Atom Transfer Polymerization of Methyl Methacrylate Mediated by Alkylpyridylmethanimine Type Ligands, Copper(I) Bromide, and Alkyl Halides in Hydrocarbon Solution

David M. Haddleton,* Martin C. Crossman, Bogdan H. Dana, David J. Duncalf, Alex M. Heming, Dax Kukulj, and Andrew J. Shooter

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

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ABSTRACT: Schiff bases of types **1**, **2**, and **3**, easily prepared by the condensation of primary amines with pyridine-2-carboxaldehyde, glyoxal, or 2-acetylpyridine, respectively, are described as ligands for a copper(I) catalyst in the atom transfer polymerization of a range of methacrylates in toluene and xylene solution. Increasing the length of the alkyl group on ligands of type **1** increases the solubility of the catalyst in nonpolar solvents. The rate of polymerization increases on going from R = ethyl to propyl; however, on increasing the length of R further, we see no effect on the rate. The molecular weight distribution is narrow for all ligands where R = *n*-alkyl, and the number-average molecular weight (M_n) increases linearly with conversion. A decrease in rate and a loss of control are observed when branching is introduced in the α-position of the side chain. The polymerization is approximately first order in initiator, 0.90 ± 0.22, CuBr, 0.90 ± 0.13, and methyl methacrylate, 0.93 ± 0.01. Polymerization with CuBr in conjunction with diazabutadiene ligands does not proceed very effectively, due to the high stability of the copper(I) complexes with regard to oxidation. The mechanism of the reaction is complex and may differ on subtle changes in ligand, metal, solvent, etc. The ligand systems presented in this paper offer a wide range of versatility when choosing the most effective system for a particular application. The Schiff base ligands, when used as described, provide an excellent method for achieving the controlled polymerization of a wide range of methacrylates at relatively mild temperatures in hydrocarbon, noncoordinating, solvents.

Introduction

The controlled polymerization[1] of methacrylates to polymers of specific architecture, with a range of designed properties/effects, is of continuing widespread interest.[2,3] Living polymerization[4] is a route to a wide range of useful polymer architectures including block copolymers, graft copolymers, telechelic polymers, and star polymers. For methacrylates this has traditionally been achieved through anionic polymerization[5−7] or group transfer polymerization (GTP).[8−10]

Although anionic polymerization of nonpolar monomers such as butadiene and styrene is carried out for a range of commercial products, the need for high-purity monomers, solvents, and reagents, coupled with the low temperatures usually required, has meant that living polymerization of acrylic monomers has met with relatively little commercial success.[11] Controlled/living free radical polymerization or polymerization processes that involve homolytic bond cleavage, as opposed to ion formation, are ideally suited to circumvent these problems. Stable organic free radicals, such as TEMPO, have found success for styrene and styrenic monomers.[12−14] An area that is attracting considerable interest is transition metal mediated polymerization. This technique has been pioneered by Matyjaszewski utilizing copper(I) halide catalysts in conjunction with alkyl halide initiators[15−19] and Sawamoto using a $Ru^{II}Cl_2(PPh_3)_3$ catalyst.[20−23] This has been extended by Percec to the use of sulfonyl halides as so-called *universal initiators*.[24−27] A range of other metals have subsequently been demonstrated to be effective under appropriate reaction conditions including Ni(II),[28,29] Fe(II),[30] Pd(II),[31] and Rh(III).[32] Scheme 1 is the simplest representation of the mechanism occurring during atom transfer polymerization, where Pol* represents the active propagating species, *n* = formal oxidation state of the metal, and X = Cl or Br.

Scheme 1

$$\text{Pol-X} + \text{M(n)} \rightleftharpoons \text{Pol}^* + \text{M(n+1)-X}$$

The effectiveness of this chemistry to produce narrow molecular weight distribution polymers of controlled number-average molecular weight (M_n) depends on the position of this equilibrium. Thus, when a different monomer is used, the relative stability of Pol* and Pol−X changes leading to a shift in the equilibrium shown in Scheme 1; changes in solvent, etc., may also effect this equilibrium. Bis(ortho-chelated) arylnickel(II) complexes[28] are effective in controlled polymerization of methacrylates, as is $RuCl_2(PPh_3)_3$[20,21] in toluene. Although copper bipyridyl complexes are excellent at polymerizing styrene and acrylates in hydrocarbon solvents, more coordinating solvents such as anisole or diphenyl ether seem to give better results for methacrylates.[19] This is presumably due to weak coordination of the solvent to the metal affecting the nature of the active catalyst. We have been developing a series of Schiff base ligands which are easily prepared in quantitative yields by the reaction of pyridine-2-carboxaldehyde, glyoxal, or acetylpyridine with primary amines, at room temperature over short time periods, for use in transition metal mediated atom transfer polymerization (Scheme 2).[33−35]

These ligands are effective for the polymerization of methacrylates[36−39] in toluene or xylene solutions in conjunction with copper(I) halides and suitable alkyl

* Author for correspondence: e-mail D.M.Haddleton@warwick.ac.uk; Tel +44-1203-523-256; Fax +44-1203-524-112.

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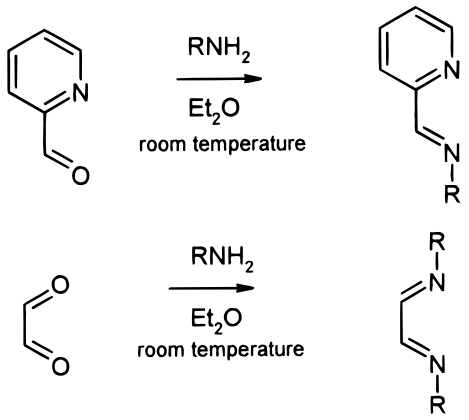
Scheme 2



halide initiators over a wide range of temperatures (even as low as −15 °C).[40] It is also noted that although there exists a certain amount of circumstantial evidence that the mechanism of this type of reaction is via a *free* radical,[41] it has been as yet impossible to obtain direct evidence for the involvement of free radicals. Attempts to detect carbon-centered radicals by EPR have proved elusive due to the *g* values of copper(II) and propagating free radicals being too similar,[42,43] and the exact mechanism of this reaction remains elusive. We have previously shown that the presence of hydrophilic or coordinating groups can effect the reaction kinetics.[44−46] In this paper we present results from a detailed study into the polymerization of methyl methacrylate (MMA) with this class of catalyst, investigating the effect of the nature and amount of ligand used in conjunction with CuBr.[36]

Experimental Section

Analysis and General. All manipulations were performed using standard Schlenk or syringe techniques under an atmosphere of dinitrogen. NMR spectra were recorded on Bruker AC250 and AC400 spectrometers. FTIR spectra were recorded on a Bruker Vector 22 spectrometer with fitted an attenuated total reflection (ATR) cell, and mass spectra were measured on a Kratos MS80 spectrometer. Crystal data were collected on a Siemens three-circle diffractometer equipped with a SMART CCD area detector and graphite-monochromated radiation, Mo−Kα radiation (λ = 0.710 73 Å). Polymer conversions were 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.

Reagents. Ethylamine (Avocado, 70% aqueous solution), *n*-propylamine (Lancaster, 98%), *n*-pentylamine (Aldrich, 99%), *n*-hexylamine (Avocado, 98%), *n*-heptylamine (Avocado, 98%), *n*-octylamine (Lancaster, 98%), *n*-nonylamine (Avocado, 98%), pyridine-2-carboxaldehyde (Avocado, 99%), glyoxal (Avocado, 40% aqueous solution), or 2-acetylpyridine (Avocado, 98%), 2-benzoylpyridine (Avocado, 99%), 4,4′-dimethylbenzil (Avocado, 98%), titanium tetrachloride (Aldrich, 1.0 M solution in toluene), diethyl ether (BDH, 98%), xylene (Fisons, 99.8%), and magnesium sulfate (Philip Harris) were all used as received. Methyl methacrylate (Aldrich, 99%), ethyl methacrylate (Aldrich, 98%), *n*-butyl methacrylate (Aldrich, 99%), isobutyl methacrylate (Aldrich, 99%), *tert*-butyl methacrylate (TCI, 98%), *sec*-butyl methacrylate (Polysciences, bp 146−148 °C), *n*-hexyl methacrylate (Polysciences, 98%), and *n*-octyl methacrylate were 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,[47] and *N*-(*n*-butyl)-2-pyridylmethanimine was prepared as described earlier.[51]

***N*-(*n*-Pentyl)-2-pyridylmethanimine (*n*-Pen-1).** An excess of *n*-pentylamine (29.0 mL, 0.25 mol) was added dropwise to a stirred solution of pyridine-2-carboxaldehyde (20.0 mL, 0.21 mol) in diethyl ether (20 mL) cooled in an ice bath. After complete addition of the amine, anhydrous magnesium sulfate (5 g) was added and the slurry stirred for 2 h at 25 °C. The solution was filtered, solvent removed, and the product purified by distillation under reduced pressure to give a golden yellow oil. Yield: 35.8 g (96.7%). Bp 80 °C/0.4 Torr. ^{1}H NMR ($CDCl_3$): δ 8.61 (m, 1H), 8.36 (s, 1H), 7.95 (m, 1H), 7.72 (m, 1H), 7.29 (m, 1H), 3.66 (t, 2H), 1.71 (sextet, 2H), 1.33 (overlapping quintets, 2H each), 0.89 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 161.6, 154.6, 149.3, 136.4, 124.5, 121.1, 61.6, 30.3, 29.4, 22.4, 14.0. IR: 1648 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1$ = 177 Da. Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.9; H, 9.2; N, 15.9. Found: C, 74.37; H, 9.16; N, 15.90.

***N*-Ethyl-2-pyridylmethanimine (Et-1).** Prepared as for *n*-Pen-**1**. Yield: 92%. Bp 60 °C/0.4 Torr. ^{1}H NMR ($CDCl_3$): δ 8.61 (m, 1H), 8.37 (s, 1H), 7.95 (m, 1H), 7.72 (m, 1H), 7.26 (m, 1H), 3.68 (q, 2H, J = 7.33 Hz), 1.30 (t, 3H, J = 7.33 Hz). ^{13}C NMR ($CDCl_3$): δ 161.2, 154.6, 149.3, 136.4, 124.5, 121.1, 55.6, 15.9. IR: 1651 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1$ = 135 Da. Anal. Calcd for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.5; H, 7.6; N, 20.7.

***N*-(*n*-Propyl)-2-pyridylmethanimine (*n*-Pr-1).** Prepared as for *n*-Pen-**1.** ^{1}H NMR ($CDCl_3$): δ 8.60 (m, 1H), 8.34 (s, 1H), 7.95(m, 1H), 7.69 (m, 1H), 7.26 (m, 1H), 3.60 (t, 2H), 1.71 (m, 2H), 0.93 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 161.7, 154.6, 149.3, 136.4, 124.5, 121.1, 63.3, 23.8, 11.8. IR: 1651 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1$ = 149 Da. Anal. Calcd for $C_9H_{12}N_2$: C, 72.9; H, 8.2; N, 18.9. Found: C, 71.1; H, 8.0; N, 18.5.

***N*-(Cyclopropyl)-2-pyridylmethanimine (cyclo-Pr-1).** Prepared as for *n*-Pen-**1.** Used without distillation following removal of ether and unreacted amine in vacuo. ^{1}H NMR ($CDCl_3$): δ 8.56 (m, 1H), 8.48 (s, 1H), 7.82 (m, 1H), 7.64 (m, 1H), 7.20 (m, 1H), 3.06 (m, 1H), 0.98 (m, 4H). ^{13}C NMR ($CDCl_3$): 159.3, 155.0, 150.0, 136.7, 124.5, 121.3, 42.3, 9.7. IR: 1634 cm^{-1} ($\nu_{C=N}$), 1586 cm^{-1}, 1567 cm^{-1}.

***N*-(*iso*-Propyl)-2-pyridylmethanimine (*iso*-Pr-1).** Prepared as for *n*-Pen-**1.** Used without distillation following removal of ether and unreacted amine in vacuo. ^{1}H NMR ($CDCl_3$): δ 8.64 (m, 1H), 8.40 (s, 1H), 7.99 (m, 1H), 7.73 (m, 1H), 7.30 (m, 1H), 3.66 (septet, 1H, J = 6.35 Hz), 1.29 (d, 6H, J = 6.35 Hz). ^{13}C NMR ($CDCl_3$): δ 159.1, 154.7, 149.2, 136.3, 124.4, 121.2, 61.3, 23.8. IR: 1647 cm^{-1} ($\nu_{C=N}$), 1588 cm^{-1}, 1566 cm^{-1}.

***N*-(*n*-Propyl)-2-pyridylethanimine (*n*-Pr-3).** A solution of 2-acetylpyridine (10 g, 82.5 mmol) in diethyl ether (50 mL) was placed in a Schlenk tube containing activated 3 Å molecular sieves under an atmosphere of dinitrogen. *n*-Propylamine (8 mL, 97.3 mmol) was added and the reaction mixture stirred at room temperature for 18 h. The reaction was filtered, and then ether and excess *n*-propylamine were removed in vacuo. *N*-(*n*-Propyl)-2-pyridylethanimine was the second fraction recovered from the reaction mixture by vacuum distillation. Yield: 45%. Bp 60 °C/0.4 Torr. ^{1}H NMR ($CDCl_3$): δ 8.40 (m, 1H), 7.94 (m, 1H), 7.48 (m, 1H), 7.05 (m, 1H), 3.42 (t, 2H), 2.28 (s, 3H), 1.72 (m, 2H), 0.95 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 166.5, 158.3, 148.5, 136.6, 124.3, 121.1, 54.6, 24.4, 14.2 (**C**H_3C=N), 12.5. IR: 1639 cm^{-1} ($\nu_{C=N}$), 1585 cm^{-1}, 1565 cm^{-1}.

***N*-(*n*-Hexyl)-2-pyridylmethanimine (*n*-Hex-1).** Prepared as for *n*-Pen-**1**. Yield: 98.1%. Bp 65 °C/0.2 Torr. ^{1}H NMR ($CDCl_3$): δ 8.60 (m, 1H), 8.35 (s, 1H), 7.96 (m, 1H), 7.71 (m, 1H), 7.28 (m, 1H), 3.64 (t, 2H), 1.70 (m, 2H), 1.30 (m, 6H), 0.86 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 161.6, 154.6, 149.3, 136.4, 124.5, 121.1, 61.6, 31.6, 30.6, 27.0, 22.6, 14.0. IR: 1650 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1$ = 191 Da. Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.7; H, 9.5; N, 14.7. Found: C, 75.3; H, 9.5; N, 14.8.

***N*-(*n*-Heptyl)-2-pyridylmethanimine (*n*-Hep-1).** Prepared as for *n*-Pen-**1**. Yield: 97.8%. Bp 87 °C/0.2 Torr. ^{1}H NMR ($CDCl_3$): δ 8.61 (m, 1H), 8.34 (s, 1H), 7.96 (m, 1H), 7.70 (m, 1H), 7.28 (m, 1H), 3.64 (t, 2H), 1.70 (m, 2H), 1.30 (m, 8H), 0.85 (t, 3H). IR: 1650 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1 = 205$ Da. Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.4; H, 9.9; N, 13.7. Found: C, 75.9; H, 9.9; N, 13.7.

***N*-(*n*-Octyl)-2-pyridylmethanimine (*n*-Oct-1).** Prepared as for *n*-Pen-**1**. Yield: 97.6%. Bp 101 °C/0.2 Torr. ^{1}H NMR ($CDCl_3$): δ = 8.62 (m, 1H), 8.35 (s, 1H), 7.97 (m, 1H), 7.71 (m, 1H), 7.28 (m, 1H), 3.65 (t, 2H), 1.70 (m, 2H), 1.30 (m, 10H), 0.85 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 161.6, 154.6, 149.3, 136.4, 124.5, 121.1, 61.5, 31.8, 30.6, 29.3, 29.2, 27.3, 22.6, 14.0. IR: 1650 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1 = 219$ Da. Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.0; H, 10.2; N, 12.8. Found: C, 76.8; H, 10.1; N, 13.0.

***N*-(*n*-Nonyl)-2-pyridylmethanimine (*n*-Non-1).** Prepared as for *n*-Pen-**1**. Yield: 98.7%. Bp 123 °C/0.2 Torr. ^{1}H NMR ($CDCl_3$): δ 8.62 (m, 1H), 8.35 (s, 1H), 7.96 (m, 1H), 7.71 (m, 1H), 7.29 (m, 1H), 3.65 (t, 2H), 1.70 (m, 2H), 1.30 (m, 12H), 0.85 (t, 3H). IR: 1650 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1 = 233$ Da. Anal. Calcd for $C_{15}H_{24}N_2$: C, 77.5; H, 10.4; N, 12.1. Found: C, 77.3; H, 10.1; N, 12.0.

***N*-(*n*-Octadecyl)-2-pyridylmethanimine (*n*-Octadec-1).** Prepared as for *n*-Pen-**1** but not distilled. Yield: 90%. ^{1}H NMR ($CDCl_3$): δ 8.62 (m, 1H), 8.35 (s, 1H), 7.96 (m, 1H), 7.71 (m, 1H), 7.28 (m, 1H), 3.65 (t, 2H), 1.70 (m, 2H), 1.30 (m, 32*H), 0.85 (t, 3H). IR: 1652 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1 = 359$ Da. Anal. Calcd for $C_{24}H_{42}N_2$: C, 80.4; H, 11.8; N, 7.8. Found: C, 80.07; H, 11.71; N, 7.54.

***n*-Propyldiazabutadiene (*n*-Pr-2).** Water (50 mL) was added to glyoxal (50 g, 0.34 mol, 40% aqueous solution), and then *n*-propylamine (50 g, 0.87 mol) was added dropwise with vigorous stirring. The product was extracted into diethyl ether and purified by vacuum distillation. Bp 85 °C/0.3 Torr. ^{1}H NMR ($CDCl_3$): δ 7.87 (s, 2H), 3.49 (t, 4H), 1.66 (m, 4H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 166.5 (Pr−**C**H═N), 63.1, 23.5, 11.6. IR: 1672 cm^{-1}, 1641 cm^{-1} ($\nu_{C=N}$).

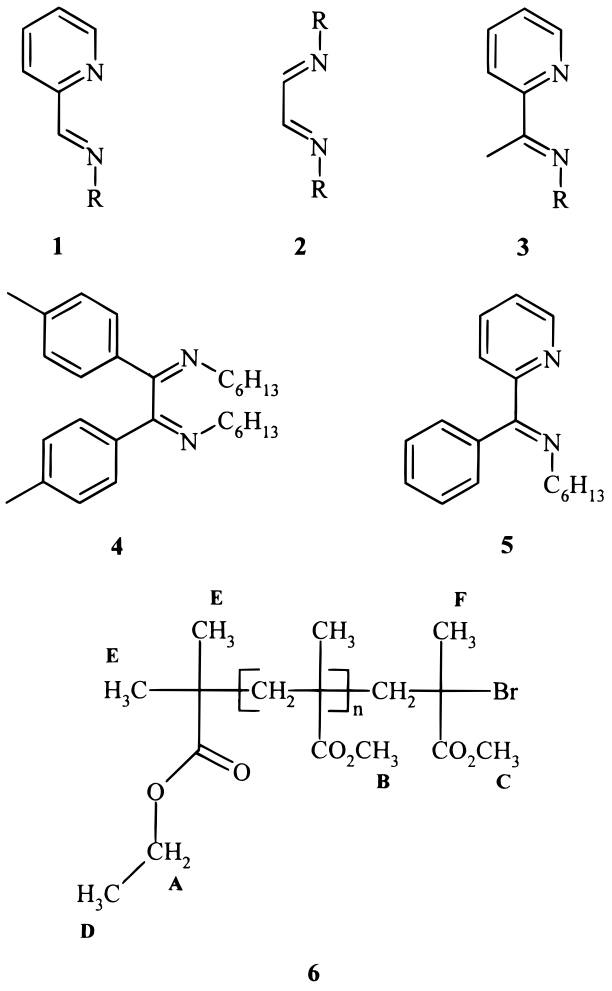
Isopropyldiazabutadiene (*iso*-Pr-2). Prepared as for *n*-propyldiazabutadiene except the product was recrystallized as white needles from diethyl ether. Yield: 89%. Mp 50 °C. ^{1}H NMR ($CDCl_3$): 7.90 (s, 2H), 3.49 (septet, 2H), 1.19 (d, 12H). ^{13}C NMR ($CDCl_3$): δ 160.2, 61.7, 24.1. IR: 1630 cm^{-1} ($\nu_{C=N}$).

Cyclopropyldiazabutadiene (*cyclo*-Pr-2). Glyoxal (10 g, 0.69 mol, 40% aqueous solution) was dissolved in methanol (10 mL), and cyclopropylamine (10 g, 0.175 mol) was added with stirring at room temperature. After 1 h the product was extracted into diethyl ether and isolated as a colorless crystalline solid that was purified by sublimation. ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 2H) 2.97 (m, 2H), 0.98 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 159.7, 42.3, 10.2. IR: 1619 cm^{-1} ($\nu_{C=N}$).

1,4-Dihexyl-2,3-diphenylmethyl-1,4-diaza-1,3-butadiene (4).[48] An excess of *n*-hexylamine (5.0 mL, 38 mmol) was added to a stirred solution of 4,4′-dimethylbenzil (1 g, 42 mmol) in toluene (15 mL) at room temperature over activated 4 Å molecular sieves. After 30 min, titanium tetrachloride (4 mL, 1 M solution in toluene) was added dropwise and the solution left for a further hour before heating to 60 °C for 2 h. Following removal of volatiles in vacuo the product was recrystallized from diethyl ether/methanol (90:10) as white crystals. Yield: 0.4 g (26.3%). ^{1}H NMR ($CDCl_3$): δ 7.71 (m, 4H), 7.24 (m, 4H), 3.38 (t, 4H), 2.43 (s, 6H), 1.76 (m, 4H), 1.34 (m, 12H), 0.93 (t, 6H). ^{13}C NMR ($CDCl_3$): δ 165.5 (s, **C**═N). IR: 1675 cm^{-1} ($\nu_{C=N}$).

***N*-(*n*-Hexyl)-2-pyridylphenylmethanimine (5).** A solution of *n*-hexylamine (11.25 mL, 86 mmol) in diethyl ether (25 mL) was added dropwise to 2-benzoylpyridine (8 g, 43 mmol) at 0 °C over activated 3 Å molecular sieves and stirred for 5 h. The solution was filtered, and the volatiles were removed in vacuo to yield the product as a bright yellow oil. Yield: 40%. ^{1}H NMR ($CDCl_3$): δ 8.69 (m, 1H), 8.56 (m, 1H), 7.31 (m, 9H), 3.37 (t, 2H), 1.68 (m, 2H), 1.27 (m, 6H), 0.88 (t, 3H).^{13}C NMR ($CDCl_3$): δ 150.55, 137.62, 136.80, 128.73, 126.73, 125.19, 124.39, 123.89, 123.60, 123.22, 54.6, 32.23, 31.66, 27.8, 23.17, 14.64. IR: 1675 cm^{-1} ($\nu_{C=N}$). MS (EI): $m/z + 1 = 266$ Da.

Typical Polymerization Procedure. For PMMA with a targeted degree of polymerization ($DP_{Theo} = 100$), CuBr (0.134 g, 0.935 mmol) was placed in a Schlenk tube and the tube purged with dry dinitrogen prior to MMA (10 mL, 93.5 mmol) being added at ambient temperature. The Schiff base ligand (2 mol equiv to CuBr, 1.87 mmol) and then deoxygenated toluene or xylene (20 mL) were added, and the Schlenk tube was immersed in a thermostated oil bath at 90 °C. When the contents reached reaction temperature, ethyl 2-bromoisobutyrate (0.137 mL, 0.935 mmol) was added via a degassed syringe (time = 0). The polymerization was sampled at suitable time periods throughout the reaction. Catalyst residues were removed by filtering through a column of basic alumina prior to SEC analysis, and polymers were isolated by precipitation into hexanes.



Results and Discussion

A range of Schiff base ligands of types **1**, **2**, and **3** can be easily prepared by the condensation of primary amines with pyridine-2-carboxaldehyde, glyoxal, or 2-acetylpyridine, respectively, in near quantitative yield and in relatively short reaction times. Type **1** has already been demonstrated to provide efficient atom transfer polymerization catalysts for methyl methacrylate.[36,44,45] The ease in which the ligands can be synthesized enables steric, electronic, and solubility parameters of the catalyst to be varied and optimized.

Polymerization of MMA with Pr-1/CuBr and Bu-1/CuBr: Effect of Branching at the α-Carbon. Previously we have reported that polymerization of methyl methacrylate with *n*-Pr-**1**/CuBr/ethyl 2-bromoisobutyrate in xylene solution was controlled as

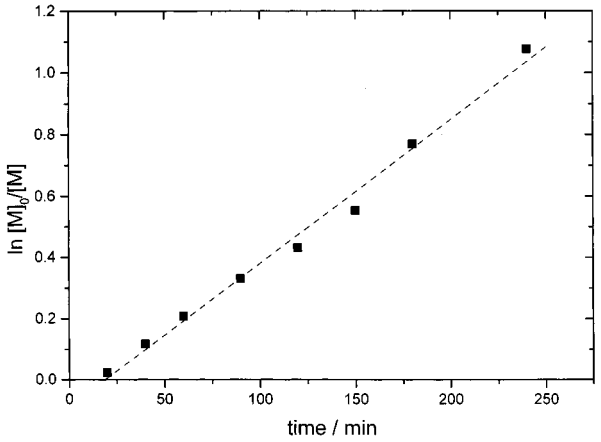


Figure 1. First-order kinetic plot for the polymerization of MMA with [*n*-Pr-**1**]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 33 vol % in xylene, 90 °C.

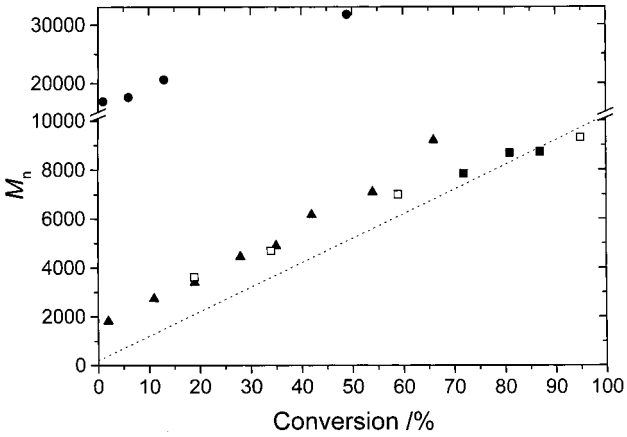


Figure 2. Evolution of M_n with conversion for polymerization of MMA with *n*-Pr-**1**, ▲; *iso*-Pr-**1**, □, ■ (duplicate experiments); and *cyclo*-Pr-**1**, ●. [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 33 vol % in xylene, 90 °C; dashed line represents the theoretical M_n.

evidenced by a linear increase in M_n with conversion, low polydispersity (PDI), and a linear first-order rate plot for the reaction.[36] These early results, however, showed polymers with an observed M_n of approximately half those expected for a controlled polymerization when ethyl 2-bromoisobutyrate is the initiator. Figure 1 shows results from a similar experiment where the first-order kinetic plot is linear, indicating that the number of active species is constant and that termination reactions are not significant. As in our earlier work, we observed an "induction" period of approximately 20 min. This induction period is often seen and is not yet fully understood but may be due to residual oxygen[49] or other impurity in the system. The M_n increases linearly with conversion (Figure 2) but is slightly higher than that predicted for both *n*-Pr-**1** and *iso*-Pr-**1**. This higher than expected M_n is more prominent at the start of the reaction, which indicates slow initiation relative to propagation or that a certain amount of initiator is lost through primary radical−primary radical reactions reducing the initiator efficiency. As the steric hindrance of the alkyl group is increased to *cyclo*-Pr-**1**, this effect becomes dominant as observed by very high M_n during the initial stages of the reaction. We usually see slightly higher than predicted M_n in all our observations of atom transfer polymerization of MMA with this type of ligand system, *in all but our earliest publication*.[36]

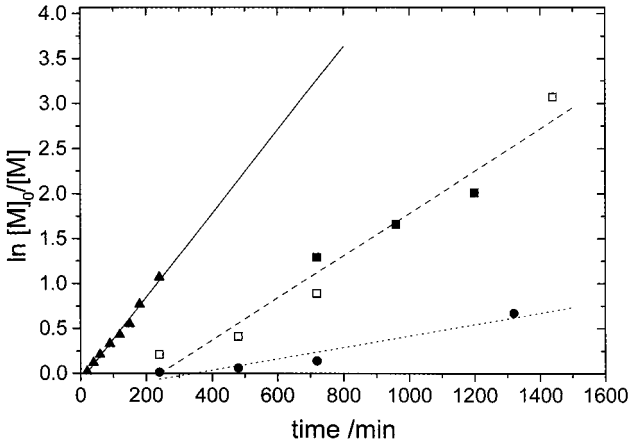


Figure 3. Comparison of Pr-**1** ligands. First-order kinetic plots for the polymerization of MMA with *n*-Pr-**1**, ▲; *iso*-Pr-**1**, □, ■ (duplicate experiments); and *cyclo*-Pr-**1**, ●. [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 33 vol % in xylene, 90 °C; lines represent best fit through data.

Table 1. Effect of Branching at the α-Carbon in Pr-1 on the Atom Transfer Polymerization of MMA[a]

ligand	time/h	conv/%	M_n	PDI	k_p[Pol*] × 10^5/s^{-1}
n-Pr-**1**	240	66	9200	1.19	7.80
iso-Pr-**1**	720	72	7840	1.45	2.50
cyclo-Pr-**1**	720	13	20600	1.49	1.05
n-Pr-**3**	240	68	6850	1.59	11.05

[a] [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 33 vol % in xylene, 90 °C; for full data sets see Supporting Information.

The effect of steric crowding around the catalyst was investigated by introducing branching at the carbon atom α to the imine, i.e., using *iso*-Pr-**1**. The result was a decrease in the rate of polymerization (Figure 3 and Table 1) accompanied by an increase of PDI; the control of M_n with conversion was similar, however (Figure 2). This experiment was carried out twice to provide duplicate data. The trend continued when *cyclo*-Pr-**1** was used as the ligand. Only 13% conversion was reached after 12 h, and the control over M_n was much reduced. This effect is surprising since both single-crystal XRD structural and variable temperature NMR studies of this type of catalyst reveal no significant differences when branching at the α-carbon is introduced.[50−52]

A Schiff base containing a methyl group in place of the imine hydrogen, *n*-Pr-**3**, was designed to increase the electron-donating ability of the ligand in an attempt to stabilize the copper(II) complex relative to the copper-(I) complex. The rate of polymerization remains very similar to the reaction using *n*-Pr-**1** attaining 68% conversion after 4 h (Table 1), but the PDI increases steadily throughout the polymerization reaching 1.65 after 8 h at 96% conversion (M_n = 8990, see Supporting Information). If the position of the Cu(I)/Cu(II) equilibrium is the dominant feature in atom transfer polymerization, it might have been expected that increasing the electron-donating ability of the ligand by the incorporation of a relatively electron-donating methyl group would have stabilized Cu(II) and resulted in an increase in the rate of polymerization; however, this is clearly not the case. The nature of both the thermodynamics and kinetics of electron transfer in these types of copper-(I) complexes is currently being examined in our laboratory by microelectrode oxidation reactions.

Table 2. Effect of Branching at the α-Carbon in Bu-1 on the Atom Transfer Polymerization of MMA[a]

ligand	time/h	conv/%	M_n	PDI	k_p[Pol*] × 10^5/s^{-1}
n-Bu-**1**	4	85.2	10400	1.33	14.8
sec-Bu-**1**	4	5.1	890	1.68	0.498
	28	75.3	9860	2.66	
iso-Bu-**1**	4	15.7	2100	1.57	0.231
	28	47.2	5400	2.38	
tert-Bu-**1**	20	0			

[a] [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 3:1:1:100, 50 vol % in xylene, 90 °C; for full data sets see Supporting Information.

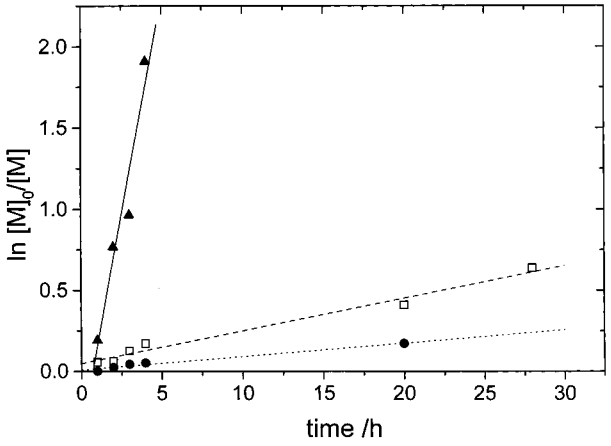


Figure 4. Comparison of butyl-**1** ligands. First-order kinetic plots for the polymerization of MMA with *n*-Bu-**1**, ▲; *iso*-Bu-**1**, □; and *sec*-Bu-**1**, ●. [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 3:1:1:100, 50 vol % in xylene, 90 °C; lines represent best fit through data.

The observation of an increase in PDI and loss of control over M_n is indicative of an increase in the amount of termination, in conjunction with the increase in M_n with percent conversion, etc. The lower reaction rates, however, suggest a lower concentration of radicals, and it would be expected that the rate of termination should be lower. These contradicting statements suggest that the reaction mechanism is more complex than that depicted in Scheme 1.

The effect of branching in the alkyl group α to the imine bond on the efficiency of the ligand was also investigated with isomeric butyl groups, viz., *n*-, *sec*-, *iso*-, and *tert*-Bu-**1** ligands (Table 2). Again, a dramatic decrease in the rate of polymerization is observed with the introduction of branching (Figure 4), such that when using *tert*-Bu-**1** no polymerization is observed (under the usual reaction conditions). It is apparent from these results that both the steric and electronic effects of the alkyl group on the ligand have a significant effect on the ability of the copper complexes to mediate controlled polymerization. Some of the Bu-**1** results have been published previously;[51] they are included here for completeness, however.

Polymerization of MMA with Various *n*-Alkyl-1 Ligands: Effect of the Length of the Alkyl Group. The synthesis of **1** is such that the length of the alkyl group can be easily varied by appropriate choice of primary amine. Table 3 reports data for the polymerization of MMA in toluene, as opposed to xylene, with a range of *n*-alkyl ligands of type **1** ranging from ethyl to octadecyl (C_{18}). Figure 5 shows the first-order kinetic plots for Et-**1**, *n*-Pr-**1**, *n*-Bu-**1**, *n*-Pen-**1**, *n*-Hex-**1**, and *n*-Oct-**1**. Very similar rates of polymerization are observed for all the reactions except for that using Et-**1**, which has a higher rate of reaction. Similar rates of polymerization are also observed when using *n*-Octadec-**1**, *n*-Non-**1**, and *n*-Hep-**1** with 83%, 70%, and 74% conversion, respectively, achieved after 4 h. The nature of the alkyl group dramatically effects the solubility of the copper complexes in a range of solvents, especially at ambient temperatures. As the length of the alkyl group is increased, the system becomes more soluble in nonpolar solvents. Indeed, polymerization with Et-**1** and CuBr in 50% toluene solution at 90 °C is a heteroge-

Table 3. Effect of the Alkyl Chain Length in Ligands of Type 1 on the Atom Transfer Polymerization of MMA[a]

ligand	time/h	M_n	PDI	conv/%[b]	k_p[Pol*] × 10^5/s^{-1}
Et-**1**	0.5	4930	1.25	33.9	18.33
	1	6470	1.21	53.5	
	1.5	7180	1.21	66.6	
	2	8260	1.19	75.9	
	3	9180	1.16	87.6	
	4	11650	1.19	93.6	
Pr-**1**	0.5	2410	1.22	22.1	12.18
	1	6970	1.22	37.3	
	1.5	5050	1.20	48.5	
	2	6580	1.20	58.2	
	3	7930	1.17	72.8	
	4	8330	1.18	82.7	
Bu-**1**	0.5	2520	1.24	23.3	11.12
	1	5030	1.22	37.7	
	1.5	5060	1.22	48.6	
	2	6340	1.21	57.3	
	3	7270	1.19	71.0	
	4	7920	1.19	81.0	
Pen-**1**	0.5	3380	1.33	20.7	12.66
	1	4630	1.27	38.6	
	2	5800	1.25	60.5	
	3	6500	1.23	73.3	
	4	8910	1.23	84.7	
Hex-**1**	0.5	3620	1.27	22.6	12.36
	1	4600	1.25	39.7	
	2	5810	1.22	62.0	
	3	6600	1.22	74.6	
	4	7670	1.19	84.0	
Hep-**1**	4	10370	1.25	73.6	*c*
Oct-**1**	0.5	5180	1.27	25.2	10.63
	1	7350	1.23	38.9	
	1.5	8220	1.23	49.8	
	2	9010	1.21	58.8	
	3	9500	1.23	71.4	
	4	9820	1.24	80.5	
Non-**1**	4	10930	1.27	70.2	*c*
Octadec-**1**	4	11910	1.23	82.7	*c*

[a] [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 50 vol % in toluene, 90 °C. [b] By ^{1}H NMR. [c] Not sampled with time.

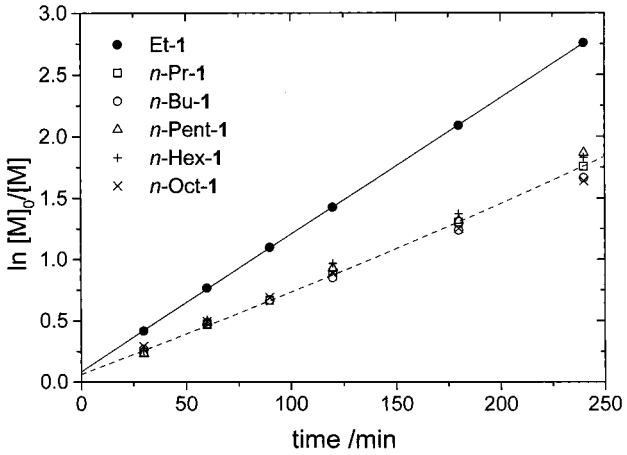


Figure 5. Comparison of alkyl chain lengths on ligands. First-order kinetic plots for the polymerization of MMA with *n*-alkyl-**1**. [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 50 vol % in toluene, 90 °C.

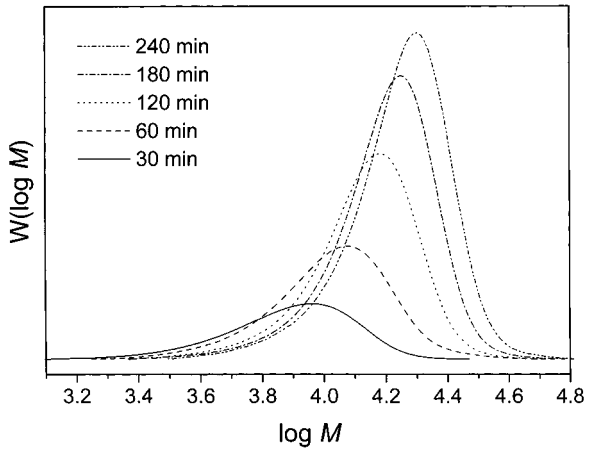


Figure 6. Evolution of molecular weight with time for the polymerization of MMA with *n*-Hex-**1**. [*n*-hex-**1**]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 2:1:1:100, 33 vol % in toluene, 90 °C; data from Supporting Information (areas scaled for conversion).

neous reaction. The reaction solution is homogeneous with *n*-Bu-**1** at 90 °C and at ambient temperature with *n*-Hex-**1**. The ligands with shorter alkyl chains tend to be more soluble in polar monomers such as MMA such that when the concentration of monomer in the reaction is increased, the solubility of the copper complexes is also increased. The *n*-Oct-**1** copper complexes are extremely soluble in nonpolar media thus the solubility of the system can be tuned by appropriate choice of ligand to allow excellent control over the M_n and PDI of the PMMA in a range of solvents. At present it is not apparent why the rate of polymerization is fastest for the heterogeneous polymerization. It is suspected that the solubility of the copper(II) complex is even less than the copper(I) complex. This would have the effect of removing the deactivator from solution resulting in a faster rate of polymerization. This effect is very reproducible, and the Supporting Information contains a second set of data for most ligands in this series. In all cases, PDI remains relatively narrow and M_n increases linearly with conversion. M_n is slightly higher than predicted at the beginning of each reaction, however. Figure 6 shows the evolution of the molecular weight distribution as a function of time for *n*-Hex-**1**. It is noted that in all cases no induction time is observed and that great care was taken to ensure these reactions were deoxygenated as efficiently as possible.

The ligand may also be modified by substitution at the imine carbon. Substituted imines are easily prepared by condensation of the appropriate ketone with primary amine, and these Schiff bases have greater hydrolytic stability, which introduces further potential to change the nature of the Cu(I)/Cu(II) couple. For example, *N*-(*n*-hexyl)-2-pyridylphenylmethanimine, **5**, is prepared by condensation of 2-benzoylpyridine with *n*-hexylamine and when used as a ligand with CuBr is very effective for the atom transfer polymerization of MMA (Table 4). Figure 7 shows the linear evolution of M_n with conversion at two different [monomer]:[initiator] ratios, and the PDI remains low throughout the polymerization. It is interesting to note that a phenyl substituent on the imine carbon yields a ligand with good performance as opposed to the methyl substituent (*n*-Pr-**3**) described earlier. This suggests that electronic effects due to substitution at the imine positions are more important than steric effects.

Table 4. Atom Transfer Polymerization of MMA with 5[a]

time/h	[MMA]/[EIBB][b]	M_n	PDI	conv/%
1	100	3390	1.21	26.1
2	100	4470	1.24	44.7
3	100	6610	1.14	62.8
4.75	100	7190	1.17	80.0
6.5	100	8070	1.17	93.8
1	200	7070	1.19	34.0
2.5	200	11300	1.16	59.7
3	200	13300	1.11	69.7
3.75	200	15300	1.17	77.5
5	200	16000	1.05	86.7

[a] [**5**]:[CuBr]:[MMA] = 2:1:100, 50 vol % in toluene, 90 °C. [b] EIBB = ethyl 2-isobromobutyrate.

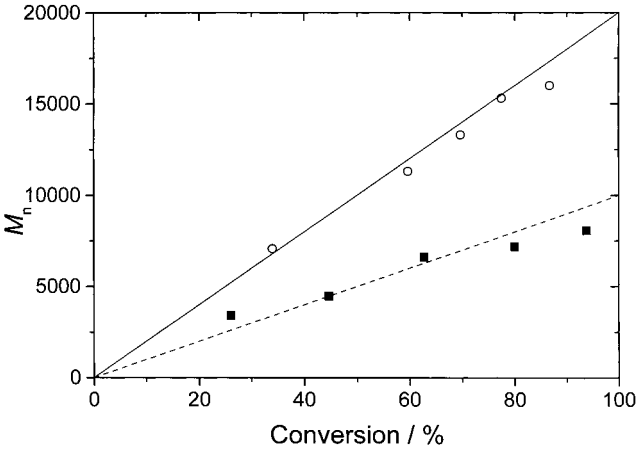


Figure 7. Atom transfer polymerization of methyl methacrylate with *N*-(*n*-hexyl)-2-pyridylphenylmethanimine, **5**: ○, [MMA]/[ethyl 2-bromoisobutyrate] = 200; ■, [MMA]/[ethyl 2-bromoisobutyrate] = 100. [**5**]:[CuBr]:[MMA] = 2:1:100, 50 vol % in toluene, 90 °C. Lines represent theoretical M_n for both experiments; for full data sets see Supporting Information.

Table 5. Use of Various Ligands of Type 2 for the Atom Transfer Polymerization of MMA[a]

ligand	time/h	M_n	PDI	conv/%
n-Pr-**2**	0.33	11 800	1.73	57
	3	13 600	1.60	100
iso-Pr-**2**	1	11 100	1.89	6
	8	10 700	1.79	30
cyclo-Pr-**2**	4	150 000	1.81	6
	24	41 500	3.88	19
n-Bu-**2**	3	11 500	2.11	93
iso-Bu-**2**	3	19 100	2.45	95
sec-Bu-**2**	3	50 700	2.27	54
tert-Bu-**2**	24			0

[a] [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[MMA] = 3:1:1:100, 33 vol % in xylene, 90 °C.

Polymerization of MMA with *N*-Alkyldiazabutadiene Ligands, 2 and CuBr. Diazabutadiene ligands, **2**, are prepared by the condensation of glyoxal with primary amines and have found widespread use as electron-accepting ligands[34] and as ligands in ethene polymerization catalysts.[35] When ligands with unbranched alkyl groups, e.g., *n*-Pr-**2**, are used in atom transfer catalysts, relatively high rates of polymerization are observed but with broad PDI (Table 5). As the branching in the α-position is increased, the rate of polymerization decreases such that with *tert*-Bu-**2** no polymerization is observed even after 24 h at 90 °C (Table 5). These results are in accord with that observed in the previous section with ligands of type **1**. A single-crystal X-ray diffraction study of [bis[*N*-*tert*-butyldiazabutadiene]copper][PF$_6$] showed a very sterically hin-

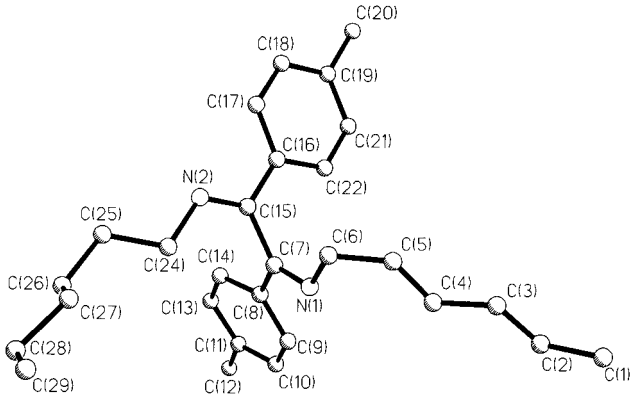


Figure 8. ORTEP diagram of 1,4-dihexyl-2,3-diphenylmethyl-1,4-diaza-1,3-butadiene, **4**.[53] The ligand exists as the *Z,Z*-isomer and so is unable to complex copper(I).

Table 6. Atom Transfer Polymerization of Various *n*-Alkyl Methacrylate Monomers[a]

monomer	time/h	M_n	PDI	conv/%
ethyl	6	11 420	1.33	75
n-butyl	6	13 380	1.27	64
n-hexyl	6	16 440	1.27	86
n-octyl	6	22 150	1.20	57

[a] [*n*-Bu-**1**]:[CuBr]:[ethyl 2-isobromobutyrate]:[monomer] = 3:1:1:100, 25 vol % in xylene, 90 °C; molecular weight data determined by SEC calibrated against PMMA standards; conversion measured by gravimetry.

dered copper(I) complex cation.[50] Hydrocarbon solutions of this compound are deep red and show no sign of discoloration to green copper(II) even after prolonged-periods of exposure to air under ambient conditions. It is envisaged that the copper(I) complex is stable with respect to either dissociation of one of the ligands or any oxidative addition at the metal. As the steric hindrance around the copper is lowered, this effect is reduced and polymerization ensues, but the equilibrium between dormant and active chains is such that the reaction is not controlled; the very much reduced rate of polymerization supports this.

Polymerization attempted with **4** in conjunction with CuBr and ethyl 2-isobromobutyrate yielded no polymer, the reaction mixture remaining completely colorless on addition of the ligand. A single-crystal X-ray diffraction study revealed that this ligand exists as the *Z,Z*-isomer and so is unable to complex copper(I). Figure 8 shows an ORTEP view of this ligand.[53] Thus, the geometric isomeric form of the Schiff base has to considered carefully when designing ligands for successful polymerization catalysts.

Polymerization of Higher Order Alkyl Methacrylates. A range of *n*-alkyl methacrylates (ethyl, butyl, hexyl, octyl) were polymerized in xylene solution (25 wt %) at 90 °C using *n*-Bu-**1** in conjunction with CuBr and ethyl 2-bromoisobutyrate. All monomers polymerize effectively with relatively narrow PDI and controlled M_n (Table 6). The molecular weights reported are relative to the poly(MMA) standards used to calibrate the SEC, and this may account for the discrepancy from the theoretical M_n.

Effect of Sterically Hindered Methacrylates. The effect of branching in the methacrylate on its atom transfer polymerization was investigated by using *n*-, *iso*-, *sec*-, and *tert*-butyl methacrylates with both *n*-Bu-**1** and *n*-Pen-**1** ligands **(**Figure 9, a and b, respectively, and Table 7). Interestingly, as soon as branching is introduced at the α carbon of the side chain, i.e., *sec*-butyl methacrylate, the rate of polymerization decreases significantly, an effect which is independent of Schiff base ligand utilized. The decrease in rate is accompanied by an increase in the PDI. When branching is further increased by using *tert*-butyl methacrylate, the polymerization is very slow, and termination reactions become very significant. It is also suspected that with *tert*-butyl methacrylate hydrolysis occurs, under these conditions, to the acid, resulting in catalyst poisoning. This is seen as an increase in PDI throughout the reaction and polymerization finally ceasing altogether at conversions of approximately 50%, yielding polymer with PDI greater than 1.5. When branching is in the β-position, i.e., isobutyl methacrylate, polymers with narrow molecular mass distribution are produced, and the first-order kinetic plot for the polymerization is linear. Thus, an increase in bulkiness at the α carbon of either the monomer ester or the ligand alkyl group results in the same effect, viz. a decrease in the rate of polymerization and loss of molecular weight control.

Table 7. Effect of Branching in the Butyl Side Group on the Atom Transfer Polymerization of Various *n*-Butyl Methacrylate Monomers[a]

monomer	ligand	M_n	PDI	conv/%
n-BMA	*n*-Bu-**1**	9410	1.18	85.0
iso-BMA	*n*-Bu-**1**	11700	1.18	80.1
sec-BMA	*n*-Bu-**1**	7630	1.34	68.0
tert-BMA	*n*-Bu-**1**	7370	1.74	52.3
n-BMA	*n*-Pen-**1**	12700	1.20	93.2
iso-BMA	*n*-Pen-**1**	9500	1.19	89.3
sec-BMA	*n*-Pen-**1**	11200	1.40	77.7
tert-BMA	*n*-Pen-**1**	6830	1.69	46.7

[a] All polymerizations sampled after 240 min; [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[monomer] = 2:1:1:100, 50 vol % in xylene, 90 °C; molecular weight data determined by SEC calibrated against PMMA standards; conversion measured by gravimetry, for full data sets see Supporting Information.

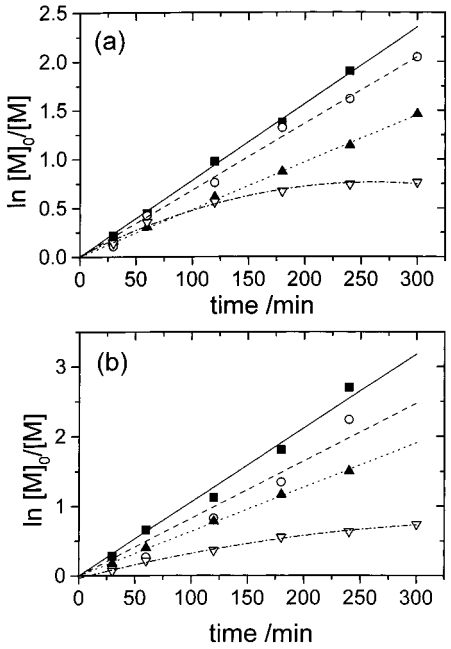


Figure 9. First-order kinetic plots for the polymerization of *n*-butyl methacrylate, ■; *iso*-butyl methacrylate, ○; *sec*-butyl methacrylate, ▲; and *tert*-butyl methacrylate, ▽. [ligand]:[CuBr]:[ethyl 2-isobromobutyrate]:[monomer] = 2:1:1:100, 50 vol % in xylene, 90 °C; (a) *n*-Bu-**1** ligand and (b) *n*-Pen-**1** ligand.

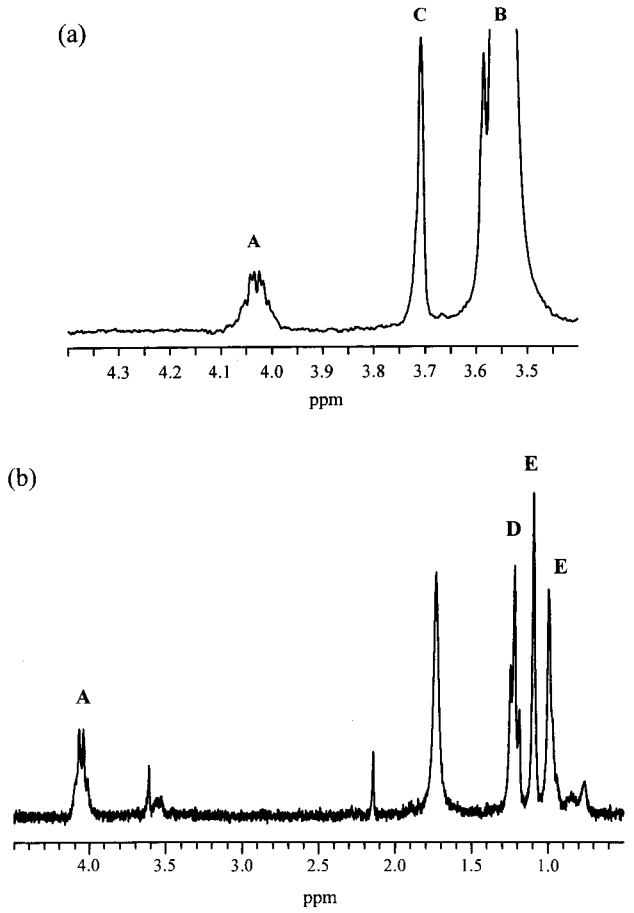


Figure 10. Partial ^{1}H NMR spectra of (a) PMMA and (b) d^8-PMMA.

NMR Characterization of PMMA from Atom Transfer Polymerization. The PMMA from atom transfer polymerization mediated by *n*-Bu-**1**, copper(I) bromide, and ethyl 2-bromoisobutyrate has structure **6**. The $-CH_2O-$ of the α terminal end, A, shows a multiplet at δ 4.03 ppm in the ^{1}H NMR spectrum (Figure 10a), and the ω-methoxy group, C, is shifted downfield from the midchain methoxy groups, B, to δ 3.71 ppm. The M_n calculated from ^{1}H NMR shows excellent agreement with that from size exclusion chromatography, both giving 4700 g mol^{-1}. Confirmation of the assignments made was obtained from the ^{1}H NMR spectrum of poly(d^8-MMA) prepared by atom transfer polymerization under the usual reaction conditions (M_n = 4590, PDI = 1.33) (Figure 10b). The triplet from the α terminal methoxy in the ester group, D, is clearly seen at 1.21 ppm with the two methyl groups, E, at 1.09 and 0.95 ppm. The peak at approximately 1.7 ppm is due to residual protons in the poly(d^8-MMA). The stereochemistry of the polymer backbone is not affected by the ligand employed and is similar to that obtained by conventional free radical polymerization (Table 8).[39,40]

Table 8. Effect of the Alkyl Chain Length in Ligands of Type 1 on the Percentage of Triads in PMMA Produced by Atom Transfer Polymerization at 90 °C[a]

ligand	*mm*	*rm*	*rr*
n-Et-**1**	1.3	40.2	58.5
n-Pr-**1**	1.4	37.3	61.4
n-Pen-**1**	1.9	39.9	58.2
n-Hex-**1**	1.7	36.5	61.8
n-Hep-**1**	1.8	39.1	59.1
n-Oct-**1**	1.7	38.8	59.5
n-Non-**1**	1.6	39.5	58.9
n-Octadec-**1**	1.4	38.6	60.0

[a] Determined from α-methyl group by ^{1}H NMR.

Kinetics of the Polymerization of Methyl Methacrylate. The order of the rate of polymerization on differing concentrations of initiator, CuBr, and monomer

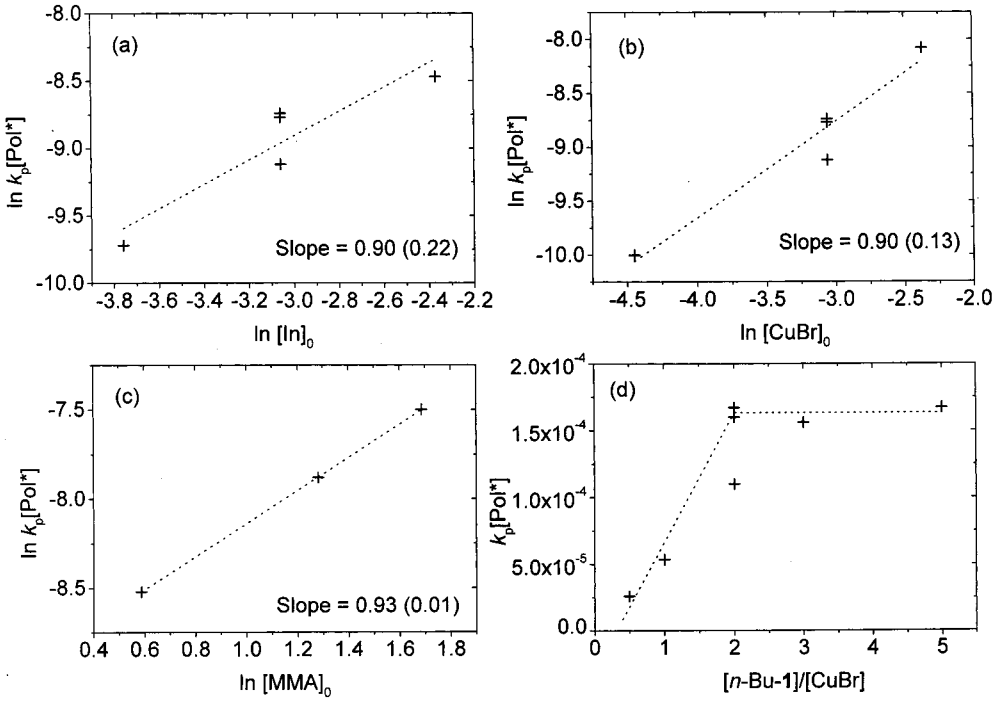


Figure 11. Determination of reaction order for the rate of propagation of MMA polymerization initiated with ethyl 2-bromoisobutyrate in xylene solution at 90 °C in conjunction with *n*-Bu-**1**/CuBr: (a) [MMA] = 4.67 mol dm^{-3}, [CuBr] = 0.0467 mol dm^{-3}, [*n*-Bu-**1**] = 0.140 mol dm^{-3}; (b) [MMA] = 4.67 mol dm^{-3}, [*n*-Bu-**1**]/[CuBr] = 3, [ethyl 2-bromoisobutyrate] = 0.0467 mol dm^{-3}; (c) [CuBr] = 0.0831 mol dm^{-3}, [*n*-Bu-**1**] = 0.249 mol dm^{-3}, [ethyl 2-bromoisobutyrate] = 0.0831 mol dm^{-3}; (d) [MMA] = 4.67 mol dm^{-3}, [CuBr] = 0.0467 mol dm^{-3}, [ethyl 2-bromoisobutyrate] = 0.0467 mol dm^{-3}.

was determined by dilatometry experiments. Dilatometry was performed on an automated system recording one data point every 5 s over the reaction period. For all first-order rate plots the gradients were taken following any observed induction periods due to both trace oxygen present in the system and possible inefficient mixing in the dilatometry reaction vessel. The following rate law was found:

$$R_p \propto [\mathrm{In}]^{0.90\pm0.22}[\mathrm{CuBr}]^{0.90\pm0.13}[\mathrm{MMA}]^{0.93\pm0.01}$$

and suggests that the reaction is essentially first order in initiator, CuBr, and MMA (Figure 11, a, b, and c, respectively). This rate law is in good agreement with that reported by both Matyjaszewski[54,55] and Percec[27] for similar systems.

Figure 11d shows the dependence of the rate on the [ligand]:[CuBr] ratio. The optimum ratio is found to be 2:1 with the rate of polymerization increasing significantly as ligand concentration is raised to this value, but further increases have no effect on the rate. Because of this, reactions are usually carried out with a 2−3 times molar excess of Schiff base ligand with respect to copper(I) halide.

General Discussion and Conclusions

A range of Schiff base ligands in conjunction with CuBr have been shown to be effective for the controlled polymerization of a range of methacrylates in hydrocarbon solvent. The solubility of the catalyst can be altered by changing the alkyl substituent on the ligand with little effect on the polymerization activity. As with other atom transfer polymerization systems the rate of polymerization is first order with respect to monomer, copper(I) bromide, and initiator with at least 2 mol equiv of ligand to copper salt being required for optimum rate of polymerization. The rate of polymerization seems to be reduced when steric hindrance is increased on *either* the ligand or the monomer, which is evidenced by not only a decrease in rate but also an associated increase in the polydispersity of the molecular weight distribution. To date, the mechanism of this type of polymerization has been assumed to be via free radical propagation,[41] and simplified mechanisms have been put forward to explain the events taking place; however, it is reemphasized that evidence of this is still only circumstantial and not conclusive. We are skeptical that the polymerization involves a pentacoordinated copper(II) species as we, and others, have previously postulated.

One of the major issues regarding exploitation of atom transfer polymerization, and related systems, is the high concentration of metal used in order to achieve acceptable rates of polymerization. The order with respect to CuBr of **1** and the time scale required to reach molecular masses of approximately 10 000 require large amounts of CuBr with respect to initiator to be used; typically equimolar amounts are the preferred reaction condition. This is an obvious limitation to this technology which needs to be addressed by the development of ligands for new, faster catalysts in order for its potential to be fully realized, and this is currently the focus of our and other research groups.[18] This will allow a reduction in the concentration of catalyst required to achieve a desired rate of polymerization and lead to fewer problems associated with high metal concentrations. The overall time taken to reach a particular molecular weight, however, will not be dramatically decreased by any improvements in catalysts of this type because increasing the rate of polymerization requires an increase in the concentration of free radicals present in the system which will in turn lead to an increase in the amount of termination.

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Supporting Information Available: Tables giving further polymerization conversion and molecular weight data. This material is available free of charge via the Internet at http://pubs.acs.org.

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