Supporting Information

Gelation Procedure

(1) After precipitation and washing, the HFIP-PT formed a dried orange-red solid.[i] It was then readily dissolved in THF at room temperature (Mallinckrodt Chemicals) in a small glass vial. The concentration of the polymer in the initial THF solution was 0.32wt% for the particular preparation used for NMR and FTIR analysis.

(2) The small vial was placed in a larger glass vial containing methanol (Mallinckrodt Chemicals).

(3) After 48h of solvent interdiffusion, the liquid in the small vial became turbid. NMR analysis of the liquid inside and outside the small vial indicated that the composition in both containers was ~96% methanol and ~4% THF. The concentration of the polymer was too small to be detected by NMR analysis but is calculated to be ~0.5wt%.

(4) Next, the liquid containing the polymer was transferred into a poly(tetrafluoroethylene) crucible and placed inside a fume-hood at room temperature and atmospheric pressure. Solvent evaporation in air resulted in the formation of an orange jelly-like substance. Under these conditions, water present in the ambient incorporated into the system. Thus, the gel contains HFIP-PT, methanol and water (estimated HFIP-PT concentration is 2wt%).

(5) When desired, the gel in a bulk or thin film form was placed inside a desiccator containing anhydrous calcium sulfate (Drierite), and connected to the vacuum line of a fume-hood (6Pa, 0.045Torr). The concentration of solvent in the gel decreases under

these conditions as illustrated by FTIR analysis, Figure S2-(c) in SI. HFIP-PT concentration in the gel after 48h at 6Pa is estimated at 88wt%.

Preparation of Thin Films

(1) The gel was first deposited on a glass slide on a Koefler bench (Leica Aktiengesellschaft) and heated to 100°C in about 15s. At this temperature, the gel melted. During heating, it is possible that water from the ambient moisture could further replace methanol in the gel as it is able to form stronger hydrogen bonding associations.

(2) The molten gel/glass slide was removed from the heating stage and transferred to a substrate at room temperature.

(3) After 15s, the razor blade was used to shear the melted gel during cool-down. Each film was sheared once with the razor blade at an angle of ~30°.

After shearing, films had a rectangular shape with area about $2x10mm^2$. The procedure employed resulted in tapering film thicknesses. The average thickness on the thinner region is 1.8µm (σ = 0.5µm) and on the thicker region is 5.4µm (σ = 1.4µm).

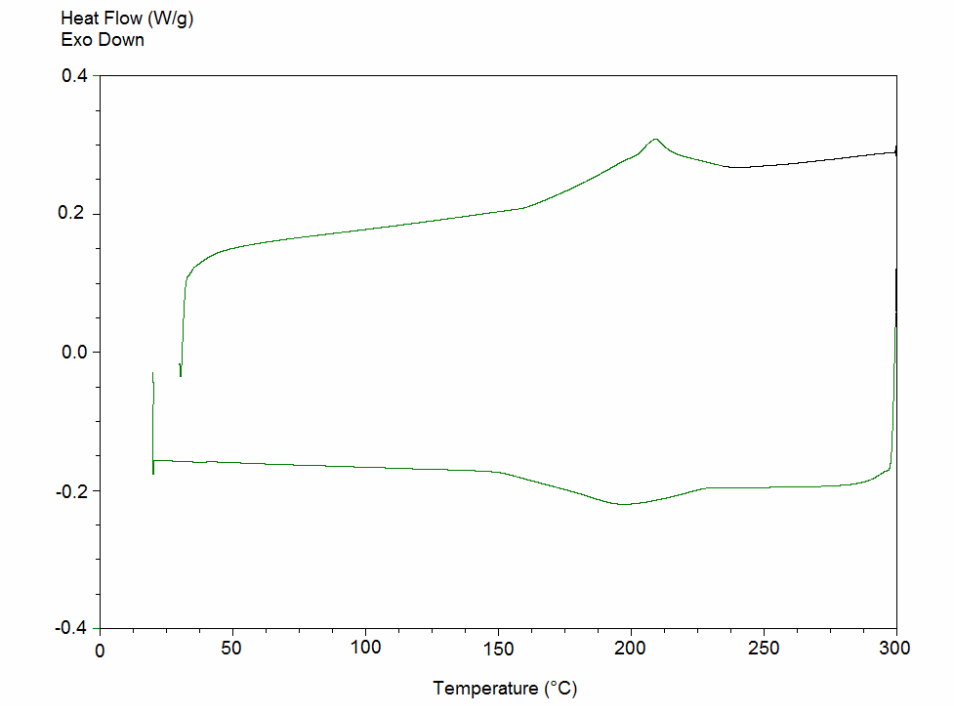

Figure S1. DSC curve for HFIP-PT. Thermal treatment is the following: equilibration at 30°C, heating ramp +10°C/min to 300°C, isothermal for 1min, cooling ramp -10°C/min to 20°C and isothermal for 1min.

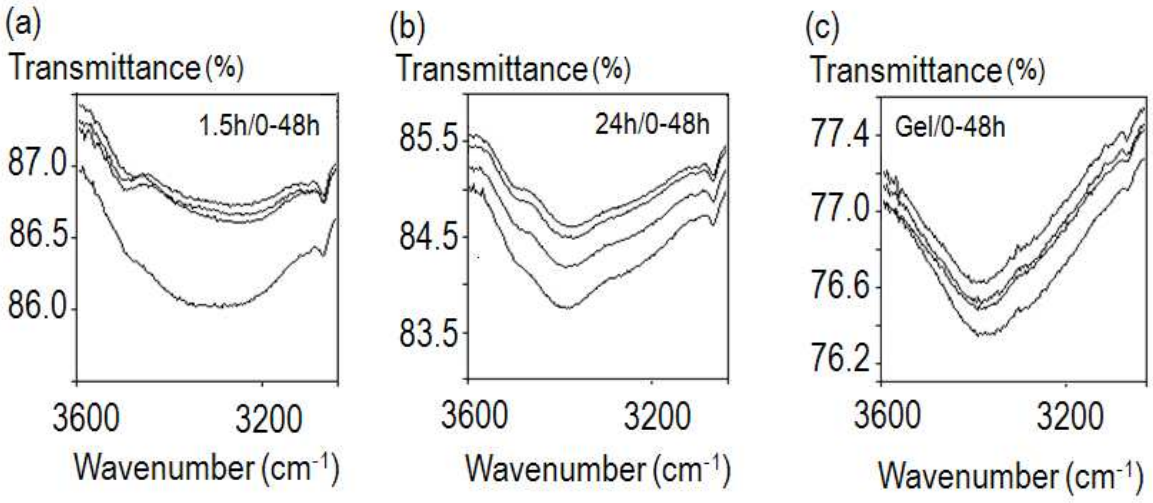

Figure S2. FTIR spectra of representative drying series. (a) 1.5h/0h, 1.5h/2h, 1.5h/24h and 1.5h/48h (b) 24h/0-48h (c) Gel/0-48h. For each interdiffusion time, higher transmittance spectra correspond to longer times under vacuum.

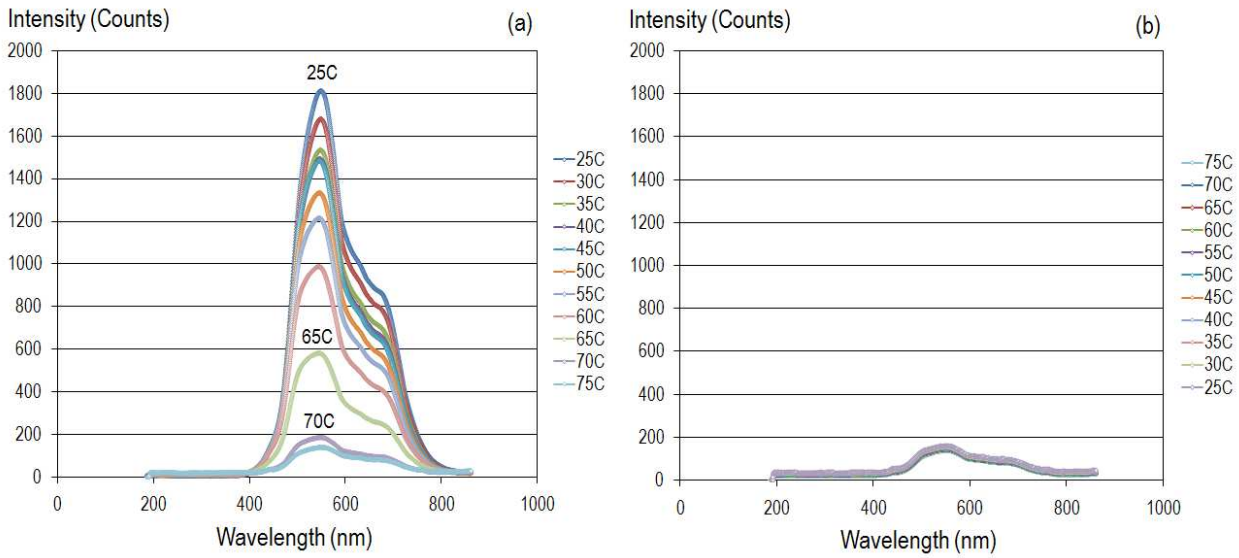

Figure S3. Reflectivity spectra monitoring the change in intensity of reflected polarized light with temperature of an oriented gel film that has been further placed under vacuum (48h 6Pa). (a) Heating ramp. (b) Cooling ramp. Thermal treatment consisted of heating at a rate of +1°C/min from 25°C to 75°C and cooling at a rate of -1°C/min from 75°C to 25°C. The residence time at 75°C was negligible.