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Alkylation of polyethyleneimine for homogeneous ligands in ATRP

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ABSTRACT

Ethylated and butylated polyethyleneimine ligands were synthesized and employed in copper catalyzed atom transfer radical polymerization of styrene and methyl methacrylate with suitable initiators in order to obtain homogeneous polymerizations, resulting in well defined polymers with low polydispersities. Linear curves drawn from kinetics and conversion–molecular weight plots indicate that all the polymerizations were successfully controlled. In ATRP reactions of S and MMA, the apparent rate of polymerization, k_p^{app}, exhibits a plateau at $[\text{Ligand}]/[\text{CuBr}] \geq 0.5$ ratio for both ligands. The apparent rate constant also decreases by increasing the alkyl chain length of the alkylated polyethyleneimine ligand. Ethylated and butylated polyethyleneimine ligands in ATRP of S and MMA were found to be faster than the existing ATRP ligands.

1. Introduction

Atom transfer radical polymerization (ATRP) [1–9] is one of the most useful controlled/radical polymerization methods in scientific area containing multi-components system; each component, which are initiator, metal catalyst, ligand, monomer and solvent, plays an important role in the system. Since the development of ATRP, a wide variety of these components have been investigated to improve the polymerization process. To achieve the minimum requirements such as fast initiation and reversible deactivation, which depends on the redox process, the choice of the ligand has a significant impact. The design of transition metal catalyst complex system allows not only control over the topologies, composition, molecular weight and molecular weight distribution of the polymers but also determines the homogeneity or heterogeneity of the polymerization media. In the literature, relationships between the structure and the effect of alkyl chain length of nitrogen based ligands have been extensively studied [10–44]. To summarize, only aliphatic-branched and aromatic long alkyl chain containing ligands have shown homogeneous polymerization, while most of other systems show heterogeneous polymerization.

The structure of the catalyst complex which depends on the complexing ligand, solvent and temperature has been reviewed extensively [45]. Ligand geometry also plays an important role during the polymerization reaction since cyclizations can occur during the polymerization [46].

The use of multidentate linear amines, N,N,N′,N″,N″-pentamethyldiethylene triamine (PMDETA) and N,N,N′,N″,N‴,N‴-hexamethyltriethylenetetramine (HMTETA) as ligands, results in faster polymerization of styrene (S) and methyl acrylate (MA) compared to catalysts prepared with dinonylbipyridine (dNbpy) in homogeneous polymerization condition. A 1:1 ratio of copper(I) salt to those ligands is often sufficient to achieve maximum rates and optimum control over polymerization [14] even under heterogeneous condition. The reports indicate that the best ratio of ligand to transition metal for any specific polymerization may depend on both the monomer and the catalyst [47].

N-alkylated linear or branched polyethyleneimines used as catalyst (charge transfer or phase transfer) and surfactants have been synthesized with a variety of short or long alkyl chain such as $-CH_3$ [48], $-C_3H_7$ [49], $-C_{10}H_{21}$ [50], $-C_{12}H_{25}$ [48,50–55], $-C_{13}H_{27}$ [56], $-C_{14}H_{29}$ [37,51,52], $-C_{16}H_{33}$ [51,52,56,57], $-C_{18}H_{37}$ [51,52], $-C_{20}H_{41}$ [52], $-C_{22}H_{45}$ [51,54].

In our previous studies, we have examined a series of alkylated linear amine ligands (ALALs) which provide fast polymerization under homogeneous conditions compared to other available and most widely used ATRP ligands. We have shown that even changing the methyl group of PMDETA to ethyl causes homogeneity and an increased reaction rate in the polymerization system [28,41,42]. In recent years, several other articles demonstrating homogeneous polymerization condition have been published on other types of ligand design such as pentasubstituted diethylenetriamine ligand [32], hexasubstituted triethylenetetramine ligand [43], hexasubstituded TREN-based amine ligands [31,34] and multisubstituted hyperbranched polyethyleneimine ligand [44].

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Herein, we report the synthesis of ethylated (EPEI) and butylated (BPEI) linear polyethyleneimine (PEI) as new ATRP ligands and their efficiency in the copper-mediated ATRP of styrene (S) and methyl methacrylate (MMA) to demonstrate 10 dentate alkylated linear amines whether useful as homogenous ligand and to enlarge the ligands library in ATRP. Ligand/catalyst ratio and comparison of the chain length of the alkyl groups were undertaken to optimize the amount of the ligands and its characteristics in homogeneous ATRP process. Additionally, the comparison of new multidentated ATRP ligands (EPEI and BPEI) with the widely used ligands such as PMDETA, DiNBpy and Me_6Tren was carried out.

2. Experimental

2.1. Materials

Linear polyethyleneimine ($M_w = 423\ g\ mol^{-1}$; EIMS m/z 375.5 (M^+)), bromobutane (99%), copper(I) bromide (CuBr, 99.99%), and potassium carbonate (99+%), N,N,N′,N″,N″-pentamethylenediethylenetriamine (PMDETA, 98+%) were purchased from the Aldrich Chemical Co.; methyl methacrylate (MMA, 99%), styrene (S, 99%), iodoethane (98%), ethyl-2-bromoisobutyrate (EBIB, 98%, used for MMA), ethyl-2-bromopropionate (EBP, 99%, used for S) were purchased from Across Organics Co.; anhydrous sodium sulphate (99%) was purchased from J.T. Baker Co. Ethylated and butylated polyethyleneimine, EPEI and BPEI, respectively, were synthesized according to literature procedure [28,41,42]. All other reagents were of analytical grade and used as received.

2.2. Synthesis

2.2.1. Synthesis of ethylated polyethyleneimine (EPEI)

Iodoethane (96.5 mL, 1.1 mol) was placed into 1 L round-bottom flask with 300 mL ethanol. While the solution was stirred at room temperature, 35 mL of polyethyleneimine (0.0885 mol) and 245 g (1.77 mol) of potassium carbonate were added to the solution and the mixture was refluxed for 3 days. After addition of a second amount of potassium carbonate (245 g, 1.77 mol), the reaction mixture was refluxed for 3 more days. Subsequently, the mixture was filtered and ethanol was evaporated in rotavap. Product was extracted by distilled water and ethyl acetate in separatory funnel. After separation, organic phase was dried over anhydrous Na_2SO_4, filtered off and ethyl acetate was evaporated in rotavap. Then the viscous product was obtained after being dried in a vacuum oven (conversion: 19%). EIMS m/z 771 (M^+); M_{EPEI} (calculated) = $770\ g\ mol^{-1}$, ^1H NMR ($CDCl_3$): δ 2.6–2.3 ppm (5H, s), 1.0–0.9 ppm (3H, s).

2.2.2. Synthesis of butylated polyethyleneimine (BPEI)

Bromobutane (63 ml, 0.56 mol) was placed into 1 L round-bottom flask with 300 mL ethanol. While the solution was stirred at room temperature, 18 mL of polyethyleneimine (0.045 mol) and 122.3 g (0.89 mol) of potassium carbonate were added to the solution. Same procedure was performed as EPEI, to achieve the synthesis and purification process of BPEI. Viscous product was obtained (conversion: 69.5%). M_{BPEI} (calculated) = $1306\ g\ mol^{-1}$, ^1H NMR ($CDCl_3$): δ 2.6–2.0 ppm (5H, m), 1.6–1.1 ppm (4H, m), 1.1–0.7 ppm (3H, s).

2.2.3. Polymerization of S and MMA using EPEI and BPEI

A typical ATRP procedure was performed as follows. Catalyst, CuBr (74.6 mg, 5.2×10^{-4} mol for S and 53.8 mg, 3.75×10^{-4} mol for MMA) was placed in a 48 ml of custom-made Schlenk flask, which was sealed with a Teflon stopper and contained a side arm with a Teflon valve. Then the flask was deoxygenated by vacuum-thaw-nitrogen cycles three times. 12 ml of S (0.104 mol) or 8 ml of MMA (0.075 mol), solvent (6 ml of toluene for S and 8 ml of anisole for MMA) and EPEI or BPEI as ligand at different ratios were added to the flask, respectively. Finally, suitable initiator 0.068 ml of EBP (5.2×10^{-4} mol, for S) or 0.055 ml of EBIB (3.75×10^{-4} mol, for MMA) was added. Then the flask was immediately placed in a thermostatically controlled oil bath at 400 rpm stirring rate (110 °C for S, 80 °C for MMA). All liquid components were pre-bubbled by nitrogen and added into the flask under nitrogen atmosphere. An aliquot was taken periodically via a syringe under nitrogen atmosphere to follow the kinetics of the polymerization process. The aliquot either precipitated in methanol, filtered and dried in order to have gravimetric measurements or after dilution in THF or dichloromethane, methanol was added as internal standard in order to have gas chromatography (GC) measurements.

2.3. Characterization

The ^1H NMR spectra were recorded on a Bruker spectrometer (250 MHz) in $CDCl_3$ solution using tetramethylsilane (TMS) as internal standard for the characterization of ligands. Mass spectra were recorded at an ionizing voltage of 70 eV. Elemental analysis was carried out by Thermo Finnegan (Flash 1112 series).

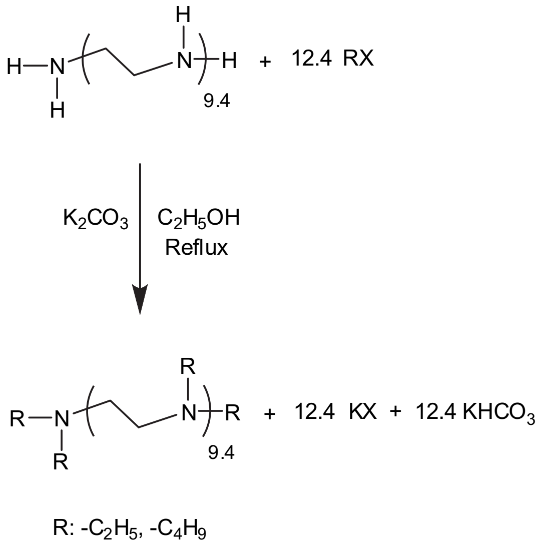
Molecular weight (M_n) and polydispersity index (M_w/M_n) of the polymers were determined by a gel permeation chromatography (GPC) instrument. An Agilent Model 1100 consisting of a pump, a refractive index detector and four Waters Styragel columns as HR 5E, HR 4E, HR 3, HR 2, and THF was used as eluent at a flow rate of 0.3 ml/min at 30 °C. Molecular weights were calibrated using polystyrene or poly(methyl methacrylate) standards.

Monomer conversion was determined by gravimetrically and/or ATI Unicam 610 Series Gas Chromatography equipped with an FID detector using a J&W Scientific 15 m DB WAX Widebore. Injector and detector temperatures were kept constant at 280 and 285 °C, respectively. Initial column temperature is 40 °C, finally reaching up to 200 °C with a heating rate of 40 °C/min.

3. Results and discussions

3.1. Synthesis of ethylated and butylated polyethyleneimine (EPEI, BPEI)

EPEI and BPEI were synthesized according to Scheme 1, using the procedure reported in our earlier work [28,41,42]. During the



Scheme 1. General route for the synthesis of EPEI and BPEI.