Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/polymers

COMMUNICATION

Hydrogen Bonding Promoting Controlled Radical Polymerization of 2-Vinyl Pyridine: Supramonomer for A Better Control

Huaqiao Wu,[1] Yingbo Wan,[1] Wenxiang Wang,[1,2] Yong Wang,[1] Nianchen Zhou,[1] Wei Zhang,[1] Xiaohong Li,[1]* Zhengbiao Zhang,[1]* Xiulin Zhu[1]

Received (in XXX, XXX) Xth XXXXXXXXX 201X, Accepted Xth XXXXXXXXX 201X
DOI: 10.1039/b000000x

Monomer-activating effect imposed by hydrogen bonding has been long acknowledged, however, the in-depth understanding was still lack. In this work, for the first time, the monomer-activating effect was elucidated with 2-vinyl pyridine (2VP) as model monomer and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as hydrogen bonding donor (solvent). A strong hydrogen bonding between HFIP and 2VP was revealed by careful ^{1}H NMR analysis and computer simulations. Upon this solid hydrogen bonding, 2VP underwent a well-controlled radical polymerization with improved control over molecular weight in contrast to those under non-hydrogen bonding environment. The well-controlled polymerization manner was ascribed to the electron induction effect of monomer molecules under hydrogen bonding interaction, *i.e.*, the electron redistribution of the monomer's vinyl double bonds, activating the monomers. The hydrogen bonding interactions between HFIP and growing radicals or HFIP and terminal monomer units of dormant polymeric species might also contribute to the good control. The unprecedented explanation of hydrogen bonding promoting controlled radical polymerization or monomer-activating effect was testified for other monomers, and some reasonable discussions were made.

Poly(vinyl pyridine)s based polymers are intriguing polymers due to the basic nitrogen atoms of pyridine group, which have strong interaction with various ions and polar groups and can make many reactions possible.[1, 2] So far, poly(vinyl pyridine)s and their ionic derivatives, especially those with hierarchically ordered structures, have been frequently explored for potential applications in the area of polyelectrolyte, polymer reagent, electrics and so on.[2-7] It is well-known that the molecular weight of the functional polymers can exert profound effects on the polymer's properties, functions, as well as the types of self-assembled hierarchical structure. Therefore, efficient synthesis of functional polymers with predictable molecular weights is highly desirable. Thanks to the advent of controlled/''living'' radical polymerization (CRP)[8] techniques, the synthesis of a variety of polymers with prescribed molecular weights is easy to implement. Up to now, many CRP techniques have been well developed and widely used to produce macromolecules with well-defined molecular weights and topologies.[9-14] Lochon *et al.* reported the CRP of 4-vinyl pyridine (4VP) by using β-phosphonylated nitroxide as a mediator *via* nitroxide-mediated radical polymerization (NMRP) technique.[15] The polymerization of 4VP was well controlled up to high monomer conversions. McCormick *et al*. demonstrated the first successful reversible addition-fragmentation transfer (RAFT) polymerizations of 2-vinylpyridine (2VP) and 4VP. Significantly, the polymerizations can be conducted in the absence of organic solvents up to high conversion while maintaining good control.[16] Matyjaszewski *et al*. studied the controlled polymerization of 4VP *via* atom transfer radical polymerization (ATRP). Good polymerization control and narrow molecular weight distribution was achieved with chloride-containing ATRP initiating/catalytic system in aqueous media at 30 °C. However, bromide-containing ATRP initiating/catalytic system produced poorly controlled polymerization manner due to more unfavorable reactions of the monomer or polymer with secondary alkyl bromide-type dormant chain ends compared to their alkyl chloride counterparts.[17] Recently, Cu(0)-mediated CRP of 4VP in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was successfully accomplished in our research group.[18, 19] The formation of strong hydrogen bonding interaction between HFIP and 4VP provided an ideal environment for polymerization at room temperature, reflecting in an improved control over molecular weight and an increased syndiotacticity. The simultaneous control over molecular weight and tacticity by using fluoroalcohols as solvent have been frequently reported in CRP area.[20-23] The increased syndiotacticity had been well explained. However, the exact reason for a better control over molecular weight in the presence of fluoroalcohol was unclear. Okamoto *et al.* proposed a monomer-activating effect originating from the hydrogen bonding between less-active monomer (such as vinyl acetate) and fluoroalcohol.[24] The monomer-activating effect was supposed to be an electronic effect by manifesting the conversion of the monomer to an electron-poor monomer. Consequently, the reaction activity between a nucleophilic radical and electron-poor monomer increased. However, the monomer-activating effect was just a theoretical derivation and was not proved by experimental facts.

In view of the structural similarity between 2VP and 4VP, analogous hydrogen bonding interaction between 2VP and fluoroalcohol is expected. Furthermore, since that the nitrogen atom is neighboring at the vinyl bond of 2VP, the hydrogen bonding interaction between 2VP and HFIP should be reinforced and can impose more pronounced effects on the polymerization behavior. Upon the strengthened hydrogen bonding interaction, some explorations with the purpose of getting a reasonable explanation for better control over molecular weight are meaningful. In this work, Cu(0)-mediated CRP of 2VP in the presence of fluoroalcohol was explored. Different kinds of fluoroalcohols were scanned, and an optimal condition for a better hydrogen bonding interaction between fluoroalcohol and 2VP was used. The influence of hydrogen bonding on the

polymerization behavior was investigated, aiming at a comprehensive understanding of the hydrogen bonding effects on polymerization behavior.

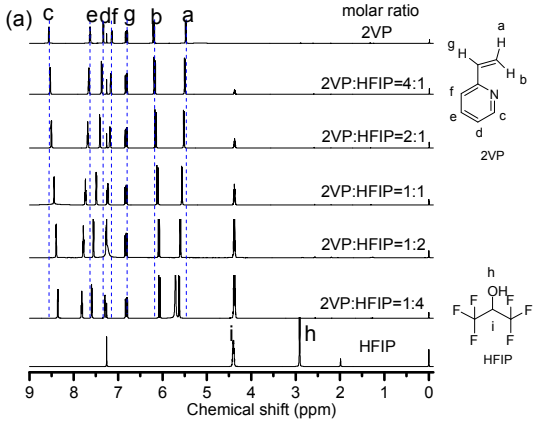
The controlled polymerizations of 2VP *via* some CRP techniques have been reported elsewhere.[16, 25-29] However, transition metal-mediated CRP of 2VP has not yet been realized, which may be ascribed to the possibility of the formation of pyridine-coordinated metal complexes as well as the poor monomer activity.[30] In this work, the Cu(0)-mediated CRP method[13, 25] is selected for the controlled polymerization of 2VP.[13, 31] Firstly, different solvents were scaned for searching an optimal solvent. As a comparison, different kinds of non-hydrogen bonding donor solvents were used. All the polymerizations were carried out at 25 °C with molar ratio of $[2VP]_0/[ECPA]_0/[Cu(0)]_0$ = 200/1/1. The polymerization results are concluded in Table 1. From the results, it can be found that in anisole and 2-propanol, the polymerization was poorly controlled with uncontrollable molecular weights and wide molecular weight distributions (entries 1&2). In toluene, the polymerization produced no conversion within 72 hours (entry 3). In N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF), the polymerizations were also poorly controlled by manifesting uncontrollable molecular weights and high M_w/M_n values (M_w/M_n>1.90) (Table 1, entries 4&5). Whereas, with fluoroalcohols as solvents under identical conditions (entries 6-11, Table 1), the polymerization conveyed reasonably controlled features with controllable molecular weights and relatively narrow molecular weight distributions, especially with HFIP as solvent.

Table 1. Polymerization of 2VP in different solvents

Entry[a]	Solvent	Time (h)	Con. (%)	$M_{n,SEC}$ (kg/mol)	M_w/M_n	$M_{n,th}$ (kg/mol)
1	anisole = 1.0 mL	72	12.7	154.2	2.02	3.6
2	2-propanol = 1.0 mL	70	32.1	329.8	1.90	8.9
3	toluene = 1.0 mL	72	0	--	--	--
4	NMP = 1.0 mL	46	39.3	85	2.04	10.8
5	DMF = 1.0 mL	46	19.7	120.7	1.96	5.5
6	$(CF_3)_2CHOH$ = 0.98 mL	40	43.3	13.4	1.40	9.3
7	$(CF_3)_3COH$ = 1.3 mL	40	21.8	15.9	1.30	4.8
8	$CHF_2CF_2CF_2CF_2CH_2OH$ = 1.29 mL	40	51.4	19.1	1.38	11.0
9	CF_3CH_2OH = 0.68 mL	4.8	14	81.2	1.50	3.1
10	$CHF_2CF_2CH_2OH$ = 0.83 mL	3.2	17.6	60.9	1.47	3.9
11	$PhC(CF_3)_2OH$ = 1.56 mL	24	27.8	36	1.55	6.0

[a] 25 °C, 2VP = 1.0 mL, entries 1-5: $[2VP]_0/[ECPA]_0/[Cu(0)]_0$ = 200/1/1; entries 6-11: $[2VP]_0/[solvent]_0/[ECPA]_0/[Cu(0)]_0$ = 200/200/1/1. ECPA = Ethyl-2-chloro-2-phenylacetate

From above results, the good control over molecular weight with fluoroalcohol as solvent could be attributed to the hydrogen bonding interaction between 2VP and fluoroalcohol, similar with those in 4VP polymerization.[18] However, different with 4VP, the nitrogen atom is neighboring at the vinyl bond of 2VP, the hydrogen bonding interaction between 2VP and HFIP may exert more effects on the polymerization behavior, including the good controllability. The hydrogen bonding interaction between 2VP and HFIP was confirmed by ^{1}H NMR titration with elaborate and careful analysis. Upon the addition of 2VP to HFIP, the chemical shifts of 2VP protons changed obviously, as shown in Figure 1. At 2VP:HFIP = 1: 1 (molar ratio), the signal of c ascribed to the proton of pyridine ring adjacent to nitrogen atom significantly moved to high field. The signals of other protons (d, e and f) of pyridine ring uniformly transferred to low field. Notably, the signals of the protons (a and b) of vinyl's methylene also changed, chemical shifts of "a" changed to low field, while "b" to high field. With continuously increasing HFIP concentration, all the above chemical shifts gradually changed. The signals of the protons of hydrogen bonding were found as the dash rectangle shown in Figure 1b. With increasing HFIP concentration, the signal of protons of pyridinium arising from HFIP-interacted 2VP moved to the high field. It is another convincing evidence for the existence of hydrogen bonding. The results denoted that the occurrence of a definite and strong hydrogen bonding interaction between 2VP and HFIP with HFIP as hydrogen bonding donor and 2VP as acceptor. The hydrogen bonding interaction dramatically changed the electron density of 2VP due to the strong electron-withdrawing ability of HFIP, reflecting in the significant changes of chemical shifts of 2VP monomer's protons, including those of the pyridine rings and vinyl bonds. Computer simulation for optimized geometries of 2VP and 2VP-HFIP with a 6-311++G (2df,p) basis set confirmed that the charge of α carbon at the double bond of 2VP is -0313, while it was -0.298 when HFIP was associated with 2VP molecule (Figures S1, ESI†). Meaningfully, the transfer of the electron density of vinyl bond denoted the enhancement of vinyl double bond activity (*i.e.*, be more readily attacked by propagating radicals) as well as the intermediate propagating radical (Figure S2, ESI†). Meanwhile, the hydrogen-bonding interaction with the terminal 2VP unit of poly(2VP) might also facilitate the activation of the dormant C-Cl bond, enabling faster interconversion between the dormant and active species and thus allowing a good control. To determine the stoichiometry of the complex, another set of ^{1}H NMR spectra with a constant total concentration of H-bond donor and acceptor was recorded.[32] The resulting Job plot (Figure 2a) shows a maximum at a HFIP molar fraction of 0.50, suggesting that a 1:1 complex formed between the fluoroalcohol and 2VP.



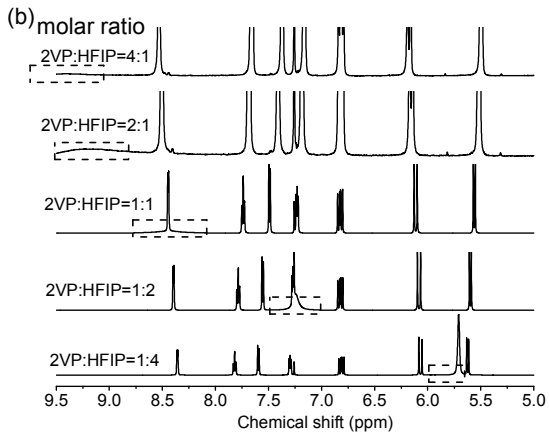


Figure 1. Full ^{1}H NMR titration spectra (a) and enlarged spectra (5~10 ppm) (b) of 2VP with HFIP at various molar ratios in $CDCl_3$.

$$\text{HFIP+2VP} \overset{K}{\rightleftharpoons} \text{2VP-HFIP} \quad (1)$$

$$[\text{HFIP-2VP}] = [\text{2VP}]_0 \Delta\delta/\Delta\delta_0 \quad (2)$$

$$[\text{HFIP-2VP}] = K([\text{2VP}]_0\text{-}[\text{HFIP-2VP}])([\text{HFIP}]_0\text{-}[\text{FOH-2VP}]) \quad (3)$$

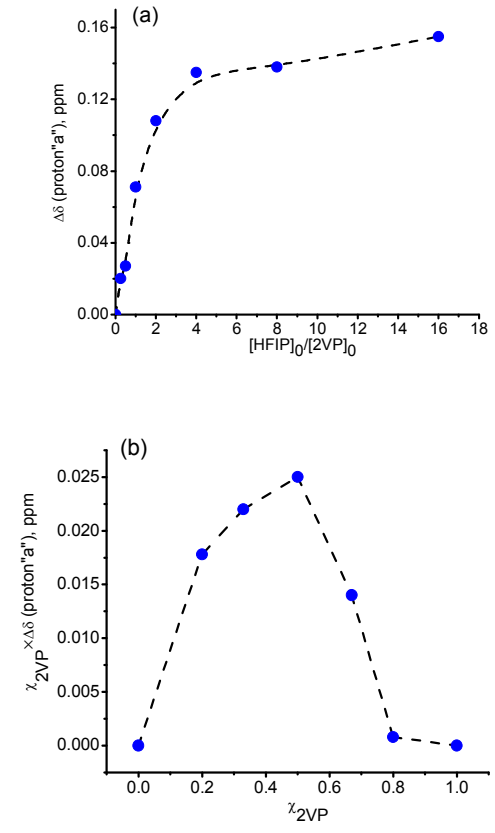


Figure 2. (a) Variations of the chemical shift of the double bond proton "a" in the presence of HFIP ($[2VP]_0$ = 0.25 mM, 600 MHz, $CDCl_3$, 25 °C). (b) Job plots for the association of HFIP with 2VP evaluated from the chemical shift changes of the double bond "a" ($[2VP]_0$+$[HFIP]_0$ = 0.31 mM, 600 MHz, $CDCl_3$, 25 °C). χ_{2VP}: molar fraction of 2VP.

The equilibrium constant (K) of the complex between 2VP and HFIP was calculated to be 6.31 L·mol^{-1} based on eqs (1) to (3), where Δδ was the difference in the observed double bond proton chemical shift of 2VP between the absence and the presence of a certain amount of HFIP, $\Delta\delta_0$ was the difference in the chemical shift of double bond proton between the absence of HFIP and that saturated with HFIP, and $[2VP]_0$ and $[HFIP]_0$ represent the initial concentration of the corresponding component, respectively. K = 6.31 L·mol^{-1} and the hydrogen bonding length of approximate 1.751 Å (Figure S3, ESI†) quantificationally confirmed a strong hydrogen bonding between 2VP and HFIP,[33] constructing the 2VP-HFIP supramonomer; Compare to the naked 2VP monomer, the formed 2VP-HFIP supramonomer would express different polymerization behavior due to electron induction as well as steric effects.

The polymerization behavior of Cu(0)-catalyzed 2VP was carefully explored with equiv 2VP and HFIP under different temperatures (25, 40 and 60 °C). The results are illustrated in Figure 3. It is easy to find that all the polymerization kinetics are in first-order linear relationship. The polymerization rate at 25 °C (k_p^{app} of 0.016 h^{-1}) was slightly higher than that at 40 °C ($k_p^{app} \approx$ 0.014 h^{-1}). While, the polymerization rate obviously decreased at 60 °C with k_p^{app} of 0.009 h^{-1}. In a normal radical polymerization, since the overall activation energy (Ep) is larger than 0, the polymerization rate will undoubtedly increase with the elevation of polymerization temperature. In this work, the polymerization rate at 60 °C was unexpectedly lower than that at 40 °C or 25 °C. The plausible reason is that the reaction activity of monomer may be changed with the change of temperature. Furthermore, as from Figure 3b, the polymerizations at 25 °C and 40 °C were well controlled with linearly increased molecular weights and relatively narrow molecular weight distributions, the experimental molecular weights agreed well with the corresponding theoretical ones; and the SEC profiles conveyed unimodal and symmetric distributions (Figures S4, ESI†). However, the polymerizations at 60 °C produced uncontrollable molecular weights. It was reported that high temperature is unfavorable for the formation of hydrogen bonding.[34, 35] In this work, at 25 °C, a 2VP-HFIP supramonomer was formed *via* a solid hydrogen bonding interaction. While, at 40 °C or 60 °C, the hydrogen bonding may be partly destroyed or weakened. To validate the temperature effects on hydrogen bonding, ^{1}H NMR was used to monitor the change of hydrogen bonding interaction at 25 °C, 40 °C and 60 °C, respectively. As shown in the enlarged ^{1}H NMR spectra (5.0-9.0) ppm (Figure 4a), when increasing temperature from 25 °C through 40 °C to 60 °C in the absence of HFIP, there was almost no change of the chemical shifts of 2VP protons, such as the signal "a" of 2VP. Whereas, when HFIP was added, the chemical shift of "a" tended to move to the low field. In the presence of HFIP, by increasing temperature, the chemical shifts of 2VP protons tended to recover to the original values (chemical shifts without HFIP). Further investigation by quantitative ^{1}H NMR showed that when the integration of signal "a" was 100, the total number of signal b-g with hydrogen bonding was changed with temperature as shown in Figure 4b. At 25 °C, the number of hydrogen bonding was the largest. This result clearly shows that with the increase of temperature, the hydrogen bonding between 2VP and HFIP is somewhat destroyed. Through the investigation of temperature-hydrogen bonding dependence, the monomer activation effect imposed by hydrogen bonding was further proved to be electron induction effect. Within experimental range, the most suitable temperature for the formation of strong hydrogen bonding is 25 °C.

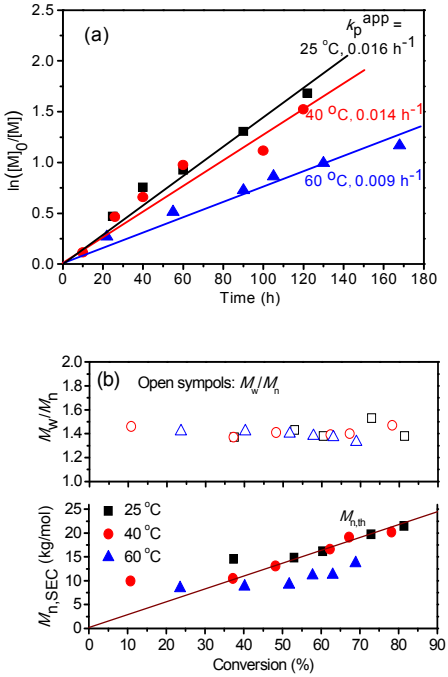


Figure 3. (a) ln([M]$_0$/[M]) as a function of time and (b) number-average molecular weights ($M_{n,SEC}$) and molecular weight distributions (M_w/M_n) versus conversion for Cu(0)-mediated CRP of 2-vinylpyridine (2VP) without additional ligand with [HFIP]$_0$/[2VP]$_0$=1/1 at different temperatures. 2VP =1.0 mL. [M]$_0$ and [M] refer to the initial concentration and instant concentration of 2VP, respectively. Theoretical molecular weight $M_{n,th}$ = ([2VP]$_0$/[ECPA]$_0$) ×M_{2VP} × Conversion + M_{ECPA}, where M_{2VP} and M_{ECPA} represent the molecular weights of 2VP and ECPA, respectively.

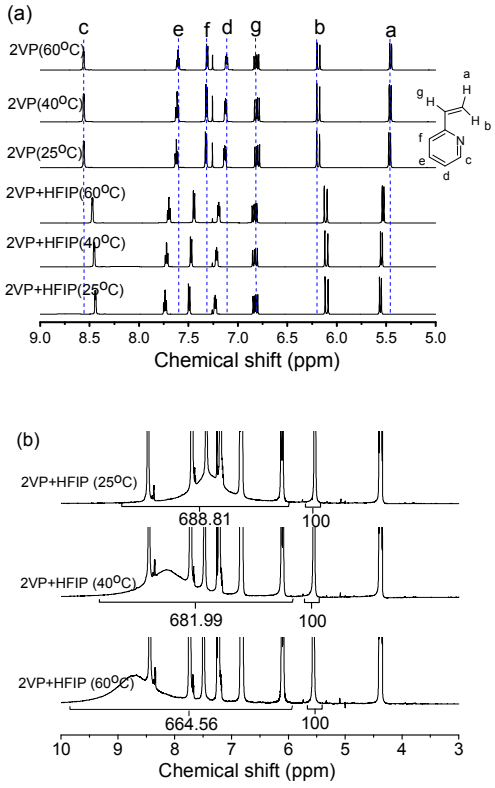


Figure 4. Enlarged ^{1}H NMR spectra of 5-9 ppm (a) and 3-10 of [2VP]$_0$:[HFIP]$_0$ = 1:1 in $CDCl_3$ at different temperatures (b).

To further demonstrate the livingness of the polymerization of 2VP under hydrogen bonding, the chain end of P2VP ($M_{n,SEC}$ = 14.8 kg/mol, M_w/M_n = 1.43) prepared under [HFIP]$_0$/[2VP]$_0$=1.0/1.0 at 25 °C was analyzed by ^{1}H NMR spectroscopy (Figures S5, ESI†). The molecular weight of P2VP sample calculated from the ^{1}H NMR spectrum ($M_{n,NMR}$) was 15.4 kg/mol, which was close to the SEC value (16.0 kg/mol), indicating that the P2VP was end-capped by ECPA species with high fidelity.

The above polymerization results clearly demonstrated that the hydrogen bonding activated the 2VP monomer by the electron-withdrawing inductive effects. Under this effect, the 2VP-HFIP supramonomer was thus more active for polymerization than the naked 2VP, supporting a better control over polymerization. Simultaneously, the formation of the supramonomer 2VP-HFIP effectively inhibited the detrimental coordination of Cu ion with pyridine moiety, which was also possibly in favour of a good control. Inspired by these results, the ever reported Cu(0)-mediated CRP of 4VP under favourable hydrogen bonding interaction[18] was re-examined by elaborate ^{1}H NMR characterizations. Electron induction effects were found (Figure S6, ESI†), however, the changes of chemical shifts of vinyl double bonds (a and b protons of α carbon) was slight and different from those of 2VP in HFIP. Encouraged by the concept of monomer-activating effects, some monomers with electron-rich vinyl double bonds were supposed to be activated and would be well controlled under the activation of hydrogen bonding. It is well known that some less-active monomers, such as vinyl acetate (VAc) and N-vinylpyrrolidone (NMP) cannot undergo well-controlled polymerization under ATRP or other metal-mediated CRP conditions. The electron-withdrawing induction effects of these monomers under hydrogen bonding were investigated by ^{1}H NMR. The results are summarized in Figure S7 and Figure S8 (ESI†). The ^{1}H NMR results clearly revealed that the vinyl double bonds of both monomers were more or less activated by electron-withdrawing induction effects arising from the hydrogen bonding interaction between monomer and fluoroalcohol. However, Cu(0)-mediated CRP of both monomers in the presence HFIP presented extremely low polymerization rate at 25 °C, and the controlled polymerization was not yet realized at current stage. Despite of this, the results afforded a concrete explanation of monomer-activating effect in literature.[24] In the presence of HFIP, other vinyl pyridine monomers, 3-vinyl pyridine (3VP) and 2-vinylpyrazine (2VPZ) were also explored by ^{1}H NMR characterization (Figures S9 & S10, ESI†). The ^{1}H NMR spectra of 3VP-HFIP indicated a similar electron induction effects on the vinyl double bonds (Figure S8, ESI†) compared with that of 4VP-HFIP. While, ^{1}H NMR spectra of 2VPZ-HFIP denoted similar electron induction effects on vinyl double bonds by HFIP (Figure S10, ESI†) as that of 2VP-HFIP, but the changes of chemical shifts were much smaller. The Cu(0)-mediated CRP of 3VP or 2VPZ in the presence of HFIP were explored, and the results are concluded in Table S1 (ESI†). Either in 3VP or 2VPZ polymerization, the presence of fluoroalcohol, including HFIP, cannot remarkably improve the polymerization controllability comparing with the non-fluoroalcohol solvent (Table S1, ESI†). The reason was unclear at current stage. Since that the effects of hydrogen bonding interactions (with monomer, growing radical and dormant polymeric chain) were profound and complex both in electron induction and steric effects, the comprehensive understanding needed more and in-depth explorations.

In this work, by using quantitative ^{1}H NMR analysis and

computer simulation, the hydrogen bonding interaction between HFIP and 2VP was found to be strong enough to redistribute the electron density of 2VP monomer, especially that of vinyl double bond. The constructed 2VP-HFIP supramonomer with altered electron density can thus undergo well-controlled Cu(0)-mediated CRP with improved controllability compared with naked 2VP monomer. The hydrogen bonding interaction between fluoroalcohol and growing radical or fluoroalcohol and terminal monomer unit of dormant polymeric chains might also contribute to the better control. The concept of hydrogen bonding promoting CRP or monomer-activating effect undoubtedly opened a new avenue to improve the controllability of those less active monomers.

Acknowledgement

The financial support from the National Nature Science Foundation of China (Nos. 21174094, 21374068), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, the Nature Science Key Basic Research of Jiangsu Province for Higher Education (No. 12KJA150007) are gratefully acknowledged.

Notes and references

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou Industrial Park, Suzhou 215123, China. Fax: (+)86-512-65112796; E-mail: lxh83@suda.edu.cn or zhangzhengbiao@suda.edu.cn

† *Electronic Supplementary Information (ESI) available: Experimental section including materials, characterizations, and typical Experimental; 2VP-HFIP at the level of B3LYP/6-311++G (2df,p), SEC traces, ^{1}H NMR spectra of 4VP-HFIP, VAc-HFIP, NMP-HFIP, 3VP-HFIP and 2VPZ-HFIP. See DOI:*

(1) Yang, T.; Ferrali, A.; Sladojevich, F.; Campbell, L.; Dixon, D. J. *Journal of the American Chemical Society* 2009, **131**, 9140-9141.
(2) Park, S.; Chang, T. *Macromolecules* 2006, **39,** 3466-3468.
(3) Aydogdu, Y.; Erol, I.; Yakuphanoğlu, F.; Aydogdu, A.; Ahmedzade, M. *Synthetic Metals* 2003, **139**, 327-334.
(4) Sfika, V.; Tsitsilianis, C.; Kiriy, A.; Gorodyska, G.; Stamm, M. *Macromolecules* 2004, **37**, 9551-9560.
(5) Li, X.; Lau, K. H. A.; Kim, D. H.; Knoll, W. *Langmuir* 2005, **21**, 5212-5217.
(6) Li, Y.; Yang, M. J.; She, Y. *Sensors and Actuators B: Chemical* 2005, **107**, 252-257.
(7) Lin, Y.; Boker, A.; He, J.; Sill, K.; Xiang, H.; Abetz, C.; Li, X.; Wang, J.; Emrick, T.; Long, S.; Wang, Q.; Balazs, A.; Russell, T. P. *Nature* 2005, **434**, 55-59.
(8) Otsu, T.; Yoshida, M. *Die Makromolekulare Chemie, Rapid Communications* 1982, **3**, 127-132.
(9) Otsu, T.; Yoshida, M.; Tazaki, T. *Die Makromolekulare Chemie, Rapid Communications* 1982, **3**, 133-140.
(10) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, **26**, 2987-2988.
(11) Wang, J.-S.; Matyjaszewski, K. *Journal of the American Chemical Society* 1995, **117**, 5614-5615.
(12) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, **31**, 5559-5562.
(13) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *Journal of the American Chemical Society* 2006, **128**, 14156-14165.
(14) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, **28**, 1721-1723.
(15) Diaz, T.; Fischer, A.; Jonquières, A.; Brembilla, A.; Lochon, P. *Macromolecules* 2003, **36**, 2235-2241.
(16) Convertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; McCormick, C. L. *Macromolecules* 2003, **36**, 4679-4681.
(17) Tsarevsky, N. V.; Braunecker, W. A.; Brooks, S. J.; Matyjaszewski, K. *Macromolecules* 2006, **39**, 6817-6824.
(18) Wang, W.; Zhang, Z.; Cheng, Z.; Zhu, J.; Zhou, N.; Zhu, X. *Polymer Chemistry* 2012, **3**, 2731-2734.
(19) Wang, W.; Zhao, J.; Yu, H.; Zhou, N.; Zhang, Z.; Zhu, X. *Polymer* 2013, **54**, 3248-3253.
(20) Kamigaito, M.; Satoh, K. *Macromolecules* 2008, **41**, 269-276.
(21) Miura, Y.; Satoh, T.; Narumi, A.; Nishizawa, O.; Okamoto, Y.; Kakuchi, T. *Macromolecules* 2005, **38**, 1041-1043.
(22) Kamigaito, M.; Satoh, K. *Journal of Polymer Science Part A: Polymer Chemistry* 2006, **44**, 6147-6158.
(23) Miura, Y.; Satoh, T.; Narumi, A.; Nishizawa, O.; Okamoto, Y.; Kakuchi, T. *Journal of Polymer Science Part A: Polymer Chemistry* 2006, **44**, 1436-1446.
(24) Yamada, K.; Nakano, T.; Okamoto, Y. *Journal of Polymer Science Part A: Polymer Chemistry* 2000, **38**, 220-228.
(25) Lokaj, J.; Holler, P. *Journal of Applied Polymer Science* 2001, **80**, 2024-2030.
(26) Chalari, I.; Pispas, S.; Hadjichristidis, N. *Journal of Polymer Science Part A: Polymer Chemistry* 2001, **39**, 2889-2895.
(27) Lokaj, J.; Poláková, L.; Holler, P.; Starovoytova, L.; Štěpánek, P.; Diat, O. *Journal of Applied Polymer Science* 2007, **105**, 1616-1622.
(28) Feng, C.; Li, Y.; Yang, D.; Li, Y.; Hu, J.; Zhai, S.; Lu, G.; Huang, X. *Journal of Polymer Science Part A: Polymer Chemistry* 2010, **48**, 15-23.
(29) Zhai, S.; Song, X.; Yang, D.; Chen, W.; Hu, J.; Lu, G.; Huang, X. *Journal of Polymer Science Part A: Polymer Chemistry* 2011, **49**, 4055-4064.
(30) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* 1999, **32**, 3531-3533.
(31) Rosen, B. M.; Percec, V. *Chemical Reviews* 2009, **109**, 5069-5119.
(32) Wan, D.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules* 2005, **38**, 10397-10405.
(33) Biczók, L.; Bérces, T.; Linschitz, H. *Journal of the American Chemical Society* 1997, **119**, 11071-11077.
(34) Kihara, H.; Kato, T.; Uryu, T.; Fréchet, J. M. J. *Chemistry of Materials* 1996, **8**, 961-968.
(35) Kolesov, B. A.; Mikhailenko, M. A.; Boldyreva, E. V. *Physical Chemistry Chemical Physics* 2011, **13**, 14243-14253.