

Supplementary Information

Unexpected LCST-type phase behaviour of a poly(vinyl thiazolium) polymer in acetone

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Experimental:

Materials

2,6-Ditertbutylo-4-methylphenol ($\geq 99\%$, Sigma Aldrich), lithium tetrafluoroborate (98%, Sigma), lithium bis(trifluoromethylsulfonyl)imide (99%, Io-li-tec), methyl iodide (99%, Alfa Aesar), 4-methyl-5-vinylthiazole ($\geq 97\%$, Sigma Aldrich), potassium hexafluorophosphate (99%, Alfa Aesar) and tetrabutylammonium bromide ($\geq 99.0\%$, Sigma Aldrich) were used without further purification. 2,2'-Azobis(2-methylpropionitrile) (Sigma Aldrich, 98%) was recrystallized from methanol. All used organic solvents were of analytic grade.

Synthesis of monomers and polymers

3,4-Dimethyl-5-vinylthiazol-3-ium iodide (MVT⁺I⁻): Methyl iodide (0.31 mol, 19.5 mL) was added dropwise under vigorous stirring to a mixture of 4-methyl-5-vinylthiazole (20.0 g, 0.155 mol) and 2,6-ditertbutylo-4-methylphenol (100 mg, 0.45 mmol) in a 250 mL round bottom flask. The flask was closed with a stopper and thermostated at 40 °C for 20 h. The solid product was dissolved in DMSO (200 mL) and subsequently precipitated into 4.0 L of 1:1 volume mixture of diethyl ether and THF. The precipitate was filtered off on a Büchner funnel, washed with 1:1 volume mixture of diethyl ether and THF, and dried overnight at 40 °C, at high vacuum

(37.6 g of MVT⁺I, 88% yield). ¹H-NMR (400 MHz, DMF-*d*₇) δ 10.38 (s, 1H), 7.19 (dd, J = 17.2, 11.1 Hz, 1H), 6.02 (d, J = 17.2 Hz, 1H), 5.66 (d, J = 11.1 Hz, 1H), 4.36 (s, 3H), 2.69 (s, 3H); ¹³C-NMR (101 MHz, DMF- *d*₇) δ 158.38, 144.50, 135.92, 125.98, 121.95, 41.81, 12.50.

3,4-Dimethyl-5-vinylthiazol-3-ium hexafluorophosphate (MVT⁺PF₆⁻): an aqueous solution of KPF₆ (44,5 mmol, 8.35 g in 100 mL of MiliQ® water) was added dropwise, under vigorous stirring to an aqueous solution of MVT⁺I (8.0 g, 30.0 mmol in 100 mL of MiliQ® water). After stirring for 30 min, the brown precipitate was centrifuged out and washed twice with water. The product was dried overnight at 40 °C, at high vacuum (4.36 g of MVT⁺PF₆⁻, 51 % yield). ¹H-NMR (400 MHz, DMF-*d*₇) δ 10.24 (s, 1H), 7.16 (dd, J = 17.2, 11.1 Hz, 1H), 6.03 (d, J = 17.3 Hz, 1H), 5.69 (d, J = 11.1 Hz, 1H), 4.32 (s, 3H), 2.74 (s, 3H); ¹³C NMR (101 MHz, DMF-*d*₇) δ 158.00, 144.29, 135.93, 125.69, 121.88, 41.27, 11.89.

Poly(3,4-dimethyl-5-vinylthiazol-3-ium hexafluorophosphate) [P(MVT⁺PF₆⁻)]: Monomer MVT⁺PF₆⁻ (1.0 g, 3.5 mmol), DMF (1.0 g) and AIBN (20 mg, 0.12 mmol) were charged into a 10 mL Schlenk flask. After dissolution, the mixture was degassed / filled with argon 5 times and then polymerization was conducted for 20 h at 90 °C. The crude product was dissolved in 4.0 mL of DMF and precipitated into 100 mL of THF. The precipitate was collected by centrifugation, washed with THF and dried overnight at 80 °C (940 mg of P(MVT⁺PF₆⁻), 94 % yield).

Instrumentation and characterization methods

Attenuated Total Reflection Fourier-transform infrared spectroscopy (ATR-FTIR) was performed at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR.

Differential scanning calorimetry (DSC) measurements were done under nitrogen flow using a Mettler-Toledo DSC-1 STARe System instrument.

Gel permeation chromatography (GPC) was performed using NOVEMA Max linear XL column with mixture of 80 % of acetate buffer and 20 % of methanol (flow rate 1.00 mL min⁻¹, Pullalan standards using RI detector - RI -101 Refractometer (Shodex). Prior to the measurement, the polymer was turned hydrophilic by exchanging the counterion from PF₆⁻ to Br⁻. Anion exchange reaction was performed by adding dropwise 1.2 equiv. of tetra-n-butylammonium bromide in pure acetone to the acetone solution of 1.0 equiv. of P(MVTh⁺PF₆⁻

). The reaction mixture was stirred for 30 min, followed by collecting the precipitate by filtering. The hydrophilic product dried at 40 °C overnight under high vacuum.

Solubility tests were performed by mixing 10 mg of samples with different solvents (1 wt% and 0.1 wt%) in a glass vial. After 24 hours of shaking, the presence of solid inside vials was checked.

Thermogravimetric analysis (TGA) experiments were performed under nitrogen flow at a heating rate of 10 K min⁻¹ using a Netzsch TG209-F1 apparatus.

Turbidity measurements were performed using Varian Cary 100 Bio UV-Visible Spectrophotometer equipped with Varian Cary Temperature Controller. The measurements were performed at $\lambda = 700$ nm using 1K/min heating rate.

Figures:

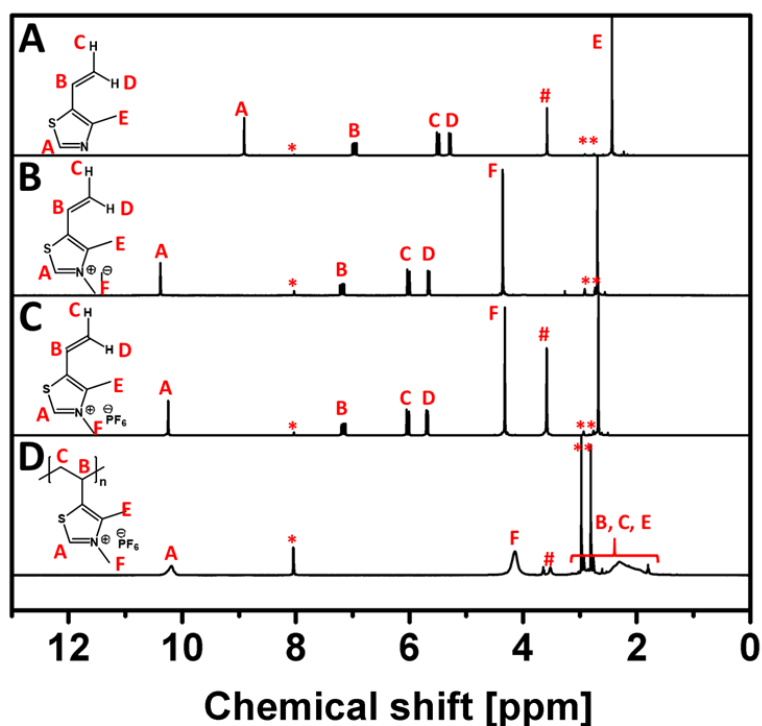


Figure S1. ¹H-NMR spectra of A - 4-methyl-5-vinyl thiazole, B – MVTh⁺I, C - MVTh⁺PF₆⁻, D – P(MVTh⁺PF₆⁻); * - DMF.

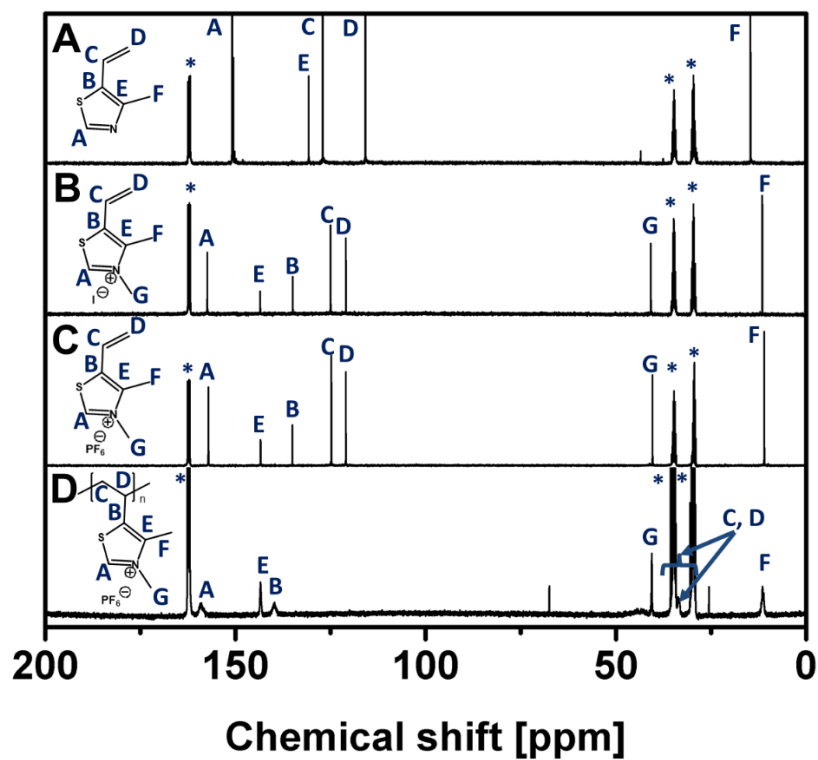


Figure S2. ^{13}C -NMR spectra of A - 4-methyl-5-vinyl thiazole (the absence of peak B is due to overlap with peak C), B - MVTh $^+\text{I}^-$, C - MVTh $^+\text{PF}_6^-$, D - P(MVTh $^+\text{PF}_6^-$), peaks C and D overlap with solvent peaks; * - DMF.

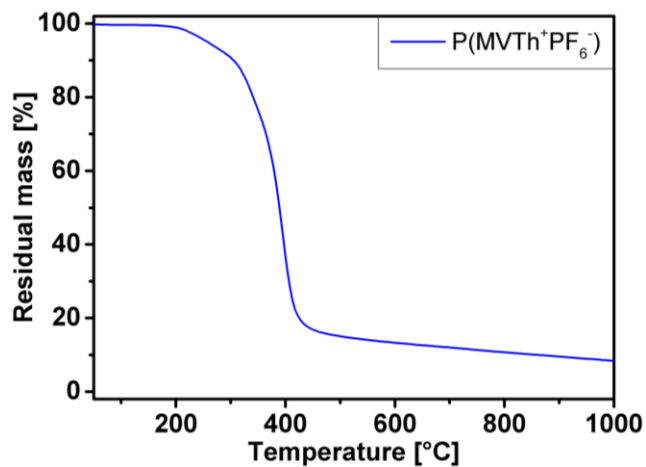


Figure S3. TGA curve of P(MVTh $^+\text{PF}_6^-$) recorded under N_2 , at a heating rate of 10 K/min.

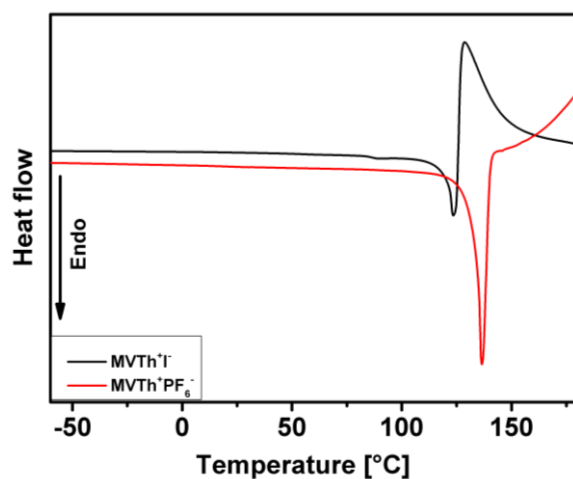


Figure S4. DSC traces recorded for MVTh⁺I⁻ and MVTh⁺PF₆⁻.

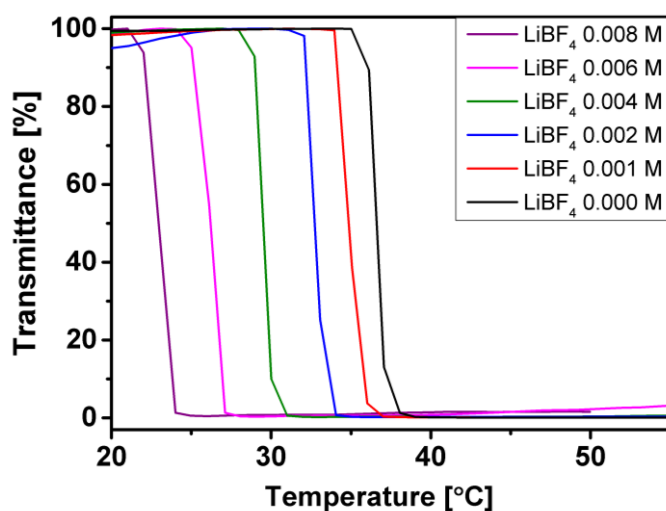


Figure S5. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of LiBF₄.

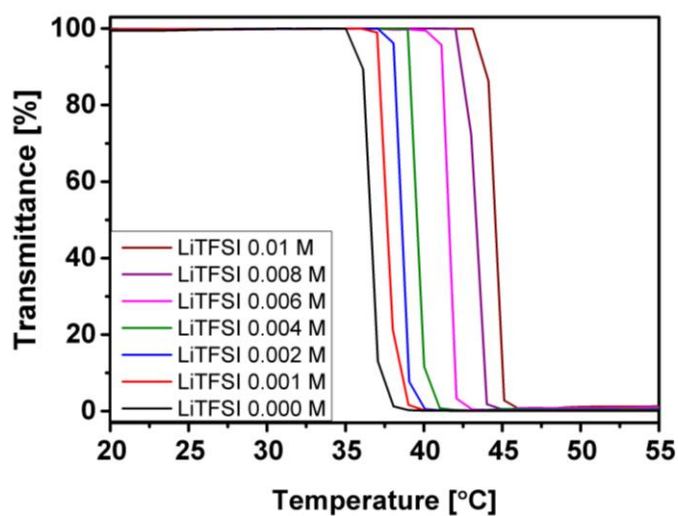


Figure S6. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of LiTFSI.

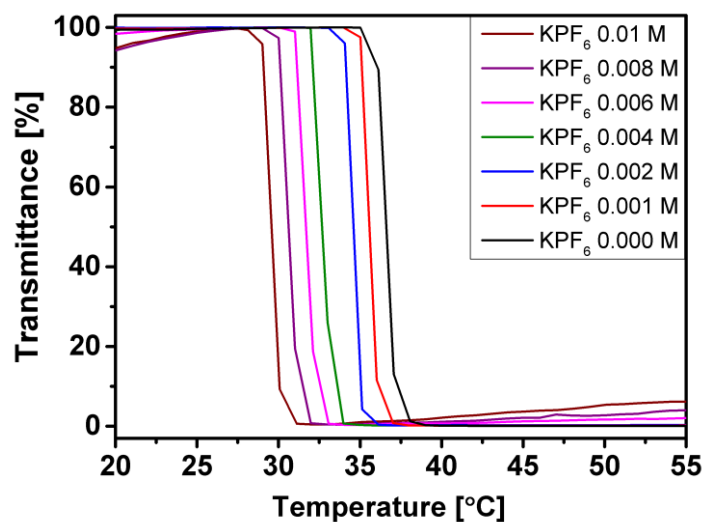


Figure S7. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of KPF₆.

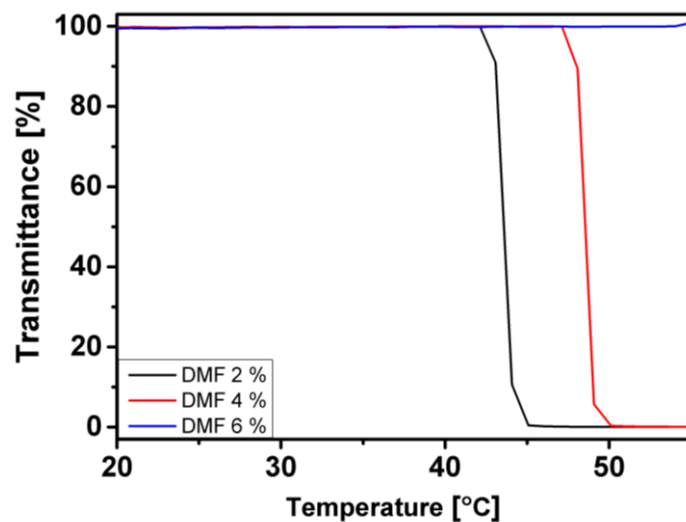


Figure S8. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of DMF as a cosolvent.

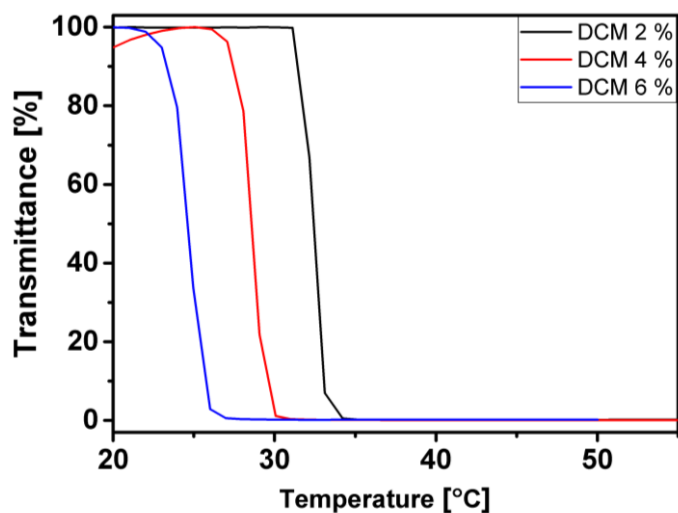


Figure S9. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of DCM as a cosolvent.

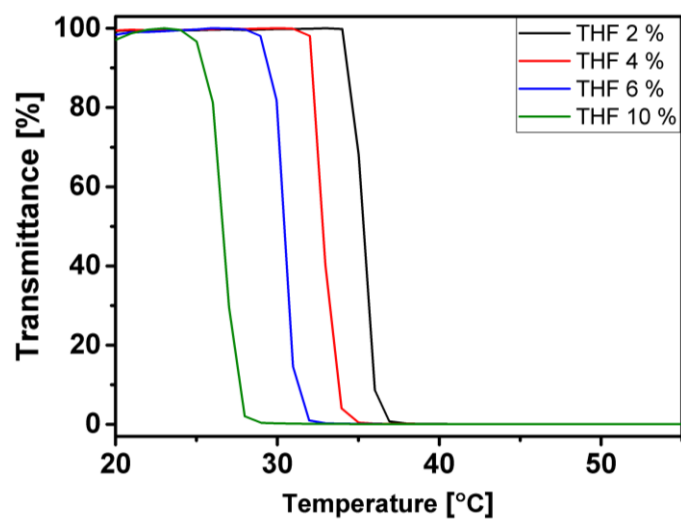


Figure S10. Turbidity curves measured for 3 wt% P(MVTh⁺PF₆⁻) acetone solutions at various concentrations of THF as a cosolvent.