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A Copper-Based Reverse ATRP Process for the Living Radical Polymerization of 4-Vinylpyridine: Discussion on Optimum Reaction Conditions

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In this original experiment, reverse atom transfer radical polymerization technique using CuCl_2 /hexamethyl tris[2-(dimethylamino)ethyl]amine ($\text{Me}_6\text{-TREN}$) as catalyst complex was applied to living radical polymerization of 4-vinylpyridine (4VP) with azobisisobutyronitrile (AIBN) as initiator. *N,N*-Dimethylformamide was used as solvent to improve the solubility of the reaction system. The polymerization not only showed the best control of molecular weight and its distribution, but also provided a rather rapid reaction rate with the molar ratio of $[\text{4VP}]:[\text{AIBN}]:[\text{CuCl}_2]:[\text{Me}_6\text{-TREN}]=400:1:2:2$. The rate of polymerization increased with increasing the polymerization temperature and the apparent activation energy was calculated to be $51.5 \text{ kJ}\cdot\text{mol}^{-1}$. Use of Cl as the halogen in copper halide had many advantages over the use of Br. The resulting poly(4-vinylpyridine) was successfully used as the macroinitiator to proceed the block polymerization of styrene in the presence of $\text{CuCl}/\text{Me}_6\text{-TREN}$ catalyst complex via a conventional ATRP process in DMF.

Keywords: living polymerization; reverse atom transfer radical polymerization; 4-vinylpyridine

1 Introduction

Well-defined poly(4-vinylpyridine) (P4VP) with predefined molecular weight, narrow molecular weight distribution and high degree of chain end functionalization has attracted much interest in recent years due to its application as molecular imprinting polymers (1), ion-exchange resins (2, 3), bio-sorption/biosensor materials (4) and microfiltration membranes (5, 6). Anionic polymerization has traditionally been one of the best ways to prepare P4VP, but this polymerization often involves complex catalysis or side reactions (7, 8). Therefore, controlled radical polymerization is becoming increasingly important, as it gives polymers with predictable molecular weight, low polydispersity and well-defined architecture. The nitroxide mediated polymerization of 4-vinylpyridine (4VP) has made great progress in the last few years resulting from the introduction of new types of nitroxides (9, 10), however, elevated reaction temperature is required during the whole process. Reversible addition-fragmentation chain transfer polymerization (RAFT) has been recently studied to obtain homo

and block copolymerization of 4VP (11, 12). High conversions and low polydispersities could be easily obtained, but low molecular weight tailing is also observed. Atom transfer radical polymerization (ATRP) is one of the most widely used methods in the controlled radical polymerization, which involves an equilibrium reversible redox reaction between a transition metal complex, and the halogen containing initiator, or dormant species forming a radical and the metal halide in a higher oxidation state (13–22). With this method, the homo and some block copolymerizations of 4VP have already been described by Matyjaszewski (23–25) and the other researchers (26–28). However, the solvent used in these polymerizations was mainly 2-propanol, or ethanol/water mixture.

To overcome the oxidation of the catalyst M_n^t/LX in ATRP, the use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state has been reported and referred to as reverse ATRP by Matyjaszewski (29–31) and the other researchers (32). To the best of our knowledge, only Cohen (33) reported that reverse ATRP of 4VP in an aqueous/1-methyl-2-pyrrolidone mixture through the use of a 2,2'-azobis(2,4-dimethylpentanitrile) initiator and a $\text{CuCl}_2/2,2'$ -bipyridine catalyst-ligand complex. Pyridine-coordinated copper complexes are not effective catalyst for ATRP, because there are significant complexing behavior of

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the pyridine rings of both monomer and polymer with copper catalyst. So the ligand with high complexing constant to copper is very important. Multi-dentate ligand hexamethyl tris[2-(dimethylamino)ethyl]amine ($\text{Me}_6\text{-TREN}$) can strongly complex copper catalyst and compete with the pyridine units, could be used as the ligand (23).

The optimization of the reaction conditions to prepare P4VP by reverse ATRP was investigated by this research. $\text{Me}_6\text{-TREN}$ was chosen to be the ligand and N,N -dimethylformamide (DMF) was used as a solvent to solubilize the ligand, monomer and polymer. The successful approach of the well-controlled reverse ATRP of 4VP with a new $\text{CuCl}_2/\text{Me}_6\text{-TREN}$ catalyst system by using azobisisobutyronitrile (AIBN) as the initiator in DMF was described for the first time, as well as the effects of $\text{CuCl}_2/\text{Me}_6\text{-TREN}$ catalyst system on the polymerization. Influence of temperature on the polymerization, the overall activation energy for the polymerization and effects of different copper halide on reverse ATRP of 4VP were also discussed. Block polymerization of styrene using P4VP as macroinitiator was also approached.

2 Experimental

2.1 Materials

4VP (Acros, 96%) was dried over CaH_2 and distilled under reduced pressure just before polymerization. Anhydrous CuCl_2 (Shanghai Chemical Reagents Co., A. R. grade) was dried under vacuum at 60°C before use. AIBN (Shanghai Chemical Reagents Co., Shanghai, China) was recrystallized from analytical-reagent-grade ethanol and dried in a desiccator. $\text{Me}_6\text{-TREN}$ was synthesized from tris(2-(aminoethyl)amine according to the literatures (34, 35). N,N -Dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co.) was distilled at reduced pressure and stored over type 4-Å molecular sieves before use.

2.2 Polymerization

A typical example of the general procedure was as follows. A dry flask was filled with the reagents in the order of DMF, $\text{Me}_6\text{-TREN}$, CuCl_2 , AIBN and 4VP. It was degassed and charged with N_2 (three times). The mixture was sealed under N_2 and stirred at room temperature until the catalyst was dissolved. The flask was then immersed in an oil bath at the desired temperature detected by a thermostat, then followed by cooling in ice water after a definite time. A small amount of sample was taken out for chemical analysis. The resultant mixture was then dissolved in 2-propanol, and the solution was passed through a short alumina column for removal of the copper complexes. A rotary evaporator was employed to concentrate the eluent solution, and then precipitate was obtained by pouring residual liquid into a

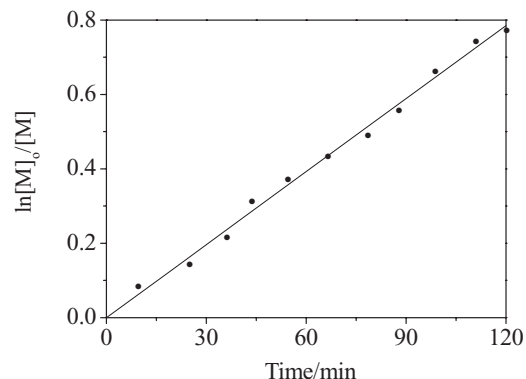


Fig. 1. First-order kinetic plot of monomer consumption as a function of time during reverse ATRP of 4VP with $[4VP] = 4.5 \text{ M}$ and $[4VP]:[AIBN]:[\text{CuCl}_2]:[\text{Me}_6\text{-TREN}] = 400:1:2:2$ at 75°C .

large amount of diethyl ether. Finally the products were filtered several times and dried at 50°C under vacuum.

2.3 Characterization

The conversion of the monomer was determined by $^1\text{H-NMR}$ data. $^1\text{H-NMR}$ spectra were recorded on a Bruker Avance300 NMR spectrometer, using CDCl_3 as a solvent and tetramethylsilane (TMS) as the internal reference.

The molecular weight (M_n) and polydispersity index (PDI) of P4VP were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$ through a combination of Waters HT3, HT4, and HT5 styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 35°C with purified high-performance-liquid-chromatography-grade DMF as an eluent. A Waters 2414 differential refractometer was used as the detector.

According to the characteristics of living polymerization, the theoretical molecular weight (M_{th}) could be calculated

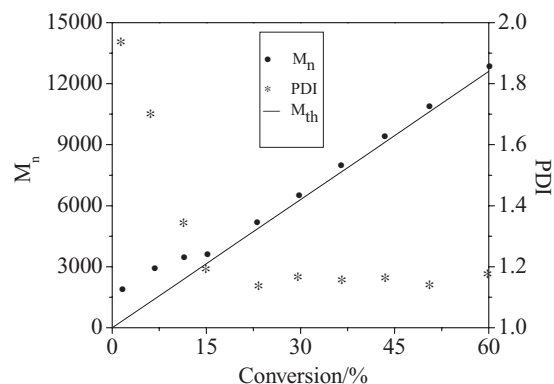


Fig. 2. Dependence of M_n and PDI on the monomer conversion for reverse ATRP of 4VP with $[4VP] = 4.5 \text{ M}$ and $[4VP]:[AIBN]:[\text{CuCl}_2]:[\text{Me}_6\text{-TREN}] = 400:1:2:2$ at 75°C .

Table 1. Data for reverse ATRP of 4VP catalyzed by CuCl₂/Me₆-TREN

Entry	[AIBN]:[CuCl ₂]:[Me ₆ -TREN]	Time/min	Conversion/%	M _{th}	M _n	PDI	k _p ^{app} × 10 ⁵ (s ⁻¹)
1	1:1:1		60.5	12705	14560	1.26	12.9
2	1:2:2		54.3	11403	12140	1.18	10.9
3	1:4:4		48.9	10269	11320	1.15	9.32
4	1:6:6		40.2	8442	9560	1.11	7.14
5	1:2:1	120	59.4	12474	13680	1.17	12.5
6	1:2:3		50.5	10605	11920	1.19	9.77
7	1:2:4		46.7	9807	10670	1.20	8.74
8	1:1:2		62.3	13083	14240	1.29	13.5
9	1:3:2		46.1	9681	10450	1.12	8.58
10	1:4:2		39.8	8358	9750	1.09	7.05

[4VP] = 4.5 M, [4VP]:[AIBN] = 400:1, t = 75°C.

from the following equation (36),

$$M_{th} = \frac{[4VP]}{2[AIBN]} \times M_{w4VP} \times \text{Conversion}$$

Where M_{w4VP} is the molecular weight of 4VP.

3 Results and Discussion

3.1 Reverse ATRP of 4VP

4VP was polymerized with CuCl₂/Me₆-TREN as catalyst and AIBN as initiator at 75°C ([4VP]:[AIBN]:[CuCl₂]:[Me₆-TREN]=400:1:2:2). Figure 1 showed kinetic plots of ln[M]₀/[M] vs. time. The linearity of the plot indicated that the polymerization was approximately first-order with respect to the monomer concentration. It was suggested by the slope of the kinetic that the number of active species in the polymerization process was constant and the termination reactions could be neglected. The monomer conversion reached about 54.3% within 120 min. The corresponding value of the apparent rate constant (k_p^{app}) calculated from the kinetic plot was 10.9 × 10⁻⁵ s⁻¹.

Figure 2 represented Mn and PDI of the resulting P4VP, determined by GPC. The Mn increased with the monomer conversion, and agreed well with those of the theoretical values (M_{th}) beyond 15% of the conversion. The higher molecular weight at conversion less than 15% indicates the incomplete decomposition of AIBN at the beginning of the reaction resulting in a small amount of the polymer chain. The polydispersities were narrow when the conversion was in the range of 15–55% and the value of PDI of P4VP could reach 1.16. The broader PDI at conversion less than 15% suggested there was some termination or side reaction at the beginning of the reaction because the radicals were not immediately deactivated. These results revealed that the polymerization of 4VP with AIBN/CuCl₂/Me₆-TREN initiating system was a living/controlled radical polymerization process.

3.2 Effect of CuCl₂/Me₆-TREN Catalyst System on Reverse ATRP of 4VP

ATRP of 4VP poses a very challenging problem since both 4VP and P4VP are strong coordinating ligands that can compete for the binding of the metal catalysts in these systems. In this study, Me₆-TREN was used as the ligand. In order to further investigate effects of the CuCl₂/Me₆-TREN catalyst system on reverse ATRP of 4VP, a series of experiments of reverse ATRP of 4VP were carried out. The results have been compiled in Table 1. As more CuCl₂/Me₆-TREN catalyst system was added (entries 1, 2, 3, 4), slower polymerization rates and narrower molecular weight distributions were observed, which suggested that the concentration of CuCl₂/Me₆-TREN had a favorable influence on the activation as well as equilibrium of reverse ATRP. The increasing amount of Me₆-TREN in the catalyst system (entries 2, 5, 6, 7) caused a decrease on the rate of polymerization, while the molecular weight distribution of polymers remained narrow. It can be illustrated that a large amount of Me₆-TREN had a role in catalyzing the elimination of the initiator. When the ratio of CuCl₂/Me₆-TREN was changed from 1:2 to 4:2 (entries 2, 8, 9, 10), the molecular weight distribution of polymers decreased from 1.29 to 1.09, and the rate of polymerization decreased prominently.

Table 2. Kinetic data for reverse ATRP of 4VP at different temperature

Temperature (°C)	k _p ^{app} × 10 ⁵ (s ⁻¹)
65	6.43
70	8.45
72	9.34
75	10.9
80	14.1
85	17.9

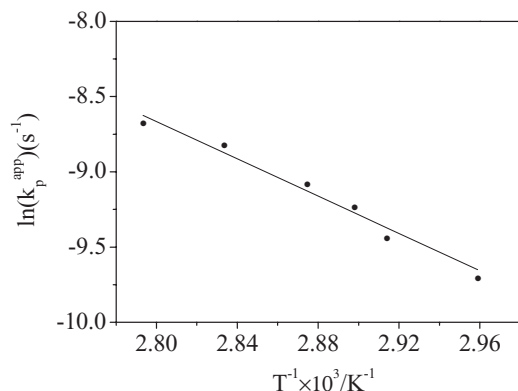


Fig. 3. Effect of temperature on k_p^{app} .

3.3 Effect of The Polymerization Temperature on Reverse ATRP of 4VP

Effect of the polymerization temperature on reverse ATRP of 4VP was investigated with $[4VP] = 4.5 \text{ M}$ and $[4VP]:[AIBN]:[CuCl_2]:[Me_6\text{-TREN}] = 400:1:2:2$ in DMF. The experimental results were given in Table 2. The apparent rate constant became larger with increasing temperature. The Arrhenius plot obtained from the experimental data in Table 2, was shown in Figure 3. In addition, the apparent activation energy was calculated to be $51.5 \text{ kJ}\cdot\text{mol}^{-1}$.

3.4 Effect of Different Copper Halides on Reverse ATRP of 4VP

Different metal catalysts in the polymerization merit further discussion. Effects of different copper halide on reverse ATRP of 4VP were discussed with $[4VP] = 4.5 \text{ M}$ and $[4VP]:[AIBN]:[\text{copper halide}]:[Me_6\text{-TREN}] = 400:1:2:2$ in DMF at 75°C . Table 3 showed the outcomes for the polymerization of 4VP with both $CuCl_2$ and $CuBr_2$ as the catalyst. When $CuBr_2$ was used as the catalyst (entries 5, 6,

Table 3. Data for reverse ATRP of 4VP catalyzed by different copper halide

Entry	Copper halide	Reaction time (min)	Conversion (%)	M_{th}	M_n	PDI
1	$CuCl_2$	50	27.9	5859	6420	1.18
2		80	40.7	8547	9560	1.17
3		100	48.1	10101	11120	1.19
4		120	54.3	11403	12140	1.18
5	$CuBr_2$	50	21.1	4431	5010	1.19
6		80	36.6	7686	8120	1.21
7		100	40.1	8421	9810	1.29
8		120	42.5	8925	10150	1.37

7, 8), a slower polymerization rate and a sharp increase of polydispersity as conversion beyond 42.1% were observed, implying that the use of Br as the halogen might have many disadvantages and the polymerization was ill-controlled as conversion beyond 42.1%. A similar phenomenon has also been reported by Matyjaszewski (23) when ATRP of 4VP was carried out in 2-propanol. The strong C-Cl bond could balance the activation/deactivation by the $CuCl_2/Me_6\text{-TREN}$ complex for a suitable concentration of the active radicals, and the inferior ability of chlorine atom as the leaving group rendered it less susceptible for SN_2 type nucleophilic attack of pyridine molecules on the terminal and initiating alkyl halide headgroups. In contrast, the use of Br as the halogen resulted in an obvious amount of termination reactions, and this was demonstrated by the fact that the polymerization solution employing Br showed much darker color than that with Cl due to the presence of a higher concentration of Cu^{2+} in the solution.

3.5 Chain Extension of P4VP

According to the initiation mechanism of AIBN and the mechanism polymerization of reverse ATRP using AIBN/ $CuCl_2/Me_6\text{-TREN}$ system, the well-defined P4VP with an ω -chlorine atom end groups was obtained. Therefore, the obtained P4VP can act as a macroinitiator for the extension polymerization. For further confirmation of the controlled polymerization, block polymerization of styrene using P4VP ($M_n = 5450$, $PDI = 1.16$) as macroinitiator was carried out in DMF at 80°C in the presence of the $CuCl/Me_6\text{-TREN}$ catalyst system via a conventional ATRP process. When $[St] = 5.0 \text{ M}$, $[St]:[P4VP]:[CuCl]:[Me_6\text{-TREN}] = 500:1:2:2$, the block copolymer P4VP-b-PSt was with $M_n = 54320$, $PDI = 1.28$ (Fig. 4). It was clearly verified that the block polymerization of styrene did take place.

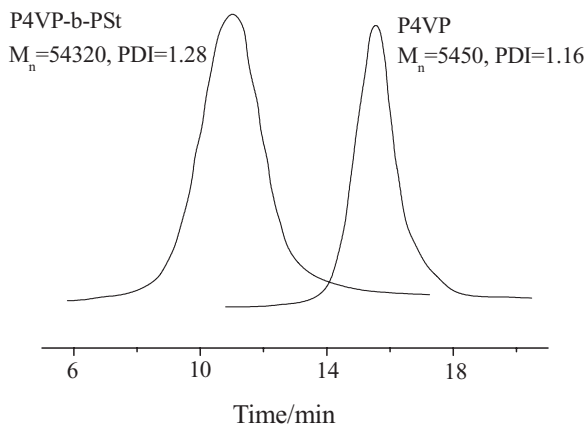


Fig. 4. GPC curves of P4VP before and after chain extension

4 Conclusions

The new catalyst system, $CuCl_2/Me_6\text{-TREN}$, was successfully used in reverse ATRP of 4VP in DMF

with AIBN as the initiator. When the molar ratio of [4VP]:[AIBN]:[CuCl₂]:[Me₆-TREN] was 400:1:2:2, the polymerization showed the best control of molecular weight and its distribution. The rate of polymerization increased with increasing the polymerization temperature and the apparent activation energy was calculated to be 51.5 kJ·mol⁻¹. Use of Br as the halogen resulted in a slower polymerization rate and a sharp increase of polydispersity. The resulting P4VP was end-functionalized by chlorine atoms and was acted as a macroinitiator for the block polymerization of styrene.

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