

## Supporting Information to

# A Favorable Hydrogen Bonding in Room-temperature Cu(0)-Mediated Controlled Radical Polymerization of 4-Vinylpyridine

Wenxiang Wang, Zhengbiao Zhang,\* Zhenping Cheng, Jian Zhu, Nianchen Zhou, Xiulin Zhu\*

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China.

E-mail: zhangzhengbiao@suda.edu.cn (Zheng B. Zhang) or xlzhu@suda.edu.cn (Xiu L. Zhu)

### Experimental part:

#### Materials

4-vinylpyridine (4VP, 95%, J & K Scientific LTD.) was distilled under reduced pressure. Ethyl-2-bromo-2-phenylacetate (EBPA, 95%, Alfa Aesar), Ethyl-2-chloro-2-phenylacetate (ECPA)<sup>1</sup> and 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN)<sup>2</sup> were synthesized according to literatures report. Copper (75  $\mu\text{m}$  powder, 99%, Sigma-Aldrich). 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Shanghai Daishang Chemical Co.), 2-propanol (99%), Dimethyl sulfoxide (DMSO, 99.9%), N, N-dimethylformamide (DMF, 99.9%) were purchased from Shanghai Chemical Reagents and used as received. All other chemicals were obtained from Shanghai Chemical Reagents and used as received unless mentioned.

#### Characterization

The number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2412), using HR 1 (pore size: 100 Å, 100-5000 Da), HR 2 (pore size: 500 Å, 500-20,000 Da), and HR 4 (pore size 10,000 Å, 50-100 000 Da) columns (7.8  $\times$  300 mm, 5  $\mu\text{m}$  beads size) with molecular weights ranging from 10<sup>2</sup> to 5  $\times$  10<sup>5</sup> g/mol. 50 mM solution of LiBr in DMF

was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with polystyrene standards purchased from Waters. The <sup>1</sup>H NMR spectrum of the precipitated polymer was recorded on an INOVA 300 MHz nuclear magnetic resonance instrument using DMSO-d<sub>6</sub> as the solvent. The UV-vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer.

#### **UV-Vis spectroscopic analyses of the interreaction of 4VP with different amount of HFIP**

4VP (0.50 mL) and HFIP (0.25, 0.50, or 0.75 mL) were placed in a quartz UV-vis cell (1 mm path length) and Supplement to 3 mL with methylene dichloride (CH<sub>2</sub>Cl<sub>2</sub>). After vigorous shaking, the cell was placed in the UV-vis spectrometer for measurement. Then the cell was put into a water bath equipped with a thermostat at 25 ± 1 °C for reaction and get out for measurement after a preset time, the absorbance was recorded in the 200-800 nm range.

#### **The UV-Vis spectroscopic for stoichiometry study of 4VP/HFIP complex**

1 mL (9.4 mmol) of 4VP/HFIP mixed solution was added to a 2 mL-ampoule, the ampoule was then flame sealed and placed in a stirred water bath equipped with a thermostat at 25 ± 1 °C under the protection of Ar. After 2 hours, the ampoule was opened and the content was poured into a quartz UV-Vis cell (1 mm path length) and supplement to 3 mL with methylene dichloride (CH<sub>2</sub>Cl<sub>2</sub>). After vigorous shaking, the cell was placed in the UV-vis spectrometer for measurement. Similarly, a series of solutions with molar ratios of 4VP/HFIP, from 0:1 through 0.5:0.5 to 1:0.25, were measured.

#### **Typical procedures for Cu(0)-mediated CRP of 4VP without additional ligand in HFIP**

The monomer (4VP, 1.0 mL, 9.4 mmol), initiator (ECPA, 7.5 μL, 0.038 mmol), catalyst (Cu(0), 3.0 mg, 0.047 mmol), and solvent (HFIP, 1.0 mL) were added to a 5 mL-ampoule in the following order: Cu(0), 4VP, solvent, and initiator. The solution deoxygenated with six standard freeze - pump - thaw cycles. The ampoule was then flame sealed and placed in a stirred water bath equipped with a thermostat at 25 ± 1 °C. After 15 hrs, the ampoule was cooled by immersion in iced water. Afterward, the ampoule was opened and the contents were dissolved in 5 mL 2-propanol, then the solution was washed with isopropyl alcohol saturated base solution (NaOH). The solution was passed through a small basic Al<sub>2</sub>O<sub>3</sub> chromatographic

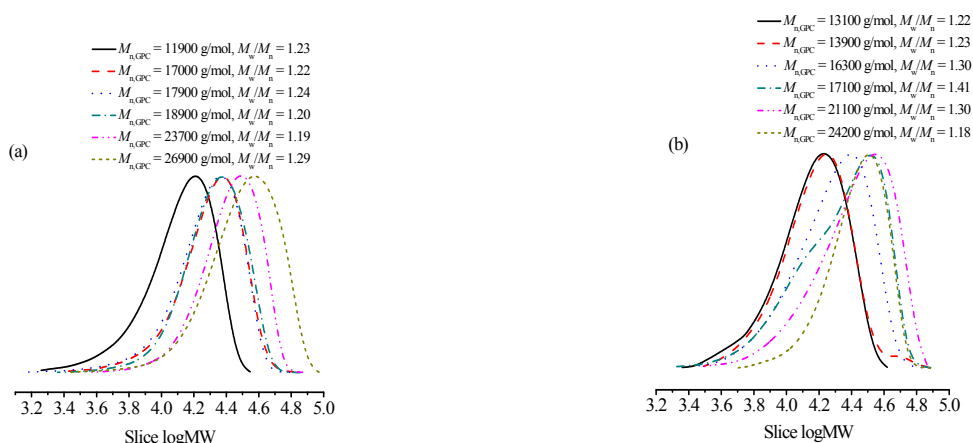
column to remove any residual Cu(0) powder and Cu-ion compounds. The resulting solution was precipitated into 200 mL of cold hexane with stirring. The polymer was isolated by filtration and dried under vacuum until a constant weight at room temperature. The monomer conversion was 25.7% determined by gravimetric calculation. The  $M_n$  and  $M_w/M_n$  values were determined by GPC (DMF) with polystyrene (PSt) standards ( $M_{n,GPC} = 11\,800$  g/mol,  $M_w/M_n = 1.23$ ).

### **Activation of Commercial Cu(0) powder**

In this work, activation of commercial Cu(0) powder was achieved on treatment of the Cu(0) powder with hydrazine hydrate at room temperature.<sup>3</sup> 10 g commercial Cu(0) powder was added to a 25 mL beaker with hydrazine hydrate (50 mM) and distilled THF (10 mL) under N<sub>2</sub>. After stirring for 1 h, the mixture was filtered to remove the suspended substance. Then the Cu(0) powder was rinsed with 10 mL of deoxygenated THF followed by absolute ethanol under positive N<sub>2</sub> pressure. The Cu(0) powder was then transferred to a small vial and dried under vacuum at ambient temperature. The activation process was conducted in glove box, and the dried active-Cu(0) powder was also stored in glove box to minimize contact with air.

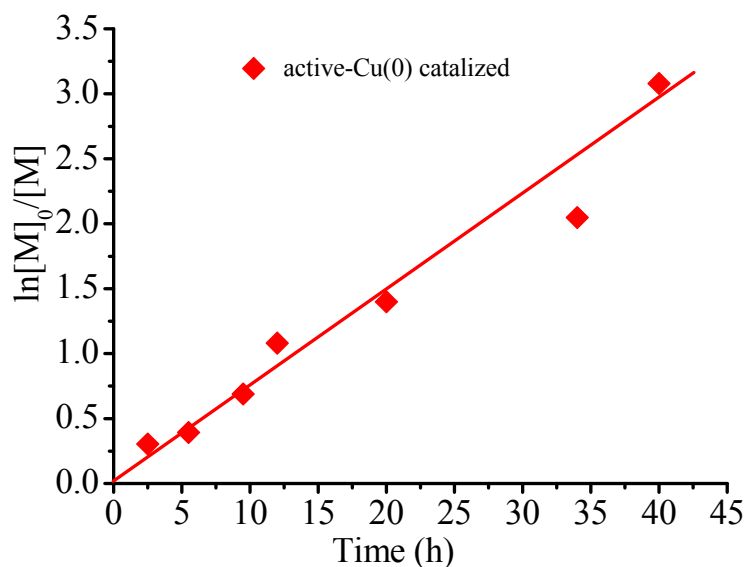
### **Chain extension of P4VP using P4VP as macroinitiator**

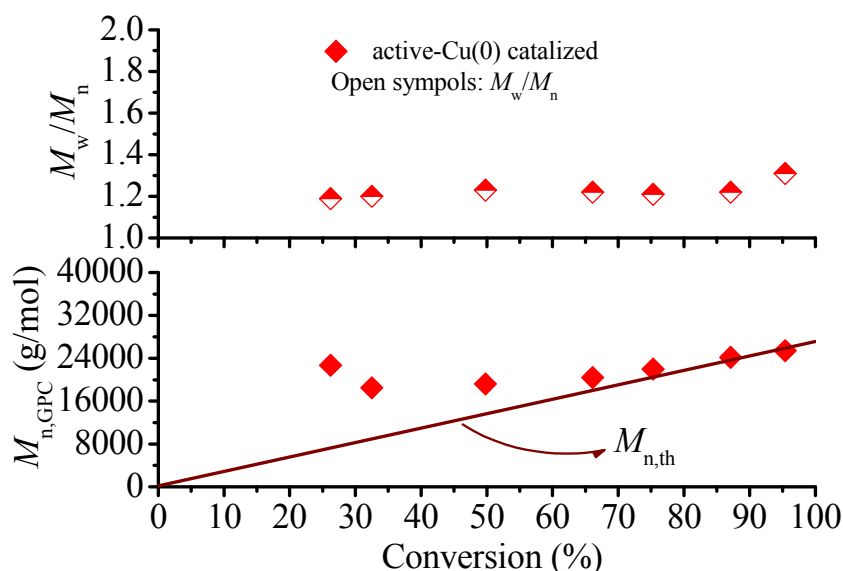
A predetermined quantity of obtained P4VP was dissolved in solution with predetermined quantity of 4VP and HFIP. The polymerization temperature was then stabilized at  $25 \pm 1$  °C. The rest of the procedure was identical to that described earlier except that ECPA replaced by obtained P4VP.



**Figure S1.** Evolution of GPC traces of the prepared polymers in HFIP with  $[HFIP]_0/[4VP]_0 = 1/1$  (a)  $[4VP]_0/[ECPA]_0/[Cu(0)]_0 = 250/1/1.25$ , (b)  $[4VP]_0/[EBPA]_0/[Cu(0)]_0 = 210/1/1$ .

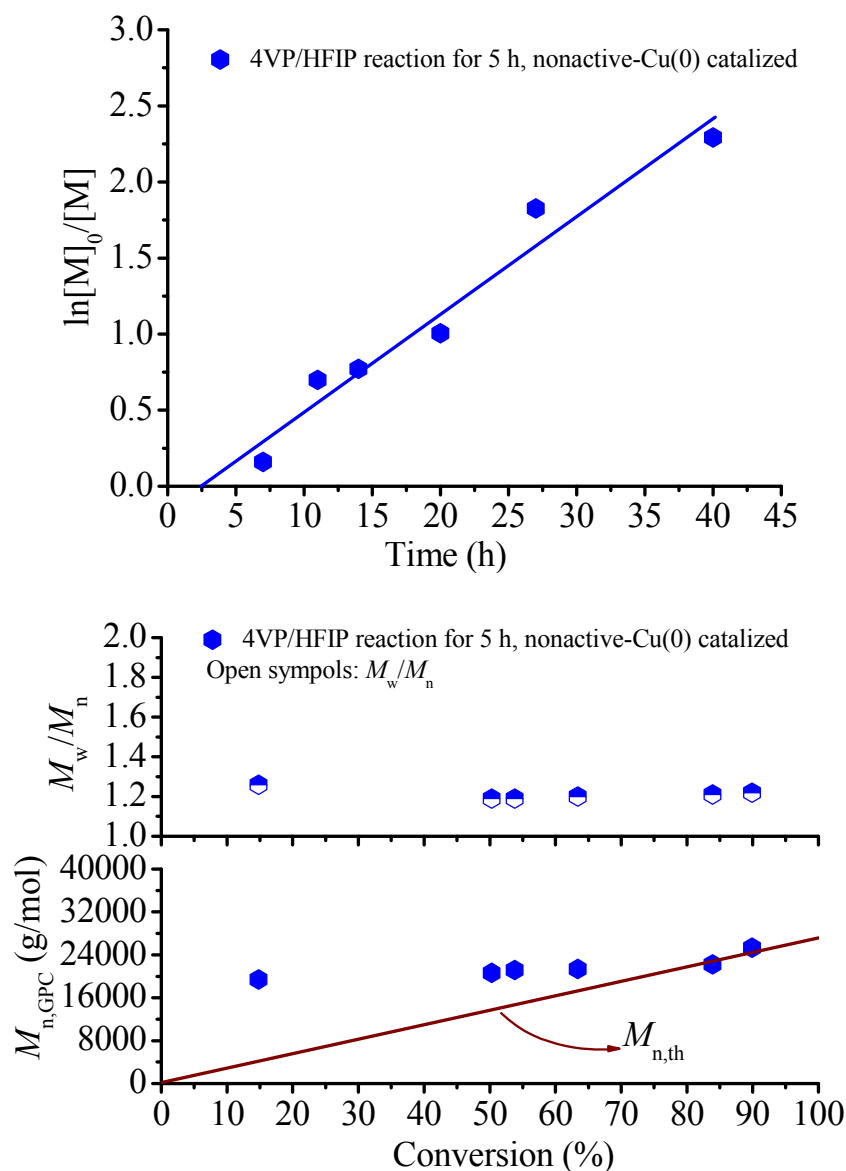
The polymerizations of 4VP mediated with activated  $Cu(0)^3$  were conducted (Fig. S2). The kinetic plots showed linear relationship, and passed through original point. The polymerization mediated with active  $Cu(0)$  was proceeded much faster than that with nonactive  $Cu(0)$  in Fig. 1. However, the molecular weights were higher than calculated values at the early stage of the polymerization reaction, which was due to that the highly active  $Cu(0)$  can generate a high polymerization rate with an intense radical generation and less deactivation.<sup>4,5</sup>





**Figure S2.**  $\ln([M]_0/[M])$  as a function of time (a) and evolution of molecular weight ( $M_{n,GPC}$ ) and polydispersity ( $M_w/M_n$ ) vs. conversion (b) for active-Cu(0)-mediated polymerization of 4-vinylpyridine (4VP) without additional ligand with  $[HFIP]_0/[4VP]_0 = 1.0/1.0$ . 4VP = 1.0 mL, temperature = 25 °C. Theoretical molecular weight  $M_{n,th} = ([4VP]_0/[ECPA]_0) \times M_{4VP} \times \text{Conversion} + M_{ECPA}$ .

In the polymerization process of Figure S3, nonactivated-Cu(0) was added when 4VP/HFIP complex was completely formed after 5 hrs at 25 °C. The polymerization proceeded with a linear kinetic plot, and the induction period was obviously shortened (about 2.5 hrs) compared with that in Fig. 1 (about 5 hrs). Also the rate of the polymerization was markedly accelerated. The molecular weights deviated from calculated values at the earlier stage of the polymerization with narrow  $M_w/M_n$  ( $< 1.30$ ). These results shown that the induction period observed in Fig. 1(a) and Fig. 2(a) was probably due to the oxidized Cu(0) surface and the time needed for the complexation of 4VP and HFIP.



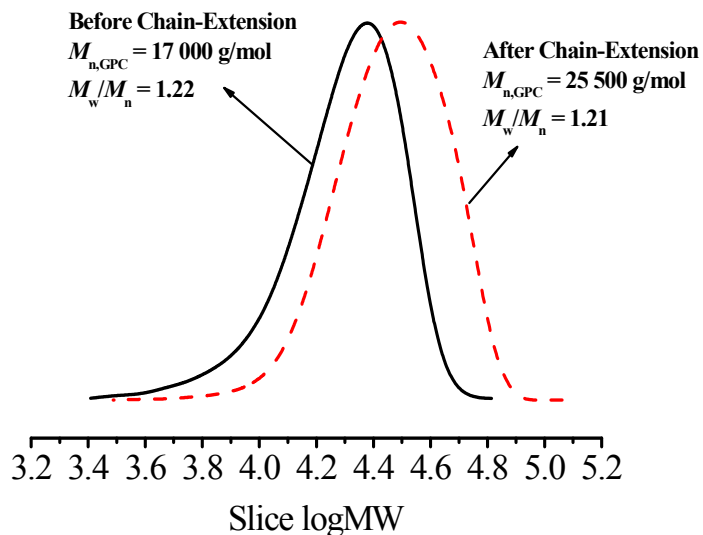
**Figure S3.**  $\ln([M]_0/[M])$  as a function of time (a) and evolution of molecular weight ( $M_{n,GPC}$ ) and polydispersity ( $M_w/M_n$ ) vs. conversion (b) for nonactivated Cu(0)-mediated polymerization of 4-vinylpyridine (4VP) without additional ligand with  $[HFIP]_0/[4VP]_0 = 1.0/1.0$ . nonactivated Cu(0) was added after 4VP/HFIP reaction for 5 hrs. 4VP = 1.0 mL, temperature = 25 °C. Theoretical molecular weight  $M_{n,th} = ([4VP]_0/[ECPA]_0) \times M_{4VP} \times \text{Conversion} + M_{ECPA}$ .

### Analysis of Chain End and Chain Extension

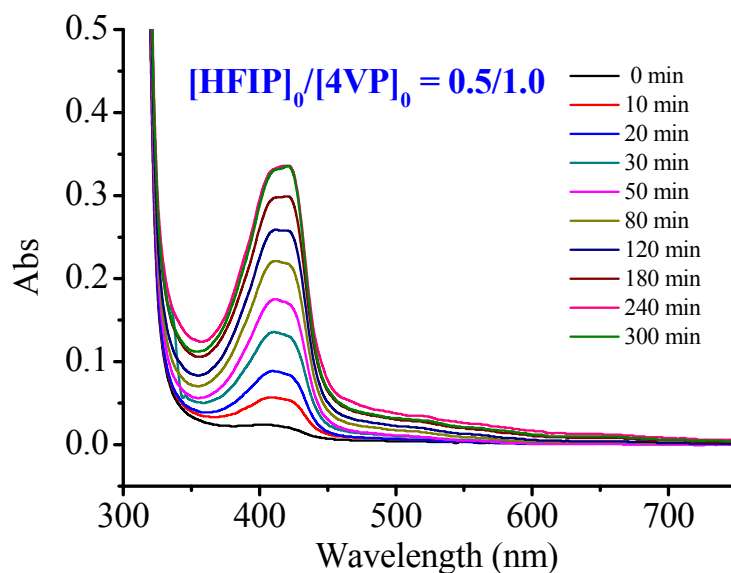
The chain end of the P4VP ( $M_{n,GPC} = 11\,800$  g/mol,  $M_w/M_n = 1.23$ ) prepared with  $[HFIP]_0/[4VP]_0 = 1.0/1.0$  in the absence of ligand was analyzed by  $^1\text{H}$  NMR spectroscopy, as shown in Figure S4. The chemical shifts at 4.36 ppm and 3.76 ppm could be assigned to the protons of the methylene (a in Fig. S4) and methine (b in Fig. S4) from the initiator moieties of ECPA. The chemical shifts at 6.00-9.00 ppm were attributed to the pyridyl groups of monomer repeat units and the phenyl group from ECPA. And the



this result that most of the end groups are active for participation in chain extension reaction, and the chlorine end groups can be reactivated as the macroinitiator.

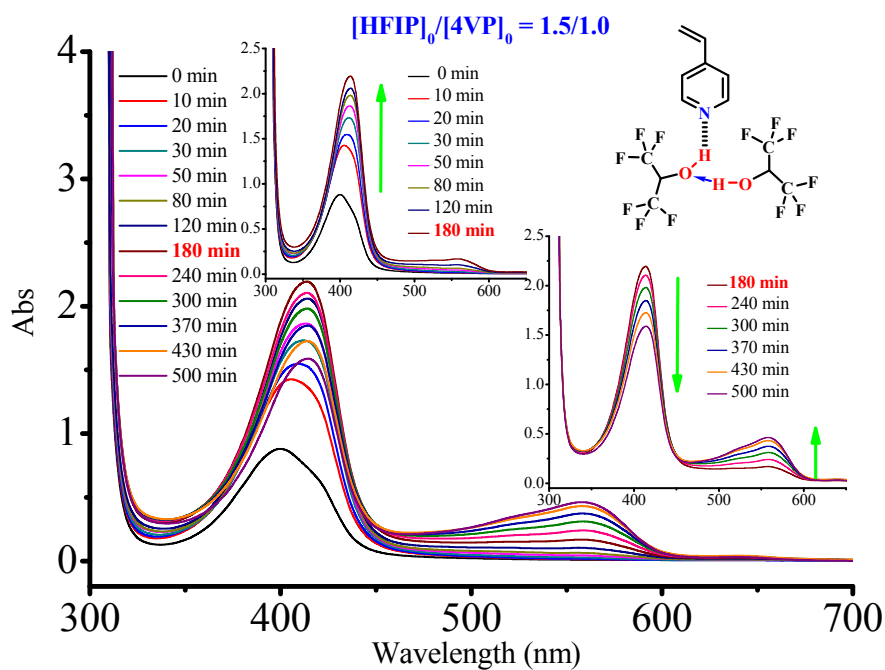


**Figure S5.** GPC curves before and after chain extension with P4VP as the macroinitiator of Cu(0)-mediated polymerization at 25 °C.  $[4VP]_0/[P4VP]_0/[Cu(0)]_0 = 300/1/1$ , 0.56 mL of 4VP,  $[HFIP]_0/[4VP]_0 = 1.0/1.0$ , 48 h, 69.1% conversion.

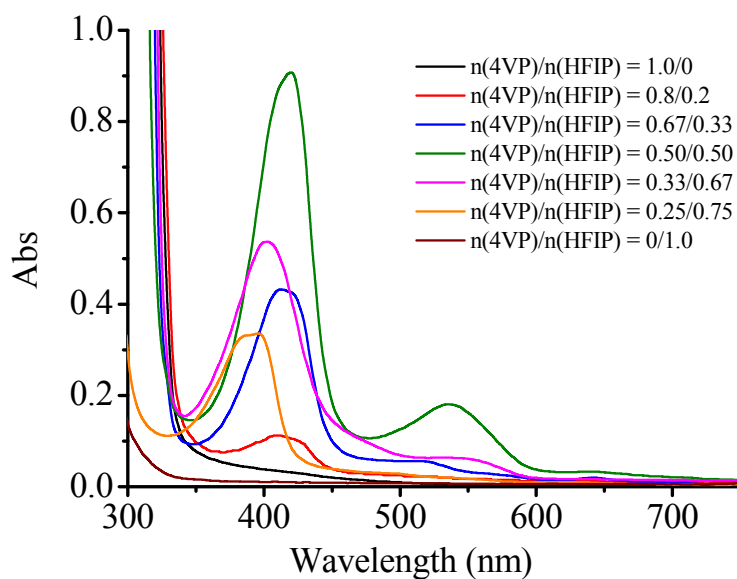


**Figure S6.** UV-vis spectra of 4VP/HFIP mixture with  $[HFIP]_0/[4VP]_0 = 0.5/1.0$  changed over time.





**Figure S7.** UV-vis spectra (a) of 4VP/HFIP mixture with  $[\text{HFIP}]_0/[\text{4VP}]_0 = 1.5/1.0$  changed over time.



**Figure S8.** UV-Vis spectra for the association of 4VP and HFIP, with molar ratios of 4VP/HFIP, from 0:1 through 0.5:0.5 to 1:0. Methylene dichloride ( $\text{CH}_2\text{Cl}_2$ ) was used as solvent.

**Table S1.** Polymerizations of 4VP under various conditions.

Entry	Conditions	T (°C)	Solvent	Time (h)	Conv. (%)	$M_{n, GPC}$ (g/mol)	$M_w/M_n$	$M_{n, th}$ (g/mol)
1	[4VP] <sub>0</sub> /[CPDN] <sub>0</sub> /[AIBN] <sub>0</sub> = 200:1:0.2	60	DMF	192	82.1	17 700	1.05	17 300
2		60	2-propanol	52	82.5	23 300	1.03	17 300
3		60	HFIP	192	47.3	10 300	1.07	9 900
4	[4VP] <sub>0</sub> /[ECPA] <sub>0</sub> /[CuCl] <sub>0</sub> = 250:1:1.25	40	HFIP	24	42.9	15 400	1.17	11 800
5		40	HFIP	240	58	21 500	1.13	15 800
6		60	HFIP	24	47.3	18 400	1.12	12 900
7		60	2-propanol	96	0	--	--	--
8	[4VP] <sub>0</sub> /[ECPA] <sub>0</sub> /[Cu(0)] <sub>0</sub> = 250:1:1.25	60	HFIP	18	56	29 700	1.2	15 100
9		60	HFIP	48	58.4	39 000	1.25	15 900

Polymerization conditions: 4VP = 1.0 mL, Solvent = 1.0 mL.

## References

- [1] K. Y. Baek, M. Kamigaito and M. Sawamoto, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1937–1944.
- [2] J. Zhu, X. L. Zhu, Z. P. Cheng, F. Liu, J. M. Lu, *Polymer*, 2002, **43**, 7037–7042.
- [3] N. H. Nguyen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* 2010, **48**, 5109–5119.
- [4] X. Jiang, B. M. Rosen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* 2010, **48**, 403–409.
- [5] A. G. West, B. Hornby, J. Tom, V. Ladmiral, S. Harriison, S. Perrier, *Macromolecules*, 2011, **44**, 8034–8041.