Supporting Information

ACS Applied Polymer Materials

Fluorinated Glycidyl Triazolyl Polymers Exhibiting Thermally Stable Layered Structures and Sticky Hydrophobic Surfaces

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1. Materials and methods

1.1. Materials

Polyepichlorohydrin (PECH, Average molecular weight: 700 kg mol^{-1}) was purchased from Scientific Polymer Products. Propiolic acid, diethylene glycol monomethyl ether, diiodomethane, ethylene glycol and 1*H*,1*H*,2*H*,2*H*-tridecafluoro-1-*n*-octanol were purchased from Tokyo Chemical Industry. Sodium azide (NaN_3), sodium hydroxide (NaOH), sodium hydrogen carbonate ($NaHCO_3$), anhydrous magnesium sulfate ($MgSO_4$), toluene, ethyl acetate, methanol, diethyl ether, 1,1,1,3,3,3-hexafluoro-2-propanol, and distilled water were purchased from Nacalai Tesque. Dry *N,N*-dimethylformamide (DMF) was purchased from Kanto Chemical. Cation exchange resin Amberlite™ HPR2900 H (hydrogen form) was purchased from Merck. Before use, the resin was washed with distilled water followed by acetone, and then dried under vacuum. Propiolic acid, diiodomethane, and ethylene glycol were purified by distillation under reduced pressure prior to use, while all other chemicals were used as received. EG2-alkyne was prepared according to a previously reported procedure.[S1]

1.2. Instrumental analysis

NMR spectra were recorded using a JEOL ECZ 400S spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei, with residual solvent peaks serving as internal standards. IR spectra were obtained using a Shimadzu IRSpirit-X spectrometer with KBr pellet samples. Size exclusion chromatography (SEC) was conducted at 50 °C using 0.01 M Li·NTf_2 in DMF as the eluent on a Shimadzu Nexera XR system equipped with a Shim-pack GPC-80MD column. Polystyrene standards (PStQuick A and B, Tosoh Bioscience) were employed for molecular weight calibration. Sample concentration was 2 mg mL^{-1}. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60 Plus instrument at a heating/cooling rate of 10 °C min^{-1} under a nitrogen flow. Thermogravimetric analysis (TGA) was carried out using a Shimadzu DTG-60 instrument under a nitrogen atmosphere. X-ray diffraction (XRD) patterns (2θ = 1−30°) were recorded by a Rigaku Miniflex 600 diffractometer (Ni-filtered Cu Kα radiation) equipped with an Anton Paar thermal control system BTS500. Prior to XRD measurement, the solid GTP samples were placed on a sample holder and heated above T_{iso} to prepare films with flat surfaces. The optical textures of materials were observed by an Olympus BX51N-31P-O3 polarized optical microscope (POM) linked to a DP22 digital camera with a temperature control system of LINKAM T95-HS, LTS420E. DFT calculation (B3LYP, 6-31G* in Nonpolar solvent) was conducted by using Spartan 24 software (Wavefunction Inc). Rheological properties were characterized using an MCR702 rheometer equipped with a CTD 600 temperature-controlled oven (Anton Paar). The sample was first heated above the mesophase transition temperature (T_{meso}) on the sample stage, then compressed with a parallel plate (20 mm diameter) to a thickness of 1.0 mm. After cooling the sample to the glass transition temperature (T_g), measurement was initiated. The shear strain and frequency were set to 1%

and 1 Hz, respectively. The heating rate was 3 °C min^{-1}, and data were collected at intervals of 1 °C. GTP films were prepared using hot press machines MP-SCL and MP-SCH (Toyoseiki). The samples were hot-pressed at 150 °C with a stainless-steel spacer (thickness: 0.5 mm). Test specimens for tensile test were prepared by cutting the GTP film using an ISO 37-4 dumbbell-shaped cutter (Kobunshi Keiki). Tensile tests were performed at room temperature (16–17 °C) using a digital force gauge ZTS-50N (Imada) in combination with a vertical motorized test stand MX2-500N (Imada). Data were recorded using Force Logger Next software (version 1.05, Imada). The GTP film for Atomic force microscope (AFM) and contact angle measurements was prepared by drop-casting 0.5 mL of a hexafluoro-2-propanol solution containing 1wt% GTP onto a glass plate (2.5 × 2.5 cm^2). The solvent was evaporated at 50 °C in a fume hood. The resulting films were annealed at 200 °C for 2 h under vacuum, followed by cooling to room temperature. AFM imaging of the GTP film surface was performed using the S-image system controlled by an SPI 4000 probe station (SII Nano Technology). Topographic images were acquired in dynamic force mode (DFM) using an SI-DF20 AFM tip (SII Nano Technology).

1.3. Contact angle measurements

The surface free energies of the GTP films were estimated from contact angle measurements using a drop shape analyzer (DSA25S, Krüss) and the Owens, Wendt, Rabel, and Kaelble model (OWRK model) using a software Krüss Advance (Version 1.13).[S2] Distilled water, ethylene glycol, and diiodomethane were utilized as probe liquids. The dispersion and polar components of surface tension are 21.8 and 51.0 mN m^{-1} for water, 30.9 and 16.8 mN m^{-1} for ethylene glycol, and 46.8 and 4.0 mN m^{-1} for diiodomethane, respectively (these values are pre-installed in the software). A 2 μL liquid was dispensed from the needle tip and deposited onto the film surface by lowering the needle. The contact angle was determined by fitting the droplet shape by Young–Laplace equation with the help of the software Krüss Advance. The baseline was set manually. Measurements were conducted at five different locations for each sample.

For advancing contact angle (θ_A) measurements,[S3] a 2 μL water was dispensed from the needle tip, and the sample stage was then raised until the droplet contacted the surface. The needle tip was positioned at the center of the droplet. An additional 1 μL of water was dispensed inside the droplet at a flow rate of 0.1 μL s^{-1}. After waiting for 30 s to make sure that the system is in equilibrium, the droplet was inflated at a flow rate of 0.1 μL s^{-1} until it reached a total volume of 15 μL. Contact angles were collected at a rate of one data per second. The contact angle was determined by fitting the droplet shape using the Young–Laplace equation. When the droplet shape could not be fitted using the Young–Laplace equation, alternative fitting methods provided by the software (Ellipse, Tangent, and Height/Width manual) were applied. The θ_A value was calculated as the average of fifty consecutive data points within the plateau region of the contact angle profile plotted against droplet volume. Measurements were conducted at five different locations for each sample.

For receding contact angle (θ_R) measurements,[S3] the needle tip was positioned within 0.3 mm of the sample surface, and water (150 μL for GTP-EG2-*co*-C_6F_{13}25 and GTP-EG2, and 100 μL for the other GTPs) was dispensed at a flow rate of 5 μL s^{-1}. After adjusting the syringe position, water was aspirated at a flow rate of 1 μL s^{-1} until the droplet volume reached 27 μL. An additional 2 μL of water was aspirated at a flow rate of 0.1 μL s^{-1}. After waiting for 30 s to make sure that the system is in equilibrium, the droplet was deflated at a flow rate of 0.1 μL s^{-1} until it reached a total volume of 5 μL. Contact angles were collected at a rate of one data per second. The contact angle was determined by fitting the droplet shape using the Young–Laplace equation. When the droplet shape could not be fitted using the Young–Laplace equation, alternative fitting methods provided by the software (Ellipse, Tangent, and Height/Width manual) were applied. The θ_R value was calculated as the average of fifty consecutive data points within the plateau region of the contact angle profile plotted against droplet volume. Measurements were conducted at five different locations on each sample.

The laboratory conditions during the contact angle measurements were as follows: Temperature: 20 °C, Relative humidity: 15–20%.

2. IR spectra

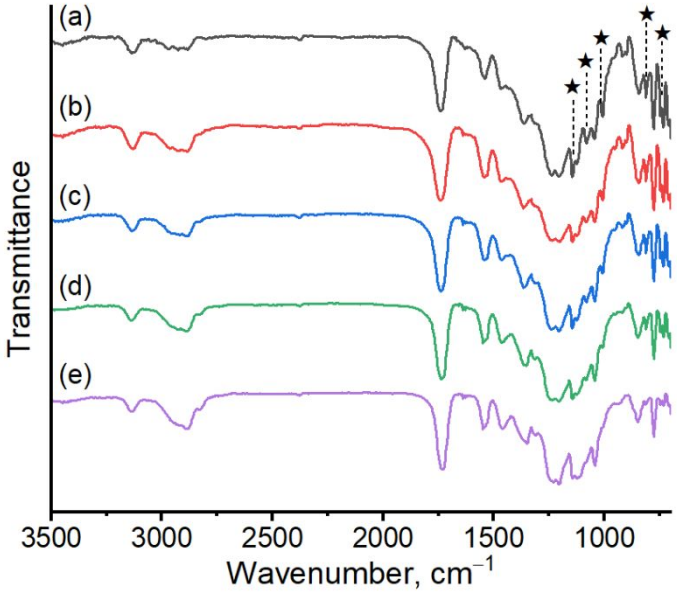

Figure S1. IR spectra of (a) GTP-C_6F_{13} homopolymer, (b) GTP-EG2-*co*-C_6F_{13}75, (c) GTP-EG2-*co*-C_6F_{13}60, (d) GTP-EG2-*co*-C_6F_{13}50, and (e) GTP-EG2-*co*-C_6F_{13}25. KBr pellets.

3. ^{1}H and ^{13}C NMR spectra

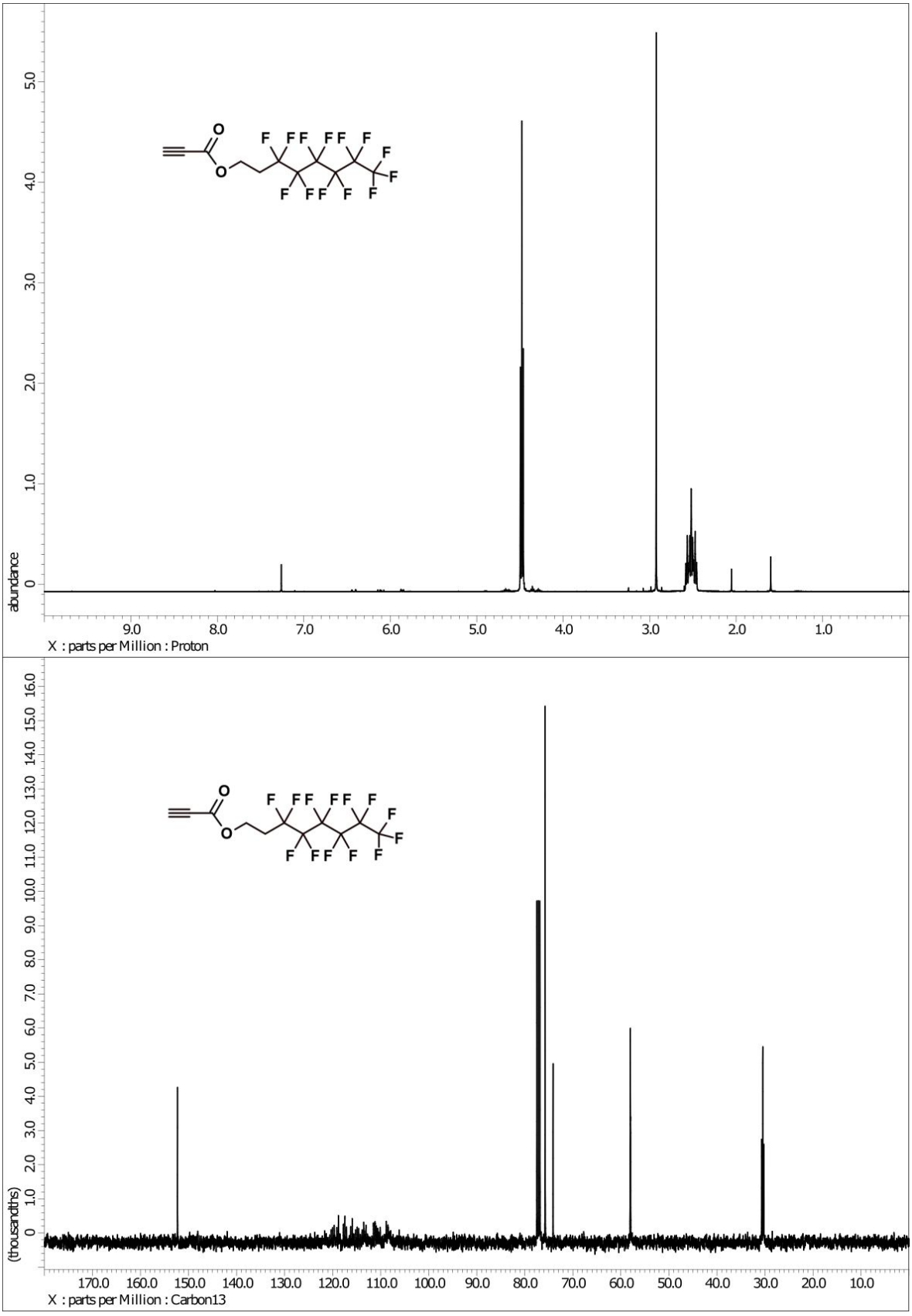

Figure S2. ^{1}H and ^{13}C NMR spectra of C_6F_{13}**-alkyne** (Solvent: $CDCl_3$).

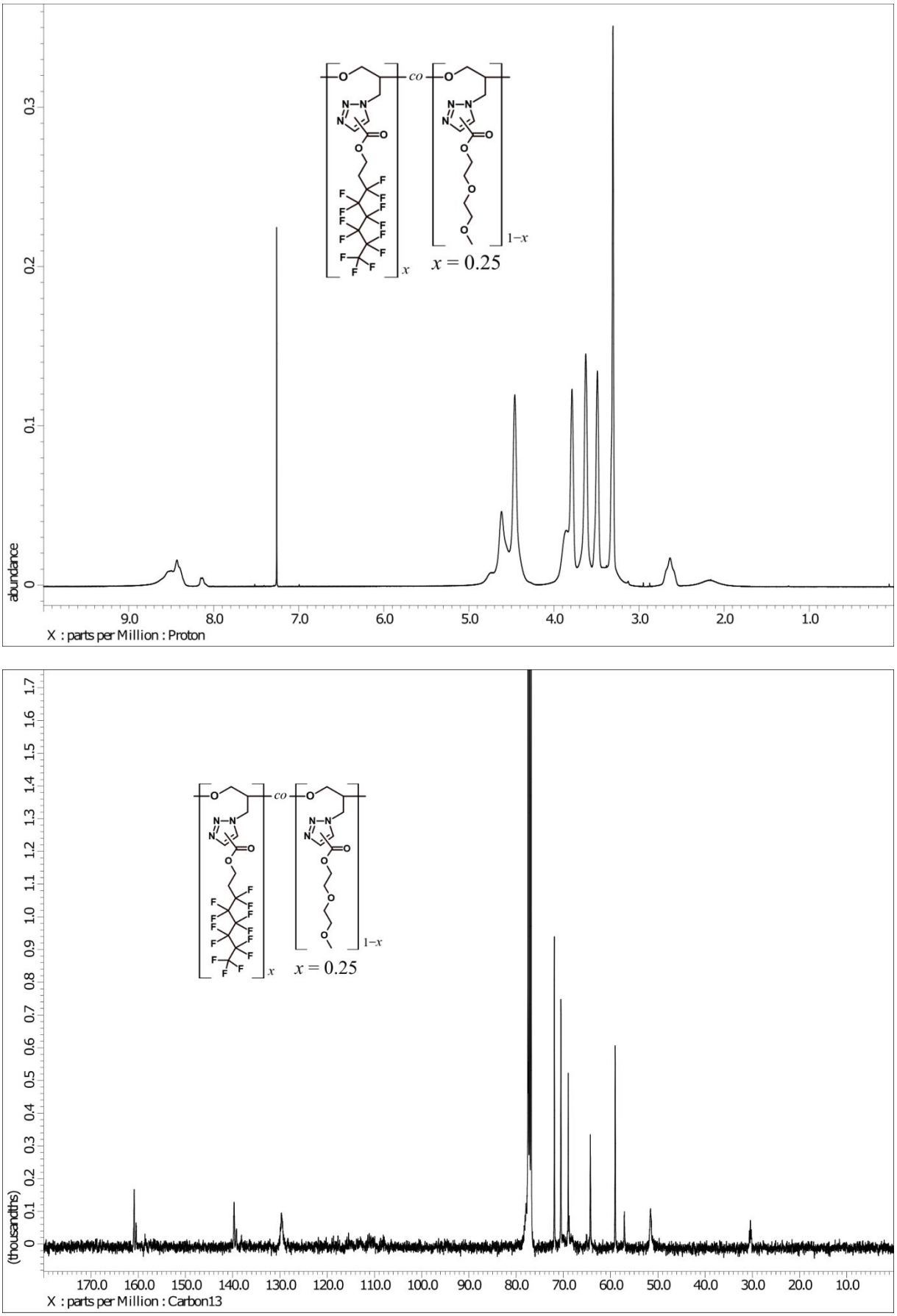

Figure S3. ^{1}H and ^{13}C NMR spectra of GTP-EG2-*co*-C_6F_{13}25 (Solvent: $CDCl_3$).

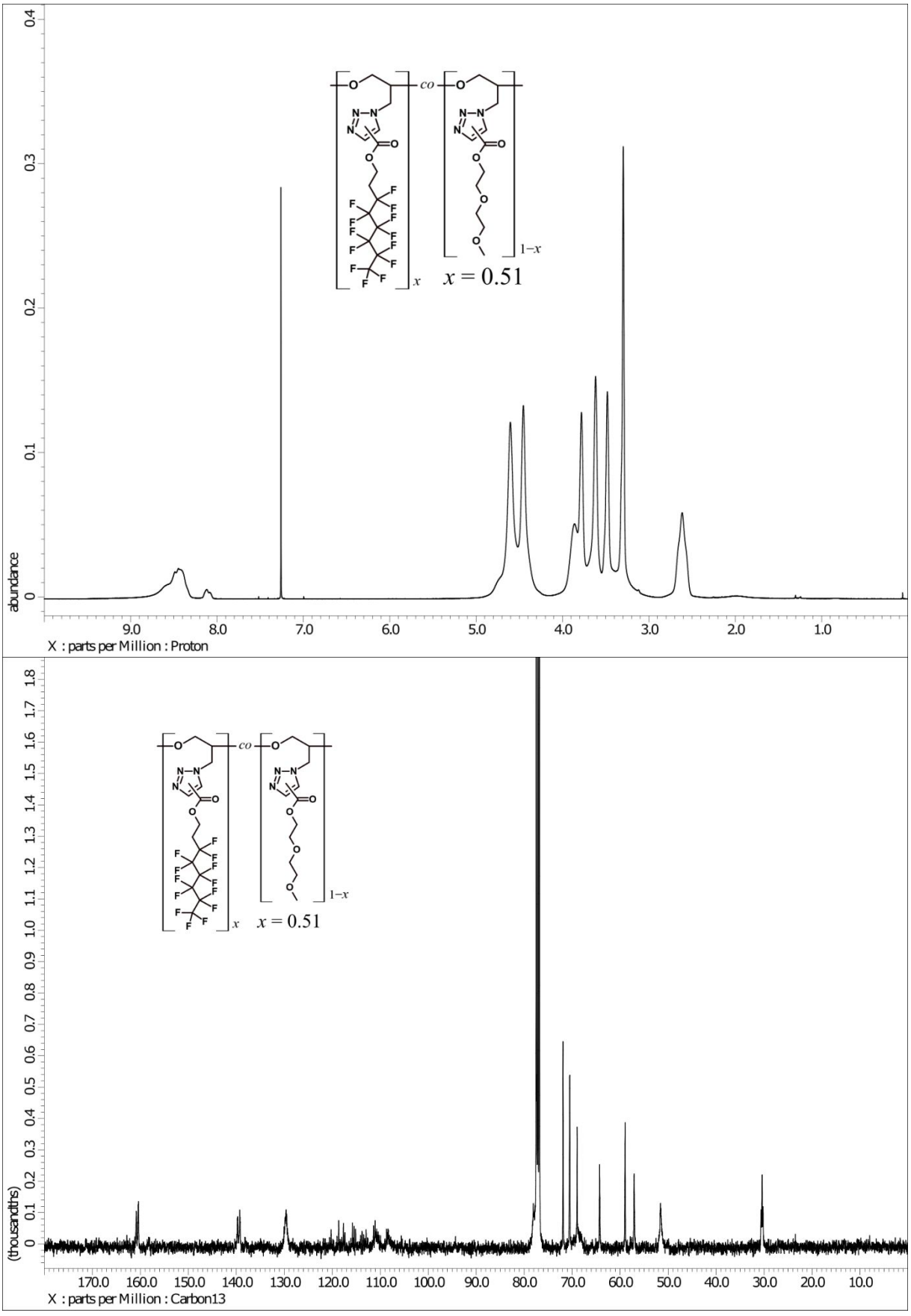

Figure S4. ^{1}H and ^{13}C NMR spectra of GTP-EG2-*co*-C_6F_{13}50 (Solvent: $CDCl_3$).

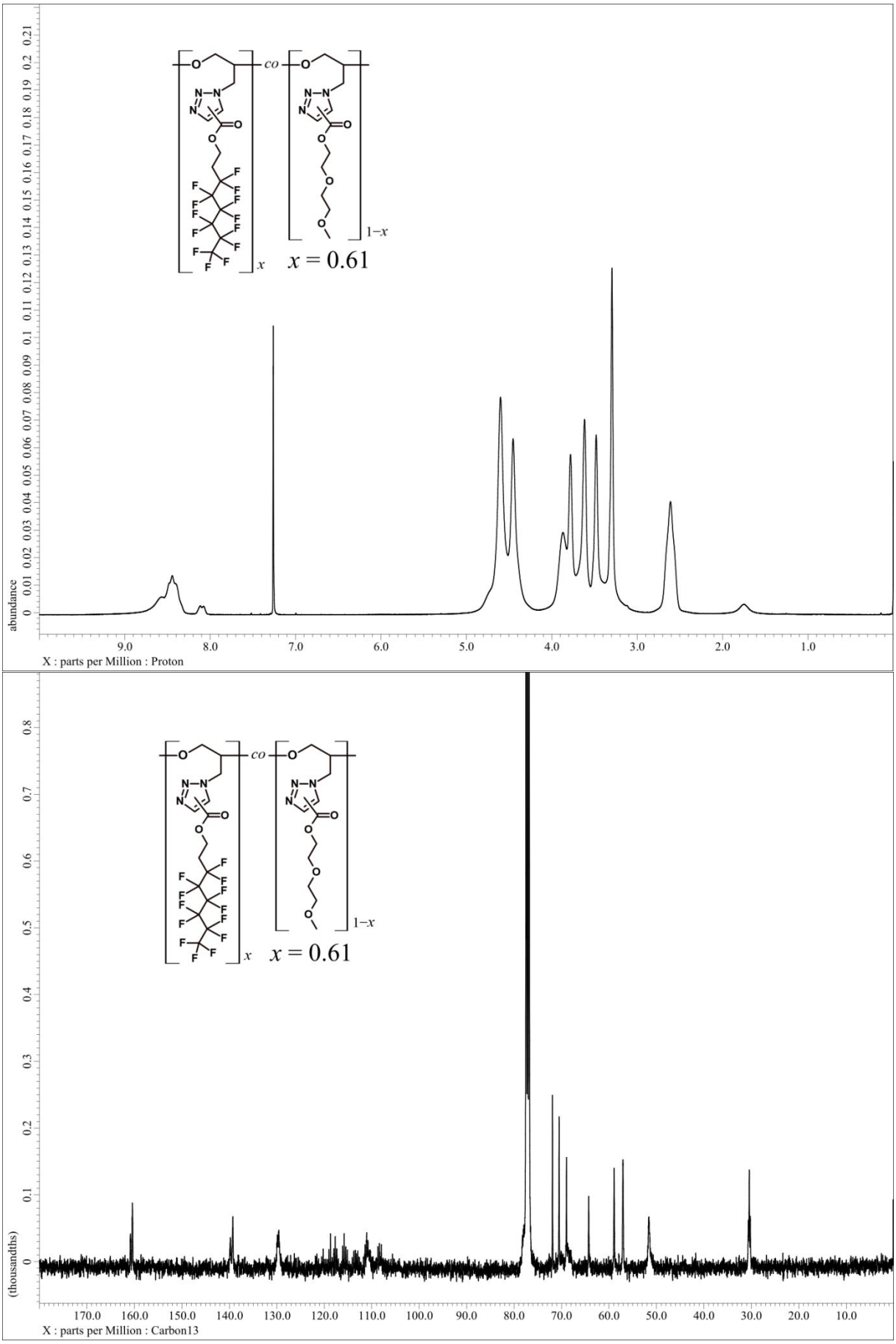

Figure S5. ^{1}H and ^{13}C NMR spectra of GTP-EG2-*co*-C_6F_{13}60 (Solvent: $CDCl_3$).

4. Size exclusion chlomrtography

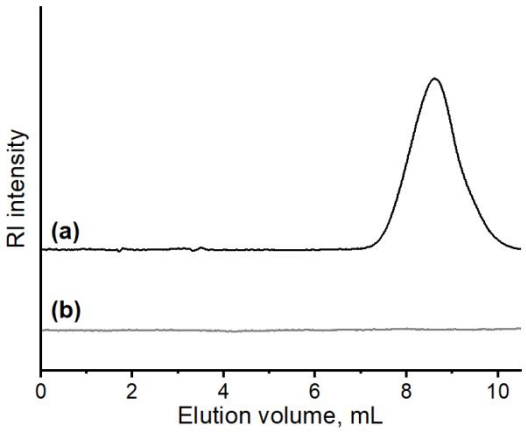

Figure S6. SEC traces of (a) GTP-EG2-*co*-C_6F_{13}25, and (b) GTP-EG2-*co*-C_6F_{13}50. Eluent: 0.01 M Li·NTf_2 in DMF.

5. Temperature-dependent XRD profiles

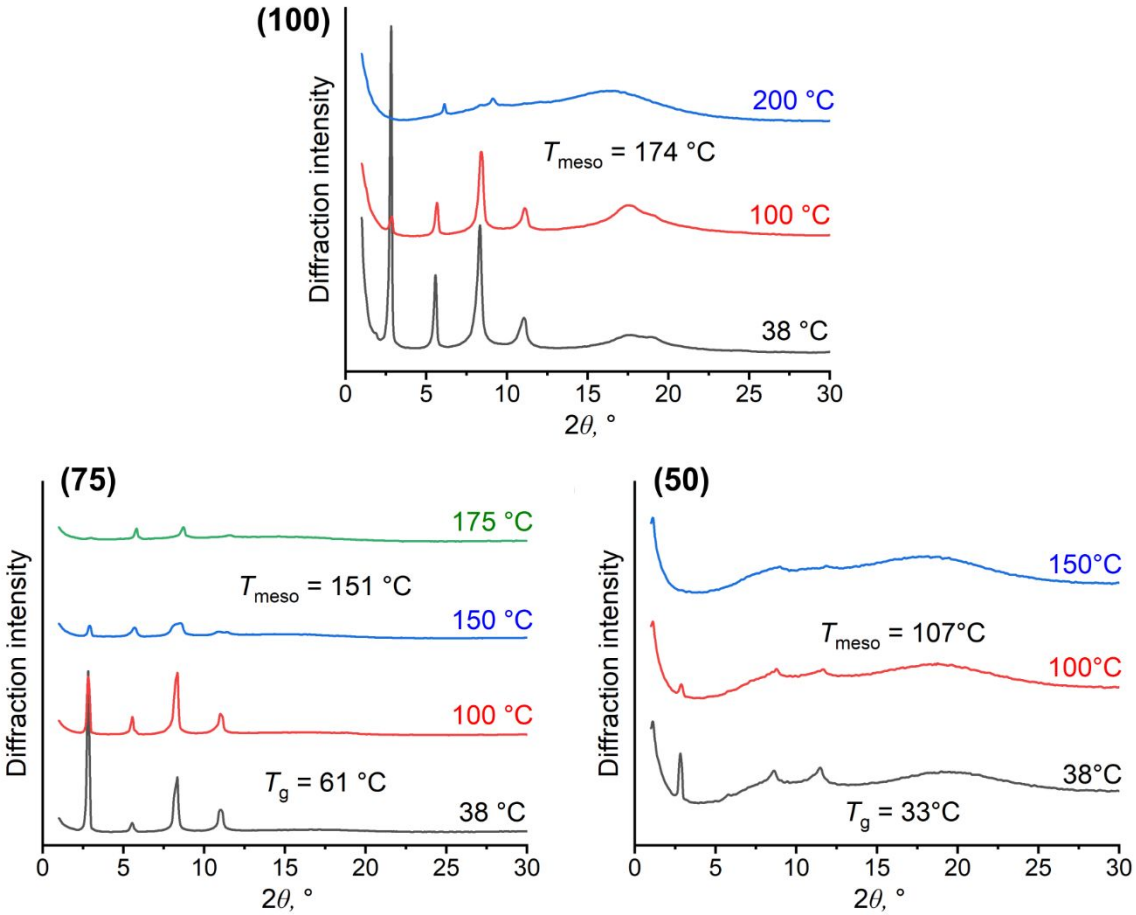

Figure S7. Temperature-dependent XRD profiles of GTP-C_6F_{13} homopolymer and GTP-EG2-*co*-C_6F_{13}*x* copolymers. The number in parentheses indicates the C_6F_{13} content.

6. AFM measurements

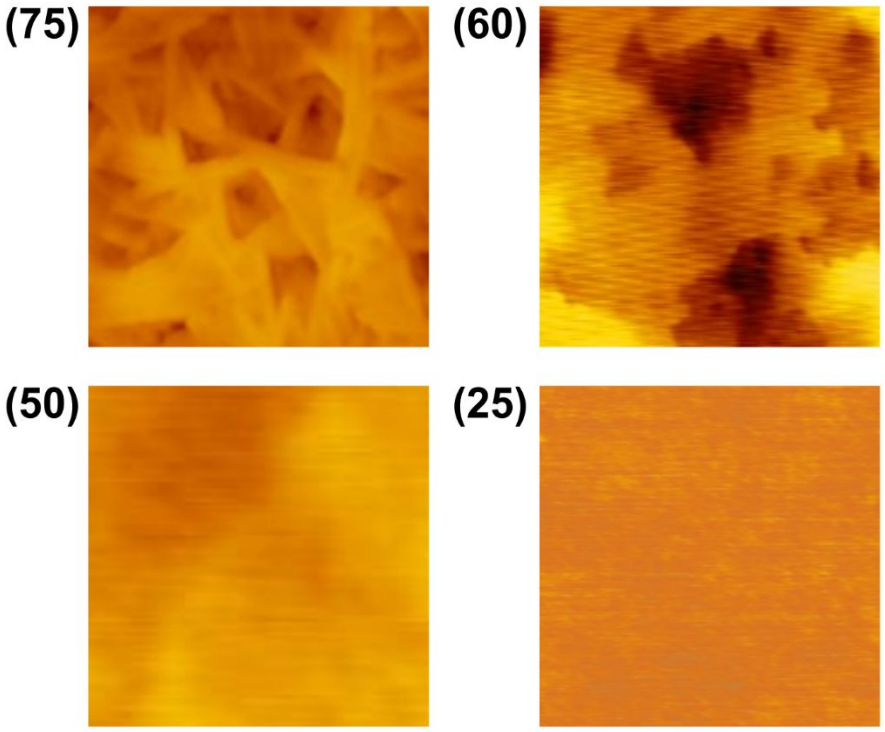

Figure S8. AFM images of the GTP-EG2-*co*-$C_6F_{13}x$ film surfaces to visualize organized structures. The number in parentheses indicates the C_6F_{13} content. Scan area: 400 nm × 400 nm.

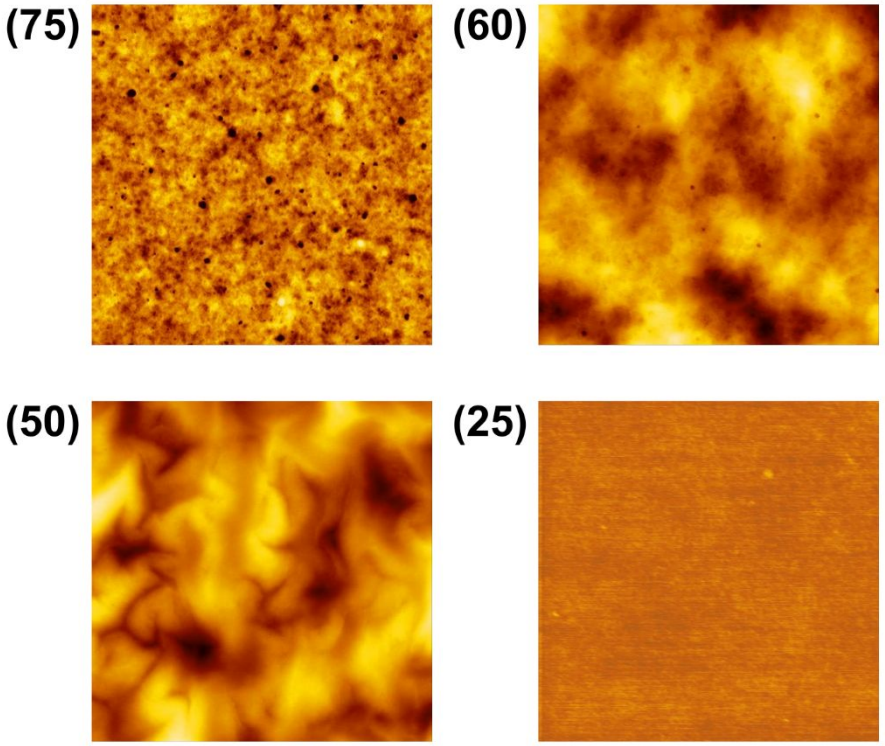

Figure S9. AFM images of the GTP-EG2-*co*-$C_6F_{13}x$ film surfaces to measure surface roughness. The number in parentheses indicates the C_6F_{13} content.. Scan area: 10 μm × 10 μm.

7. Rheological measurements

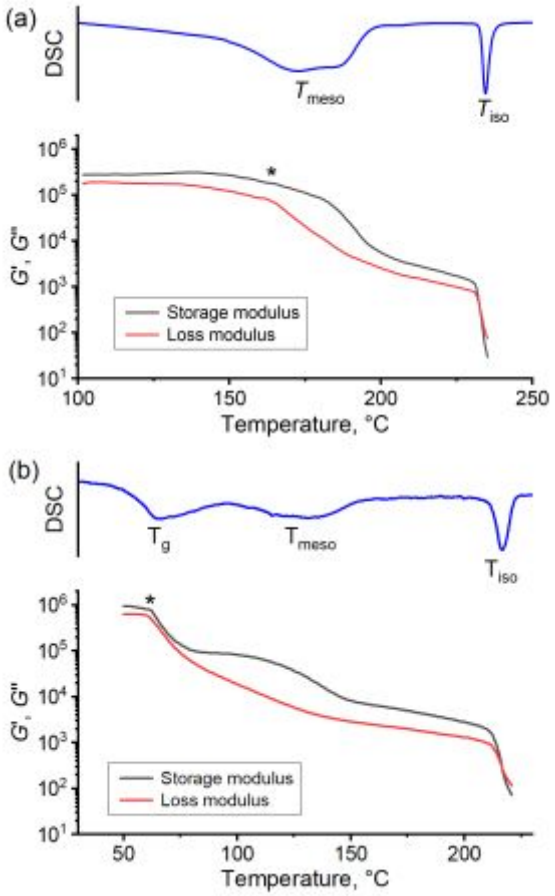

Figure S10. Temperature-dependent mechanical properties of (a) GTP-C_6F_{13} homopolymer and (b) GTP-EG2-*co*-C_6F_{13}60. The storage modulus (*G*') and loss modulus (*G*") are shown as black and red curves, respectively, while the DSC traces are depicted in blue.

8. Contact angle measurements

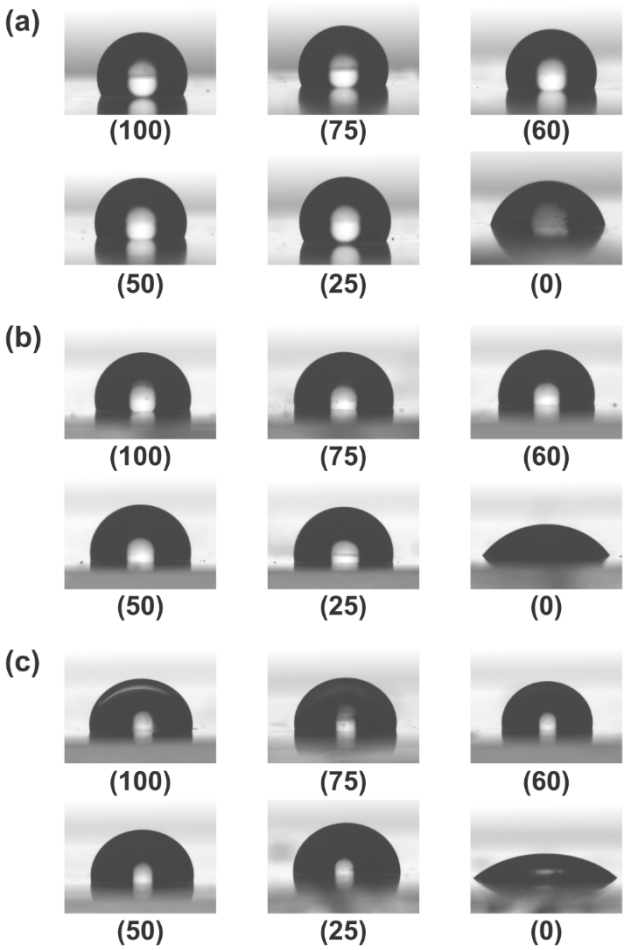

Figure S11. Representative photographs of (a) water, (b) ethylene glycol, and (c) diiodomethane droplets on the GTP films for contact angle measurement. The number in parentheses indicates the C_6F_{13} content. The photographs of (100) and (25) in (a) are identical to those in Figure 6b and are shown here for comparison with the other images. Droplet volume: 2 μL. All measurements were conducted at 20 °C and 15–20% relative humidity.

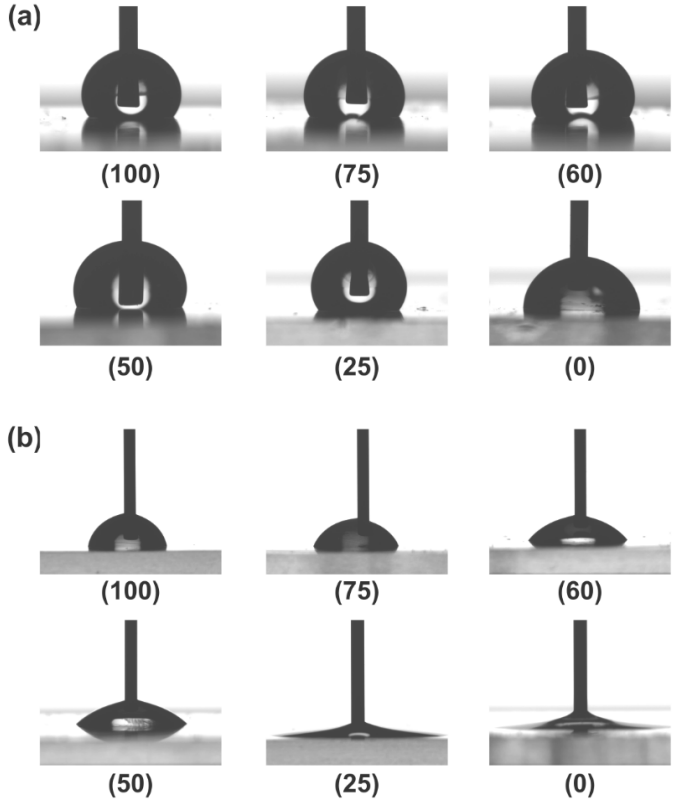

Figure S12. (a) Representative photographs of the water droplets on on the GTP films for advancing contact angle measurements. The number in parentheses indicates the C_6F_{13} content. Droplet volume: 8 μL. (b) Representative photographs of the water droplets on the GTP films droplet for receding contact angle measurements. The photographs of (100) and (25) in (b) are identical to those in Figure 7b and are shown here for comparison with the other images. Droplet volume: 11 μL. All measurements were conducted at 20 °C and 15–20% relative humidity.

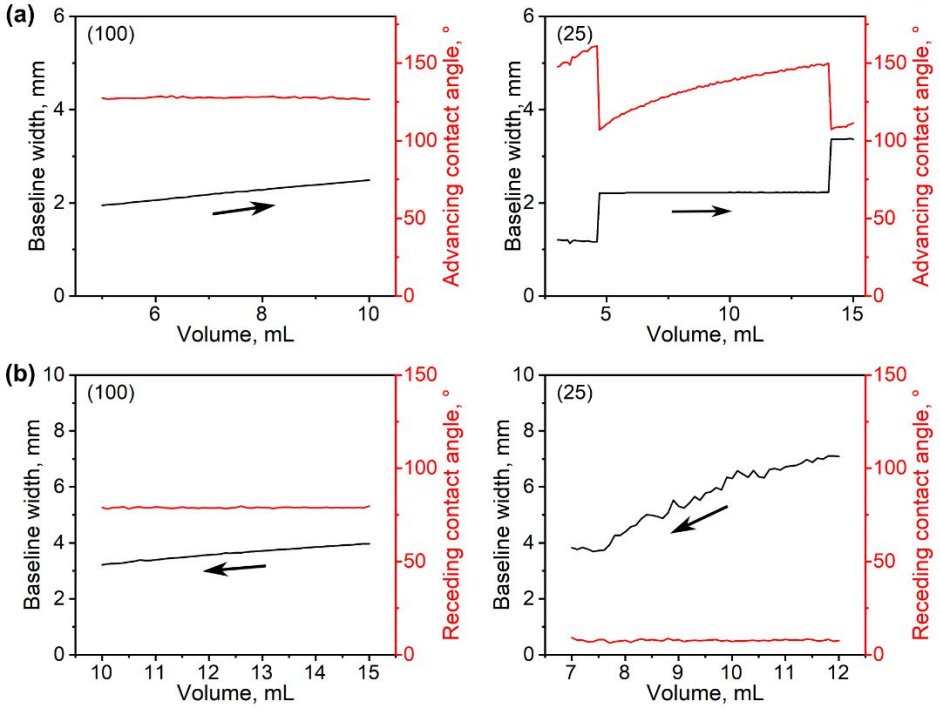

Figure S13. (a) Relationship between baseline width and advancing contact angle. (b) Relationship between baseline width and receding contact angle. The number in parentheses indicates the C_6F_{13} content.

References

S1. Ikeda, T.; Hosoda, N. Facile, Efficient, and Safe Copper-Free Synthesis of Glycidyl Triazolyl Polymers. *J. Polym. Sci.* **2025**, *63*, 2568–2578.

S2. Owens, D. K.; Wendt, R. C. Estimation of the Surface Free Energy of Polymers. *J. Appl. Polym. Sci.* **1969**, *13*, 1741–1747.

S3. Huhtamäki, T.; Tian, X.; Korhonen, J. T.; Ras, R. H. A. Surface-Wetting Characterization Using Contact-Angle Measurement. *Nat. Protoc.* **2018**, *13*, 1521–1538.