm region of the spectrum corresponding to the quaternary backbone carbon using assignments from the literature.[37,38] At 90 °C, 59.1% *rr* triads are obtained with a persistence ratio of 0.924, Table 4. This is close to that expected for a Bernouillion distribution where stereochemistry is determined only by the last monomer unit, as is observed for conventional free-radical polymerization. Lowering the temperature has the result of increasing the racemic content such that, at −15 °C, *rr* = 71.5%. This is again consistent with what would be expected for a free-radical polymerization

Table 3. Polymerization of MMA under Various Atom Transfer Polymerization Conditions[a]

T/°C	ligand	[MMA]/[**3**]	solution	time/h	conv/%	$M_n^{theo\ b}$	M_n^{SEC}	PDI
−15[c]	**1**	100	bulk	116	67.8	6980	10200	1.28
−15	**1**	100	bulk	193	27.8	2980	8600	1.29
25	**2**	100	bulk	20	92	9410	8680	1.34
25	**2**	500	bulk	72	89	45500	43800	1.24
40	**2**	200	bulk	15	62	12600	13100	1.24

[a] [MMA]:[CuBr]:[ligand] = 100:1:3. [b] Calculated using eq 1. [c] Added MeHQ; [MeHQ]:[CuBr] = 10:1.

Table 4. Fractions of Triads and Diads in Poly(methyl methacrylate) Prepared by Atom Transfer Polymerization at Various Temperatures

	triads			diads		
T/°C	mm	mr/rm	rr	m	r	ρ[a]
90	0.0350	0.374	0.591	0.222	0.778	0.924
60	0.0237	0.336	0.641	0.191	0.809	0.922
40	0.0281	0.344	0.628	0.200	0.800	0.931
15	0.0148	0.286	0.700	0.158	0.842	0.929
−15	0.0177	0.267	0.715	0.151	0.849	0.962

[a] Persistence ratio, $\rho = 2(m)(r)/(mr)$

following Bernoullian statistics at this temperature.[39−41] The persistence ratio is close to unity over all temperatures studied which is again similar to that observed in normal radical polymerization.

Conclusions

Atom transfer polymerization of MMA has been shown to proceed effectively at temperatures down to as low as 15 °C with narrow polydispersity indexes and control over M_n. The reaction even proceeds even at −15 °C, yielding narrow polydispersities; however, control over M_n is less effective. The polymerization is mediated by CuBr complexed with *N*-alkyl-2-pyridylmethanimine ligands and α-bromo esters in hydrocarbon solvent. At lower temperatures the reaction is accelerated by the addition of phenol or MeHQ, which is reflected in a lowering of the activation energy for k^{app}. It is believed that phenols act as a coordinating ligands for copper(I), facilitating formation of the active propagating center. The stereochemistry of the poly(MMA) produced is similar to that for a free-radical propagation mechanism with the fraction of syndiotactic arrangements in the polymer increased at reduced temperatures. The present study illustrates that with the appropriate Schiff base ligands for copper(I), acceptable rates of polymerization can be achieved either in bulk or hydrocarbon solvent at low temperatures.

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Supporting Information Available: Tables giving further polymerization conversion and molecular weight data for the reactions at 90, 60, 40, and 15 °C and M_n vs conversion figures for the data at 90, 60, and 15 °C (7 pages). Ordering and Internet accesss information is given on any current masthead page.

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