Communications

Alkoxy Bipyridine Ligands for ATRP of Styrene and Methyl Methacrylate

Young-Je Kwark

Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul 156-743, Korea

Introduction

Since the first report in the last decade, atom transfer radical polymerization (ATRP) has been drawn flourishing interests from researchers due to its possibilities in wide applications.[1-11] One of the advantages in ATRP process, compared to other controlled free radical polymerization techniques, is its diversity in applying to various systems. Since the process is composed of many components, such as metal, ligand, halide, initiator, and temperature, those parameters should be optimized for the controlled polymerization of a certain monomer. In other words, if the parameters are optimized properly, it might be possible to polymerize any monomer in controlled way.

Many metal/ligand catalyst systems have been developed for ATRP process.[12-16] Among them, copper halides/bipyridines based systems were the one firstly developed and still one of the most widely used systems.[17] Especially, 4,4'-dinonyl-2,2'-bipyridine (dNbpy) has been very popular due to its effectiveness in controlling polymerization of various monomers such as styrenes and acrylates.[18] The long alkyl substituents make the catalyst soluble in those monomers, which provide excellent control in the polymerization. However, the rate of polymerization is rather slow and the reactions need high temperature for an extended time to complete polymerization.

We believed that the tuning of electron density on nitrogen centers in bipyridines would affect the relative stability of the metal complex between lower and higher oxidation state, and eventually control the rate of polymerization. For example, increased electron density on bipyridines with electron-donating substituents, such as alkoxy groups, would increase stability of higher oxidation state of the metal com-

plex, and make the polymerization faster. In this work, we prepared various alkoxy substituted bipyridines and checked possibilities of using them as ligands of catalyst systems for the ATRP of styrene and MMA.

Results and Discussion

We synthesized various bipyridines with different alkoxy substituents (Figure 1). Since the electron donating nature of the alkoxy substituent was expected to enhance the relative stability of the higher oxidation state of the metal complex, the alkoxy bipyridine ligands were expected to increase rate of polymerization.

2,2'-Bipyridine (bpy) was first oxidized with hydrogen peroxide to increase reactivity in nitration on aromatic ring. The nitropyridine oxide was reacted with sodium alkoxide to introduce alkoxy groups to the ring, and the product was finally reduced to generate alkoxy bipyridines. The products were recrystallized and characterized using FTIR and NMR as pure crystals.

Styrene was polymerized using the synthesized alkoxy bipyridines as a ligand to CuCl. Table I shows the results. As comparison, bpy and dNbpy were also tested. All the synthesized alkoxy bipyridines were effective in ATRP of styrene to give polystyrenes with controlled structure. For all case, the molecular weight determined using GPC was similar to the theoretical values, and polydispersity index (PDI) was less than 1.2. The polymerization using eby was less controlled than others, considering higher values of M_n and PDI, due to the poor solubility of the CuCl/eby complex in styrene. The other four phenoxy bipyridines formed styrene-soluble complex with CuCl, and showed better control in polymerization. CuCl/pby and CuCl/epy complexes gave
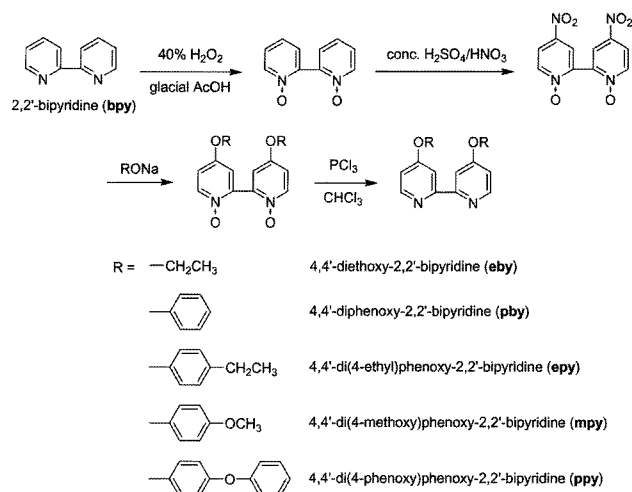

Figure 1. Synthesis of alkoxy bipyridines.

*Corresponding Authors. E-mails: ykwark@ssu.ac.kr

Table I. ATRP Using Various Alkoxy Bipyridine Ligands

| Monomer	Ligands	Time (h)	Yield (%)	$M_{n,theory}{}^{d}$	$M_{n,exp}$	PDI	Remark
Styrene[a]	bpy	10	80	10,810	10,810	1.47	heterogeneous
	dNbpy[c]	3	high	14,500	14,500	1.09	
	eby	10	80	9,810	9,810	1.23	heterogeneous
	pby	5	82	7,440	8,360	1.16	
	epy	10	80	8,110	8,110	1.09	
	mpy	5	90	8,450	8,450	1.17	
	ppy	11	82	6,920	6,920	1.14	
MMA[b]	bpy	1	71	9,500	9,500	1.65	heterogeneous
	dNbpy[c]	1	67	12,920	12,920	1.45	
	pby	1	63	8,800	8,800	1.28	
	epy	1	93	10,200	10,200	1.22	

[a]CuCl; initiator, benzyl chloride; Mt/L/I/styrene = 1/2-3/1/100; 130 °C. [b]CuBr; initiator, methyl α-bromoisobutyrate; Mt/L/I/MMA = 1/2-3/1/100; 90 °C. [c]4,4'-Dinonyl-2,2'-bipyridine. [d]The theoretical values of M_n can be calculated by $(MW_{monomer} \times 100 \times \frac{conversion}{100})$.

the lowest value of PDI as low as 1.05. The rate of polymerization using phenoxy bipyridines was not as high as expected, and similar or slower than that using dNbpy. However, there was a rough trend that the rate of polymerization was higher for the bipyridines with substituents of increased electron donating character (pby and mpy). A kinetic study was performed for the CuCl/pby system (Figure 2). $\ln([M]_0/[M])$ increased linearly with time up to 70% of conversion, indicating no termination taking place. Molecular weight also increased linearly with conversion, indicating no chain transfer reaction. PDI was 1.19 at 30% of conversion and decreased as low as 1.05 at 70% of conversion, which is one of the best results for the ATRP of styrene. These results confirmed that the polymerization of styrene using CuCl/pby initiation system was well-controlled. Chain extension reaction was also performed to see the living character of the growing chain end (Figure 3). Bulk styrene $(([M]/[I])_0=100)$ was polymerized using CuCl/pby catalyst system to give polystyrene $(M_n=10,180, \text{PDI}=1.11)$. After the reaction mixture was completely solidified, additional 100 equivalence of styrene was added to continue the polymerization. The resulting polymer had controlled structure of $M_n=18,160$ and PDI=1.14. The unimodal increase of molecular weight on this experiment indicated that the polymerization using the catalyst system had living character.

MMA was also polymerized using the alkoxy bipyridines ligands along with CuBr. Generally, bipyridines have not been known as good ligand for the ATRP of MMA. Only dNbpy showed some level of control for MMA.[19] Our result was also similar to give PDI of 1.45 with dNbpy. On the other hand, the alkoxy bipyridines showed better performances. When pby and epy, which showed the best results in the ATRP of styrene, were used for the ATRP of MMA, the prepared PMMA had lower PDI of 1.22~1.28. The M_ns were
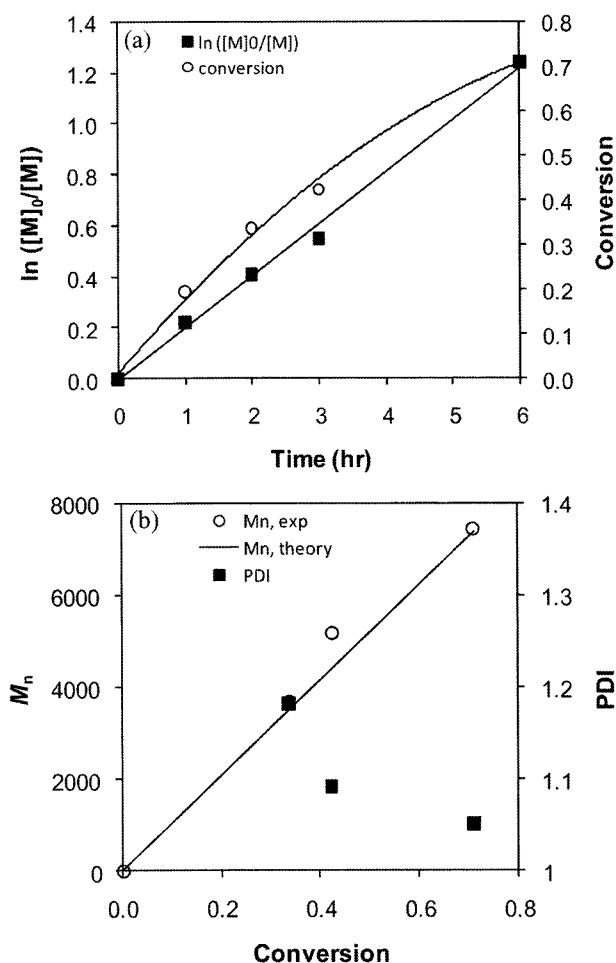
Figure 2. Kinetics of bulk polymerization of styrene using CuCl/pby catalyst system at 130 °C. [styrene]$_0$/[benzyl chloride]$_0$/[CuCl]$_0$/[pby]$_0$=100/1/1/2. (a) $\ln([M]_0/[M])$ and monomer conversion; (b) M_n and PDI.
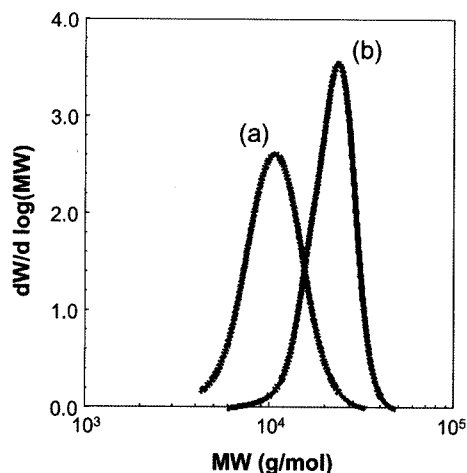
Figure 3. Chain extension reaction of ATRP of styrene using CuCl/pby catalyst system at 130 °C. (a) Polystyrene prepared with initial ratio of [styrene]/[benzyl chloride]/[CuCl]/[pby]=100/1/1/2. (b) Extended polymer by adding additional 100 equivalences of styrene.

also closer to the theoretical values. Especially, the polymerization using the CuBr/epy system was very fast and reached 93% of yield in 1 h.

Conclusions

Various alkoxy bipyridines were synthesized to be used as ligands of ATRP catalyst systems. Among them, phenoxy bypyridines formed monomer soluble complexes with copper halide and the complexes were very effective in control polymerization of styrene and MMA to prepare polymers with defined molecular weight and low PDI. Also they showed enhanced reaction rate in the polymerization of MMA. This result demonstrated another example of tuning activity of ATRP catalyst systems by simply modifying substituent on ligands. For example, substituents on bypyridine with more electron donating nature, such as long alkyloxy groups, would make very reactive ATRP catalyst that is sufficiently active even at lower temperature. Researches in this field will be followed in future.

Supporting Information: Detailed experimental procedures including the synthesis of alkoxy bipyridines ligands are available via the Internet at http://www.polymer.or.kr.

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