

SUPPORTING INFORMATION

Low T_g , strongly segregated, ABA triblock copolymers: a rheological and structural study

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Materials and methods

All chemicals were purchased from Sigma-Aldrich (Merck), Acros, or Fluorochem. Solvents of analytical grade were used unless otherwise stated. Monomers were passed through a short column filled with activated basic aluminium oxide before use. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from diethyl ether.

¹H-NMR spectra were recorded on a 500 MHz Advance Bruker spectrometer at 25 °C. Chemical shifts are given in ppm downfield from Tetramethylsilane (TMS). Size exclusion chromatography (SEC) was carried out on a system composed of two PSS SDV columns (1000 Å and 10000 Å) connected to an Agilent differential refractometer, with THF as eluent (30 °C, 1 mL.min⁻¹). Polystyrene standards were used for calibration.

SAXS measurements were performed at different temperatures with an in-house setup of the Laboratoire Charles Coulomb, Université Montpellier, France. A high brightness low power X-ray tube, coupled with aspheric multilayer optics (GeniX3D from Xenocs), was employed. It delivers an ultralow divergent beam (0.5 mrad, $\lambda=0.15418$ nm). Scatterless slits were used to give a clean 0.6mm beam diameter with a flux of 35 Mphotons/s at the sample. We worked in a transmission configuration, and scattered intensity was measured by a 2D “Pilatus” 300K pixel detector by Dectris (490*600 pixels) with a pixel size of 172×172 μm^2 , at a distance of

1.9 m from the sample. All Intensities were corrected by transmission, and the empty cell contribution (two mylar foils) was subtracted. The copolymer samples were placed between two mylar foils, heated to 130°C for one hour, and cooled down to room temperature before starting the measurements. For each temperature, ten scans of 30 min were performed, and a Mettler F12 stage was employed to control the sample temperature.

Dynamic mechanical analyses were performed with a DMTA/SDTA861e from Mettler Toledo (Greifensee, Switzerland). Disc specimens of 6 mm diameter and 0.5 mm thickness were heated from -70 to 200°C at 3°C/min. The samples were analysed under shear at a constant frequency of 1 Hz, a constant force of 0.1 N, and by a maximum strain imposed of 0.2%.

Rotational shear rheological experiments were performed in the linear regime on an ARES (TA Instruments) strain-controlled rheometer equipped with an oven. All experiments were carried out at given temperatures, using 8 mm plate-plate geometries. The gap was adjusted between 0.8 and 1 mm to fill the geometry. All samples were equilibrated for about an hour in the rheometer at a temperature of 130°C, and normal forces were checked to be relaxed prior to any measurement. Samples were measured at several temperatures from T= -20 to 200°C, depending on the samples. Measurements were conducted from low to high and then from high to low temperatures to prove the reversibility of the measurements. For the PnBA homopolymer reference sample, a master curve was built at the reference temperature of 25°C, following a Willian-Landel-Ferry (WLF) equation with the constant c1= 6.2 and c2= 131.17K.¹ In addition, a vertical shift factor :

$$b_T = \frac{\rho(T_{ref}) \cdot T_{ref}}{\rho(T) \cdot T}$$

with $\rho=1.2571-6.89 \times 10^{-4}T$ has been applied in order to account for the temperature dependence of the sample density and elasticity.² For the triblock master curves, the reference temperature was shifted to iso-Tg compared to the reference PnBA. In such a way, only the influence of temperature and the phase separation is considered, allowing us to discuss the impact of the phase separation in a wide range of temperatures (from - 25°C to 200°C) on the dynamics of the triblock copolymers.

Copolymer synthesis

PHFBA macro-CTA

The procedure for the PHFBA of 10000 g/mol is given as representative example. 2,7 mL of HFBA (1.5×10^{-2} mol, 100 eq.), 44 mg of S,S-Dibenzyl trithiocarbonate (DBTTC) (1.5×10^{-4} mol, 1 eq.) as RAFT agent, 3,7 mg of AIBN (2.25×10^{-5} mol, 0.15 eq.), and DMF (1.0 mL) as solvent were added in a Schlenk tube equipped with a magnetic stirrer. Five freeze-pump-thaw cycles were applied to degas the solution. The reaction tube was filled with argon, sealed, and placed in a pre-heated oil bath at 70°C for 3h30. The reaction was stopped by plunging the flask into liquid nitrogen and opening it to air. The polymer was subsequently precipitated twice into a MeOH/H2O (1/1, v/v) mixture. The polymer was finally dried under vacuum at 35 °C for 48h.

For the PHFBA of 21000 g/mol, the same conditions were used but with a HFBA/CTA ratio of 200, and the polymerization time was of 4 hours.

$^1\text{H-NMR}$ (500 MHz, THF- d_8 , ppm): 7.38-7.09 (m, $\text{H}_{\text{aromatic}}$), 4.70 (t, O- $\text{CH}_2\text{-CF}_2$), 2.55 (br, - CH-CO-), 2,15 -1,15 (m, - $\text{CH}_2\text{-CH-}$). SEC: PHFBA 10k: $\bar{M}_w/\bar{M}_n = 1,15$; PHFBA 21k: $\bar{M}_w/\bar{M}_n = 1,21$

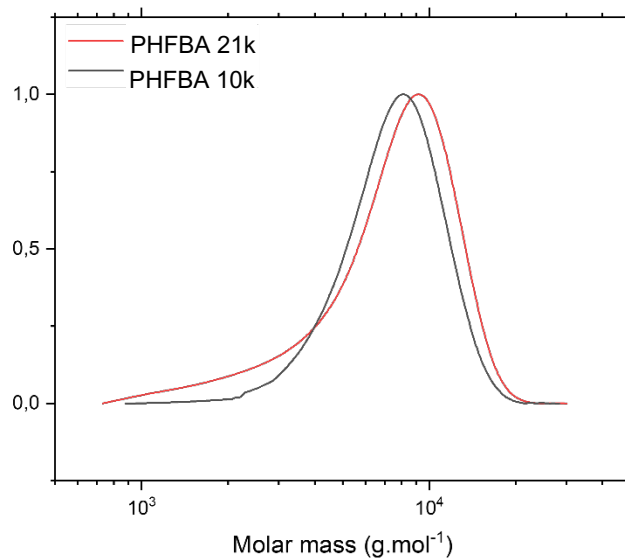


Figure S1: Molar mass distribution (PS calibration) of the two PHFBA macro-CTA

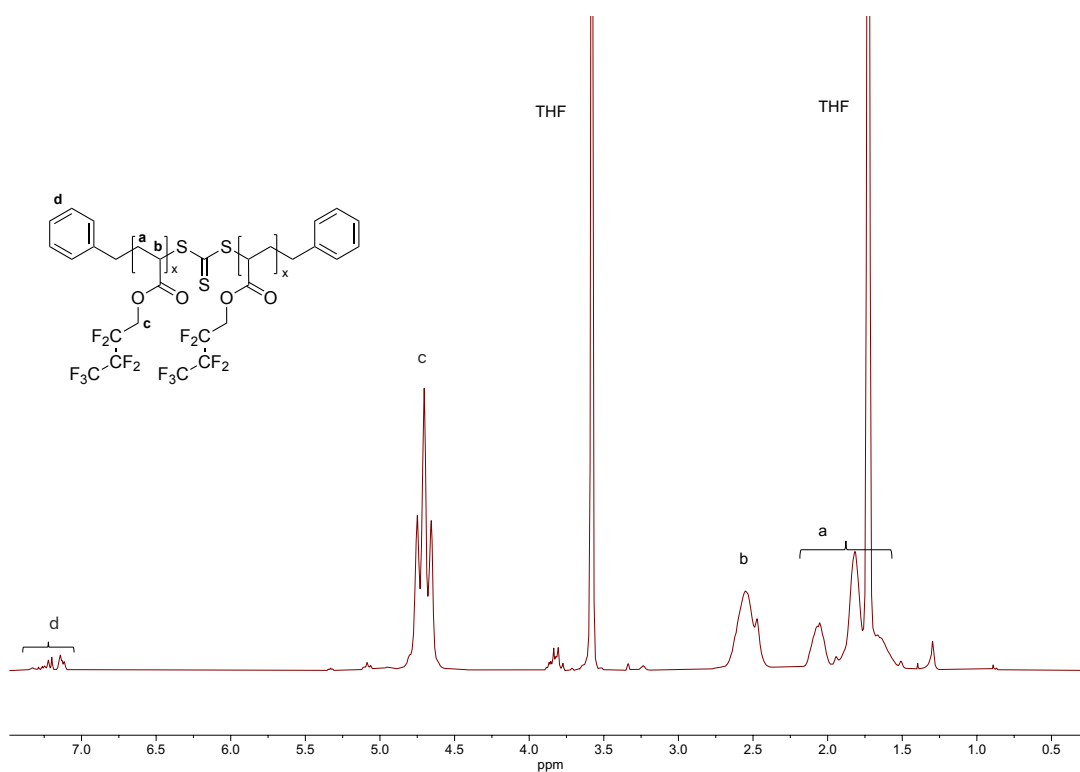


Figure S2: Representative NMR spectrum (THF- d_8) of a PHFBA macro-CTA

PHFBA-*b*-P*n*BA-*b*-PHFBA triblock copolymers

The procedure for the F₁₀A₁₁₃F₁₀ copolymer is given as representative example. 3.3 mL of *n*-butyl acrylate (*n*BA) (23 mmol, 1100 eq), 615 mg of PHFBA macro-CTA (2.1×10^{-2} mmol, 1 eq) and 1,5 mg of AIBN (9.2×10^{-3} mmol, 0,15 eq) collected from a stock solution, and trifluoroethanol as solvent (20 %wt) were added in a Schlenk tube (25 mL) equipped with a magnetic stirrer. Five freeze–pump–thaw cycles were applied to degas the solution. The reaction tube was filled with argon, sealed, and placed in a pre-heated oil bath at 70°C for 3 hours. The polymerization was stopped by placing the Schlenk tube into liquid nitrogen and opening it to air. The final mixture was dissolved in a minimum amount of dichloromethane and purified by precipitation (two times) into a mixture of MeOH/water (1/1, v/v). The copolymer was finally recovered by filtration and dried in a vacuum oven at 35°C for 48h.

For the F₅A₆₀F₅ copolymer, the same conditions were used but with a *n*BA/CTA ratio of 520, and the polymerization time was of 5 hours.

¹H-NMR (500 MHz, THF-*d*8, ppm): 7.38-7.09 (m, H_{aromatic}), 4.70 (t, O-CH₂-CF₂), 4.04 (m, O-CH₂-CH₂), 2.65–1.32 (m, H_{backbone}), 1,61 (m, O-CH₂-CH₂), 1,40 (m, -CH₂-CH₃), 0,95 (t, -CH₂-CH₃). SEC: F₅A₆₀F₅: Đ = 1,42; F₁₀A₁₁₃F₁₀: Đ = 1,45

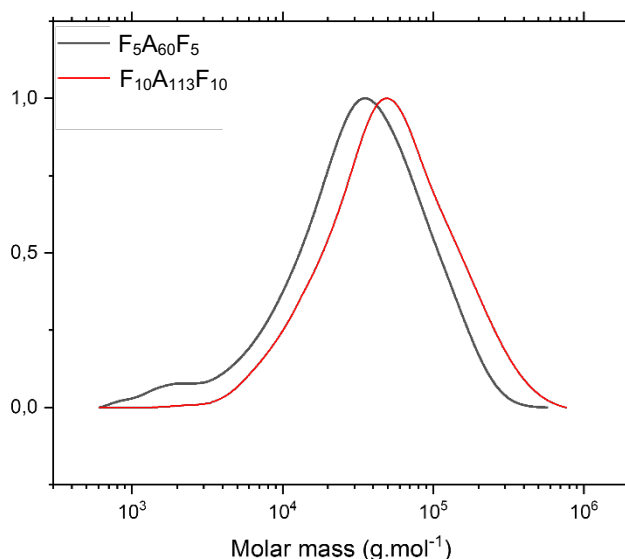


Figure S3: Molar mass distribution (PS calibration) of the two copolymers

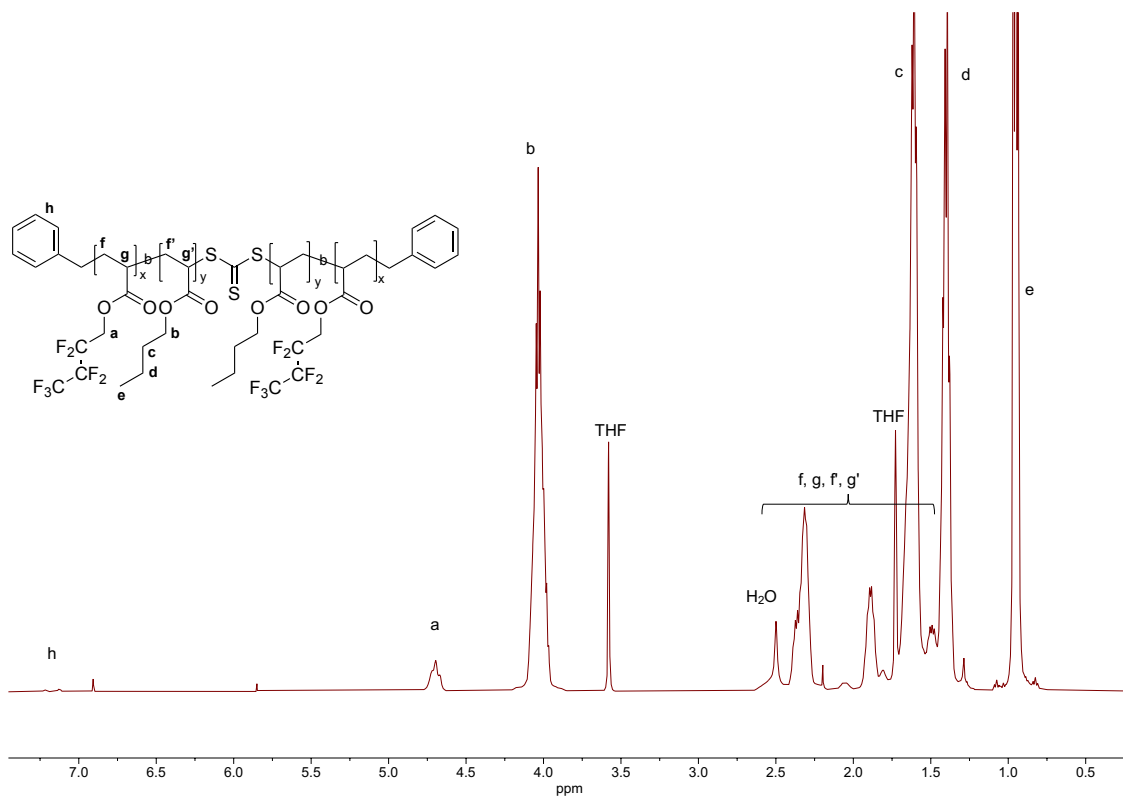


Figure S4: Representative NMR spectrum (THF-d8) of a FAF copolymer

References

- 1 Y. Li, C. Pyromali, F. Zhuge, C. A. Fustin, J. F. Gohy, D. Vlassopoulos, E. van Ruymbeke, *J. Rheol.*, 2022, **66**, 1223.
- 2 E. van Ruymbeke, E. B. Muliawan, D. Vlassopoulos, H. Gao, K. Matyjaszewski, *Eur. Polym. J.* 2011, **47**, 746.