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Research Article

A kinetic study of atom transfer radical polymerization of styrene with bis(2-pyridyl)ethylenedimethanimine derivative ligands

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Abstract: Atom transfer radical polymerization (ATRP) of styrene was carried out with multidentate nitrogenbased ligands, namely N,N'-bis[phenyl(pyrid-2-yl)methylene] ethane-1,2-diamine (BPDA) and N,N'-bis[methyl(pyrid-2-yl)methylene] ethane-1,2-diamine (BMDA), and catalyst systems at catalyst/ligand molar ratios of 1/0.33, 1/0.5, 1/1, and 1/1.5 by using 2 different initiators, (1-bromoethyl)benzene (BEB) and ethyl-2-bromopropionate (EBP). Linear first-order kinetic plots were observed for ATRP of styrene upon using BPDA as a ligand with both initiators. Even though the linear slopes indicate that radical concentration remains constant during reactions, high molecular weights were obtained at low conversion and showed a linear relation thereafter. To investigate the molecular weight effect, reactions were also performed in the presence of (1-bromoethyl)benzene initiator in dimethylformamide (DMF) for BPDA and in toluene for BMDA using a catalyst/ligand ratio of 1/1.

Key words: Polymer synthesis, controlled radical polymerization, ATRP, imine ligand

1. Introduction

Atom transfer radical polymerization (ATRP) has developed as one of the strongest and most commonly used synthetic techniques in polymer science. Synthesis of polymers via ATRP employs an alkyl halide as initiator and a metal complex in the lower oxidation state as catalyst. This process, separately improved by Matyjaszewski, Sawamoto, and Percec in 1995, allows the synthesis of polymers of various compositions with predetermined molecular weight and narrow molecular weight distribution.^{1–3} A series of metals such as Cu(I), Ru(II), Fe(II), Pd(II), Rh(III), and Re(II) have been used as catalysts for ATRP.^{4–6} For copper-based ATRP nitrogen-donor compounds have been used as ligand. A wide range of monomers like (meth)acrylates, styrenes, acrylonitrile, acrylamides, and vinyl pyridines have been polymerized and copolymerized successfully with Cu-based catalysts using ligands with amine, pyridine, or imine substructures.^{7–9}

The amine ligands can be classified as aliphatic amine ligands such as 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), cyclic amine ligands such as 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄ Cyclam) and dimethyl cross-bridged cyclam (DM-CBCy), and branched amine ligands such as tris[2-(dimethylamino)ethyl]amine (Me₆ TREN) and tetramethyl-guanidino-tris(2-aminoethyl)amine (TMG₃-TREN), N,N'-bis[(2-pyridyl)methyl]-2-aminomethylpyrrolide (BPPY),

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tris [2-(diethylamino)ethyl]amine (Et $_{6}\,\mathrm{TREN}$), and 2,4-dimethyl-6-bis (2-(dimethyl amino)ethyl)aminomethylphenoxy (N-tetramethyl triamine phenoxy) (Me $_{4}\,\mathrm{TAPH}$). $^{10-18}$

Commonly used imine ligands can be classified as N-alkyl-(2-pyridyl) methanimine (PyMIm-R) such as N-(n-hexyl)pyridyl methanimine (NHPyMIm), N-(n-pentyl) pyridyl methanimine (NPPyMIm), N-(n-pentyl) pyridyl methanimine (NPPyMIm), 2,6-bis[1-(2,6-diisopropyl phenylimino)ethyl]pyridine (BPIEP), glyo-xaldiimine-type (GlIm-R), and bis(2-pyridyl)methanimine.¹⁹⁻²⁵

The strong character of ATRP such as its tolerance to the most functional groups present in reagents, solvents, and impurities makes it attractive. This precludes the extensive use of protecting group chemistry and laborious reagent and solvent purification. To date, macromolecules with several configurations have been synthesized using ATRP.^{10,12,13,16,26-44}

Recently studies have been conducted to develop new ligands and metal complexes that increase the activity and selectivity of the catalyst.^{9,15,21,24,42,45} The choice of ligand is one of the key factors influencing the reactivity of the catalyst. Due to the continuous search for a new ligand for Cu-based ATRP, in this presentation derivatives of the ligands bispyridyl methanimine, N,N'-bis-(phenyl(pyrid-2-yl)methylene)-ethane-1,2-diamine (BPDA), and N,N'-bis-(methyl(pyrid-2-yl)methylene)-ethane-1,2-diamine (BMDA) were used to investigate ligand effects in Cu-based ATRP.⁴⁶⁻⁴⁹

2. Experimental

2.1. General

BPDA and BMDA ligands were prepared as in the literature.⁵⁰ All other chemicals were supplied from Merck, Sigma-Aldrich, or Carlo Erba and used without purification while only toluene was distilled before use. The quoted IR spectra were recorded on a Jasco FT-IR 300E spectrophotometer in CHCl₃ or KBr pellets in the range of 4000–600 cm⁻¹. GPC measurements were conducted with a Knauer gel permeation chromatograph equipped with a WellChrom Interface Box, RI Detector K-2301, and WellChrom HPLC pump K-501 and 3 Waters Styragel HR columns (guard, 4, 3) set with CHCl₃ as eluent at 35 °C and a flow rate of 1 mL/min using ChromGate software. Monodisperse polystyrenes (Polyscience) were used as standard polymer.

2.2. ATRP of styrene

The procedure was performed with minor changes to that in the literature.⁴⁴ ATRP of styrene was carried out using BPDA and BMDA as ligands and EBP and BEB as initiators in 2 different solvents (toluene and DMF) by the following experimental procedure. A given amount of CuCl and ligand were placed in a 50-mL round-bottom flask sealed with a rubber septum. The flask was deoxygenated by 3 cycles of vacuum-nitrogen. Given amounts of monomer (styrene), solvent, and initiator were added to the flask via a syringe and the flask was placed in a silicon oil bath at 110 °C. All liquid components were bubbled with nitrogen prior to transferring them into the flask. Polymerizations were performed at various molar ratios of CuCl/ligand (1/0.33, 1/0.5, 1/1, and 1/1.5), while the molar ratio of monomer/initiator/CuCl was 200/1/1. The liquid partition was taken regularly through a syringe to keep track of the kinetics of the polymerization process. Polymers were precipitated in methanol, filtered, and dried to constant mass in a vacuum oven at 35 °C. The conversion was gravimetrically determined. Polymers were characterized by gel permeation chromatography (GPC) and FT-IR spectrometry.

3. Results and discussion

N,N'-Bis[phenyl(pyridine-2-yl)methylene]ethane-1,2-diamine (BPDA) and N,N'-bis[methyl(pyridine-2-yl)methylene] ethane-1,2-diamine (BMDA) ligands were synthesized according to the literature (Scheme 1).⁵⁰



Scheme 1. Scheme for the synthesis of ATRP ligands.

CuCl-BPDA complex (brown color) is not soluble in styrene and toluene at room temperature. The mixing of CuCl, BPDA, EBP, styrene, and toluene generated a heterogeneous solution at 110 $^{\circ}$ C and thus polymerizations took place in a heterogeneous medium (Scheme 2). Initial conditions and results of the polymerizations are listed in Table 1.



Scheme 2. ATRP mechanism using BMDA and BPDA as ligands.

A semilogarithmic kinetic graph of the monomer consumption versus time for ATRP of styrene using BPDA ligand is presented in Figure 1. First-order kinetic curves were observed for all reaction conditions, indicating that the number of active species is constant during the polymerization and that termination reactions are absent or limited.

The apparent rate constant values of the polymerizations (k_p^{app}) were calculated from the slope of the $\ln([M]_o/[M])$ -time graphs for different ligand ratios in Figure 1 and are listed in Table 1. The obtained apparent rate constant of ATRP of styrene is relatively high compared to those of other ligands such as Bpy (Table 1, run 5) used in the literature.⁴⁷⁻⁴⁹ It is observed that $M_{n,GPC}$ values are higher than $M_{n,th}$ values and thus $f_{ini.eff}$

values $(M_{n,th}/M_{n,GPC})$ are fairly low, between 0.08 and 0.28, and polymers possess a broad molecular weight distribution $(M_w/M_n = 1.32-2.22, \text{ Table 1})$. Similar results were reported in the literature. ^{14,22,45,51,52} These results can be attributed to the heterogeneity of the polymerization system because CuCl/BPDA complex is not completely soluble in styrene and toluene at room temperature or even at 110 °C.

Run no.	$[BPDA]/[CuCl]^a \ge$	$\operatorname{Conv.}^{b}$	$\frac{\text{Time}^{b}}{(\min)}$	$M^b_{n,th}$ (g mol ⁻¹)	$M^b_{n,GPC}$ (g mol ⁻¹)	M_w/M_n^b	k_p^{app} (10 ⁻⁴ s ⁻¹)	$f^{b,c}_{ini.eff}$
1	0.33	16.5	90	3440	13100	2.22	0.35	0.26
2	0.50	28.8	89	6000	76000	1.32	0.65	0.08
3	1.00	45.5	90	9480	34200	2.02	1.00	0.28
4	1.50	45.7	90	9520	48100	2.09	1.03	0.20
5^d	1	24	300	5000	3200	1.21	0.15	1.00

Table 1. ATRP of styrene using ethyl-2-bromopropionate as initiator.

a) $[S]_o = 7.9 \text{ mol } L^{-1}$ in toluene at 110 °C. $[S]_o / [EBP]_o / [CuCl]_o / [BPDA]_o = 200/1/1/x$

b) Last point of kinetic data. Molecular weights were measured by GPC using polystyrene standards.

c) $f_{ini.eff.} = M_{n,th}/M_{n,GPC}$

d) $[S]_o = 7.9 \text{ mol } L^{-1}$ in toluene at 110 °C. $[S]_o / [EBP]_o / [CuBr]_o / [Byr]_o = 200/1/1/1.^{48}$

All polymerizations were also performed by using BEB as initiator at the same conditions with EBP in order to investigate the issue of high molecular weights, since CuCl and BPDA were not completely soluble even at 110 $^{\circ}$ C and the polymerizations also took place in heterogeneous medium. The initial conditions and results of the polymerizations are listed in Table 2.

The semilogarithmic kinetic plots of $\ln([M]_o/[M])$ versus time for ATRP of styrene using BPDA as ligand and BEB as initiator in toluene at 110 °C are presented in Figure 2. First-order kinetic plots were observed for all reactions, indicating that radical concentration remains constant during polymerization, i.e. polymerizations were carried out in a controlled manner. Apparent rate constant values of polymerizations (k_p^{app}) were calculated from the slope of the graphs in Figure 2 and are listed in Table 2.



Figure 1. Kinetic plots for ATRP of styrene using EBP in toluene at 110 °C. $[S]_o = 7.9 \text{ mol } L^{-1}$. $[S]_o/[EBP]_o/[CuCl]_o/[BPDA]_o = 200/1/1/x$.



When different amounts of ligand (BPDA) were used in the ATRP of styrene with both initiators (EBP and BEB), apparent rate constant versus ligand ratio showed the same trend and plateau above the

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[ligand]/[catalyst] ratio at one for both ligands, i.e. every BPDA and BMDA molecule binding one molecule of catalyst that can be seen from Figure 3. The molecular weights increased rapidly at the beginning of the styrene polymerization (at 5%–10% conversion) and after that generally increased linearly with conversion, but remained higher than the theoretical values. As a representative example, molecular weight versus conversion plots of ATRP of styrene using BPDA for both initiators are shown in Figure 4. Initiator efficiency ($f_{ini.eff}$) varied between 0.12 and 0.26 and polymers possessed a broad molecular weight distribution (MWD = 1.31–2.29, Table 2).

Table 2. ATRP of styrene using 1-bromoethylbenzene as initiator.

Run no.	$[BPDA]/[CuCl]^a \ge$	Conv. ^b	Time^{b}	$M_{n,th}^b$	$M^b_{n,GPC}$	M_w/M_n^b	k_p^{app}	$f^{b,c}_{ini.eff}$
		(%)	(min)	$(g \text{ mol}^{-1})$	$(g \text{ mol}^{-1})$		(10^{-4} s^{-1})	
1	0.33	23.1	90	4800	23400	2.29	0.38	0.21
2	0.50	29.8	90	6200	50100	1.31	0.62	0.12
3	1.00	33.7	91	7000	48000	2.10	0.97	0.15
4	1.50	41.6	90	8700	33800	1.68	1.03	0.26

a) $[S]_o = 7.9 \text{ mol } L^{-1}$ in toluene at 110 °C. $[S]_o / [BEB]_o / [CuCl]_o / [BPDA]_o = 200/1/1/x$

b) Last point of kinetic data. Molecular weights were measured by GPC using polystyrene standards. c) $f_{ini.eff.} = M_{n,th}/M_{n,GPC}$





Figure 3. Apparent rate constant versus ligand/catalyst ratio for ATRP of styrene using EBP and BEB in toluene at 110 °C. $[S]_o/[I]_o/[CuCl]_o/[BPDA]_o = 200/1/1/x$. $[S]_o = 7.9 \text{ mol L}^{-1}$.

Figure 4. Molecular weight versus conversion plots for ATRP of styrene using BEB and EBP in toluene at 110 °C. $[S]_o/[I]_o/[CuCl]_o/[BPDA]_o = 200/1/1/1$. $[S]_o = 7.9 \text{ mol } L^{-1}$.

Unfortunately, the molecular weight could not be controlled by changing the initiator. It is thought that the insufficient solubility of the copper-ligand complex in the monomer and the solvent, i.e. heterogeneity of the polymerization system, was responsible for this behavior. Teodorescu and Matyjaszewski reported similar observations for ATRP of (meth)acrylamides with Me₄Cyclam as a ligand and attributed this to the slow deactivation rate of the catalytic system.¹⁴ Slow deactivation can also explain why high conversions of (meth)acrylamides can be achieved when Me₄Cyclam is used as a ligand, but other ligands, such as bipyridine or linear amines, which are successfully employed in the ATRP of styrene and (meth)acrylates, afford very low conversions (which may be explained by a slow activation in conjunction with a fast deactivation process).

It was predicted that the addition of a solvent able to solve the complex would lead to a recovery in the polymerization behavior and thus the basic necessities for controlled/living polymerization could be accomplished.

The solubility of the CuCl/ligand complex was tested in the number of solvents and it was observed that CuCl/ligand complex is partially soluble in dimethylformamide (DMF) and acetonitrile at room temperature.

In order to investigate the issue of high molecular weights, polymerizations were performed in DMF as polar solvent, using a catalyst/ligand molar ratio of 1/1 because the apparent rate constant (k_p^{app}) versus [ligand]/[catalyst] ratio plot showed a plateau above the [ligand]/[catalyst] ratio of one.

Mixing of CuCl, BPDA, BEB, and styrene in DMF provided a heterogeneous mixture of dark brownishred color at 100 °C subject to the CuCl/BPDA complex (brown color) partially soluble in DMF at room temperature. First-order kinetic plots were observed for the polymerization. Apparent rate constant values of polymerization (k_p^{app}) were calculated as $6.67 \times 10^{-5} \text{ s}^{-1}$ from the slope of the graph (Figure 5). The molecular weight increased rapidly at the beginning of the styrene polymerization and after that increased linearly with conversion, but remained higher than the theoretical values ($f_{ini.eff} = 0.29$) (Figure 6).





Figure 5. Kinetic plots for ATRP of styrene using BMDA in toluene and BPDA in DMF at 110 °C. [S]_o = 7.9 mol L^{-1} . [S]_o/[BEB]_o/[CuCl]_o/[L] = 200/1/1/1.

Figure 6. Molecular weight versus conversion plot for ATRP of styrene using BMDA in toluene and BPDA in DMF at 110 °C. $[S]_o/[BEB]_o/[CuCl]_o/[L]_o =$ 200/1/1/1. $[S]_o = 7.9$ mol L⁻¹.

The ATRP of styrene was also performed in toluene as a nonpolar solvent using BMDA at a catalyst/ligand molar ratio of 1/1. Although CuCl-BMDA complex (yellow color) is partially soluble in styrene and in toluene at room temperature, CuCl, BMDA, BEB, styrene, and toluene mixtures were not soluble completely even at 110 °C; therefore, polymerization was also carried out in heterogeneous media. First-order kinetic plots were also observed. Apparent rate constant values of polymerization (k_p^{app}) were calculated as 8.67 × 10⁻⁵ s⁻¹ from the slope of the graph (Figure 5). The molecular weight increased rapidly at the beginning and after that increased linearly with conversion, but remained higher than the theoretical values ($f_{ini.eff} = 0.15$) (Figure 6). It can be concluded that replacing of the methyl group with a phenyl group in the ligand structure does not affect the coordination of ligand with CuCl, namely the stability of CuCl/ligand complex, and hence does not alter the results of the ATRP of styrene.

4. Conclusions

Two imine ligands (BPDA and BMDA) were synthesized by simple and straightforward reactions according to the literature.⁵⁰ Linear first-order kinetic plots were observed for the ATRP of styrene using the BPDA and BMDA ligands. The polymerization proceeded at a moderate rate and in a controlled manner. The apparent rate constant versus [ligand]/[catalyst] ratio plots showed a plateau above the [ligand]/[catalyst] ratio of one, i.e. catalyst complex containing 1 mol of CuCl per mol of ligand molecule. The molecular weights increased rapidly at the beginning of the styrene polymerization and after that increased linearly with conversion; however, they were higher than the theoretical values. This was attributed to the slow deactivation rate of the catalytic system, which causes a rapid increase in the molecular weight at the beginning of polymerization. The introduction of a methyl group instead of the phenyl group into the ligand structure did not affect the solubility of catalyst and the polymerization systems remained heterogeneous.

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