Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Influence of Microstructural Variations on Morphology and Separation Properties of Polybutadiene-based Polyurethanes

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1. Analysis of One-Dimensional Correlation Function

Figure S2 shows the SAXS curves obtained in this study for our samples. In this study, the morphology of PUs is assumed to be lamellar, which is a widely accepted assumption for Pus.[1] Accordingly, for a system with lamellar morphology, one-dimensional correlation function, $\gamma_1(x)$, is calculated from the scattering intensity, $I(q)$, as follows:[2]

$$\gamma_1(x) = \frac{\int_0^\infty (I(q) - I_b) q^2 \cos(qx) dq}{\int_0^\infty (I(q) - I_b) q^2 dq} \tag{S1}$$

In which, x (nm) is the length in the direction normal to the lamellae, and I_b is the background scattering due to thermal density fluctuations.

Here, modified Porod's law, as defined below, is used to calculate I_b and to extrapolate the scattering curves to the high-q values beyond the available data by fitting the tail of the scattering patterns for each sample.[3]

$$\lim_{q \to \infty} I(q) = \frac{K \times \exp(-\sigma^2 q^2)}{q^4} + I_b \tag{S2}$$

In this equation, K is Porod's constant, and $\sigma\,(nm)$ is the sigmoidal gradient interphase boundary parameter. For PU(0,0,7), the range of suitable data for fitting was limited to higher q range where the effect of σ is negligible. Therefore, original Porod's law ($\lim_{q \to \infty} I(q) = \frac{K}{q^4} + I_b$) was employed for extrapolating the data for this sample.

The calculated correlation functions for our samples are presented in Figure S3. The number-average thickness of the hard and soft microdomains, as well as their volume fraction for a corresponding ideal two-phase system with sharp phase boundaries are obtained from the graphical analysis of the correlation functions.[4, 5] Figure S4 shows an example of this procedure. In this Figure, **C** is the intercept of the straight line fitted to the linear part of the self-correlation section of the correlation function curve; A is the line tangent to the first minimum of the curve; z_1 is the intersection of A and the line fitted to the linear section of the curve, which is equal to the number-average thickness of the hard microdomains; and L is the long period. Furthermore, the volume fraction of the hard domains, ϕ_h, is obtained from the following equation:

$$\phi_h = \frac{-A}{C-A} \qquad \text{(S3)}$$

The thickness of the soft microdomains is obtained by subtracting the thickness of the hard microdomains from the value of the long period. Similarly, the volume fraction of the soft microdomains is obtained by subtracting the volume fraction of the hard microdomains from unity.

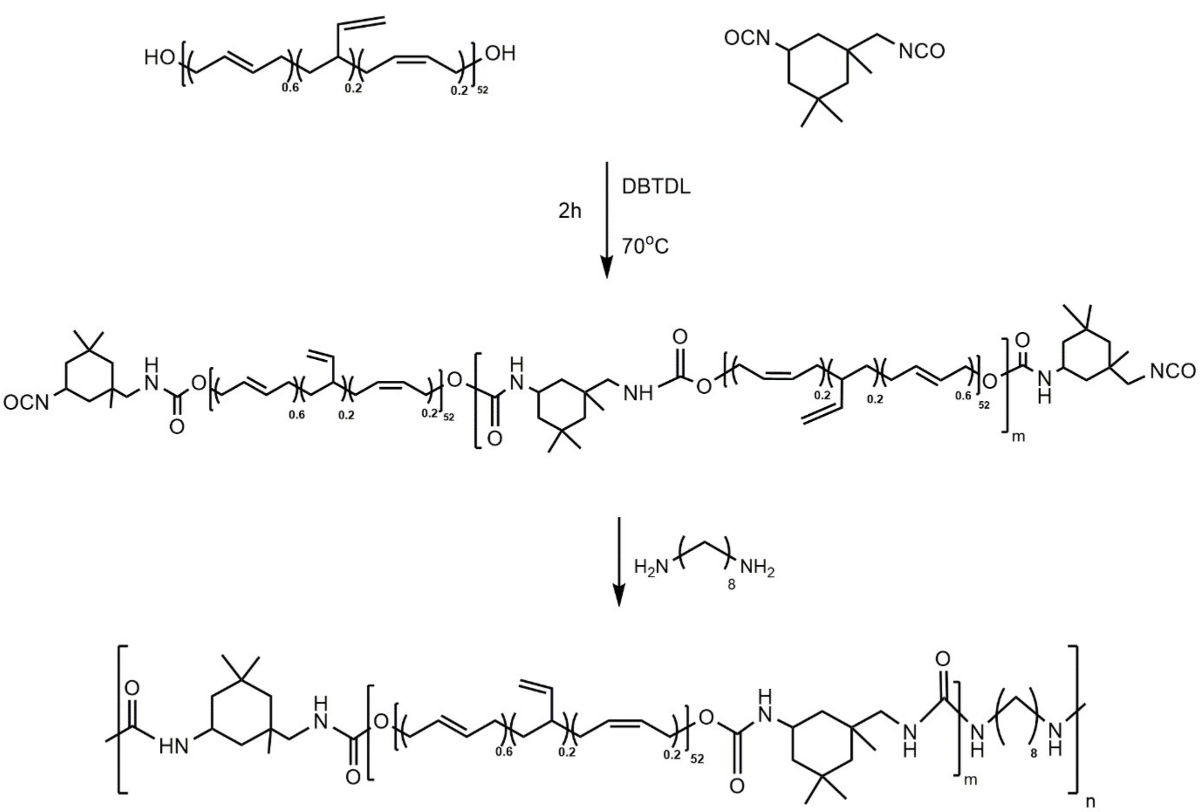

Figure S1. Schematic representation of polyurethane synthesis via a two-step bulk polymerization

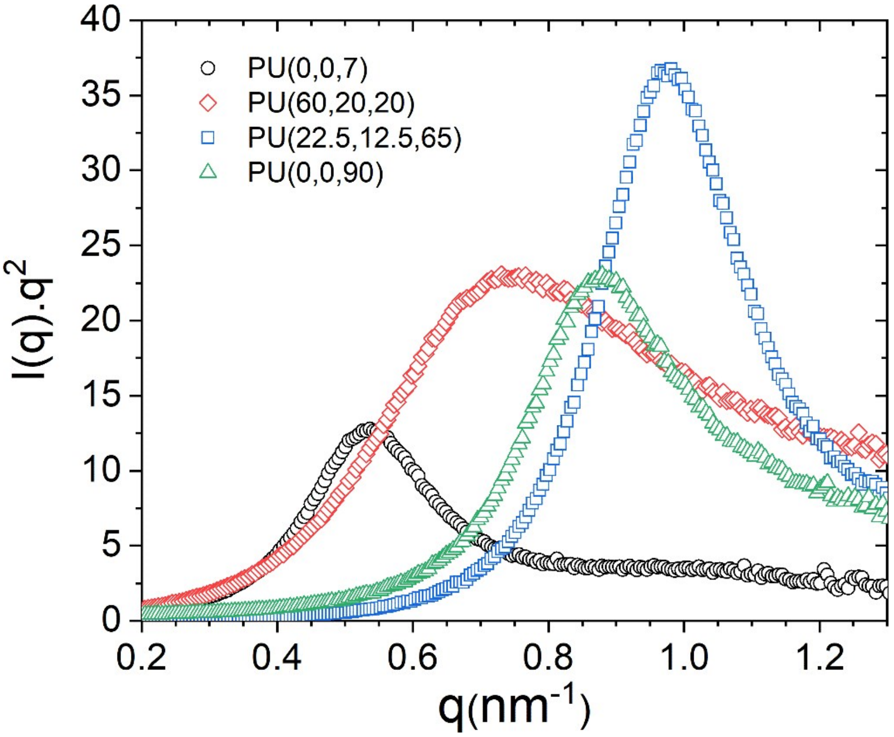

Figure S2. Lorentz- corrected SAXS curves for the synthesized PUs

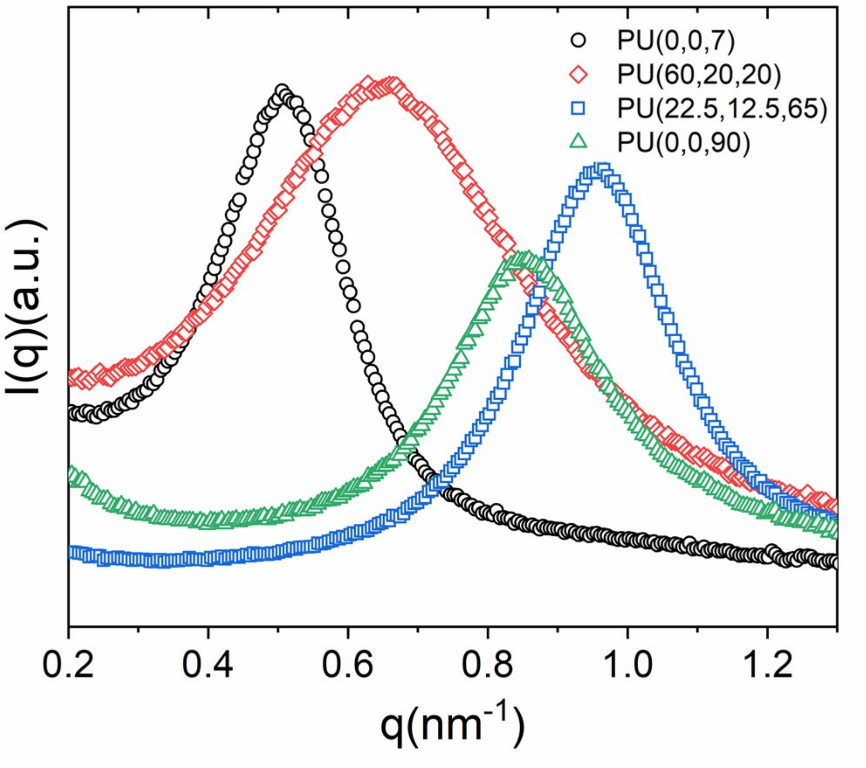

Figure S3. Scattering patterns of the PU samples.

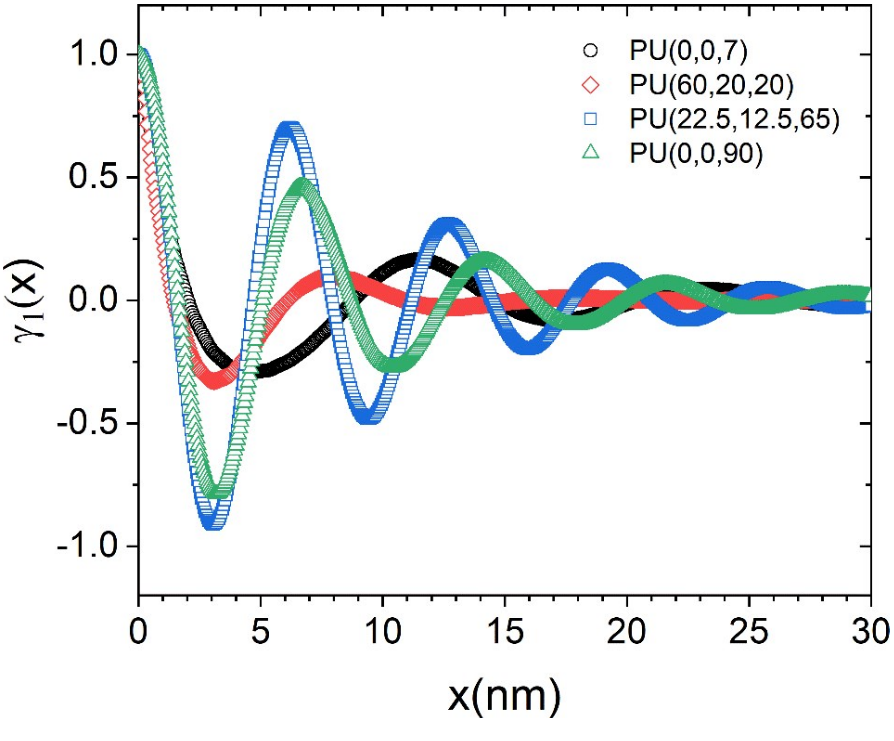

Figure S4. Calculated correlation functions obtained for the PU samples.

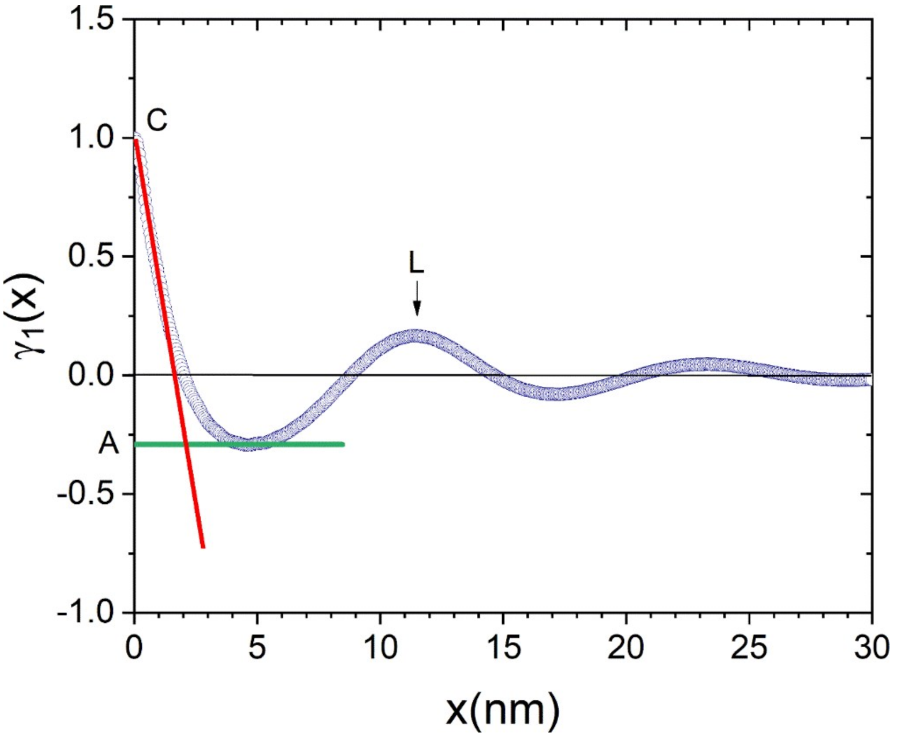

Figure S5. An example of the graphical analysis of the one-dimensional correlation function.

Table S1. Thermal stability and glass transition temperature of the synthesized PUs

Sample	$T_{10\%}$ (°C)[a]	$T_{50\%}$ (°C)[b]	Residual Char (%)	T_g (°C)	ΔT_g (°C)[c]
PU(0,0,7)	360.1	430.0	2	-34.7	3.3
PU(60,20,20)	334.8	455.1	3	-73.9	6.1
PU(22.5,12.5,65)	321.7	447.0	5	-40.5	7.5
PU(0,0,90)	342.8	450.0	8	-2.0	15

[a] the temperature at which 10% weight loss occurs.

[b] the temperature at which 50% weight loss occurs.

[c] $\Delta T_g = T_g$ (polymer) T_g (polyol)

Table S2. The parameters obtained from the analysis of the one-dimensional correlation function

Sample	HD volume fraction	SD volume fraction	HD lamella thickness (nm)	SD lamella thickness (nm)	Long period (nm)	Nominal volume fraction of HS	Long Period (Bragg's Law) (nm)
PU(0,0,7)	0.23	0.77	2.29	9.21	11.40	0.15	11.71
PU(60,20,20)	0.25	0.75	1.88	6.22	8.10	0.17	8.60
PU(22.5,12.5,65)	0.39	0.61	2.60	3.60	6.20	0.15	6.40
PU(0,0,90)	0.37	0.63	2.30	4.40	6.70	0.16	7.15

References

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