

Supporting Information

THERMOPLASTIC ELASTOMER OBTAINED BY PHOTOPOLYMERIZATION-INDUCED CONCOMITANT MACROPHASE AND MICROPHASE SEPARATIONS

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Experimental part

Materials. Poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate) (PMMA-*b*-PnBA-*b*-PMMA) triblock copolymers synthesized by nitroxide-mediated radical polymerization (named T_{NMRP}) is provided by Arkema. The second triblock copolymers synthesized by anionic polymerization (named T_{AP}) is provided by Kuraray (Kuraray LA4285). The monomer, *n*-butyl acrylate (*n*BA), is purchased from Aldrich. It is first purified with hydroquinone to remove the inhibitor (0.2 wt-% for 50 ml of monomer), then filtered and conserved in freezer. Finally, the UV photoinitiator (named PI) of type I, α -hydroxy-cyclohexyl-phenyl-ketone, is purchased from Lamberti (Esacure KS300) and used as received.

Photopolymerization. The *n*BA radical polymerization is photo-initiated during 300 seconds with a xenon-mercury UV lamp from Loctite (reference 97034) whose emission spectrum is spread between 250 nm and 600 nm with a total irradiance of 70 mW cm⁻² in our configuration. A bespoke set-up allowed us to perform in situ infrared spectroscopy to monitor the monomer conversion. The initial liquid formulations are placed in the 25 mm diameter barium fluoride cuvette transparent to infrared. The final film thicknesses are roughly 500 μ m and their top surfaces are in contact with air during polymerization.

Characterizations methods.

Time-resolved Fourier Transform Infra-Red spectroscopy (FTIR) is systematically performed during films preparation with a Perkin Elmer Spectrum One spectrometer. The IR spectra are collected every 2.5 seconds during polymerization to monitor the evolution of the absorption band at 6160 cm⁻¹ associated to the carbon-carbon acrylate double bond of the *n*BA monomer.^[1] Then integration of the absorption pic allows the determination of the conversion rate, *C*, versus time using the following expression: $C(t) = 100 \times (A_0 - A(t)) / A_0$. Where A_0 and $A(t)$ are the integrals under the considered absorption band, initially and at time *t* respectively.

Size-Exclusion Chromatography (SEC) is performed for the macromolecular characterization. The SEC setup operates in THF, at 30 °C (flow rate: 1 mL min⁻¹) and is equipped with a Viscotek VE 1122 automatic injector, a set of Shodex columns (KF 801, KF 8025, KF 804 et KF 806 from Waters) working in series, a Wyatt Heleos II Multi Angle Laser Light Scattering detector (MALLS, 18 angles, $\lambda_0 = 664.4$ nm), a refractive index (RI) detector Viscotek VE 3580. Number-average molar mass M_n , weight-average molar mass M_w and dispersity D (M_w/M_n) of block copolymers are calculated with refractive

index and light scattering signals using Astra-software. The BCP refractive index increments (dn/dc) are given in Table S1. All samples are prepared at 1 g L^{-1} concentration and filtered through PVDF 0.45 mm filters. The elution times at peak are obtained after fitting the MALLS signals with two gaussian functions, using Igor Pro (Wavemetric). In addition, to account for the tails at higher elution time the gaussian peak is smeared out by convolution with an exponential function.

Classical Nuclear Magnetic Resonance (NMR) and Diffusion-Ordered Spectroscopy (DOSY)^[2] are performed at $25 \text{ }^\circ\text{C}$ on a Bruker Avance 400 spectrometer equipped with a Bruker 5 mm BBFO probe and a gradient amplifier, which provides a z-direction gradient strength up to 47.5 G cm^{-1} . Polymer samples are prepared at 2 g L^{-1} in deuterated benzene (C_6D_6). ^1H chemical shifts are referenced to TMS (from C_6D_6) at 0.00 ppm. NMR DOSY experiments are performed with 2D sequence for diffusion measurement using double stimulated echo for convection compensation and LED (dstebpgp3s). Typically, a value of 3 ms is used for the gradient duration (δ) and 200 ms for the diffusion time (Δ). Each parameter is tuned to reach 95 % signal attenuation for the slowest diffusion species at the last experiment step. The pulse repetition delay (including acquisition time) between each scan was superior to 2 s. Data acquisition and analysis are performed with Bruker Topspin software. The Dynamics Center module of Topspin is used to calculate the diffusion coefficients and to create 2D spectra with NMR chemical shifts versus calculated diffusion coefficients.

The Atomic Force Microscope (AFM) used in this study is a Bruker Multimode VIII AFM performed in the PeakForce mode at 1 kHz. The cantilevers mounted are SCANASYST AIR with a nominal spring constant of 0.4 N m^{-1} and a nominal radius of curvature of 2 nm provided by Bruker probe. The AFM samples are sectioned at $-120 \text{ }^\circ\text{C}$ using a Leica EM UC7 microtome equipped with a 45° trimer and a 35° diamond knife, both purchased from Diatome. The AFM images presented in the paper are all topographic height images.

Small Angle X-ray Scattering (SAXS) data are collected on the SWING beamline at SOLEIL (Saclay, France) and on the BL11-NCD beamline at ALBA (Barcelona, Spain). The SWING configurations used a 1 \AA wavelength with 4 m for the sample-to-detector distance. The BL11-NCD configuration used a 1 \AA and a single sample-to-detector distance of 2.841 m. In this paper, the scattering curves are plotted as a function of the scattering vector q defined as followed: $q = 4\pi/\lambda \sin(\theta/2)$ with θ the scattering angle. Two types of samples are investigated by SAXS: (i) the final solid samples after the photopolymerization, i.e., $500 \text{ }\mu\text{m}$ thick films (SOLEIL & ALBA); and (ii) in situ experiments during the photopolymerization (SOLEIL). This last experiment is performed in mark-tubes made of quartz glass (capillaries) with a diameter of 1.5 mm, purchased from Hampton Research and Hilgenberg. The SAXS spectra are collected following a logarithmic time sequence and the setup allows a synchronization between the UV lamp and the SAXS spectra collection. Two aspects are considered as negligible during time-resolved experiments: (i) the impact of X-rays on the PI and (ii) confinement effect in capillaries.

Indeed, to evaluate the impact of X-rays photons on the formulation containing the PI, a SAXS experiment was performed without UV radiation, revealing a negligible evolution of the SAXS pattern.

Rheology is performed with a dynamic rotational rheometer AR2000 from TA Instrument, working with constant stress. The geometry used for formulations is a parallel plate geometry, with striated 8 mm diameter plates. We measured the complex shear modulus (G' , storage part and G'' , loss part) as a function of circular frequency. A stress sweep is performed before each experiment to evaluate the linear viscoelastic region. The mechanical spectroscopy experiments are performed in the frequency range 100 to 10^{-1} rad s^{-1} for the temperatures ranging between - 40 and 20 °C. At 30 °C, the frequency range is 100 to 10^{-4} rad s^{-1} . The time-temperature superposition principle is used to build all master curves at room temperature, $T_{ref} = 20$ °C.^[3, 4]

SEC MALLS data analysis

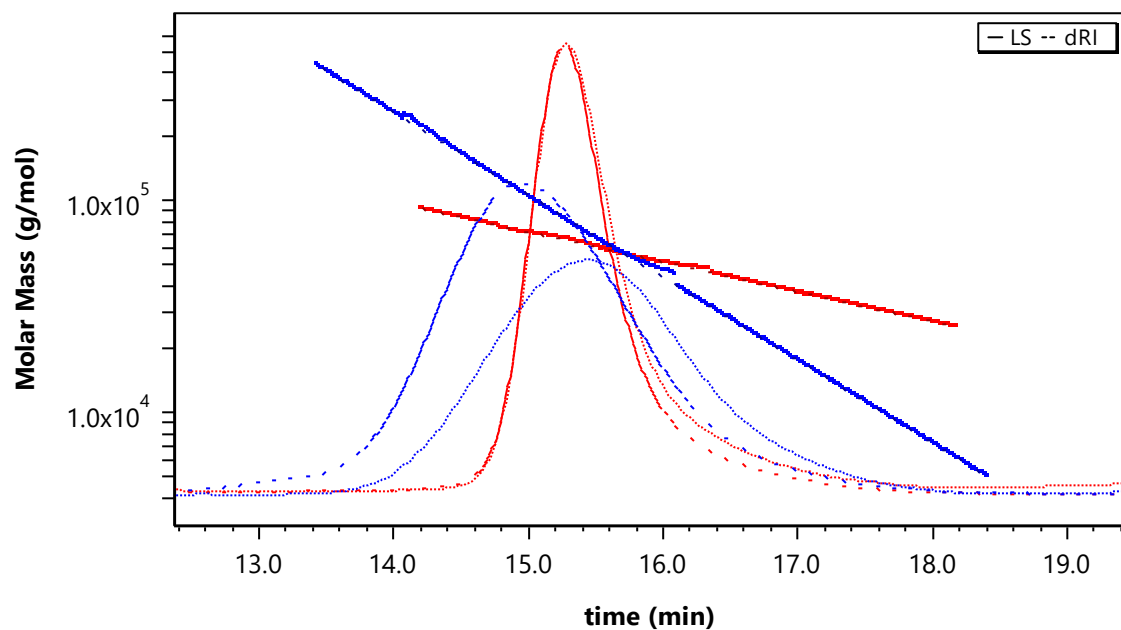


Figure S1. SEC chromatograms measured on T_{AP} (red curves) and T_{NMRP} (blue curves) BCPs. The dashed lines correspond to MALLS signal (LS), dotted lines to refractive index signal and solid straight lines to molar masses vs. elution time. The BCP refractive index increments (dn/dC) are given in Table S1. This graph is extracted from Astra software.

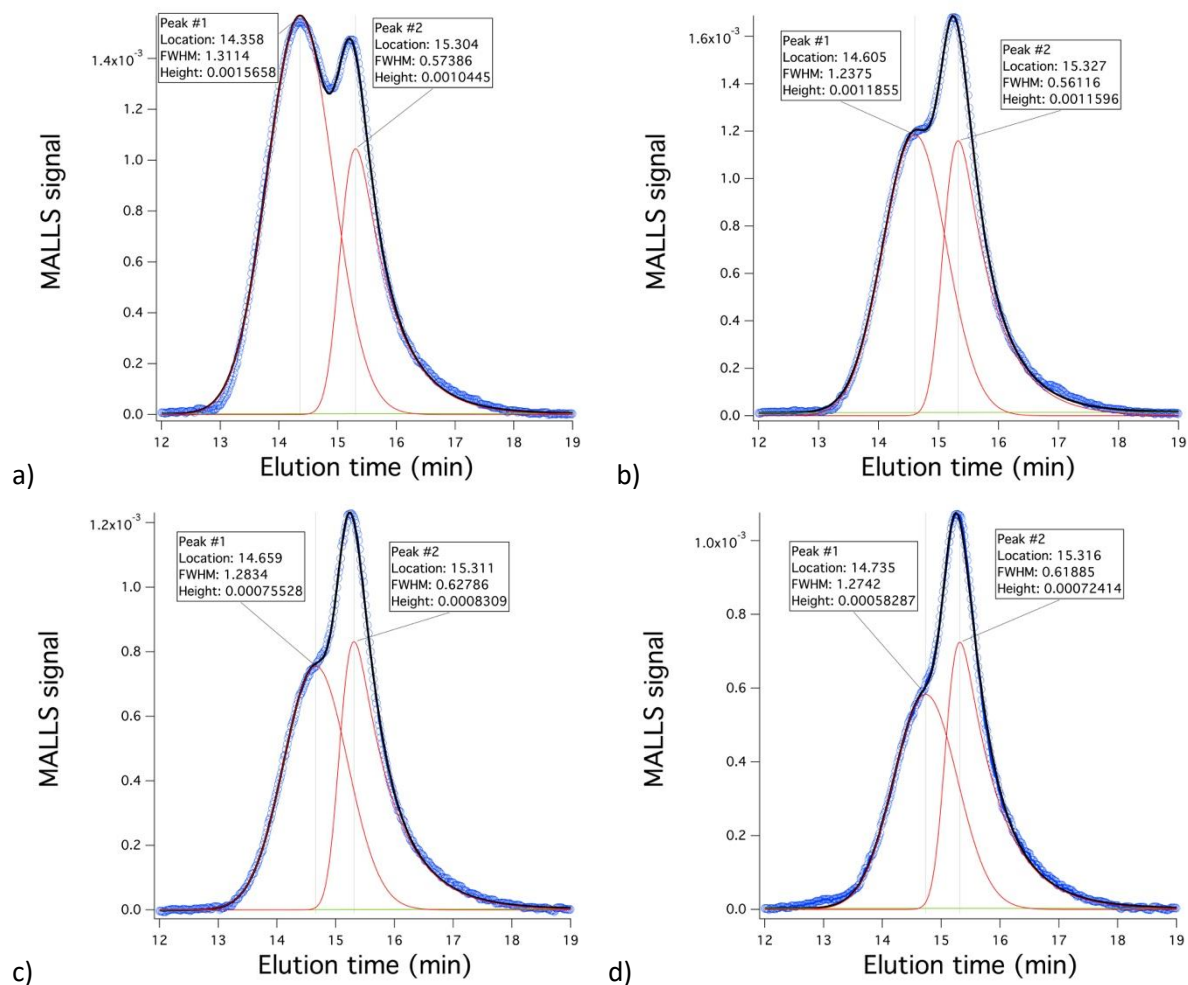


Figure S2. SEC MALLS signal versus elution time collected on T_{AP} series at different PI concentrations and fitted with two gaussian functions: (a) 30T_{AP}PI₄, (b) 30T_{AP}PI₂, (c) 30T_{AP}PI₁ and (d) 30T_{AP}PI_{0.5}.

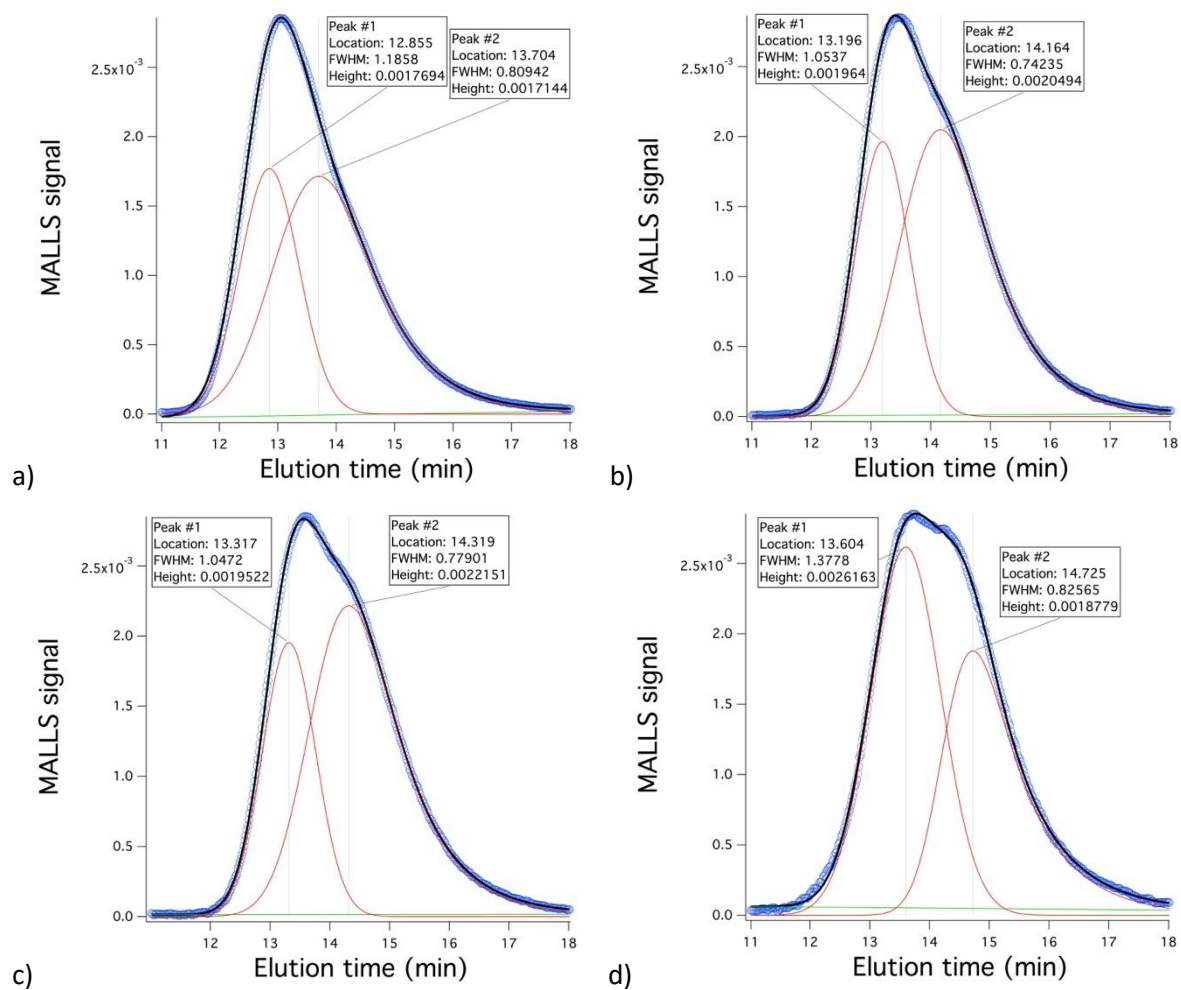


Figure S3. SEC MALLS signal versus elution time collected on T_{NMRP} series at different PI concentrations and fitted with two gaussian functions: (a) $30T_{\text{NMRP}}\text{PI}_4$, (b) $30T_{\text{NMRP}}\text{PI}_2$, (c) $30T_{\text{NMRP}}\text{PI}_1$ and (d) $30T_{\text{NMRP}}\text{PI}_{0.5}$. In addition, to account for the tails at higher elution time the gaussian peak#2 is smeared out on its right side by convolution with an exponential function. Note that the elution volume at maximum intensity of MALLS signal of T_{NMRP} is equal to 15 mL (Figure 2 and Figure S4).

Classical and DOSY NMR data analysis

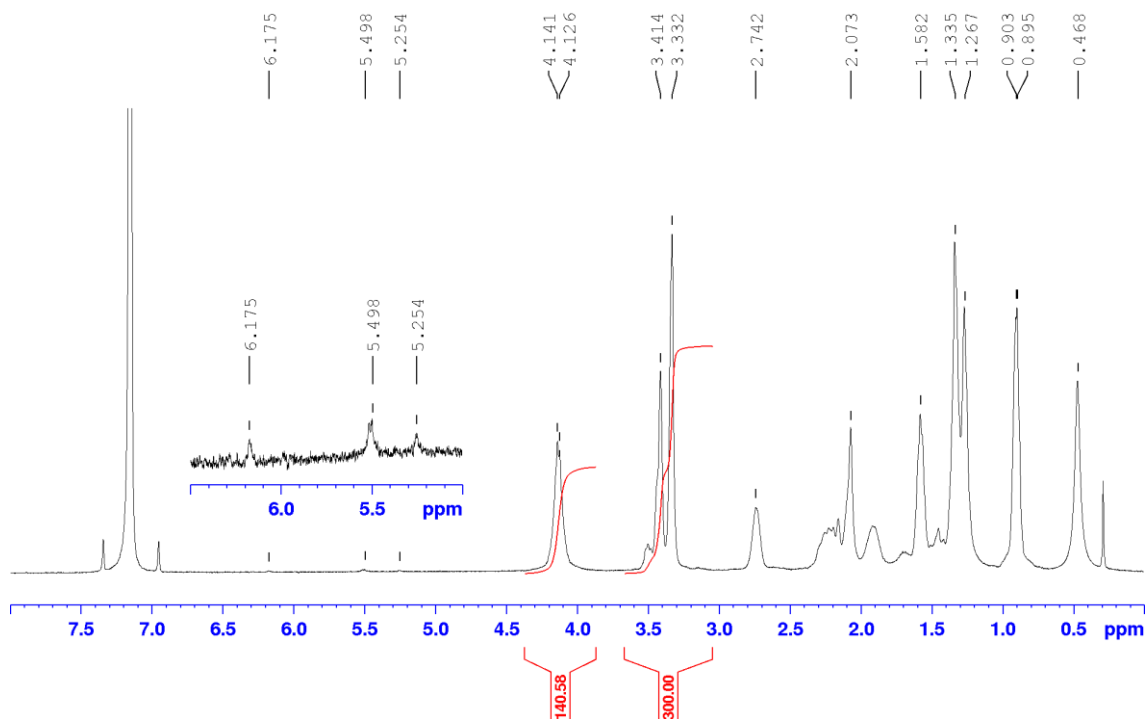


Figure S4. ^1H NMR spectra collected on the T_{NMRP} BCP in deuterated benzene at 25 °C. The inset is a higher magnification in the range 5 to 6.5 ppm; it corresponds to the unsaturated bond domain (6.175 and 5.254 ppm).

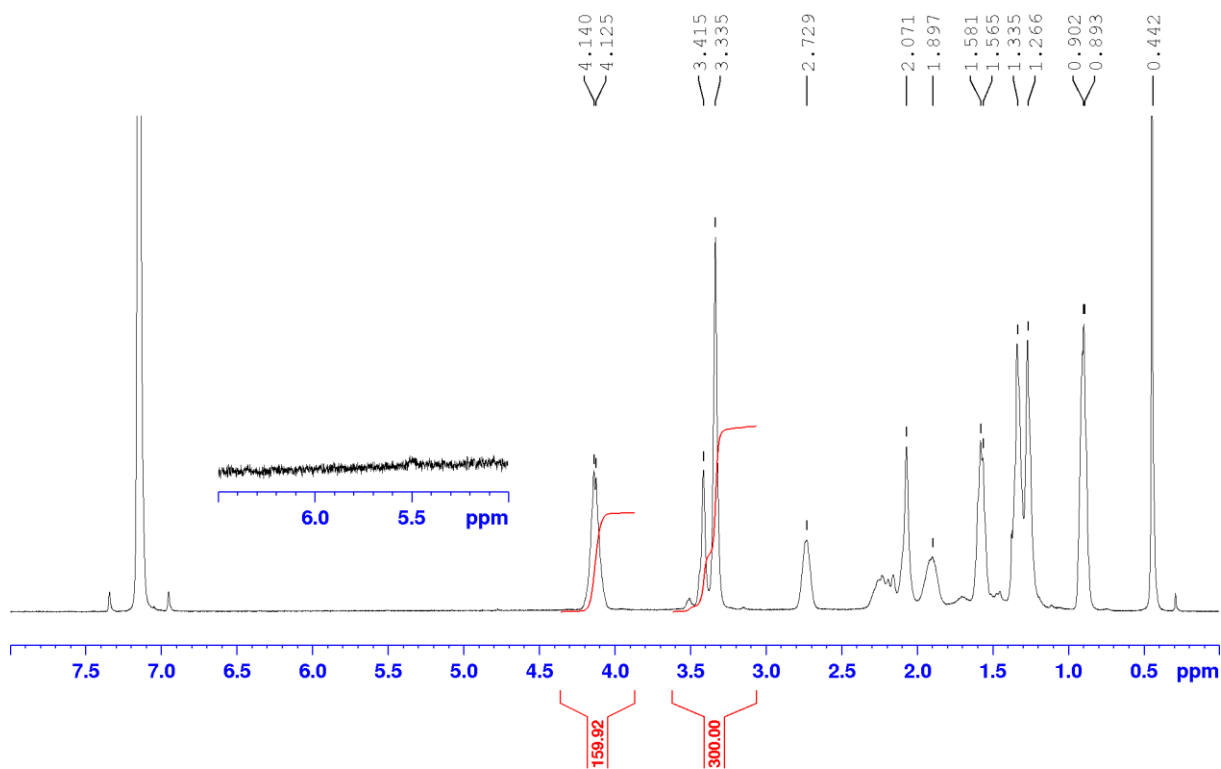


Figure S5. Proton NMR spectra collected on the T_{AP} BCP in deuterated benzene at 25 °C. The inset is a higher magnification in the range 5 to 6.5 ppm, corresponding to the unsaturated bond domain.

BCP molar compositions, x_{MMA} and x_{nBA} , are calculated from 1H NMR spectra (Figure S5 and Figure S6) using the following Equation S1 and Equation S2.

$$x_{MMA} = \frac{I_{MMA/3}}{I_{MMA/3} + I_{nBA/2}} \quad \text{Eq. S1}$$

$$x_{nBA} = 1 - x_{MMA} \quad \text{Eq. S2}$$

I_{nBA} is the integral of the 2 polymeric protons of nBA units at 4.1 ppm.

I_{MMA} is the integral of the 3 polymeric protons of MMA units in the 3.3 to 3.4 ppm range.

Table S1. BCP compositions, molar ratios, x , weight fraction of each block (W_x) and BCP refractive index increments (dn/dC).

BCP Name	x_{nBA} ^{a)}	x_{MMA} ^{b)}	W_{PnBA} ^{c)}	W_{PMMA} ^{d)}	dn/dC ^{e)}
T _{NMRP}	0.41	0.59	0.47	0.53	0.0815
T _{AP}	0.44	0.56	0.51	0.49	0.0809

^{a)} Calculated with Equation S1.

^{b)} Calculated with Equation S2.

^{c)} Calculated with Equation S3.

^{d)} Calculated with $W_{PMMA} = 1 - W_{PnBA}$

^{e)} Calculated with Equation S4.

$$W_{PnBA} = \frac{M_{nBA} \times x_{nBA}}{M_{nBA} \times x_{nBA} + M_{MMA} \times x_{MMA}} \quad \text{Eq. S3}$$

with the monomer molar masses $M_{nBA} = 128.17 \text{ g mol}^{-1}$ and $M_{MMA} = 100.121 \text{ g mol}^{-1}$.

The average values of dn/dC of both BCP are calculated from their block weight fraction (see Table S1 and Equation S4) and from the values of dn/dC of each homopolymer in THF at 30 °C: $(dn/dC)_{PMMA} = 0.090$, $(dn/dC)_{PnBA} = 0.072$.^[5]

$$\left(\frac{dn}{dC}\right)_{BCP} = W_{PMMA} \times \left(\frac{dn}{dC}\right)_{PMMA} + W_{PnBA} \times \left(\frac{dn}{dC}\right)_{PnBA} \quad \text{Eq. S4}$$

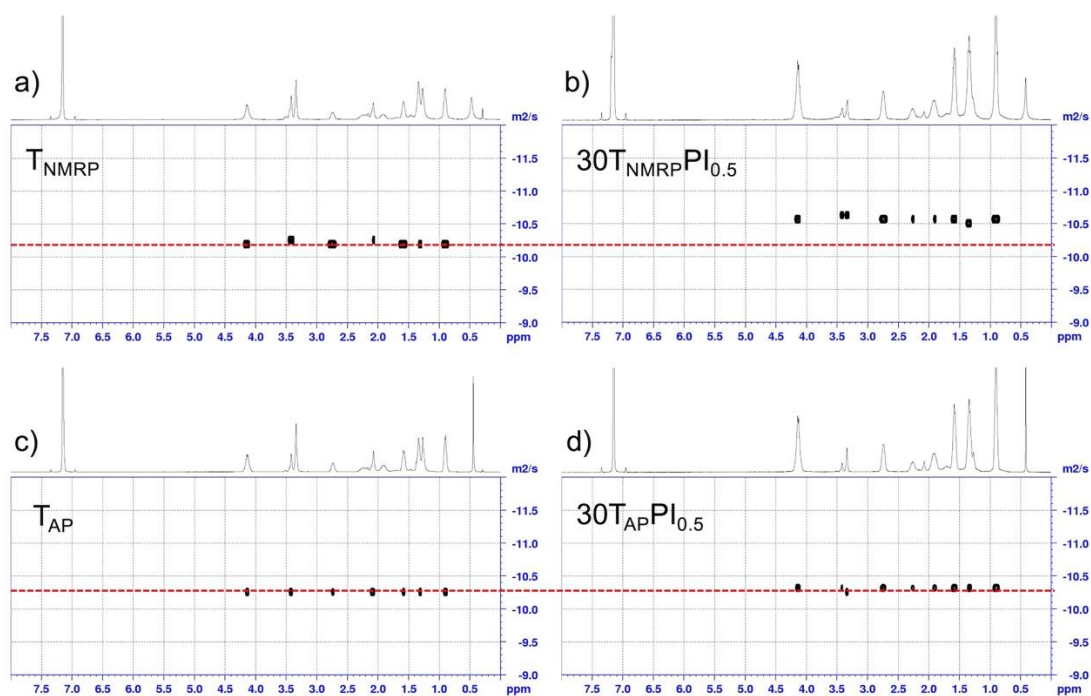


Figure S6. Proton DOSY NMR spectra collected on samples: (a) T_{NMRP} BCP, (b) $30T_{\text{NMRP}}\text{PI}_{0.5}$, (c) T_{AP} BCP, (d) $30T_{\text{AP}}\text{PI}_{0.5}$. The red dotted lines are the neat BCP diffusion coefficient lines (labelled by the PMMA peaks between 3.3 and 3.4 ppm) to be compared with the BCP diffusion coefficient lines in the formulated samples.

Table S2. DOSY NMR diffusion coefficients, D , determined with a single exponential decay on the PMMA peaks in the 3.3 to 3.4 ppm range.

Name	D [$\text{m}^2 \text{s}^{-1}$]	Name	D [$\text{m}^2 \text{s}^{-1}$]
T_{NMRP}	4.51×10^{-11}	T_{AP}	4.58×10^{-11}
$30T_{\text{NMRP}}\text{PI}_{0.5}$	2.07×10^{-11}	$30T_{\text{AP}}\text{PI}_{0.5}$	4.84×10^{-11}
$30T_{\text{NMRP}}\text{PI}_1$	2.73×10^{-11}	$30T_{\text{AP}}\text{PI}_1$	4.72×10^{-11}
$30T_{\text{NMRP}}\text{PI}_2$	2.64×10^{-11}	$30T_{\text{AP}}\text{PI}_2$	4.74×10^{-11}
$30T_{\text{NMRP}}\text{PI}_4$	2.91×10^{-11}	$30T_{\text{AP}}\text{PI}_4$	4.82×10^{-11}

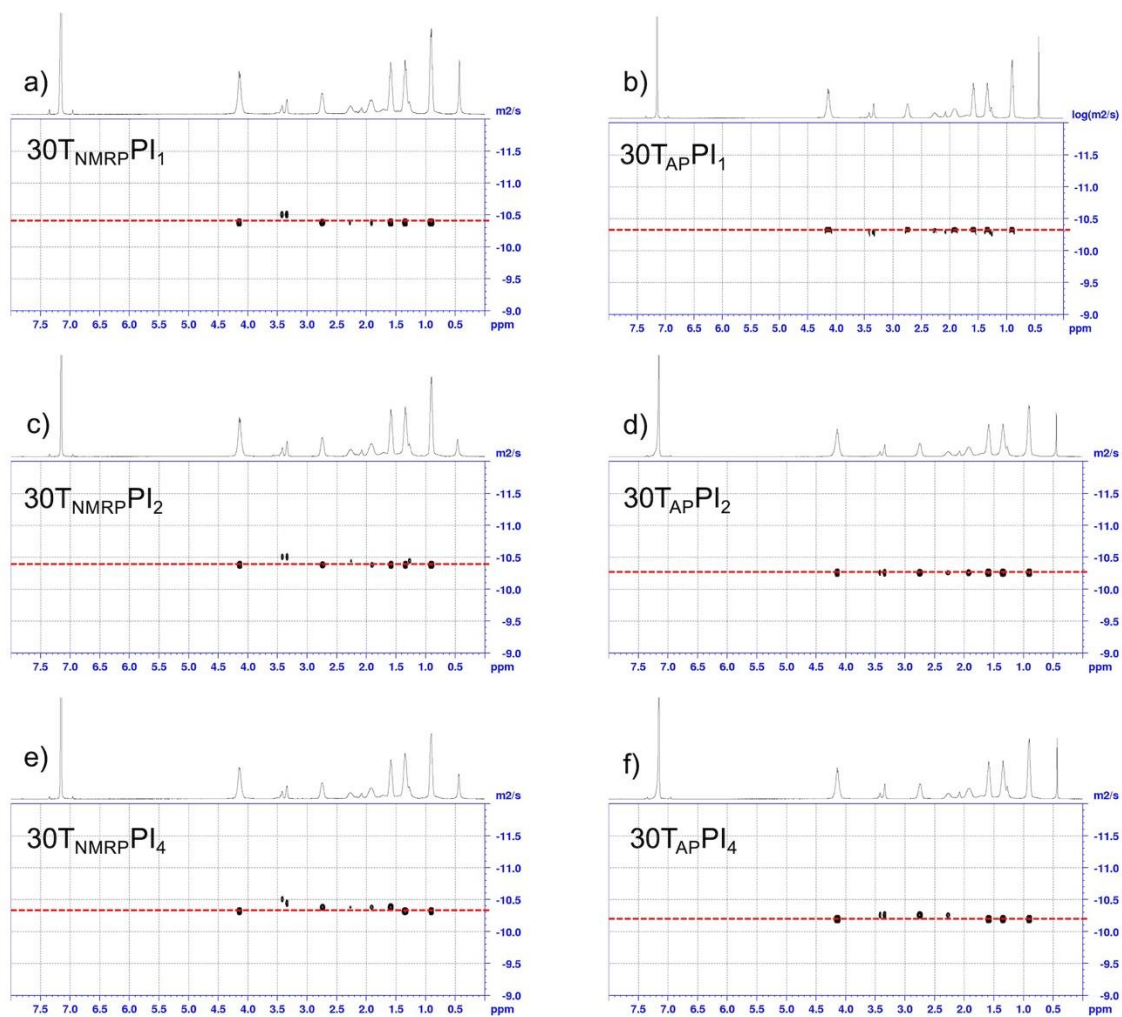


Figure S7. DOSY NMR results collected on formulated samples: (a) $30T_{\text{NMRPPI}_1}$, (b) $30T_{\text{APPI}_1}$, (c) $30T_{\text{NMRPPI}_2}$, (d) $30T_{\text{APPI}_2}$, (e) $30T_{\text{NMRPPI}_4}$ and $30T_{\text{APPI}_4}$. The red dotted lines correspond to BCP diffusion coefficient lines in the formulated samples (labelled by the PMMA peaks between 3.3 and 3.4 ppm).

Additional AFM images

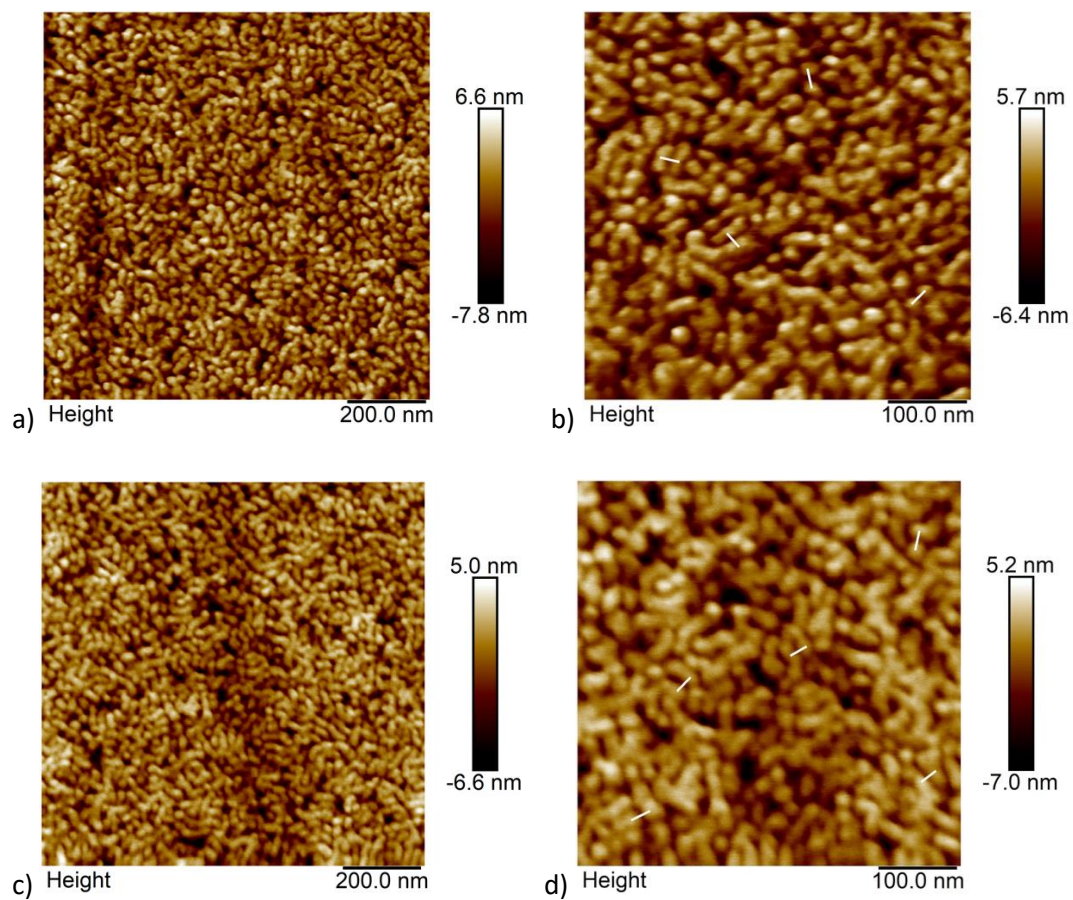


Figure S8. AFM height images collected on the neat T_{NMRP} (a & b) and T_{AP} (c & d) at two different magnifications. The white bars in (b) and (d) correspond to a distance of 25 nm.

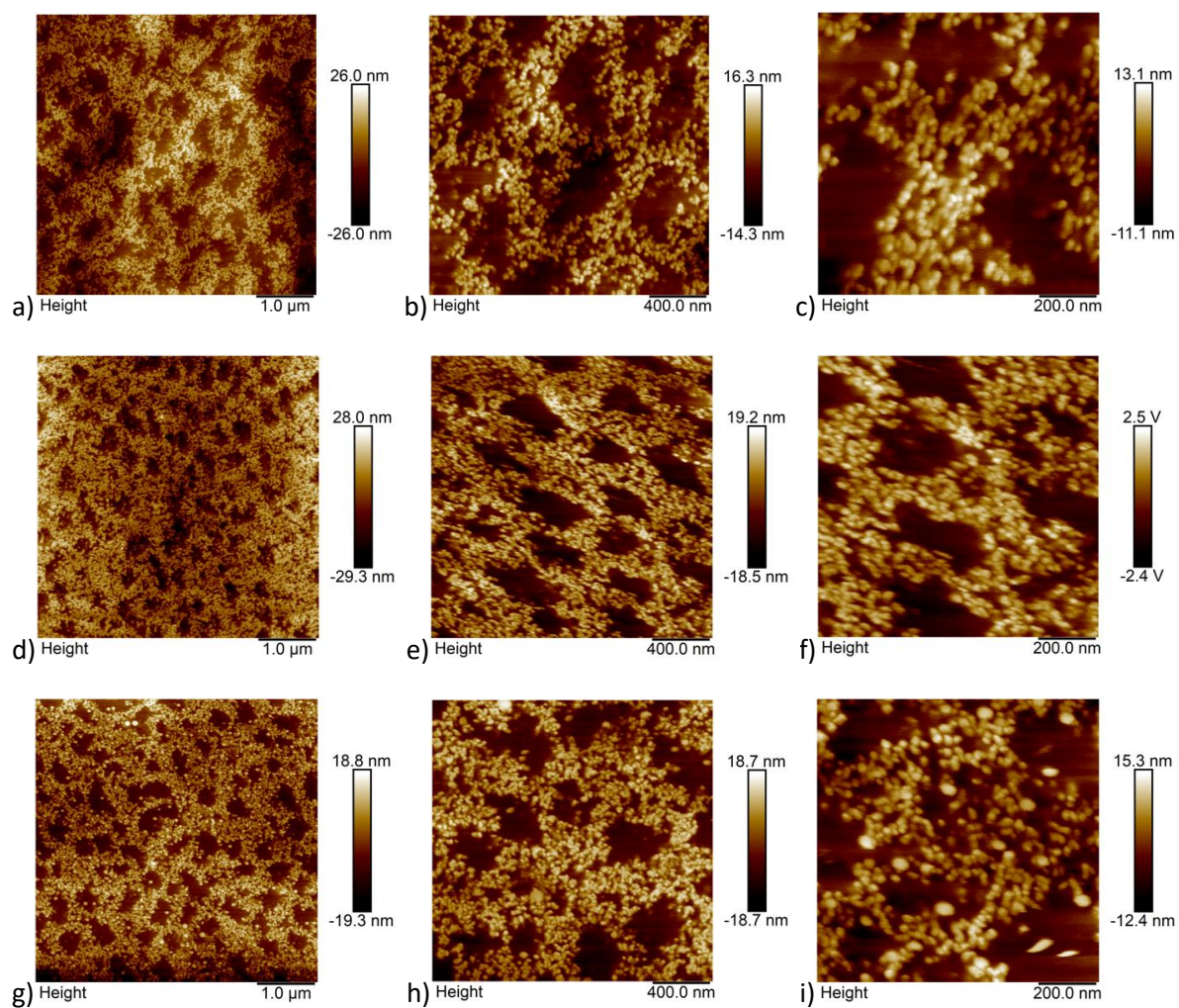


Figure S9. AFM height images collected on the 30T_{NMRP}PI₁ (a, b & c), 30T_{NMRP}PI₂ (d, e & f) and 30T_{NMRP}PI₄ (g, h & i) formulations at three different magnifications.

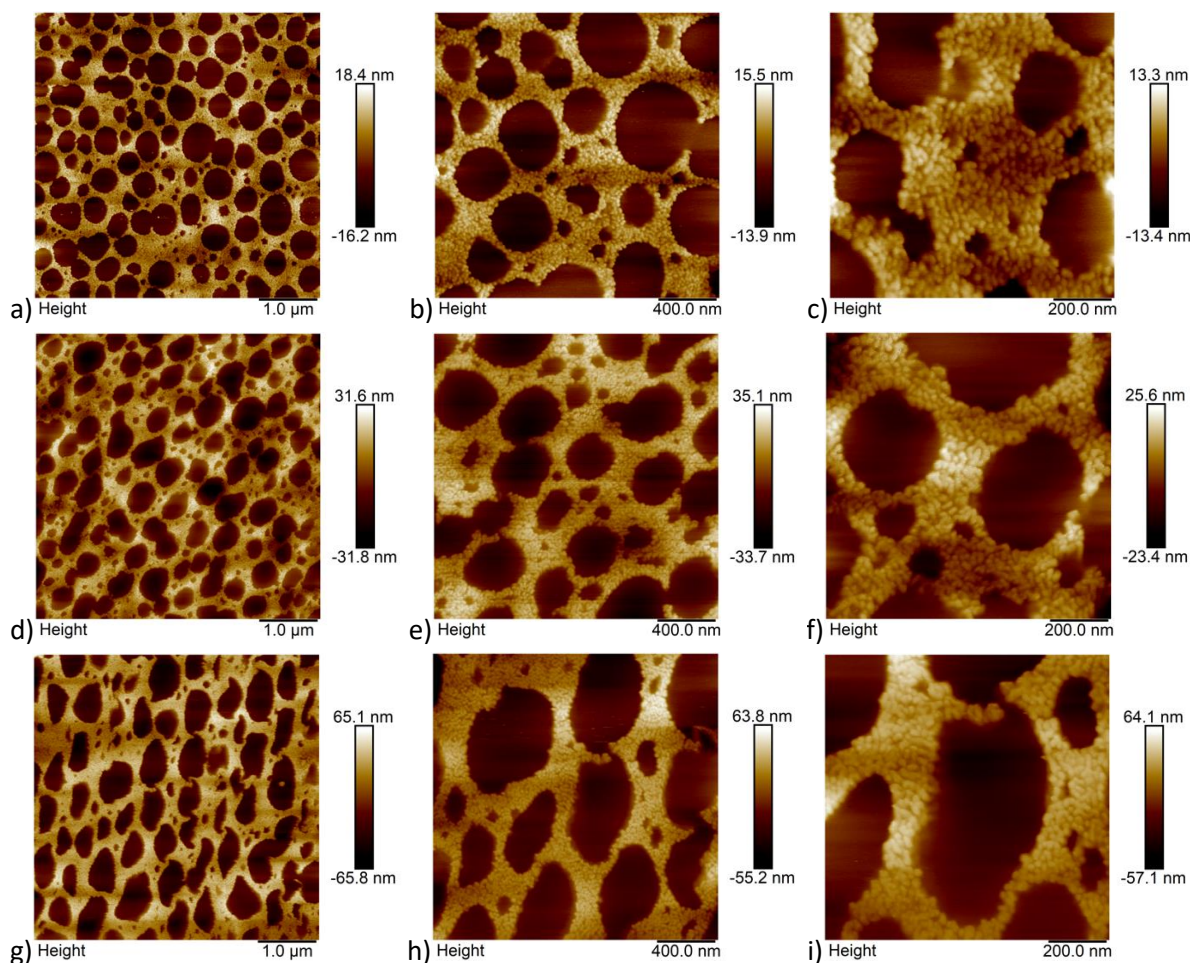


Figure S10. AFM height images collected on 30T_{AP}PI₁ (a, b & c), 30T_{AP}PI₂ (d, e & f) and 30T_{AP}PI₄ (g, h & i) formulations at three different magnifications.

SAXS data analysis

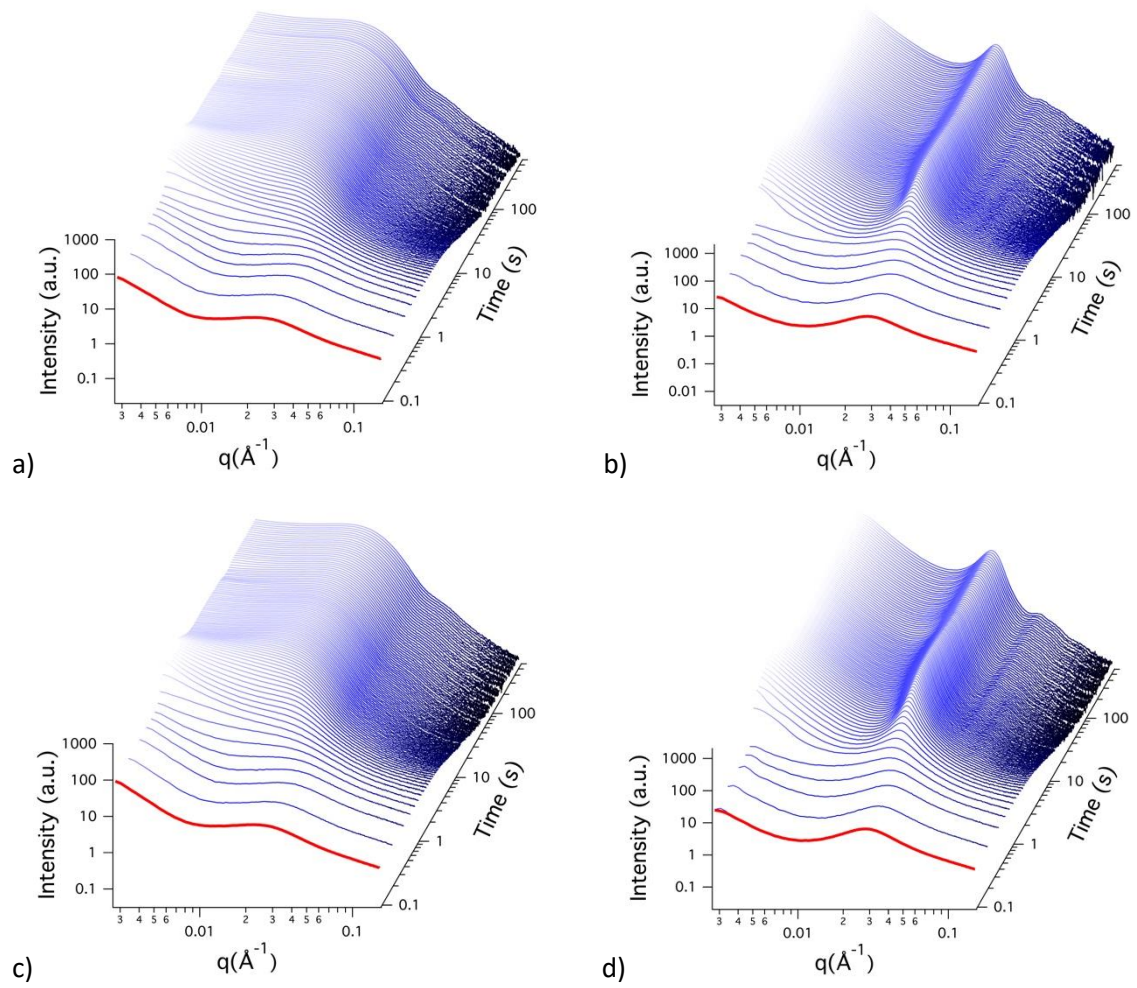
The SAXS data from Figure 5 were fitted with the Kinning–Thomas hard-sphere model.^[6] To proceed, the equations presented by Narimani *et al.*^[7] were coded under Igor Pro[®] (Wavemetric[®]). In the present paper, R and R_{HS} are respectively the domain radius and the hard sphere radius (closest approach radius). η is the hard sphere volume fraction. Note that for 30T_{AP} series, an additional power law of q^{-4} is introduced in the fitting expression to account for the low- q upturn.

Table S3. Kinning–Thomas model parameters obtained after fitting the SAXS data from Figure 5. R and R_{HS} are respectively the domain radius and the hard sphere radius (closest approach radius). η is the hard sphere volume fraction.^[6] The ratio $(R/R_{HS})^3$ gives the volume fraction of the domain within the hard sphere.

Name	R [nm]	R_{HS} [nm]	η	$(R/R_{HS})^3$
30T _{NMRP} PI _{0.5}	10.6	12.1	0.251	0.67
30T _{NMRP} PI ₁	9.9	12.2	0.238	0.53
30T _{NMRP} PI ₂	10.4	12.3	0.227	0.60
30T _{NMRP} PI ₄	10.2	12.2	0.227	0.58

30T _{AP} PI _{0.5}	9.0	11.9	0.322	0.43
30T _{AP} PI ₁	9.1	12.0	0.347	0.44
30T _{AP} PI ₂	9.2	12.0	0.377	0.45
30T _{AP} PI ₄	9.3	12.2	0.339	0.44

SAXS kinetics data



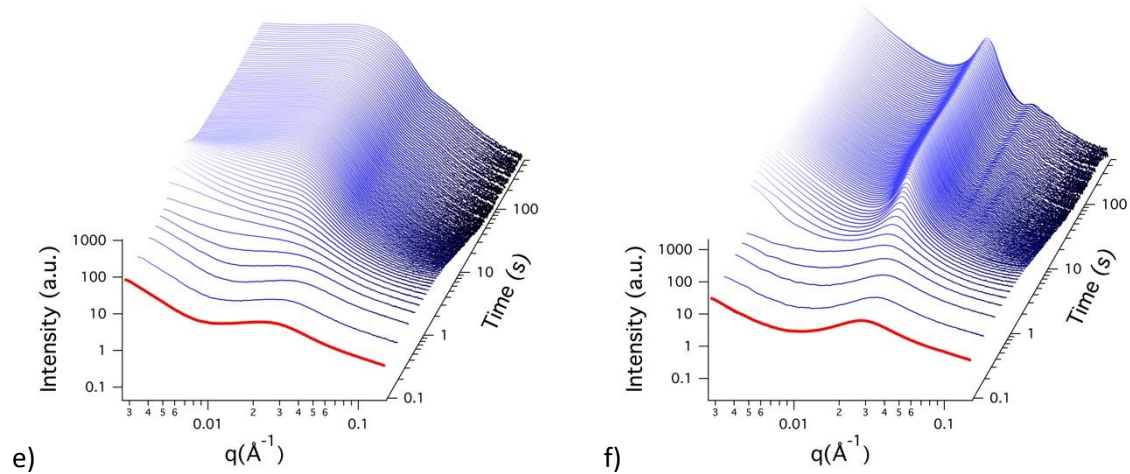
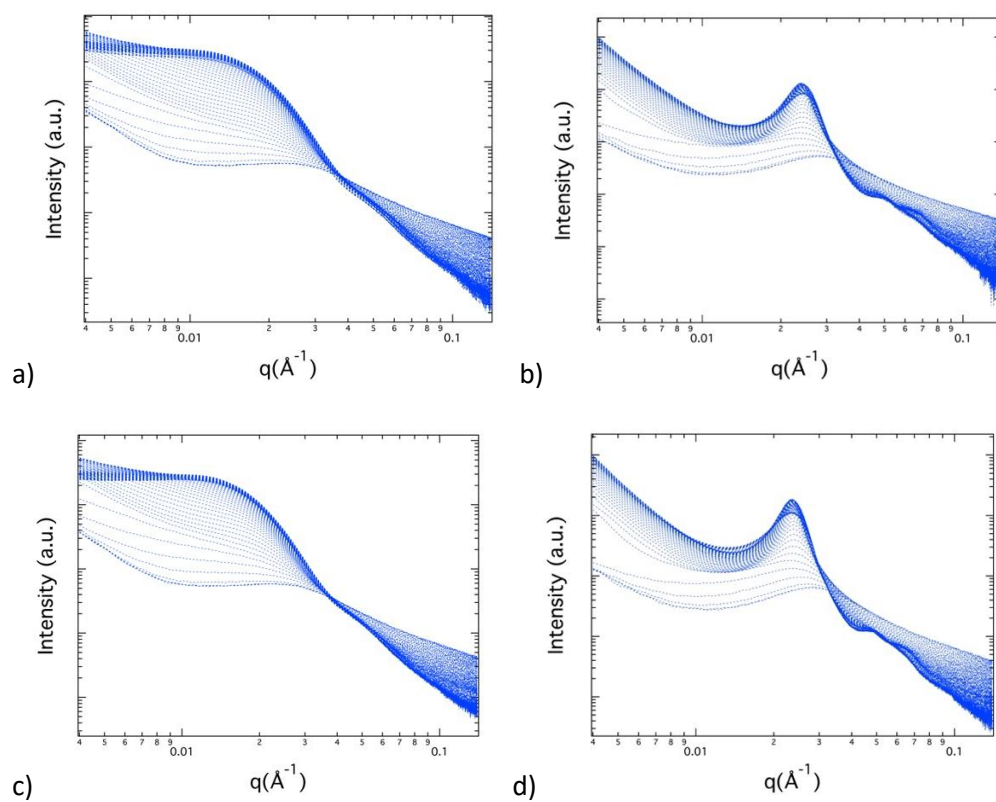


Figure S11. Time-resolved SAXS patterns collected on formulations under UV versus exposure time: (a) $30T_{\text{NMRP}}\text{PI}_1$, (b) $30T_{\text{AP}}\text{PI}_1$, (c) $30T_{\text{NMRP}}\text{PI}_2$, (d) $30T_{\text{AP}}\text{PI}_2$, (e) $30T_{\text{NMRP}}\text{PI}_4$ and (f) $30T_{\text{AP}}\text{PI}_4$. The red SAXS patterns correspond to the formulations before UV exposure.



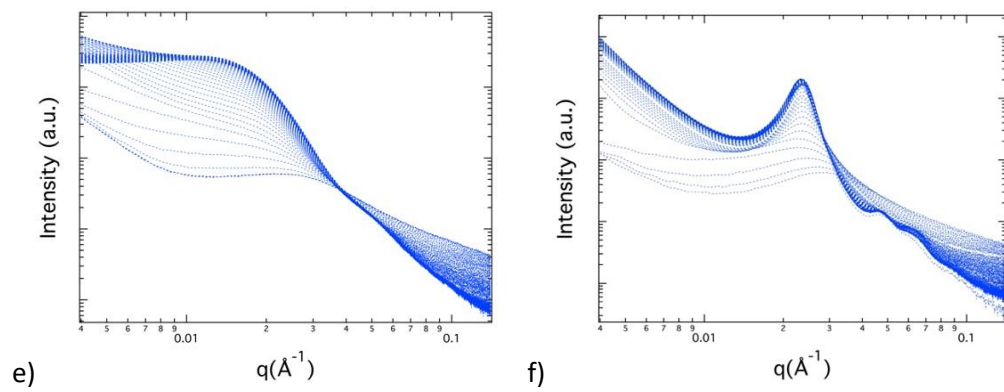


Figure S12. Time-resolved SAXS patterns collected on formulations under UV versus exposure time: (a) $30T_{\text{NMRP}}\text{PI}_1$, (b) $30T_{\text{AP}}\text{PI}_1$, (c) $30T_{\text{NMRP}}\text{PI}_2$, (d) $30T_{\text{AP}}\text{PI}_2$, (e) $30T_{\text{NMRP}}\text{PI}_4$ and (f) $30T_{\text{AP}}\text{PI}_4$.

Sample transparency



Figure S13. Photographs of 30T_{NMRP}PI_{0.5} (a) and 30T_{AP}PI_{0.5} (b).

Spectromechanical data analysis

Table S4. Values of the *WLF* coefficients to build the T_{NMRP} BCP and 30T_{NMRP} series master curves presented in Figure 9 and Figure S15.

Name	C ₁	C ₂ [°C]	G' @ low freq. [Pa]
T _{NMRP}	10.9	141.9	5.9 × 10 ⁷
30T _{NMRP} PI _{0.5}	7.2	122.5	4.4 × 10 ⁴
30T _{NMRP} PI ₁	9.9	139.9	2.6 × 10 ⁴
30T _{NMRP} PI ₂	7.8	124.5	4 × 10 ⁴
30T _{NMRP} PI ₄	9.3	137.2	1.2 × 10 ⁵

Table S5. Values of the *WLF* coefficients to build the T_{AP} BCP and 30T_{AP} series master curves presented in Figure 9 and Figure S16.

Name	C ₁	C ₂ [°C]	G' @ low freq. [Pa]
T _{AP}	11.5	146	7.3 × 10 ⁷
30T _{AP} PI _{0.5}	2.7	90.9	3.2 × 10 ⁴
30T _{AP} PI ₁	3	94.1	1.2 × 10 ⁵
30T _{AP} PI ₂	5.2	108.1	1.7 × 10 ⁵
30T _{AP} PI ₄	13.7	162.1	1.6 × 10 ⁶

It is worth to note that the values of the translation coefficients, *C*₁ and *C*₂, obtained on T_{AP} BCP and 30T_{AP} series undergo a disparity (Table S5). Thus, indicating that limit conditions to apply time-temperature equivalence are reached. On the other hand, the translation coefficients obtained on T_{NMRP} BCP and 30T_{NMRP} series are more comparable to each other.

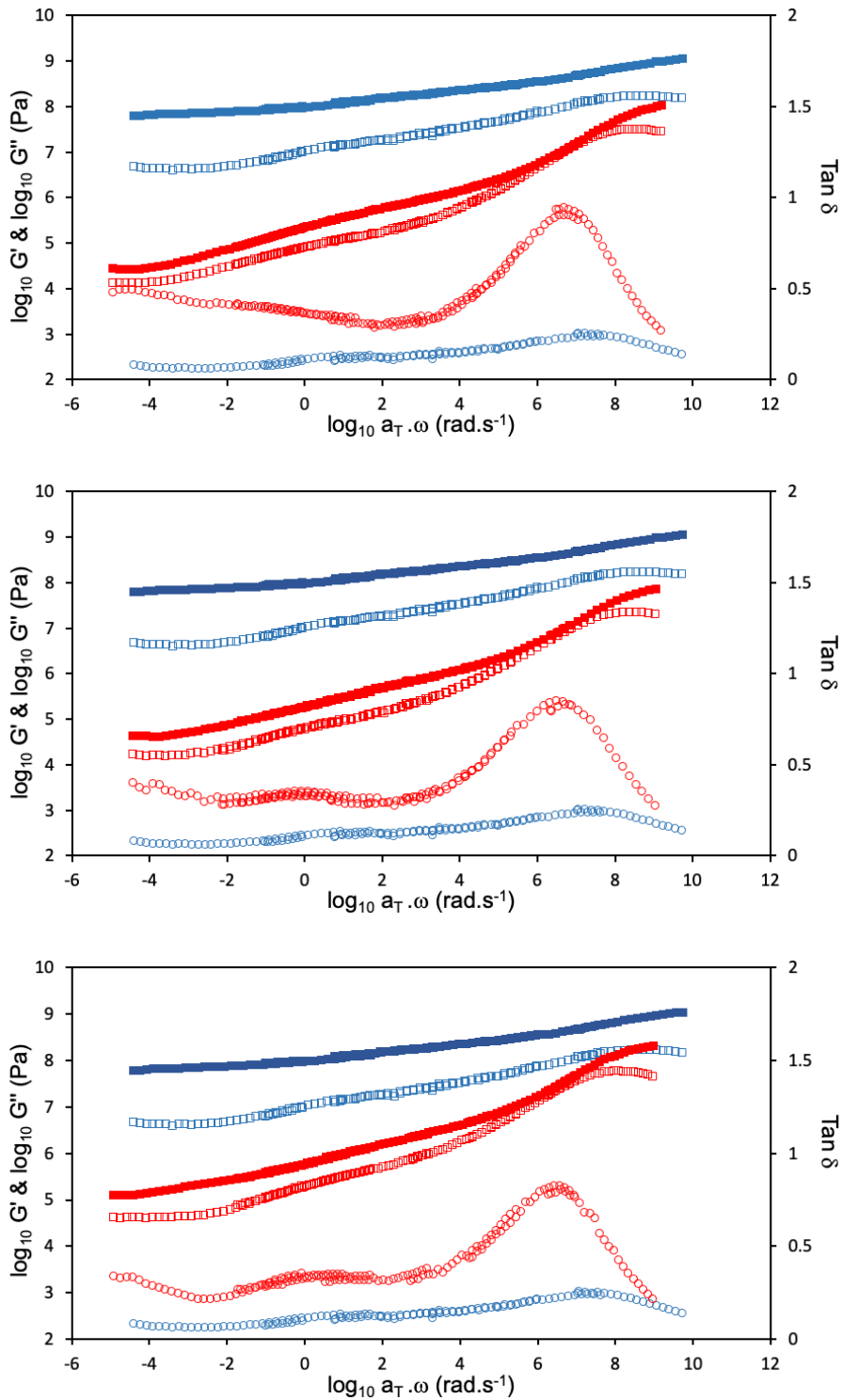


Figure S14. Spectromechanical master curves for the T_{NMRP} BCP (blue markers) and $30T_{\text{NMRP}}$ series (red markers): (a) $30T_{\text{NMRP}}\text{PI}_1$, (b) $30T_{\text{NMRP}}\text{PI}_2$ and (c) $30T_{\text{NMRP}}\text{PI}_4$. Solid square corresponds to G' , open square to G'' and open circle to $\text{Tan } \delta$. The master curves reference temperature is $T_{\text{ref}} = 20$ °C.

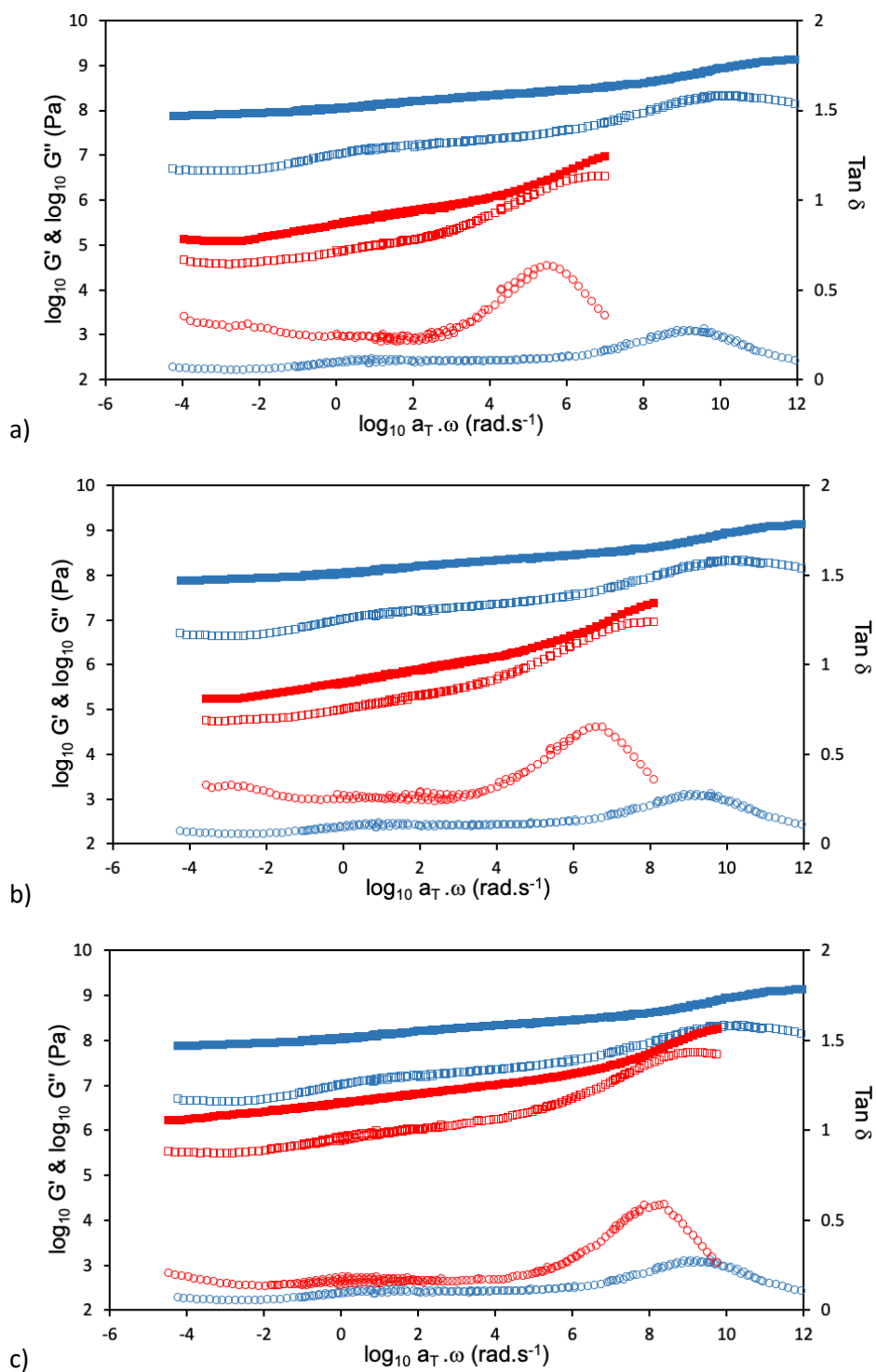


Figure S15. Spectromechanical master curves for the T_{AP} BCP (blue markers) and $30T_{AP}$ series (red markers): (a) $30T_{AP}PI_1$, (b) $30T_{AP}PI_2$ and (c) $30T_{AP}PI_4$. Solid square corresponds to G' , open square to G'' and open circle to $Tan\delta$. The master curves reference temperature is $T_{ref} = 20$ °C.

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