

Supporting Information

Post-polymerization modification of reactive polymers derived from vinylcyclopropane: 2. Poly(vinylcyclopropane) derivative with physical gel and UCST behaviour in ethanol/water mixtures

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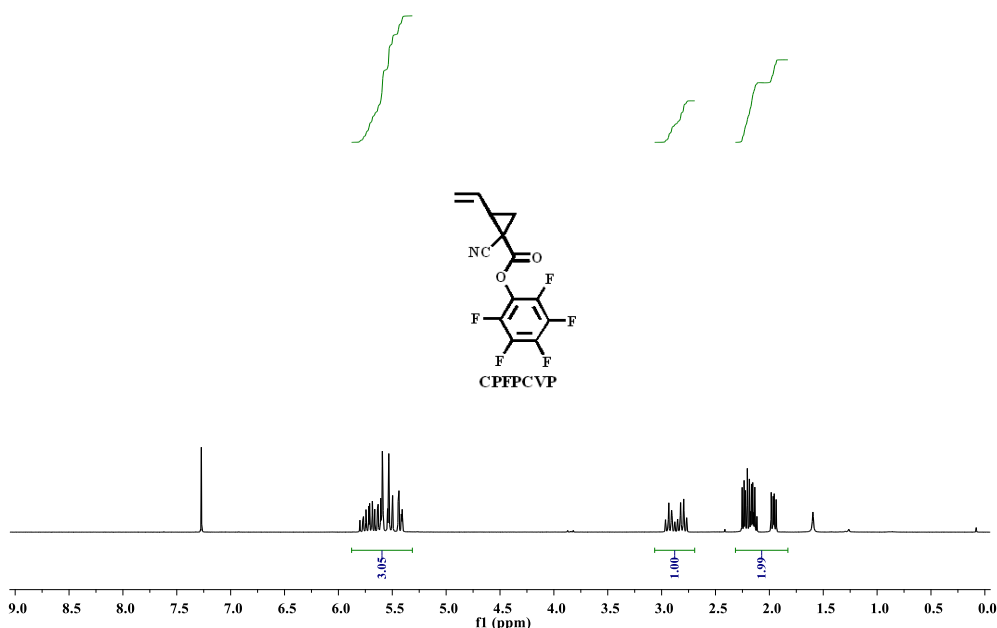
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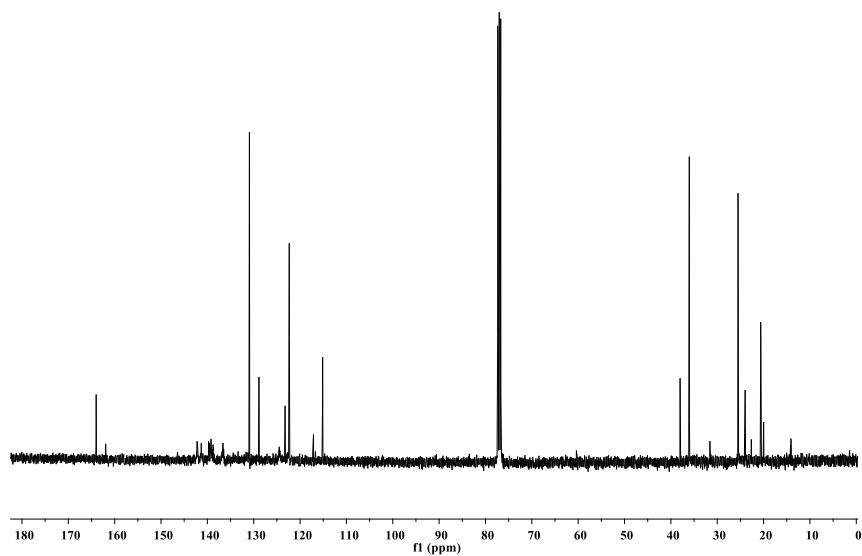
S1A. Synthesis of 1-cyano-1-pentafluorophenoxycarbonyl-2-vinylcyclopropane (CPFPCVCP).

1-Cyano-2-vinylcyclopropanecarboxylic acid (2) (10 g, 0.0730mol), pentafluorophenol (PFP) (13.8 g, 0.075 mol) and 20 ml of dried DCM were placed in a round bottomed flask under argon atmosphere and cooled in an ice bath. Dicyclohexylcarbodiimide (DCC) (15.48 g, 0.075 mol) was diluted in 20ml dried DCM and added dropwise to the flask through a septum. The mixture was stirred for 24 hours at room temperature, vacuum filtrated and the filtrate washed three times with 100ml aqueous HCl of pH 4. Then, DCM was evaporated and the remaining oil was diluted in the minimum amount of hexane and placed in a freezer at -20°C overnight to precipitate the remaining dicyclohexylurea (DCU), filtrated again, evaporated and chromatographed with chloroform to yield highly viscous oil that crystallized in the freezer (purity 92 %).

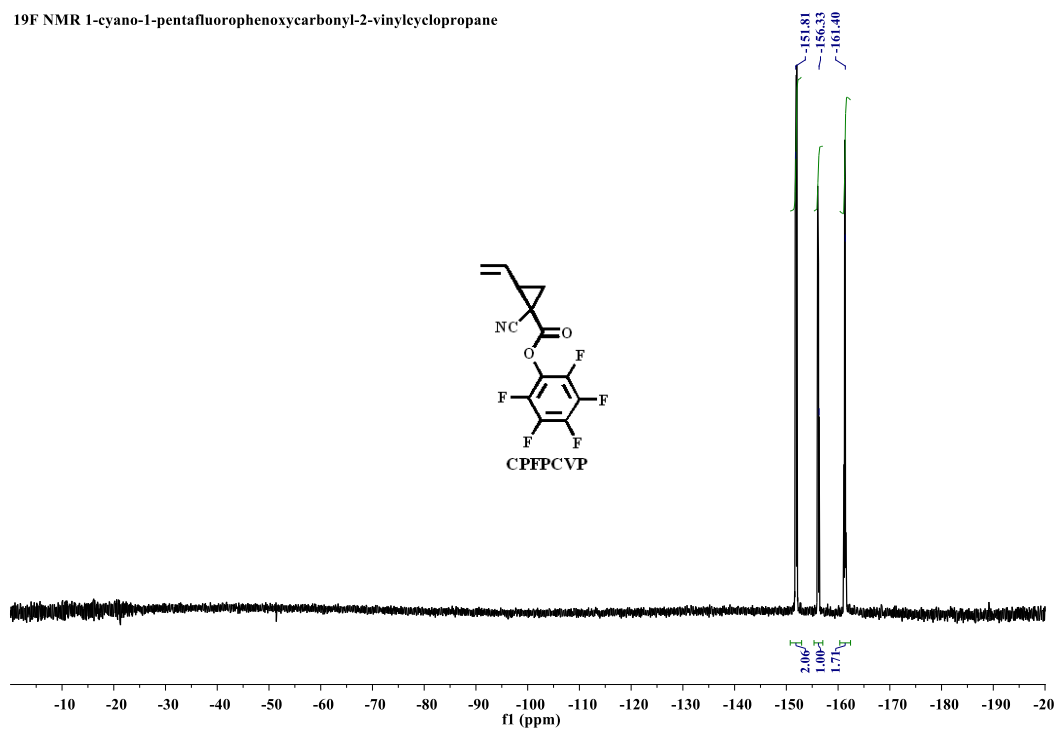
¹H NMR 1-cyano-1-pentafluorophenoxycarbonyl-2-vinylcyclopropane



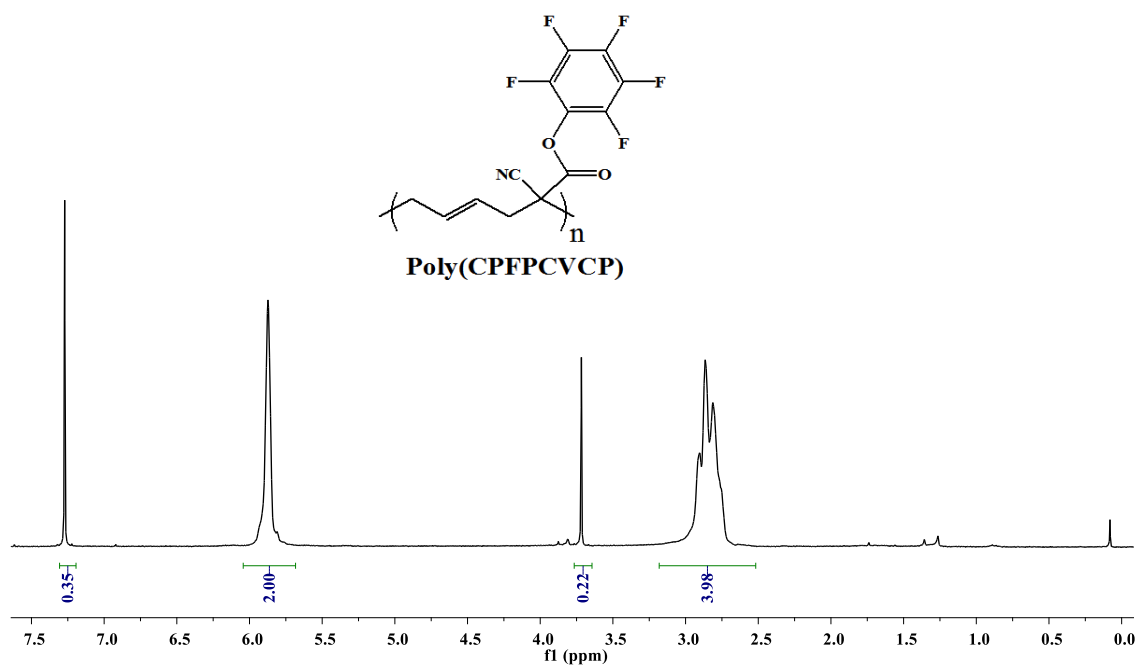
¹³C NMR 1-cyano-1-pentafluorophenoxyacetyl-2-vinylcyclopropane



¹⁹F NMR 1-cyano-1-pentafluorophenoxyacetyl-2-vinylcyclopropane

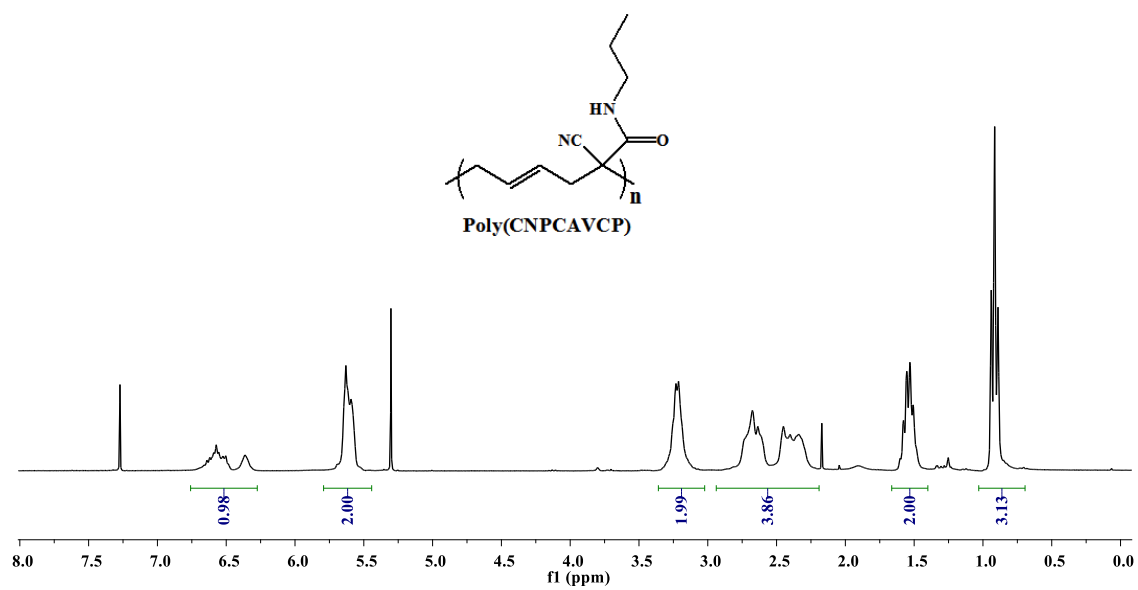


¹H NMR of Poly(CPFPCVCP) in CDCl₃

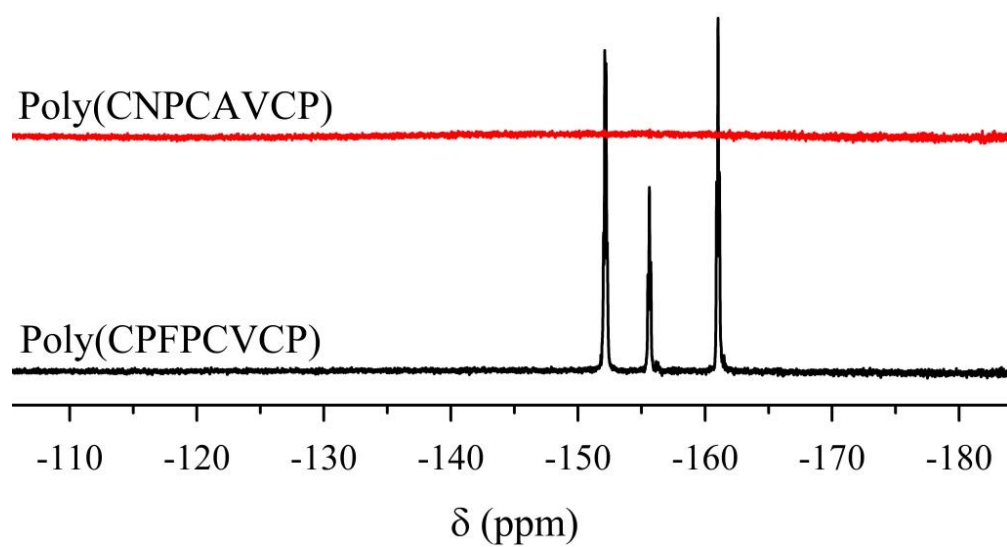


S2. ¹H NMR of 1-cyano-1-pentafluorophenoxycarbonyl-2-vinylcyclopropane

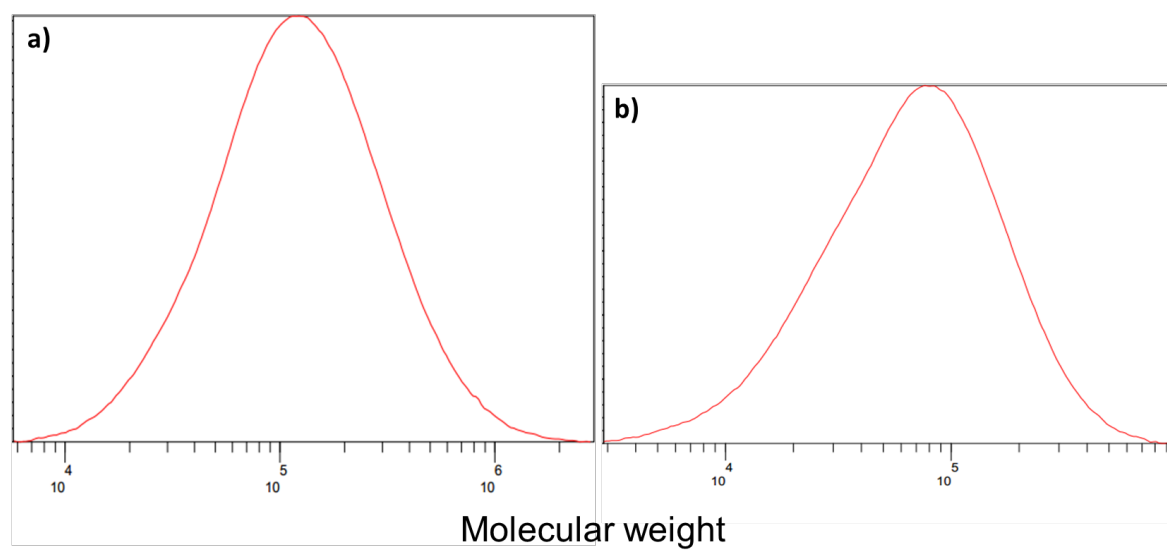
¹H NMR of Poly(CNPCAVCP) in CDCl₃



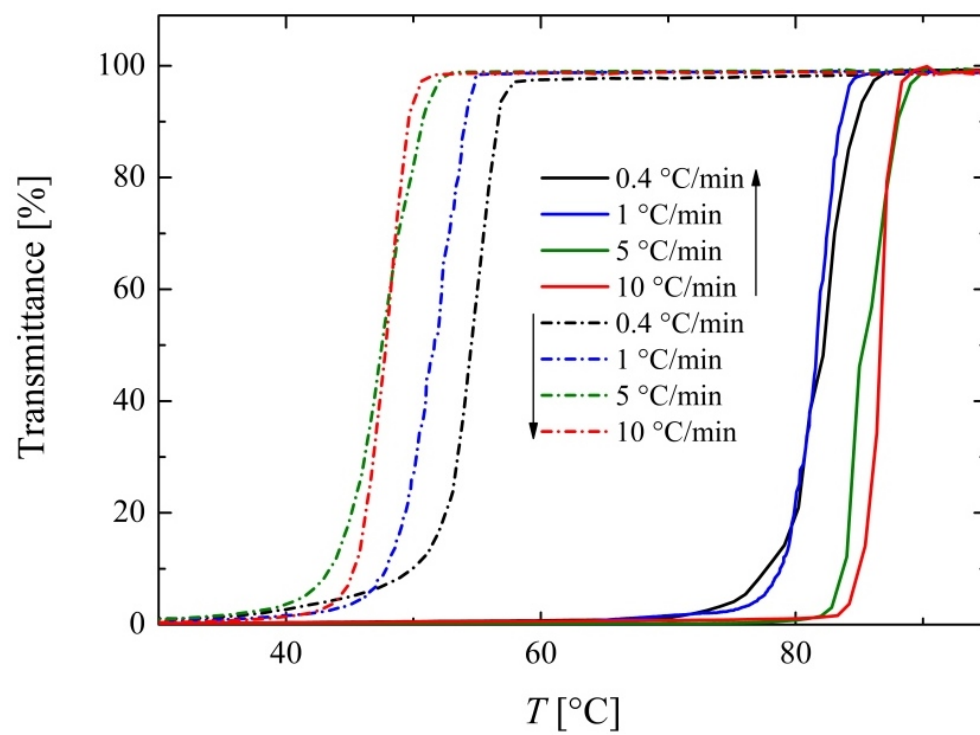
S3. ¹H NMR of Poly(1-cyano-N-Propylcarboxyamidovinylcyclopropane)



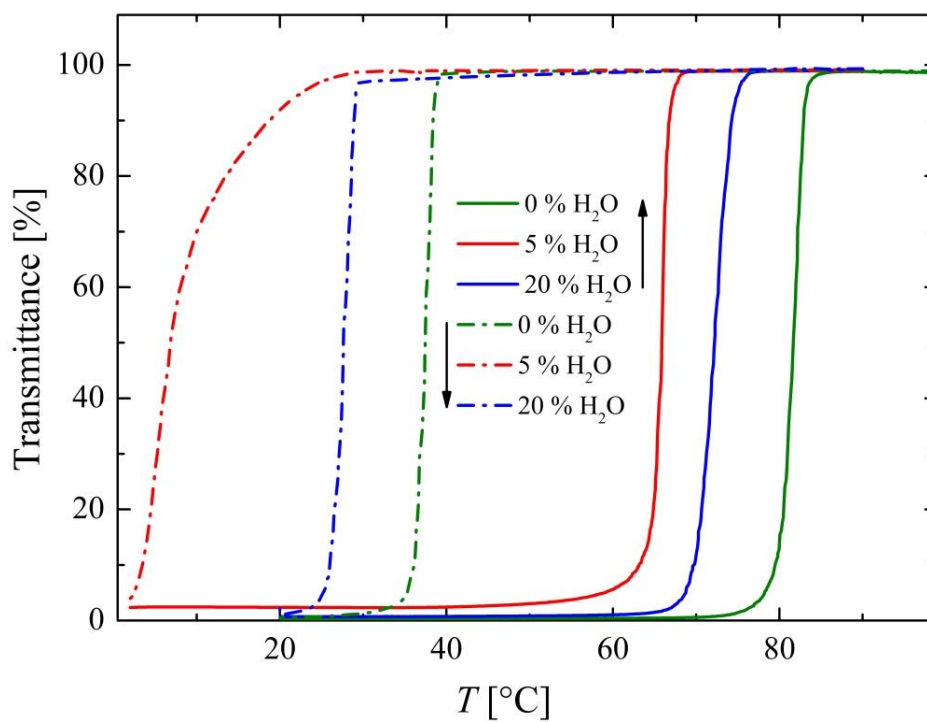
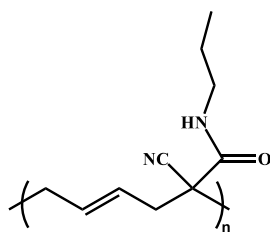
S4A. ^{19}F -NMR spectra of poly(CPFPCVCP) and Poly(CNPCA VCP)



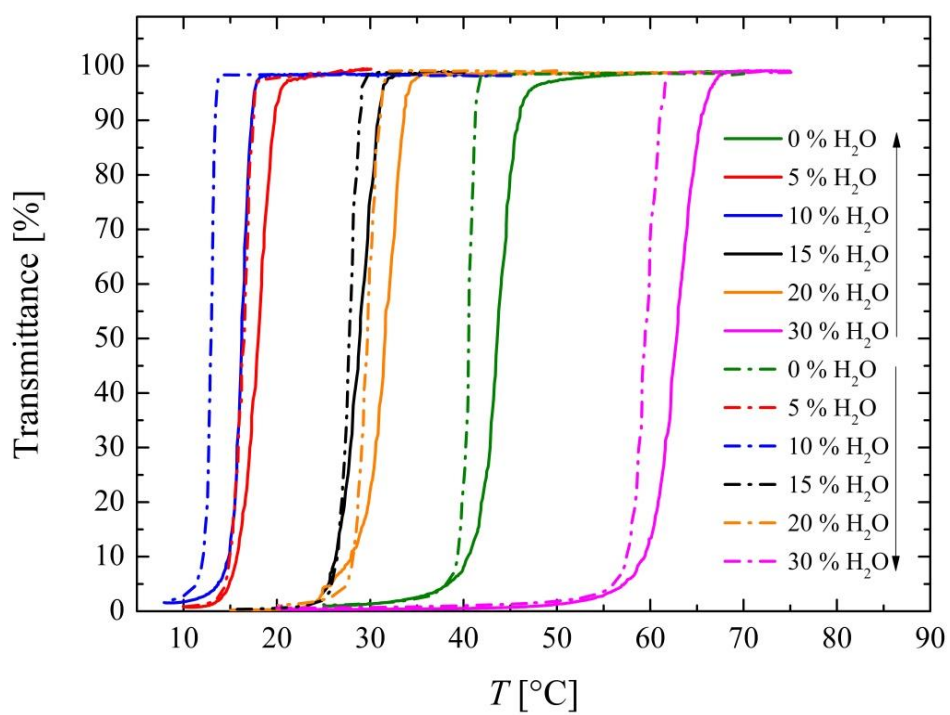
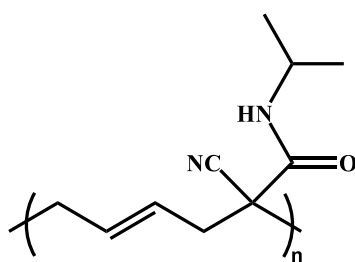
S4B. Gel permeation Chromatogram: a) poly(CPFPCVCP) and b) poly(CNPCA VCP)



S5. UCST of Poly(CNPCA VCP) in ethanol at different heating/cooling rate.

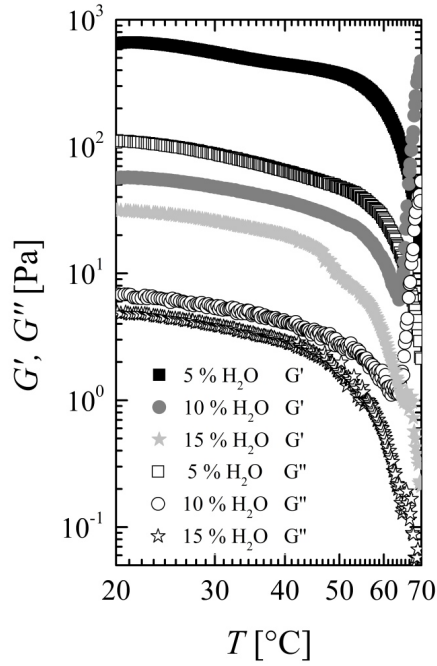


S6. UCST of Poly(CNPCAVCP) 5 mg/ml in ethanol/water mixture.

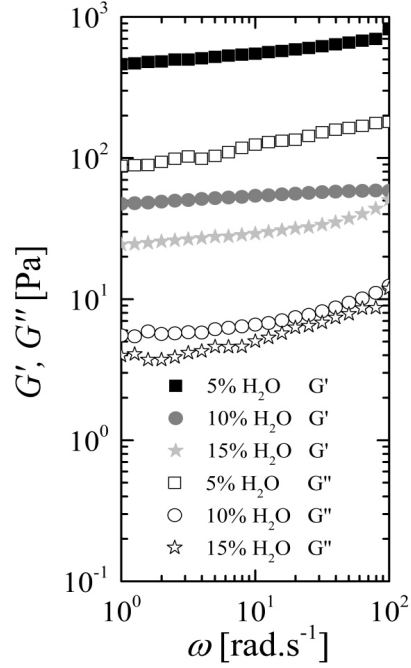


S7. UCST of Poly(CNPCAVCP) isomer (prepared using isopropylamine) in ethanol/water mixture.

a)

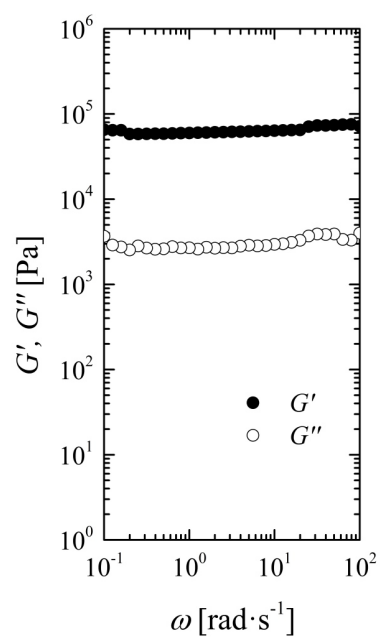


b)

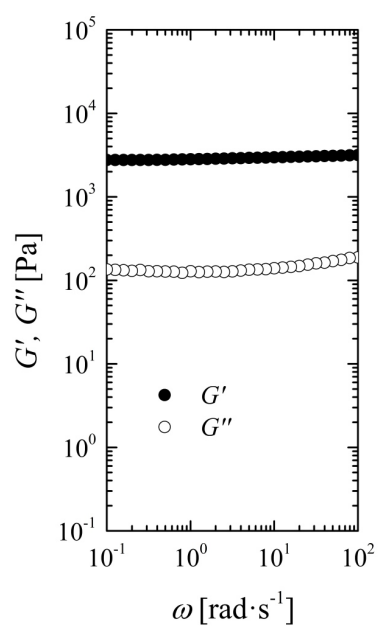


S8. (a) Temperature dependence of the dynamic moduli of a 5 mg/ml polymer gel in ethanol/water mixture at an angular frequency of 10 rad/s: storage modulus G' and loss modulus G'' . (b) Frequency sweep of a 5 mg/ml polymer gel in ethanol/water mixture at 25 °C (Measurements were made using an AR 2000ex rheometer of TA instruments with standard Peltier plates with solvent trap).

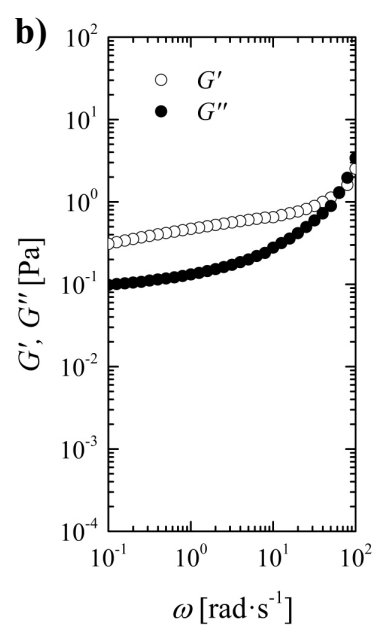
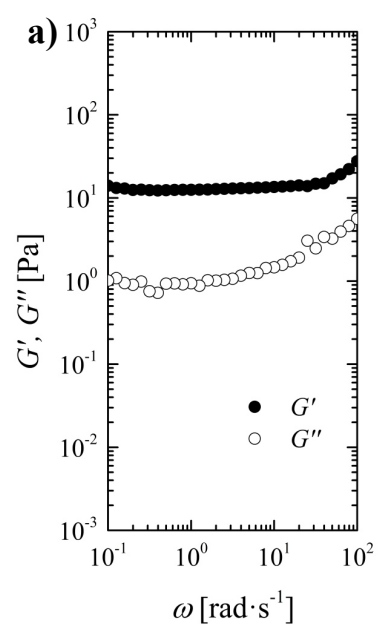
a)



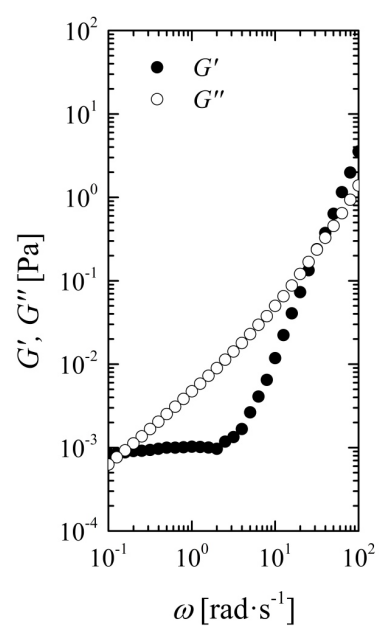
b)



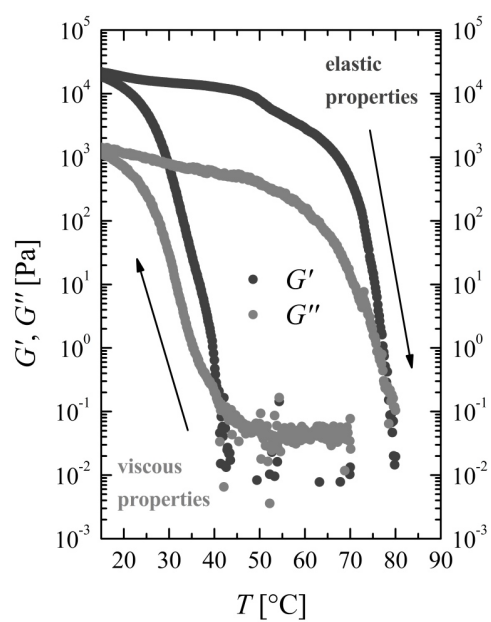
S9. Frequency sweep of polymer gel in ethanol/water at 25 °C: (a) 15 mg/ml, (b) 10 mg/ml.



S10. Frequency sweep of polymer gel in ethanol/water at 25 °C: (a) 5 mg/ml, (b) 2.5mg/ml.



S11. Frequency sweep of polymer gel in ethanol/water at 25 °C: 1 mg/ml.



S12. The storage modulus G' and the loss modulus G'' as a function of the temperature T during cooling and heating ramps (0.5 °C/min) at a gelator concentration of 10 mg/mL in ethanol/water (95:05 vol %)