RAPID COMMUNICATION

Synthesis of Hexylated Triethylenetetramine: New Ligand for Homogeneous Atom Transfer Radical Polymerization

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In the past decade, controlled radical polymerization has developed at an unparalleled pace. Since it was first reported by independent groups in 1995,[1–4] metal-mediated radical polymerization, more generally known as atom transfer radical polymerization (ATRP), has become one of the most efficient controlled/living radical polymerization methods to obtain linear polymers and copolymers with different topologies[5–10] as well as low polydispersities.

The catalyst–ligand complex in ATRP plays a key role in controlling the chain growth, polymerization rate, and polydispersity. The main effect of the ligand is to solubilize the transition-metal salt in the organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical.[11] Nitrogen-based ligands are effective for copper-mediated ATRP. The structure of the amine ligand greatly affects the catalyst activity. Better solubility can be achieved by the addition of long alkyl substituents to the ligand.[12,13] Homogeneity of the catalyst–ligand complex results in high deactivator concentration and a fast deactivation rate, which lead to a lower apparent rate constant (k_{app}) and low polydispersity.[14] Tertiary amine and pyridine-based ligands are generally preferred to suppress side reactions. Many amine ligands such as bipyridines,[4,15–18] terpyridines,[19,20] phenantrolines,[21] picolyl amines,[20,22] pyridinemethinamines,[23–27] and tri[15,20,28–30] or tetradentate aliphatic amines[11,15,31–34] have been examined and compared.[20,34–36] Solubility of the ligand and its Cu(I) and Cu(II) complexes in organic media is of particular importance to attain homogeneous polymerization conditions.[25,37] A recent survey[11] of nitrogen-based ligands revealed that the activity of an aliphatic ligand increases with the number of coordinating nitrogen atoms and decreases with the number of carbon atoms in the spacer. On the basis of these criteria, it can be deduced that tetradendate amines having two spacer carbon atoms must be efficient ligands for ATRP. The ligand with a long aliphatic chain on the nitrogen atoms provides solubility of its metal complexes in organic solvents. However, the increasing length of the alkyl substituents induces steric effects and can alter the redox potential of the metal center. Any shift in the redox potential affects the electron transfer and the activation–deactivation equilibrium.[38,39]

In this communication, our focus is to demonstrate copper-mediated ATRP in entirely homogeneous conditions, which was provided by soluble copper complexes of alkylated tetradentate linear amines. For this purpose, triethylenetetramine (TETA) was alkylated with 1-bromohexane (Scheme 1) as follows. TETA was distilled (167–171 °C/1 Torr) before use. 1-Bromohexane (43 mL, 0.305 mol) was added to a solution of 7.3 mL (0.05 mol) of TETA in 50 mL of ethanol and stirred for

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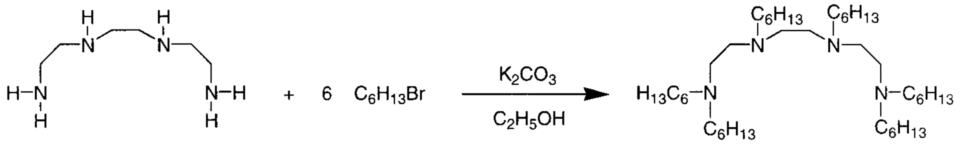

TETA

HHTETA

Scheme 1

1 h at room temperature. Potassium carbonate powder (K_2CO_3, 55 g, 0.4 mol) was added to the mixture and refluxed for 72 h under continuous stirring. While hot, the mixture was filtered and washed with 40 mL of ethanol. The filtrate was transferred into the reaction flask, and another 55 g of K_2CO_3 were added to the mixture. The mixture was refluxed for another 72 h. After cooling, the reaction content was poured into 300 mL of water in a separatory funnel. The organic layer was separated with 70 mL of ethyl acetate. The organic phase was dried with 25 g of anhydrous Na_2SO_4 and filtered. The ethyl acetate in the filtrate was removed on a rotavapor. The product was further purified by column chromatography (with basic aluminum oxide, activated, Aldrich, Brockmann I, standard grade, 150 mesh) with 80 mL of dry tetrahydrofuran (THF). Removal of the THF on a rotavapor gave a light yellow oil. The viscous oily product weighed 21.8 g (86.0%).

^1H NMR ($CDCl_3$, ppm): δ 2.3–2.6 (multiplet, 24H, —CH_2—N—), 1.2–1–6 (br doublet, 48H, —CH_2—), 0.9 (triplet, 18H, —CH_3). ELEM. ANAL. (Calcd. for $C_{42}H_{90}N_4$): C, 77.54 ± 0.56% (77.47); H, 13.81 ± 0.31% (13.93); N, 8.65 ± 0.25% (8.60).

This procedure gives a pure product, TETA, possessing six hexyl groups on the nitrogen atoms (1,1,4,7,10,10-hexakis-1,4,7,10-tetraazadecane). Gas chromatographic analysis showed no trace of 1-bromohexane residues in the product. The purity of the product can also be verified by the absence of a residual NH signal at 3.45 ppm in the ^1H NMR spectrum. Shorter reaction times cause the appearance of an NH signal that indicates incomplete hexylation.

The resulting hexahexyl triethylenetetramine (HHTETA) forms soluble copper complexes in organic solvents including styrene (S) and methyl methacrylate (MMA) because of the six hexyl groups involved. This observation prompted us to use HHTETA as a ligand in ATRP.

In this work, the efficiency of HHTETA as a ligand was investigated in copper-mediated ATRP of S and MMA in bulk conditions. In a typical procedure, 0.072 g (4.35×10^{-2} M) of CuBr, 11.5 mL (8.7 M) of S, and 0.325 g (4.35×10^{-2} M) of HHTETA were placed in a degassed Schlenk tube. The mixture was stirred for 10 min to form HHTETA-CuBr complex. The tube was placed in a silicon oil bath at 110 °C, and 67 μL (4.35×10^{-2} M) of 1-phenyl ethyl bromide (1-PEBr) were introduced with a hypodermic syringe. The kinetics of the reaction was followed by taking aliquots at appropriate time intervals. The molecular weights were monitored by gel permeation chromatography (Agillant 1100, refractive-index detector, Waters Styragel columns HR4, HR3, and HR2; with THF as the eluent and a flow rate of 0.3 mL/min). A similar procedure was followed in the polymerization of MMA, with the exception that the temperature was 75 °C, the monomer/initiator ratio was 300/1, and 65 μL (3.12×10^{-2} M) of ethyl-2-bromo propionate (EBrP) were used as the initiator, which is 1 equiv of CuBr and HHTETA.

During polymerization, the reaction mixture became homogeneous and dark brown for S and light green for MMA. Linear ln($[M]_o/[M]$) versus time plots were observed for bulk polymerization of both S and MMA (Fig. 1), which indicate first-order kinetics with respect to monomer in each case. This result reveals that the concentrations of the growing radicals remained constant throughout the polymerizations. ATRP of both monomers proceeded at reasonable rates. The k_{app} is 1.7×10^{-4} s^{-1} for S ($[S]_o/[1\text{-PEBr}]_o/[CuBr]_o/[HHTETA]_o = 200/1/1/1$) at 110 °C and 1.1×10^{-4} s^{-1} for MMA ($[MMA]_o/[EBrP]_o/[CuBr]_o/[HHTETA]_o = 300/1/1/1$) at 75 °C. In Table 1, the k_{app} of bulk S is comparable to the literature value at 110 °C.

Both of the polymerizations presented linear conversion molecular weight (M_n) relationships as shown in

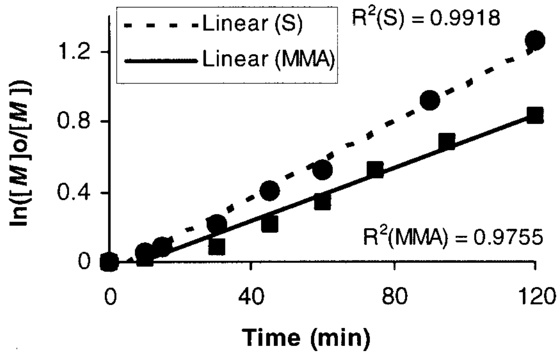

Figure 1. Kinetic plots for ATRP of S (●) and MMA (■) with HHTETA as a ligand. $[S]_o$ = 8.7 M (bulk), $[1\text{-PEBr}]_o = [CuBr]_o = [HHTETA]_o$ = 0.0435 M at 110 °C; $[MMA]_o$ = 9.36 M (bulk), $[EBrP]_o = [CuBr]_o = [HHTETA]_o$ = 0.0312 M at 75 °C.

Table 1. Apparent Rate Constants of ATRP of Bulk S Initiated by 1-Phenyl Ethyl Bromide at 110 °C

Catalyst	Ligand	Reaction Medium	k_{app} (sn^{-1})	Reference
CuBr	dNbpy[a]	Homogeneous	1.10×10^{-4}	15
CuBr	dNbpy[a]	Homogeneous	1.60×10^{-4}	37
CuCl	Bpy[b]	Heterogeneous	1.35×10^{-4}	1
CuCl	Bpy[b]	Heterogeneous	1.40×10^{-4}	18
CuBr	PMDETA[c]	Heterogeneous	4.00×10^{-4}	15
CuBr	HMTETA[d]	Heterogeneous	4.00×10^{-4}	15

[a] dNbpy: 4,4′-di(5-nonyl)-2,2′-bipyridine.
[b] Bpy: 2,2′-bipyridine.
[c] PMDETA: pentamethyltdiethylenetriamine.
[d] HMTETA: hexamethyltriethylenetetramine.

Figure 2 for S and Figure 3 for MMA. In the MMA polymerization the molecular weights are somewhat higher than the theoretical ones as usually observed in the ATRP of MMA. The M_w/M_n's remained relatively narrow (<1.20) and almost unchanged during both polymerizations.

We also attempted to alkylate TETA with 1-chloro hexadecane by the same procedure. However, low substitution yield was obtained even in prolonged reaction times. The ^{1}H NMR spectrum of the obtained product indicates only 27.6% alkylation, which corresponds to about two alkyl chains per molecule. The low conversion can be attributed to low reactivity of the alkyl chloride and steric effects of the bulky alkyl group. The resulting solid product is also soluble in S and MMA. However, very slow polymerization rates were observed when this compound was used as a ligand, and only 29% conversion was obtained after 5 h in the polymerization of S at 110 °C. The polydispersities were somewhat higher (1.2–1.3), presumably because of the remaining nonalkylated secondary or primary amine groups. Another reason for the relatively higher polydispersities might be slow halogen transfer imposed by steric effects of the two hexadecyl groups. As a result, an increase in the chain length of alkyl substitutions makes the copper complex less effective in controlling the chain growth. HHTETA seems to be appropriate for reasonable polydispersities.

In conclusion, the versatile tetradentate ligand HHTETA, which can be prepared readily and cost-efficiently, forms organic soluble copper complexes and provides entirely homogeneous ATRP conditions in the polymerization of S and MMA. Previous work has demonstrated homogeneous ATRP with long-alkyl-chain aromatic or mixed aromatic/aliphatic ligand systems. This work has demonstrated that homogeneous ATRP can be obtained with long-alkyl-chain linear aliphatic ligands. When HHTETA dissolves in S, CuBr and $CuBr_2$ can be extracted from aqueous solutions almost quantitatively. This observation implies the possible use of HHTETA as a ligand for copper-mediated ATRP in suspension or emulsion polymerization processes. Additional studies in this aspect are under consideration.

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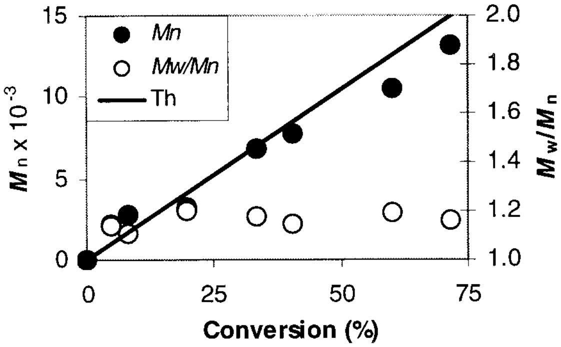

Figure 2. Dependence of molecular weight (M_n, ●) and polydispersity (M_w/M_n, ○) on monomer conversion of S with HHTETA as a ligand. $[S]_0 = 8.7$ M, $[1\text{-PEBr}]_0 = [CuBr]_0 = [HHTETA]_0 = 0.0435$ M at 110 °C.

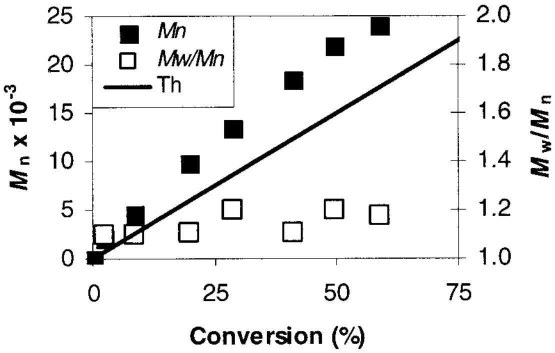

Figure 3. Dependence of molecular weight (M_n, ■) and polydispersity (M_w/M_n, □) on monomer conversion of MMA with HHTETA as a ligand. $[MMA]_o = 9.36$ M, $[EBrP]_o = [CuBr]_o = [HHTETA]_o = 0.0312$ M at 75 °C.

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