

SYNTHESIS OF ALKYLATED LINEAR AMINE LIGANDS AND THEIR EFFECTS ON HOMOGENOUS ATRP

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Introduction

Metal-mediated radical polymerization, more generally known as atom transfer radical polymerization (ATRP)¹⁻⁵ has become one of the most efficient and widely used controlled radical polymerization method to obtain polymers and copolymers with different topologies.

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. So far, a range of multidentate neutral nitrogen ligands was developed as active and efficient complexing agents for copper-mediated ATRP.⁵ Tridentate⁶⁻¹⁰ and tetradentate¹¹⁻¹⁶ aliphatic amines ligands generally provide faster polymerizations than bidentate ligands, while monodentate nitrogen ligands yield redox-initiated free radical polymerization. In addition, ligands with an ethylene linkage between the nitrogens are more efficient than those with a propylene or butylene linkage.¹⁷

Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were synthesized and examined for ATRP as ligands.⁶ Reasons for examining of these type of ligands are, they have low price, due to the absence of the extensive π -bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bipy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.

Solubility of the ligand and its metal complexes in organic media is of particular importance to attain homogeneous polymerization conditions. The rate of polymerization is also affected by the relative solubilities of the activating and the deactivating species of the catalyst. In heterogeneous systems, a low stationary concentration of the catalyst species allows for a controlled polymerization, but the polymerization is much slower than in homogeneous systems.¹⁷ 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.¹⁸

In this study, in order to demonstrate effect of homogeneity, we continued¹⁶ to synthesize a series of ligands with Hoffmann reaction of diethylenetriamine, triethylenetetramine and poly(ethylene imine) with linear alkylbromides which have different chain lengths (C_2H_5 -, C_3H_7 -, C_4H_9 -, C_5H_9 -, C_6H_{13} -). Linear amine ligands were selected because of low price, robust and versatile synthesizing conditions. After synthesizing, alkylated tri-, tetra and multidentate nitrogen ligands were used in ATRP of methyl methacrylate (MMA) and styrene (S) which was carried out in the presence of CuBr as co-catalyst with suitable initiators. The well defined polymers with low polydispersities were obtained due to the homogeneity of the polymerization facilitated by these ligands.

Experimental

Materials. Diethylenetriamine (DETA, 99%), triethylenetetramine (TETA, 60%), polyimine ($M_w=423$ g mol⁻¹), 1-bromobutane (99%), 1-bromohexane (98%), copper(I)bromide (CuBr, 99.99%), potassium carbonate (99+%), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99%), bipyridine (bpy, 98%), and dinonylbipyridine (dNBpy, 97%) were purchased

from the Aldrich Chemical Co. MMA (99 %), S (99 %), bromoethane (98%), ethyl-2-bromoisobutyrate (EiBB, used for MMA, 98%), ethyl-2-bromopropionate (EBP, used for S, 99%) were purchased from Acros Organics Co. Ethanol (99.5%) and anhydrous sodium sulphate (99%) were purchased from J. T. Baker Co. All reagents were used without further purification. Tris(2-(dimethylamino)-ethyl)amine (Me₆-TREN)¹⁹ was synthesized according to modified literature procedure.

Characterization. ¹H NMR spectra of the ligands were collected with a Bruker 200 MHz ¹H NMR using CDCl₃ as a solvent. Monomer conversion was determined by ATI Unicam gas chromatography (GC) equipped with a FID detector and a J&W scientific 15 m DB WAX widebore capillary column. Molecular weight and molecular weight distributions of polymer were measured on a gel permeation chromatography (GPC) system consisting of an Agilent 1100 series pump, four Waters Styragel HR columns (5E, 4E, 3, 2) and an Agilent 1100 RI detector, with a THF flow rate 0.3 ml min⁻¹; poly(methyl methacrylate) and polystyrene were used as standards.

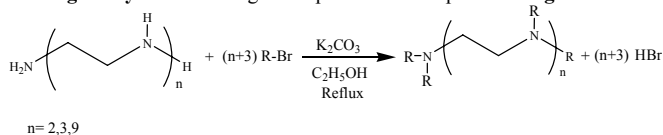
Synthesis of linear alkyl substituted amine ligands. Alkylated linear amine ligands (ALAL) that are derivatives of tridentate, tetradentate and multidentate linear amines; 1,1,4,7,7-pentaethyldiethylenetriamine (PEDETA), 1,1,4,7,7-pentapropyldiethylenetriamine (PPrDETA), 1,1,4,7,7-pentabutyl-diethylenetriamine (PBDETA), 1,1,4,7,7-pentapentyl-diethylene triamine (PPEDETA), 1,1,4,7,7-pentahexyldiethylenetriamine (PHDETA), 1,1,4,7,10,10-hexaethyltriethylenetetramine (HETETA), 1,1,4,7,10,10-hexapropyltriethylenetetramine (HPrTETA), 1,1,4,7,10,10-hexabutyltriethylene tetramine (HBTETA), 1,1,4,7,10,10-hexapentyltriethylenetetramine (HPeTETA), 1,1,4,7,10,10-hexahexyltriethylenetetramine (HHTETA), and ethyl substituted polyimine (EPI) were synthesized according to a procedure described previously.¹⁶

The synthesis of PEDETA is given as representative procedure for all ALAL: Ethyl bromide (0.255 mol) solution in ethanol (100 ml) was added dropwise to DETA. The mixture was stirred for two hours before adding potassium carbonate (0.4 mol). The mixture was refluxed for 3 days and after refreshing the potassium carbonate (0.4 mol) it was continued refluxing for 3 more days. Then ~300 ml of distilled water and 100 ml of ethyl acetate were added in order to separate the organic phase. Organic phase was dried over sodium sulphate overnight. After the filtration, ethyl acetate was evaporated in the rotavaporator. Dry THF (80 ml) was added and solution was passed through a column filled with neutral alumina. Then THF was evaporated. Yellowish oily product was obtained after distillation. ¹H NMR (200 MHz, CDCl₃): δ 0.9-1.0 (m, 18 H), 2.44 (t, 15 H).

Polymerization. A typical ATRP procedure was performed as follows. Catalyst, Cu(I)Br was placed in a 48 ml of flask, which contained a side arm with a Teflon valve sealed with a Teflon stopper. Then the flask was deoxygenated by vacuum-traw-nitrogen circles. MMA (6.24 mol l⁻¹) or S (7.93 mol l⁻¹), anisole and ligand were added to the flask. Finally, an appropriate initiator (EiBB for MMA and EBP for S) was added then the flask was replaced in thermostatically controlled oil bath at given temperatures. All liquid components were nitrogen bubbled prior to placement into the flask. Monomer/ initiator/catalyst/ligand ratio was 200/1/1/1 for both MMA and S polymerizations. Samples were taken periodically via a syringe to follow the kinetics of the polymerization process. The samples were diluted with THF and methanol was added. GC and GPC measurements were performed.

Results and Discussion

Ligand synthesis. The general procedure is depicted in **Figure 1**.



R: C_2H_5 -, C_3H_7 -, C_4H_9 -, C_5H_9 -, C_6H_{13} -

Figure 1. The synthesis of alkylated linear amine ligands

After optimization of the condition, all ALALs were used in ATRP of MMA and S, which provided homogeneous polymerization conditions. A representative kinetic plot of MMA and S polymerizations using PEDETA as a ligand under entirely homogeneous polymerization conditions shows linear relationship with time (**Figure 2**). The linearity of molecular weight versus

conversion plot and low PDI also demonstrated controlled radical polymerization behavior (Figure 3).

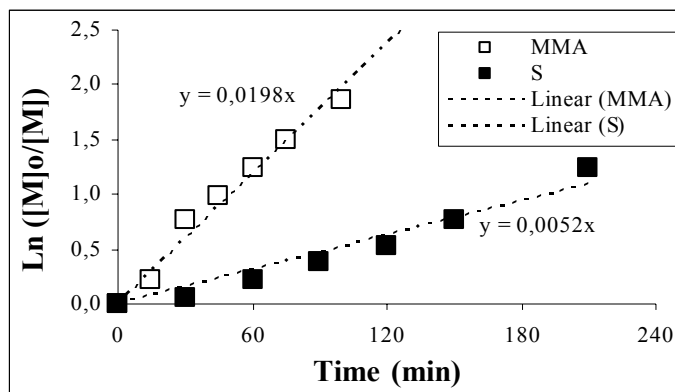


Figure 2. Kinetic plot of MMA (80 °C) and S (110 °C) polymerizations. [S]: 7.93 mol l⁻¹, [MMA]: 6.24 mol l⁻¹ in anisole; [Monomer]₀/[Initiator]₀/[Catalyst]₀/[PEDETA]₀: 200/1/1/1.

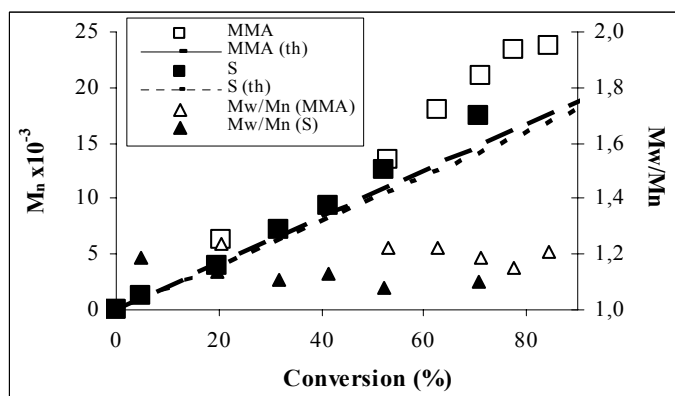


Figure 3. Molecular weight versus conversion of MMA (80 °C) and S (110 °C) polymerization. [S]: 7.93 mol l⁻¹, [MMA]: 6.24 mol l⁻¹ in anisole. [Monomer]₀/[Initiator]₀/[Catalyst]₀/[PEDETA]₀: 200/1/1/1.

Table 1. ATRP Of MMA And S Using Different Ligands.

Ligand	k _p ^{app} (10 ⁻⁴ .s ⁻¹) MMA	k _p ^{app} (10 ⁻⁴ .s ⁻¹) S
PEDETA ^a	3.30	0.87
PBDETA ^a	2.85	0.58
PHDETA ^a	2.75	0.52
HETETA ^a	2.63	1.15
HBTETA ^a	2.42	0.87
HHTETA ^a	2.17	0.80
HHTETA ^b	1.10	1.70
dNbpy ^a	0.42	0.12
Me ₆ Tren ^a	1.27	0.78
PMDETA ^a	2.30	0.78
Bpy ^a	1.88	0.15
EPI ^a	1.60	-

a)[Monomer]₀/[Initiator]₀/[Catalyst]₀/[Ligand]₀: 200/1/1/1. [S]: 7.93 mol l⁻¹ at 110 °C and [MMA]= 6.24 mol l⁻¹ at 80 °C in anisole.

b) S at 110 °C and MMA at 75 °C in bulk, [MMA]₀/[EBP]₀/[CuBr]₀/[HHTETA]₀=300/1/1/1, [S]₀/[PEBr]₀/[CuBr]₀/[HHTETA]₀: 200/1/1/1. Ref [16].

It was previously claimed that the activity of N-based ligands in ATRP decreases with the number of coordinating sites: N₄>N₃>N₂>>N₁ in the heterogeneous system.²⁰ In our study we have also observed the same trend for homogeneous S polymerization (N₄>N₃). However, for the homogeneous MMA polymerization the order of activity was reverse (N₄<N₃). Best to our

knowledge, this is the first report on the effect of alkyl chain length of the ligand in ATRP. The activity of DETA and TETA derivatives decreases with the increasing length of the alkyl chain (C₂>C₃>C₄>C₅>C₆), which may be due to the steric hindrance.

In order to compare behavior of ALALs with those of well established ATRP ligands, two sets of ATRP of MMA and S were carried out under identical experiment condition. The results are shown in Table 1. Apparently, all ALALs and only PMDETA among the conventional ligands exhibited linear relationship. The initiator efficiency is low in MMA polymerization in agreement with the literature values. The low polydispersities of PMMA and PS thus obtained (PDI ≥ 1.05) confirmed the controlled nature of the polymerization. Typical k_p^{app} values for the ligand, PEDETA, were found to be 3.30 x 10⁻⁴ s⁻¹ and 0.87 x 10⁻⁴ s⁻¹ for the polymerization of MMA and S, respectively.

Conclusions

A series of alkylated linear amine ligand were synthesized by a simple and versatile reaction. The ATRP by using ALALs can be performed under homogeneous conditions and relatively fast polymerization rates were attained. Systematic investigation revealed that by changing methyl group of PMDETA to ethyl introduces homogeneity to the polymerization system.

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