

Synthesis of poly(4-vinylpyridine) and block copoly (4-vinylpyridine–b-styrene) by atom transfer radical polymerization using 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane as ligand

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Received 8 January 2003; received in revised form 18 March 2003; accepted 19 March 2003

Abstract

Poly(4-vinylpyridine) (P4VP) and block copolymer, poly(4-vinylpyridine–b-styrene) (P4VP-b-PSt) were prepared by atom transfer radical polymerization (ATRP) using 1-phenylethyl chloride as initiator, CuCl and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane ($\text{Me}_6[14]\text{aneN}_4$) as catalyst and ligand. The polymerization of 4VP was carried out in 2-propanol at 40 °C. GPC and NMR studies show that the plot of $\ln([4VP]_0/[4VP])$ against the reaction time is linear, and the molecular weight of the resulting P4VP increased linearly with the conversion. Within 3 h, the conversion can reach almost 90%. P4VP-b-PSt amphiphilic block copolymer with low polydispersity index ($M_w/M_n \approx 1.2$) is also obtained by ATRP of St in DMF at 110 °C using P4VP–Cl as macroinitiator, CuCl/ $\text{Me}_6[14]\text{aneN}_4$ as catalyst.

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Keywords: Atom transfer radical polymerization; 4-Vinylpyridine; 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazamacrocyclotetradecane; Amphiphilic block copolymer

1. Introduction

Well-defined polyvinylpyridines (PVP)s and their block copolymers with controlled molecular weight and narrow molecular weight distribution have attracted much interests, due to their potential applications, such as coordination reagents for transition metals [1]. Anionic polymerization has traditionally been one of the best ways to prepare P2VP [2,3] and P4VP [4–6] with well-controlled molecular weights and narrow molecular weight distribution. Recently, controlled radical polymerization of 4VP was reported using stable free radical polymerization (SFRP) process [7,8]. The polydispersi-

ties of the obtained polymers were relatively broad ($M_w/M_n \approx 1.2$ –1.5), the polymerizations were carried out at high temperatures (130–145 °C). Behaviors of 2VP, 3VP and 4VP in nitroxide-mediated radical polymerization (NMRP) were also studied. The influence of temperature is high and the polydispersities of the obtained polymers were relatively broad [9–11]. The polymerization of 4VP poses a very challenging problem for atom transfer radical polymerization (ATRP) because both 4VP and P4VP are strong coordinating ligands that can compete for the binding of the metal catalysts in polymerization system. As we know, the monomer 4VP is normally present in large excess over the ligand used, the complexation of 4VP with copper might occur. The pyridine-coordinated copper complexes are not-effective catalyst [12]. When the polymerization of 4VP with 1-phenylethyl bromide(1-PEBr)/CuBr/2,2'-bipyridine (bpy)

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as initiation system was performed at 40 °C for 25 h, only a monomer conversion of 10% was achieved [13]. However, block copolymers, P(St-*b*-2VP)s with low polydispersity indexes ($M_w/M_n = 1.1\text{--}1.2$) were obtained by the ATRP of 2VP at 140 °C with chlorine-capped polystyrene/CuCl/bpy as initiation system [14]. Probable reason is the high accessibility of the nitrogen in 4VP compared to 2VP. After further investigation on the ATRP of 4VP, Matyjaszewski pointed out [13] that a stronger binding ligand, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) was used instead of bpy, the competitive coordination of 4VP to copper was evident, although faster polymerization rates were observed, the conversion rate was low. When more stronger binding ligand tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was used in the solution ATRP of 4VP, the linear increase of molecular weight with conversion was observed, and the P4VP with narrow polydispersities ($M_w/M_n \approx 1.1\text{--}1.2$) was obtained. All these facts indicate that the ligand with high complexation constant to copper is very important for controlled radical polymerization of 4VP, although other factors, such as, halide initiator and solvent, also affect the “living” nature of the polymerization. But the ligand Me_6TREN is not synthesized easily and has high price. So we take into account the macrocyclo-tetraamine because its strong binding ability with metal ion. In this paper, we select a macrocyclo-tetraamine ($\text{Me}_6[14]\text{janeN}_4$), which is synthesized easily, as ligand in the ATRP of P4VP, and investigate the “living” nature of polymerization. The block copolymerization of St with 4VP was also studied using P4VP-Cl as macroinitiator, CuCl/ $\text{Me}_6[14]\text{janeN}_4$ as catalyst and ligand.

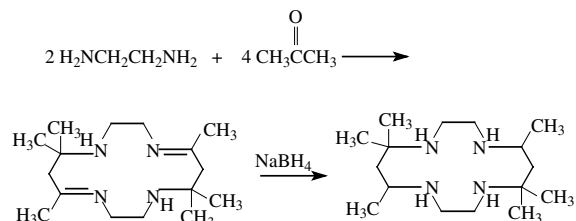
2. Experimental section

2.1. Materials

4VP (Merck-Schuchardt, Munich) was dried over CaH_2 and distilled at 55 °C/18 mm Hg before use. Styrene (St, CR, Shanghai Chemical reagents Co.) was distilled at 40 °C/14.5 mm Hg and stored at 4 °C. 2-Propanol, CuCl and CuBr were purchased from the First Shanghai Chemical Reagent Company and purified before use. 1-Phenylethyl bromide (1-PEBr, 97%, Acros), and 1-phenylethyl chloride (1-PECl) was prepared according the literature procedures [15]. 5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazamacrocyclo-tetradecane ($\text{Me}_6[14]\text{janeN}_4$) was prepared according to Scheme 1 [16]. $^1\text{H NMR}(\text{CDCl}_3, 400 \text{ MHz})$: δ 0.99 (18H,6- CH_3), 1.4~1.7(4H,4-NH), 2.3(4H,2- CH_2), 2.6 (2H,2-CH), 2.8(8H,2- CH_2CH_2).

2.2. Polymerization

Into a dried glass tube with a magnetic bar, CuCl and ligand were added, then monomer, initiator and solvent



Scheme 1.

were added. The mixture was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then immersed in an oil bath thermostated at 40 °C. After the reaction was carried out for a prescribed time, the tube was rapidly cooled down to room temperature. A small amount of sample was taken out, the conversion was measured based on $^1\text{H NMR}$ data, and calculated according to Eq. (1):

$$\text{Conv}(\%) = [(I_{8.4} - I_{5.8})/I_{8.4}] \times 100\% \quad (1)$$

where $I_{8.4}$ and $I_{5.8}$ are the integral values of the peaks at $\delta = 8.4$ and 5.5–6.0 respectively. By adding polymer solution into an excess of toluene, the polymer was precipitated, filtered and dried at 50 °C in a vacuum oven for 24 h.

The block copolymer, P(4VP-*b*-St) was synthesized by the solution ATRP of St with the molar ratio of St:P4VP-Cl:CuCl: $\text{Me}_6[14]\text{janeN}_4 = 100:1:1:3$. To a glass tube, CuCl, $\text{Me}_6[14]\text{janeN}_4$, St, P4VP-Cl and DMF were added successively. The mixture was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then immersed in an oil bath thermostated at 110 °C.

2.3. Characterization

$^1\text{H NMR}$ spectra were performed in an AV-400 NMR spectrometer, using CDCl_3 as a solvent and tetramethylsilane (TMS) as internal reference. Molecular weight and molecular weight distribution were obtained using a Waters 515 HPLC Pump, a Waters 2410 Refractive Index Detector and Waters Styragel Columns. Dimethylformamide (DMF) with Bu_4NBr (0.1 wt%) added was used as eluent at a flow rate of 1.0 ml/min.

3. Results and discussion

3.1. Homopolymerization of 4VP

4VP was polymerized in propanol using 1-PECl as the initiator, CuCl/ $\text{Me}_6[14]\text{janeN}_4$ as the catalyst and ligand. The conditions and results are listed in Table 1.

$^1\text{H NMR}$ spectrum of P4VP is shown in Fig. 1. The peaks at $\delta = 6.2\text{--}6.6$ (b) and $\delta = 8.2\text{--}8.5$ (c) are ascribed

Table 1
ATRP of 4-vinylpyridine initiated with 1-PECl/CuCl/Me₆[14]aneN₄^a

No.	Time (h)	Conversion(%) ^b	M_n (th) ^c	M_n (NMR) ^d	M_w/M_n (GPC)
1	0.5	22	2450	3930	1.20
2	1	45	4860	5700	1.15
3	1.5	64	6860	7400	1.26
4	2	76	8120	8740	1.23
5	3	87	9280	10020	1.24

^a Polymerization conditions: 4VP/1-PECl/CuCl/Me₆[14]aneN₄ = 100/1/1/3 (molar ratio); temperature: 40 °C; solvent: 2-propanol.

^b Calculated according to Eq. (1).

^c M_n (th) = ($M_m \times$ conversion $\times [M]/[I]$) + M_i , where M_m and M_i are the molar masses of monomers and initiator, respectively.

^d Calculated based on NMR data.

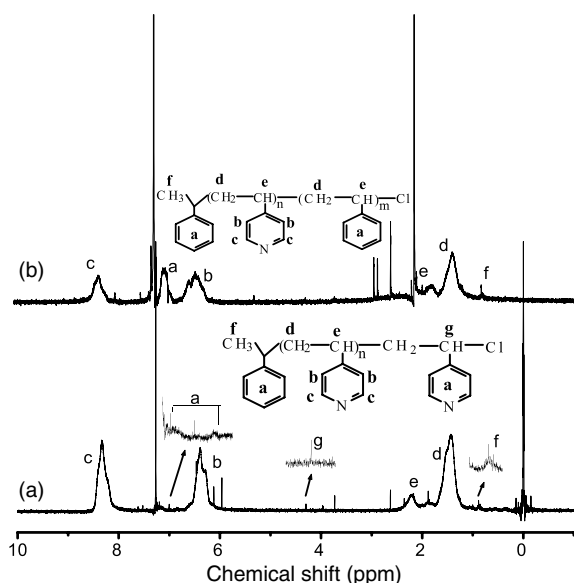


Fig. 1. ¹H NMR spectra of P4VP prepared by ATRP of 4VP at 40 °C with molar ratio 1-PECl/CuCl/Me₆[14]aneN₄ = 1/1/3 (molar ratio) and P4VP-b-PSt prepared at 110 °C with molar ratio P4VP-Cl/CuCl/Me₆[14]aneN₄ = 1/1/3 (molar ratio).

to ortho- and meta-protons of pyridine ring. The integration ratio of peaks b and c to the peaks of methylene and methane protons in the main chain is 4:3, indicating the formation of P4VP. Carefully analyzing Fig. 1(a), we will find that the residual species of 1-PECl stand at both end of P4VP chain. The peaks at $\delta = 6.8\text{--}7.2$ (a), 4.3 (g), and 0.9 (f) are corresponding to aromatic, methine and methyl protons respectively. Their integration ratio of a:g:f = 5:1:3. This must be the result from the equilibrium reactions between 1-PECl or P4VP-Cl and CuCl/Me₆[14]aneN₄. The terminative reactions are insignificant because the termination reaction will lead to the integral value decrease of the peak at $\delta = 4.3$ (g). Assumed that all P4VP chains are capped with 1-phenylethyl and chloride groups, the number-average

molecular weight M_n (NMR) can be calculated according to Eq. (2):

$$M_n \text{ (NMR)} = I_{6.4}/I_{7.0} \times 5/2 \times 105 + 140.5 \quad (2)$$

where $I_{6.4}$ and $I_{7.0}$ are integral values of peak at $\delta = 6.4$ and $\delta = 7.0$ respectively. 105 and 140.5 are molecular weights of 4VP and 1-PECl. The result are listed in Table 1.

As we mentioned above, if the coordination reaction of ligand with copper ions cannot compete against the complexation of 4VP and P4VP to copper ions, slow polymerization will occur. In order to testify the coordinating ability of Me₆[14]aneN₄, this ligand was used in the ATRP of 4VP with CuCl/1-PECl as ligand and catalyst. Fig. 2 illustrates the relationship of conversion and $\ln([4VP]_0/[4VP])$ with the polymerization time. The fast polymerization can be evidenced by almost 90% of conversion in 3 h (see Fig. 2), suggesting that a strong coordination between copper and the Me₆[14]aneN₄ ligand. A linear plot of $\ln([M]_0/[M])$ vs. time demonstrates that the number of propagating species remained constant (see Fig. 2). The molecular weights of the resulting

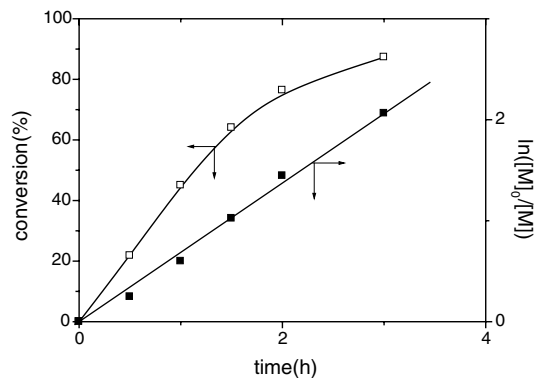


Fig. 2. Plots of conversion and $\ln([4VP]_0/[4VP])$ against polymerization time for the ATRP of 4VP in 2-propanol at 40 °C. $[4VP]_0/[1\text{-PECl}]_0/[CuCl]_0/Me_6[14]aneN_4 = 100/1/1/3$ (molar ratio).

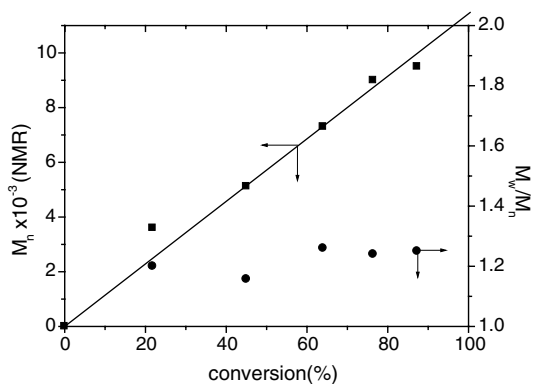


Fig. 3. Plots of M_w and M_w/M_n against conversion for 4VP polymerizations in 2-propanol at 40 °C.

P4VP increased linearly with conversion as shown in Fig. 3, so molecular weight can be controlled by the initial feed ratio of 4VP to 1-PECl and conversion. The representative GPC curve of the P4VP shown in Fig. 4 is symmetrical. The polydispersity of the P4VP remained quite low throughout the polymerization (see Fig. 3). All these facts indicate that the polymerization of 4VP with 1-PECl/CuCl/Me₆[14]aneN₄ as initiation system is of “living” nature, and a fast equilibrium reactions between the active sites and the dormant species. Fig. 3 shows that the measured molecular weights are close to

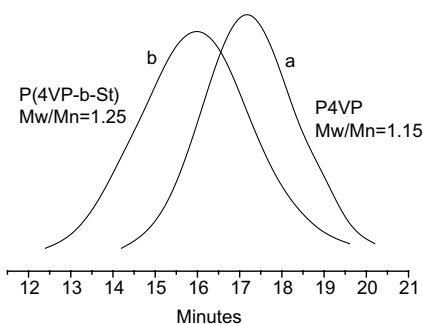


Fig. 4. GPC of P4VP macroinitiator and P(St-b-4VP) copolymer.

the theoretical values, which must be resulted from the high initiation efficiency of initiator. This result is better than that obtained from the polymerization of 4VP using Me₆TREN and CuCl as ligand and catalyst. Probably, Me₆[14]aneN₄ has stronger coordinative ability to copper ions than Me₆TREN. The Me₆[14]aneN₄-coordinated copper complexes in the polymerization system is more active in the redox reactions between 1-PECl and CuCl.

Another competition reactions in the polymerization system must be considered (see Scheme 2). The 1-PEBr is active in nucleophilic substitution reaction, and is easier to react with pyridine, due to higher accessibility of the nitrogen in 4VP. When 1-PEBr/CuBr/Me₆[14]aneN₄ was used as initiation system in the ATRP of 4VP, the plots of conversion and $\ln([4VP]_0/[4VP])$ against polymerization time are shown in Fig. 5. The fast polymerization was observed in initial 1 h, then slowed down. Probable reasons may be due to too much irresistible termination reactions between primacy and chain radicals, and fast reaction (1) in Scheme 2. Reducing the reactivity of initiator, such as PECl, will lower the rates of the reactions (1) and (2), but the effect on the rate of reaction (1)

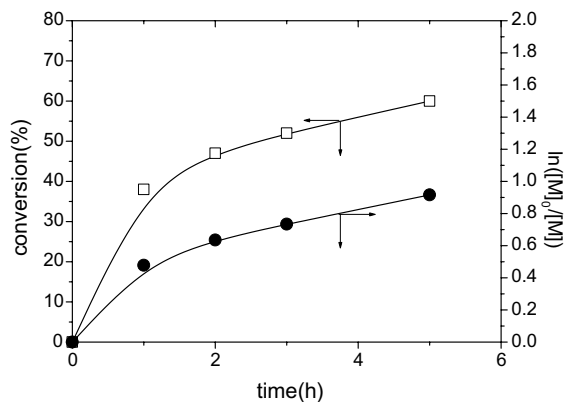
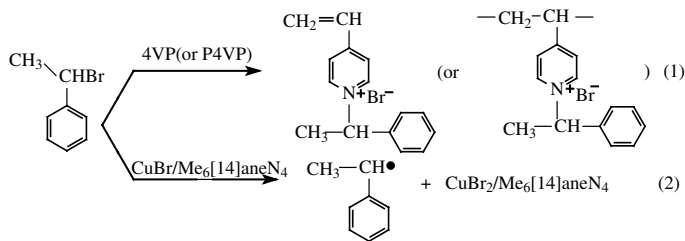


Fig. 5. Plots of conversion and $\ln([4VP]_0/[4VP])$ against polymerization time for the ATRP of 4VP in 2-propanol at 40 °C. $[4VP]_0/[1-PEBr]_0/[CuBr]_0/Me_6[14]aneN_4 = 100/1/1/3$ (molar ratio).



Scheme 2.

is greater than that of reaction (2) since redox reaction (2) has low active energy. Therefore, PECl and CuCl were used as initiator and catalyst in this investigation.

For confirming further the controlled radical polymerization, block polymerization of St using P4VP-Cl as macroinitiator, CuCl/Me₆[14]aneN₄ as catalyst and ligand was carried out in DMF at 110 °C. The block copolymer, P4VP-b-PSt, with $M_{n,NMR} = 14\,500$ and $M_w/M_n = 1.25$ was obtained. One single symmetric GPC curve shown in Fig. 4(b) is an evidence that P4VP-Cl initiated the polymerization of St, block copolymer was obtained. This can be verified further by its ¹H NMR spectrum shown in Fig. 1(b), the aromatic protons in PSt appear at $\delta = 7.0$ and 6.6. This provides another route to synthesize amphiphilic P4VP-b-PSt.

4. Conclusions

The ATRP of 4VP has been successfully carried out using a new ligand, Me₆[14]aneN₄, and the linear increase of molecular weights with conversion has been observed, and the well-defined P4VPs with controlled molecular weight and narrow molecular weight distribution were obtained. The living nature of the polymerization is evidenced by the following facts: linear evolution of molecular weight with conversion; the constant concentration of chain radical during the polymerization and low polydispersity indexes. The polymerization rate is greatly enhanced, and 90% conversion was achieved in 3 h. The amphiphilic copolymer, P4VP-b-PSt with low polydispersity index was obtained by the ATRP of St using P4VP-Cl as macroinitiator, and CuCl/Me₆[14]aneN₄ as catalyst and ligand.

Acknowledgements

The authors gratefully thank the financial support of National Natural Science Foundation of China (no. 59903006), Dr. Jingying Yuan of Beijing University for assistance with the GPC measurements.

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