Electronic Supplementary Material (ESI) for Soft Matter.

Microphase Separation Induced in the Melt of Pluronic Copolymers by Blending with a Hydrogen Bonding Supramolecular End-Capped Bisurea Polymer

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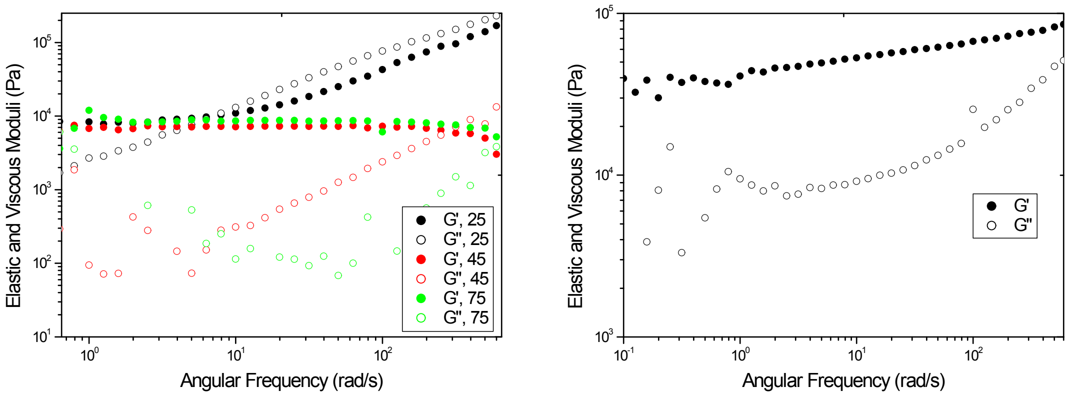
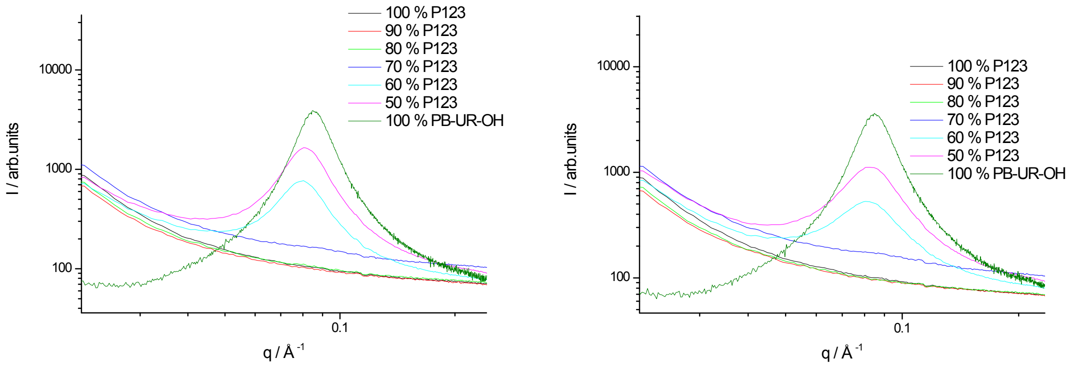
Supplementary Figures



SI Figure 1. Frequency sweeps for a 70/30 (left) and 100/0 (right) P123 / PB-UR-OH polymer blends at three temperatures as indicated. Open symbols represent the viscous modulus and the solid symbols the elastic modulus.



SI Figure 2. SAXS profiles from 100 to 40 % fraction of P123 at a) 45 °C and b) 75°C

Model for SAXS data for P123 Melt and Structure Factor of Blends

The model for 100 wt% P123 shown in SI Fig.3, comprises a Gaussian polydisperse polymer form factor, *P*(q) and mass fractal (esp cut-off) structure factor, *S*(q). Fitting was done using the program SASfit.[1]

The following are the equations for the contributions to the model SAXS profiles.[1]

Gaussian polydisperse polymer form factor:

$$P(q) = I_0 2 \frac{(1+Ux)^{-1/U} + x - 1}{(1+U)x^2}$$

Where I_0 is the forward scattering, and $x = q^2 R_g^2 / (1+2U)$, with $U = \frac{M_w}{M_n} - 1$.

Mass fractal structure factor with exponential cut-off:

$$S(q) = 1 + \frac{D\Gamma(D-1)\sin([D-1]\arctan(q\xi))}{(qr_0)^D \left[1 + \frac{1}{q^2\xi^2}\right]^{(D-1)/2}}$$

Here, D is the fractal dimension and $\Gamma(x)$ denotes the Gamma function. The cut-off parameter is defined by

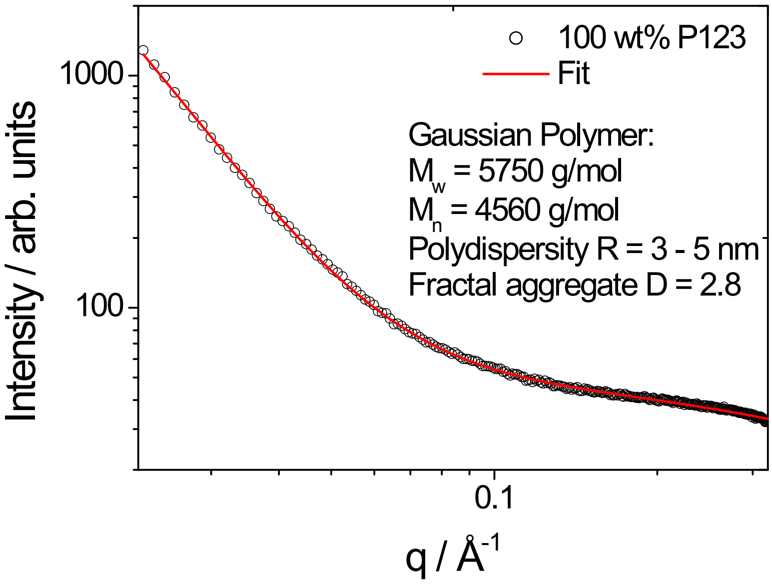
$$\xi^2 = \frac{2R_g^2}{D(D-1)}$$

A Lorentzian distribution of R_g was used, the corresponding equation for the Lorentzian is:

$$f(x, x_0, \sigma) = \frac{1}{\pi\sigma\left[1+\left(\frac{x-x_0}{\sigma}\right)^2\right]} = \frac{1}{\pi}\left[\frac{\sigma}{(x-x_0)^2+\sigma^2}\right]$$

Here x_0 is the location of the centre of the peak (Lorentzian distribution) and σ is the dispersity parameter, i.e. half-width at half-maximum (HWHM).

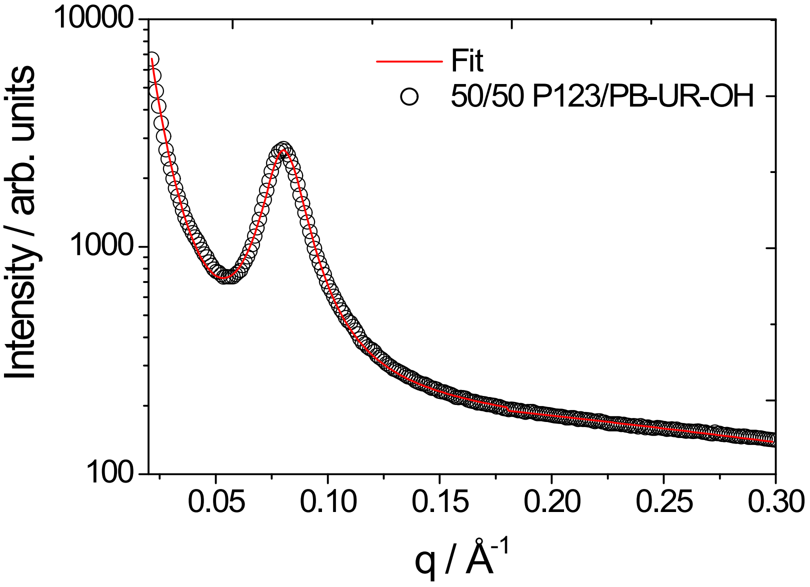
The fitted parameters for the fit to the data for P123 are given in the insert in SI Fig.3.



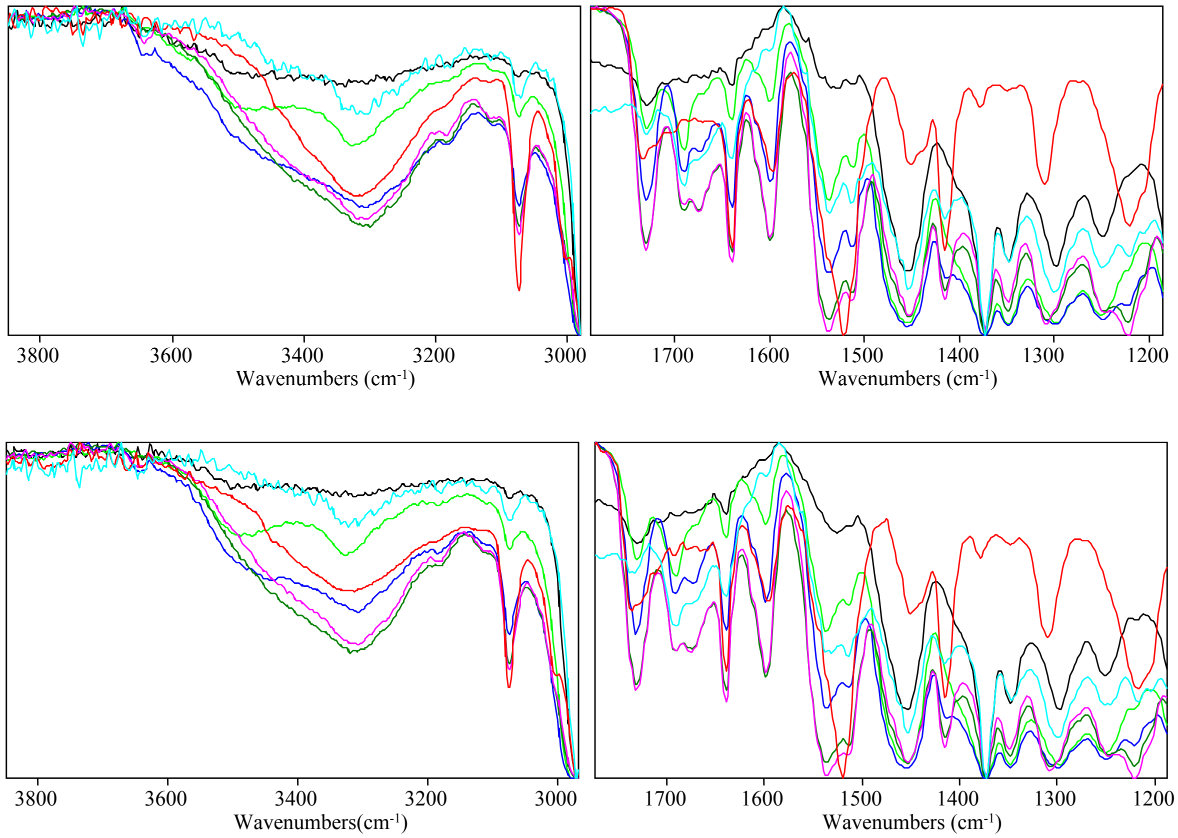
SI Figure 3. SAXS intensity profile and associated fit for 100 wt% P123.

SI Figure 4 shows an fit to the SAXS data for the 50:50 P123:PB-UR-OH blend. The base from the fit in SI Figure 3 was adjusted and a Lorentzian peak structure factor added, therefore there are 2 contributions:

1) F (q) – GaussPoly: Polydisperse R_g between 4.3 and 4.8, $M_w = 5750$, $M_n = 4560$
   S (q) – MassFractal (exp cut-off): $D = 2.9$
2) S (q) – Lorentzian: Amplitude = 11.5, $q^* = 0.08$, $\sigma = 0.0096$



SI Figure 4. SAXS intensity profile for a 50:50 P123:PB-UR-OH blend (circles) along with fitted structure factor (red line).



SI Figure 5 : FTIR spectra at (a) 45 ^{o}C and (b) 75 ^{o}C

Supplementary Tables

Sample (wt% P123/ wt% PB-UR-OH)	Temperature (ºC)	Angular Frequency (rad / s) ± 3%	Modulus (Pa) ± 5%	Relaxation Time (s) ± 3%
50/50	25	7.71	11000	0.815
	45	100	10600	0.063
	75	316	7730	0.020
60/40	25	7.21	10100	0.873
	45	279	6200	0.023
	75	No crossover point in the frequency range tested		
70/30	25	0.102	1900	61.6
	25	13.9	11300	0.452
	45	No crossover point in the frequency range tested		
	75	311	669	0.020
80/20	25	165	41000	0.038
	45	No crossover point in the frequency range tested		
	75[1]	0.102	0.280	61.6
	75[1]	269	751	0.023
	75[1]	384	981	0.016
90/10	25	0.102	10900	61.6
	25	596	71200	0.021
	45	222	259	0.028
	75[2]	101	47.6	0.062
100/0	25	No crossover point in the frequency range tested		

SI Table 1. Characteristic frequency and moduli at which crossover points occur plus the characteristic relaxation time.

Sample (P123 / PB-UR-OH)	Temperature (ºC)	R_g (Å)	*d* (Å) ± 2%
50/50	25	98.6±1.7	79.1
	45	80.6±4.8	77.6
	75	79.7±2.2	76.3
60/40	25	94.5±2.3	73.8
	45	80.1±3.8	79.4
	75	85.5±1.7	77.9
100/0	25	91.2±2.7	-
	45	92.6±2.6	-
	75	90.9±4.9	-

SI Table 2. Radius of gyration (R_g) and domain domain spacing size (*d*) for selected blends at the three temperatures.

ν/ cm^{-1}	Modes of vibration
1110-1080	C–O-C (ether stretching)
1247-1240	NH;C-N AmideIII;C–O-C(asymmetrical stretching ether)
1350	Wagging mode CH_2
1375	CH3 umbrella deformation
1460-1452	C–H (methyl and methylene)
1540-1560	H–C Amide II(urethane)
1630-1645	C=O (urea) C=O...H–N(ordered)
1660-1670	C=O (urea) C=O...H–N(disordered)
1690-1700	C=O (urea) Free
1709	C=O (urea) bonded Hydrogen bonded urethane carbonyl
1735	C=O Free urethane carbonyl
2970-2850	C–H (methylene and methyl)
3260-3290	N–H • • • O
3315-3340	N–H • • • N–H
3445-3450	free N–H
3500-3300	O–H (very broad)

SI Table 3. FTIR peak assignments.

Experimental

Materials: Pluronic copolymers were kindly donated by BASF Corporation. All reagents were used without further purification. N,N-bis(2-hydroxyethyl)ethylenediamine as purchased from Alfa Aesar. The reagents 4,4-Methylenebis(phenyl isocyanate), polybutadiene diol (Mw=2000) were kindly donated by Henkel UK Limited. Dry Tetrahydrofuran (THF) was obtained by distilling from benzophenone and sodium.

PB-UR-OH was produced via slow addition methodology employed previously[2] to generate hydroxy terminated systems. The slow addition of a highly dilute diisocyanate prepolymer solution to a solution of N,N-bis(2-hydroxyethyl)ethylenediamine to affect a large local excess of N,N-bis(2-hydroxyethyl)ethylenediamine in THF, and thys avoiding the cross-linking and detrimental polymerization.

Pluronic P123 was used as received, is denoted $E_{20}P_{72}E_{20}$ and has an average molecular weight of 5750 g mol^{-1}. Uncertainties on degrees of polymerization are typically ±3 %.

The blends of P123 / PB-UR-OH were prepared by co-dissolving the required amount of each polymer in THF (tetrahydrofuran from Sigma), pipetted on to glass slides and evoparated slowly in a THF atmosphere.

Rheology: Measurements of dynamic shear modulus were performed using a stress-controlled AR2000 rheometer from TA Instruments. Initially amplitude sweeps were employed by subjecting the polymer to strain rates between 0.01 and 10 % at a constant frequency of 5 and 50 rad/s to detect the linear viscoelastic regime. An appropriate strain rate was then chosen to carry out frequency sweeps between 0.01 and 600 rad/s. The plate-plate geometry was used with a gap setting of 100 µm and covered with a solvent trap to avoid too much evaporation.

Small – angle X-ray scattering: SAXS experiments were performed on stations 2.1 and 6.2 at the Synchrotron Radiation Source, Daresbury Lab, UK and SAXS experiments have been conducted at station BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) [29,30].The samples were introduced in pans DSC 600 heating stage from Linkam that were previously pierced and covered by mica windows and the capsules were sealed avoiding sample loss. The distance to the SAXS detector was *ca.* 5 m using a wavelength of 0.145 nm. A 2-dimensional multiwire detector was used to record SAXS patterns, with a resolution of 512 ×515 pixels and a pixel size of 260 µm^2. Standard corrections for sample absorption and background subtraction were performed.

FTIR: Variable temperature FT infrared spectroscopy: Measurements were performed using a Bruker Equinox 55 FT-IR microspectrometer fitted with a MCT D316 IR scope detector. IR measurements were conducted in transmission mode, 32 scans at 4 cm^{-1} resolution were averaged. The speciments were generated by drop casting directly on a KBr disk from a solution of THF 1% (w/v). The microspectrometer was equipped with a heating stage (Linkan TMS 94) with KBr windows in which the KBr disk is placed. FTIR experiments at different temperatures have been performed by heating the sample from 25 °C at a rate of 5 °C/min to 45 °C and 75 °C and once the desired temperature was reached the temperature was stabilised by holding the temperature (5 minutes).

References

1. Kohlbrecher, J., http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html. In 2009.
2. Hermida-Merino, D.; Slark, A. T.; Colquhoun, H. M.; Hayes, W.; Hamley , I. W., Thermo-responsive microphase separated supramolecular polyurethanes. *Polymer Chemistry* **2010,** 1, 1263-1271.