Electronic Supporting Information

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Temperature Programed Photo-induced RAFT Polymerization for Stereo-block Copolymer of Poly(vinyl acetate)

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Experimental section

Materials

Vinyl acetate (VAc) (AR, Shanghai Chemical Reagents Co., China), purified by passing through a neutral alumina column. Subsequently, it was distilled and stored at -15°C in a refrigerator. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99.5%) was obtained from Ji'Nan WeiDu Chemical Co. (China). 2-(Ethoxycarbonothioyl)sulfanyl propanoate (EXEP) was synthesized according to the literature[1] with a purity of more than 98% and stored at -15°C. All other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd and used as received unless specified.

Characterizations

The number-average molecular weight (M_w) and molecular weight distribution or polydispersity ($Đ$) of the resultant polymers were determined by TOSOH HLC-8320 (GPC) equipped with TSK gel Muliti pore HZ-N (3) 4.6×150 mm column at 40°C. Tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL/min. GPC samples were injected using a TOSOH HLC-8320 GPC plus auto sampler. The molecular weights were calibrated with PS standards purchased from Waters. Nuclear magnetic resonance spectrum was recorded on a Bruker 300 MHz nuclear magnetic resonance instrument, and about 10 mg of samples were dissolved in about 0.6 mL of $CDCl_3$ with TMS as a as an internal standard in the ^1H NMR spectra. The tacticity of the gained polymers were confirmed by ^1H NMR spectroscopy according to reference.[2]

Homopolymerization of the VAc

Typical procedure about photo-induced polymerization of vinyl acetate with EXEP was summarized as follows: amounts of VAc (2 mL, 21.6 mmol), EXEP (23.99 mg, 0.108 mmol) and HFIP (2.5 mL, 23.8 mmol) were added into a dry Schlenk tube. The solution was deoxygenated by at least three freeze-pump-thaw cycles. The tube was sealed and placed under Blue LED Lamp (460-470 nm) at constant temperature. At specific time points, aliquots were taken using syringe from the tube. The conversion of vinyl acetate was determined by ^1H NMR. The contents were then dissolved in THF and precipitated into hexane. The polymer was obtained by filtration and dried at ambient temperature under vacuum to constant weight.

Synthesis of PVAc triblock copolymers

The copolymerization reactions were performed in Schlenk tube, EXEP, VAc and HFIP in the right proportions, were introduced into the tube. The reaction mixture was submitted to at least three freeze-pump-thaw cycles, put at the desired temperature. The stirred mixture was allowed to polymerize for a certain time, a sample was withdrawn via gastight syringe for ^1H NMR analysis its conversion of VAc. The remained contents were then dissolved in THF and precipitated into hexane. The polymer was obtained by filtration and dried at ambient temperature under vacuum to constant weight to test its syndiotacticity by ^1H NMR.

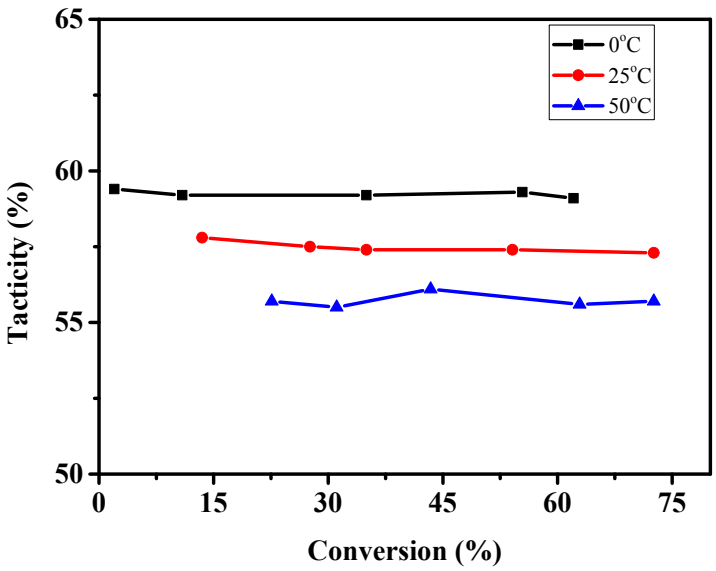

Figure S1. Conversion dependency of tacticity in the photo-induced RAFT polymerization of VAc in HFIP at different temperatures.

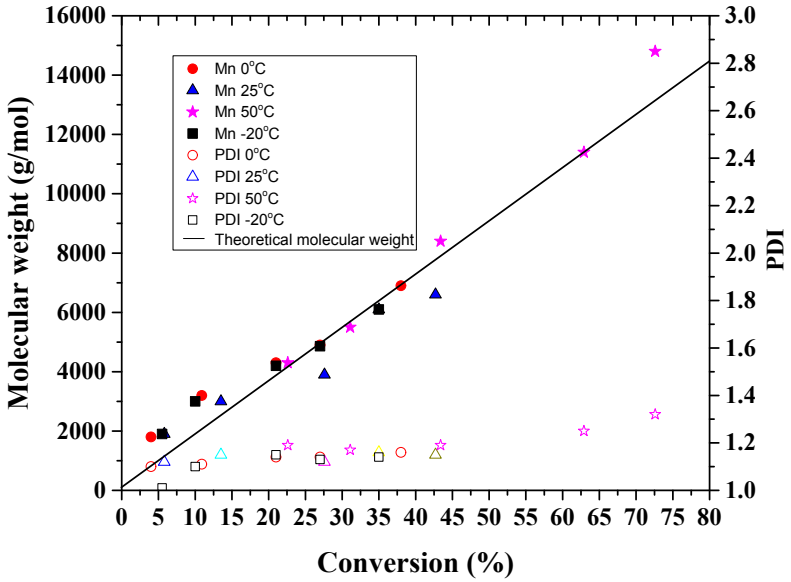

Figure S2. Dependence of M_n and $Đ$ on conversion of VAc in the presence of the EXEP with the molar ratio $[VAc]_0$:$[EXEP]_0$ =200:1 in HFIP at -20 °C, 0 °C, 25 °C, 50 °C .

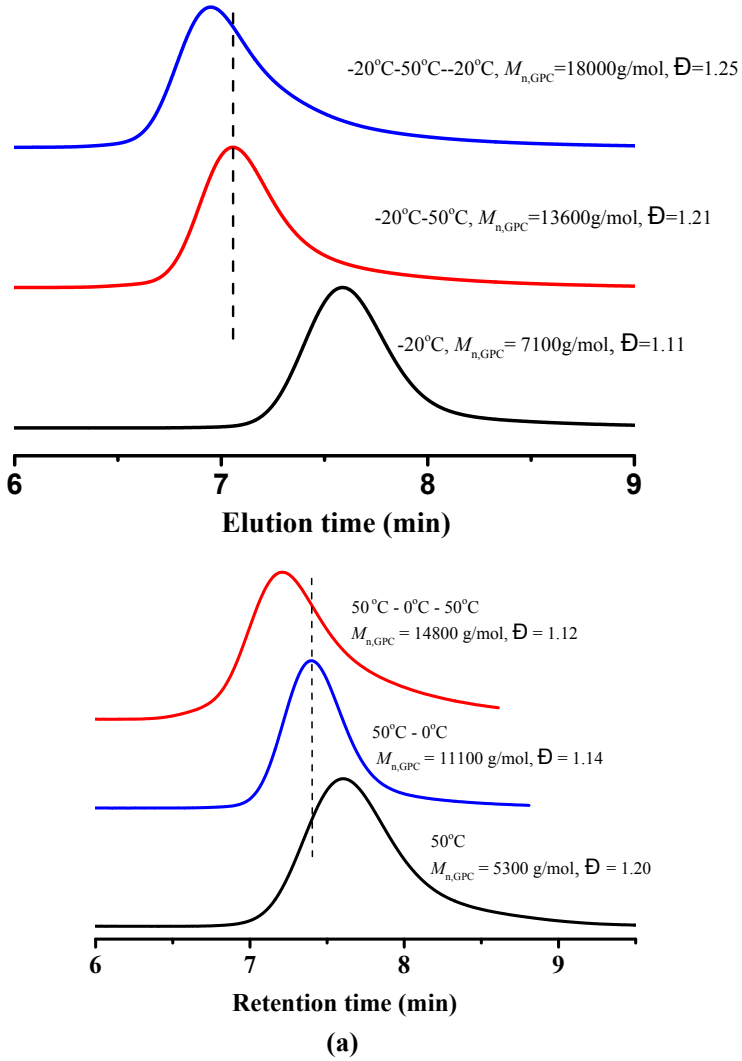

Figure S3 GPC traces of PVAc prepared in HFIP by change the polymerization temperature in the photo-induced RAFT polymerization of VAc in HFIP.

1. C. Ding, C. Fan, G. Jiang, X. Pan, Z. Zhang, J. Zhu and X. Zhu, *Macromol Rapid Commun*, 2015, **36**, 2181-2185.
2. S.-H. Shim, M.-k. Ham, J. Huh, Y.-K. Kwon and Y.-J. Kwark, *Polym Chem*, 2013, **4**, 5449-5455.