

Supporting information

Hydration influences on the phase heterogeneity of segmented copolymers

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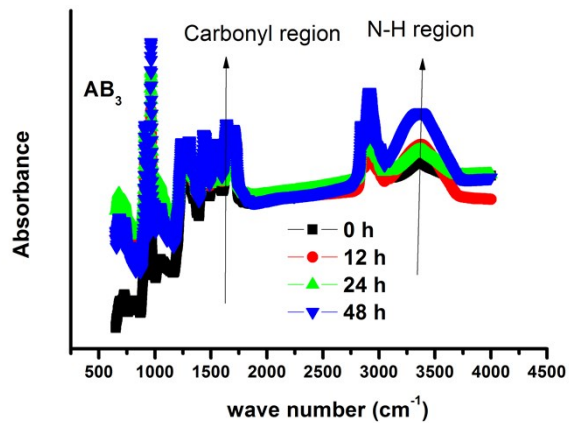
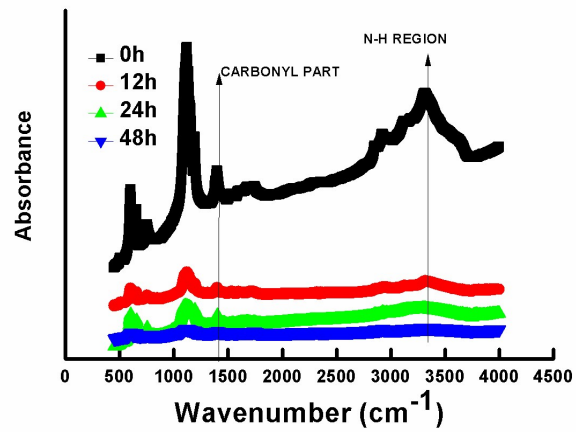
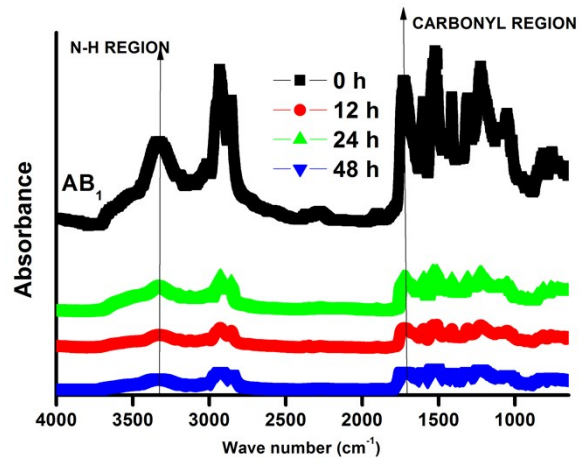


Figure S1. FTIR spectra of all systems at different durations of hydration. “0 h” is dry state. The N-H and carbonyl regions are specifically marked. Under dry conditions for AB₁, the A segments are of urethane functionality. B segments are a blend of both

urethane and urea segments. For AB₂, both A and B segments are urethane moieties. For AB₃, both A and B are formed by urethane and urea segments.

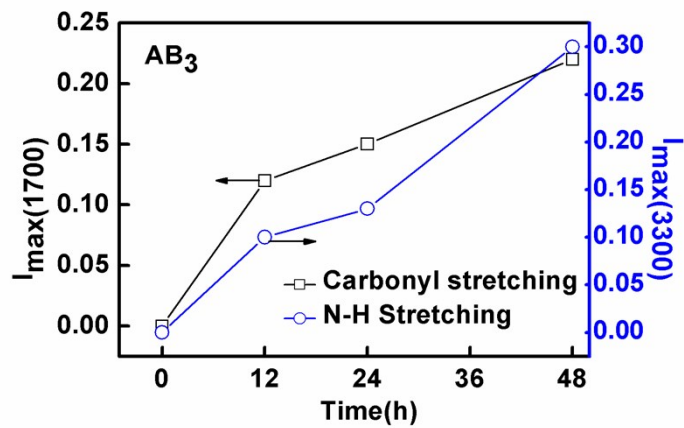
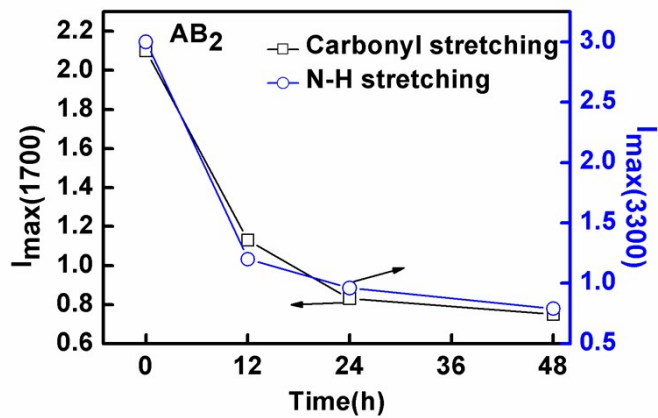
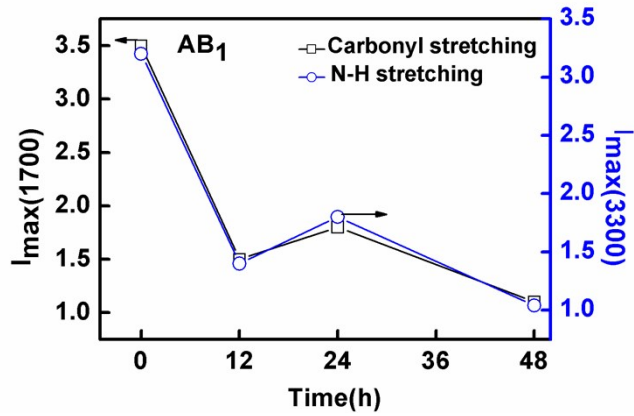


Figure S2. Change in intensities of carbonyl and N-H stretching regions with increasing durations of hydration. Upon hydration, a significant reduction in the intensities of carbonyl and –NH stretching are seen in AB₁ (intensities of peaks that spans between 1690 cm⁻¹ to 1750 cm⁻¹ and 3200 cm⁻¹ to 3500 cm⁻¹). The –NH stretching mainly originated from hydrogen bonding between soft urethane and hard urea segments^{2,3}. A reduction in intensity of peak at 1696 cm⁻¹ indicates reorientation in ordered urethane domains due to change in the hydrogen bonding interactions within the segments. In AB₂, the peak intensity of 1711 cm⁻¹ and 3450 cm⁻¹ decrease which represents ordered urethane domains⁴. Here again, decrease in hydrogen bonding indicates corroboration of the reduction in phase separation observed while quantifying degree of phase separation deduced from scattering profiles. In AB₃ an increase in intensity of carbonyl stretching (1630 cm⁻¹ to 1721 cm⁻¹) and –NH stretching (3330 cm⁻¹) upon hydration corroborates the increase in phase separation observed by scattering.

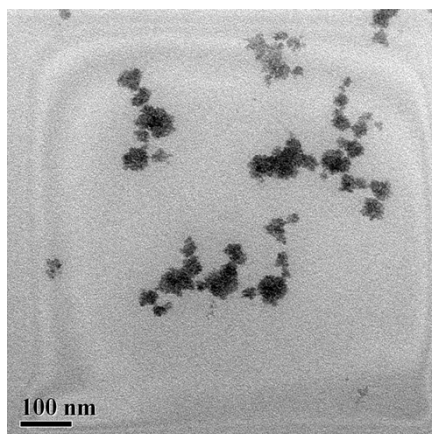


Figure S3. Representative transmission electron microscope image showing the segmented morphology of this class of polymers. The dark section indicates hard segments and the grey coloured portion, soft segments. Both individual and assemblies of hard segments can be seen.

Assessing water uptake

Water uptake experiments were assessed by gravimetric experiments. Known weight (using a weighing Balance, Citizen CY720) of samples of all the systems are immersed in double distilled water (Millipore) kept in a tightly closed container. The samples were taken out at the same intervals, at which scattering and infrared spectroscopy was performed. The difference in weight is plotted against time.

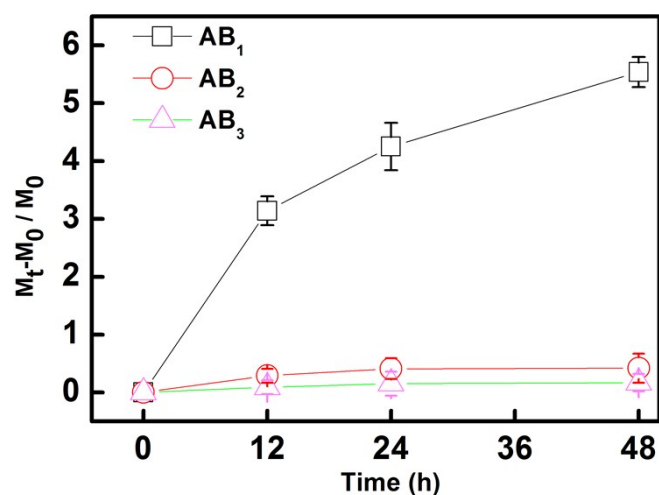


Figure S4. Gravimetric experiments for water uptake for all the three systems at the same intervals of hydration as that of SAXS, SANS and ATR-FTIR experiments. Average weight gain for three experiments with error bar is shown. The lines connecting points are only a guide to the eye.

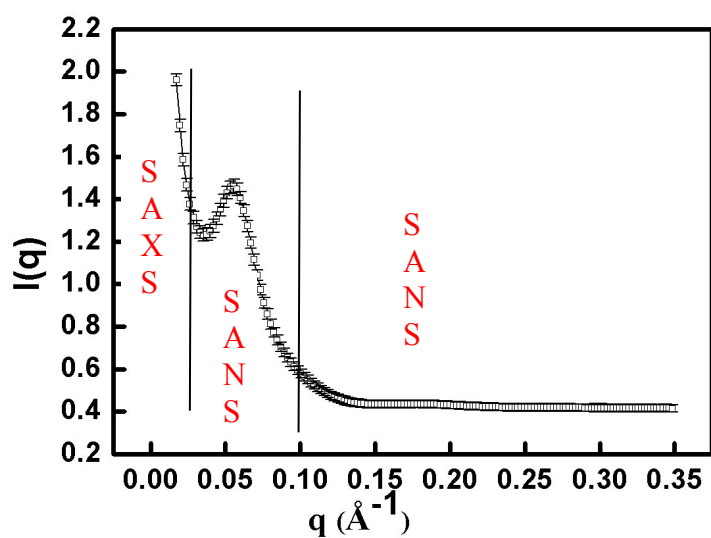


Figure S5. Identification of scattering regions (from SAXs and SANS traces) for quantification of segmentation parameters. Low q - region- SAXS, Braggs and high- q region-SANS.

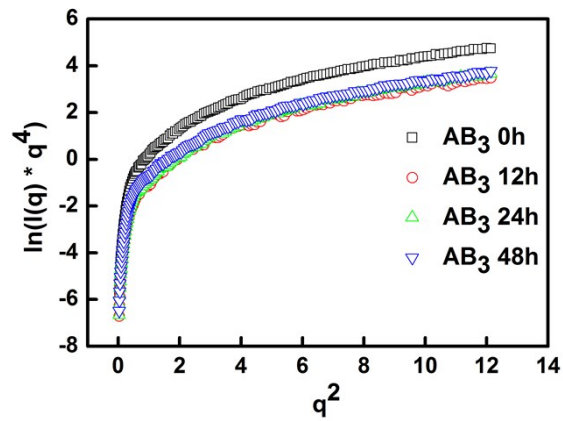
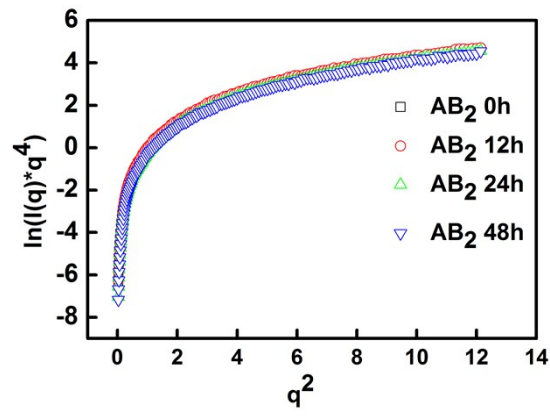
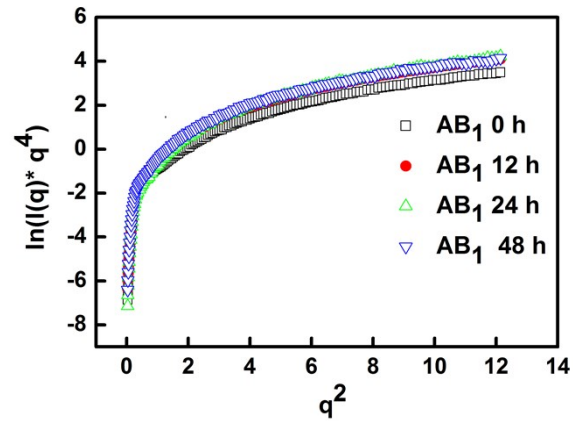


Figure S6. Plot of $\ln I(q) \cdot q^4$ against q^2 depicting the relationship shown in equation (2) of the main article.

References

1. D. P. Queiroz, M. N. de Pinho, C. Dias, *Macromolecules*. 2003, 36(11), 4195
2. S-K. Wang, C. S. P. Sung, *Macromolecules*, 2002, 35(3), 877.
3. A. M. Heintz, D. J. Duffy, C.M. Nelson, S. L. Hsu, *Macromolecules* 2005, 38(22), 9192.