Supporting Information

Assembly of Miscible Supramolecular Network Blends Using DDA-AAD Hydrogen-Bonding Interactions of Pendant Side-Chains

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Molecular Modelling

Molecular modelling was carried out to provide evidence that the desired *DDA-AAD* hydrogen bonding interaction was possible between the co-monomers. A hybrid Monte Carlo Molecular Mechanics (MCMM) conformational search was carried out in a chloroform medium, using Macromodel 10.3 from Schrödinger software and the Merck Molecular Force Field (MMFF) without restraints. 10000 conformers were generated by MCMM and low energy conformers (up to 10 kJ mol⁻¹ of relative energy) were retained. All of the conformers retained, 399 in total, displayed the desired *DDA-AAD* intermolecular hydrogen bonding interactions as well as the expected intramolecular hydrogen bonds. Figure ESI1 shows the lowest energy conformer; the methacrylate and styrene moieties point in opposite directions with potential π -stacking between the aromatic ring and the pyrimidone ring of the styrene-AIC monomer**2**.



Figure ESI 1. Molecular model diagram of the lowest energy conformation found when merge MMA-UIM monomer **1** and Styrene-AIC monomer **2** showing the desired intermolecular and intramolecular hydrogen bonding interaction. MMA-UIM monomer **1** in green, styrene-AIC monomer **2** in blue, hydrogen bonds in yellow.

Differential Scanning Calorimetry (DSC) results

To investigate the effect of addition of H-bonding motifs to PMMA and PS, respectively, DSC were performed both on the pure PMMA and PS as well as samples with different fraction of added motifs, as shown in Fig. ESI 2.



Figure ESI 2. DSC thermograms of (a, c) heat flow and (b, d) first derivative of heat flow on cooling of: PMMA homopolymer (**10**), along with copolymers of PMMA-UIM (**11**, **12**, and **13**) in indicated quantities (a, b); and PS homopolymer (**17**), along with copolymers of PS-AIC (**18**, **19**, **20** and **21**) in indicated quantities.

Figure ESI 2 compares PMMA-UIM (polymers **11** (1.5%), **12** (2%), and **13** (4%)) and PS-AIC (polymers **18** (1.5%), **19** (2.0%), **20** (5.0%), and **21** (5.5%)) copolymers to PMMA

(polymer **10**) and PS (polymer **17**) homopolymers. From these data, it is clear that the T_g values (determined as the inflection point in the heat flow vs temperature and reported in the table in the main manuscript) do not vary greatly (~ 3°C) with H-bonding motif copolymerisation up to 5.5%. With the exception of PMMA 2% **12** (which we discuss in the main manuscript).

DSC measurements across the glass transition are often performed on cooling in order to negate aging effects, which alter the shape of the calorimetric glass transition response. To avoid aging effects influencing the DSC results, we show results on cooling in the main manuscript for polymers **10** and **17**, and **12** and **20**, in Fig. 3. We also show here the corresponding experiments on heating (Fig. ESI 3).



Figure ESI 3. DSC thermograms of heat flow (a, c) and first derivative of heat flow (b, d) on heating of control sample (a, b): polymer **10** (PMMA) with polymer **17** (PS) and (c, d) blended sample: PMMA copolymer **12** (2.0% PMMA-UIM) in blue, PS copolymer **20** (5.0% PS-AIC) in red, and a 50/50 blend in purple.

Comparison between Figure ESI 3 and Figure 3 in the main manuscript demonstrates the narrowing of the glass transition observed on heating together with the presence of an enthalpy relaxation 'overshoot'.¹ We note that, as for the cooling results in Figure 3 in the main manuscript, an indication of two transitions is also apparent in the blended sample (figure ESI 3 c and d), which might indicate some degree of immiscibility as discussed in the main manuscript.

The polymer blend composition of PMMA 2% UIM and PS 4.5% AIC, as shown in Figure 3 in the main manuscript, demonstrated the strongest miscibility based on DSC. However, for comparison, DSC measurements were performed also on other polymer blend combinations, as shown in figures ESI 4, 5, and 6. These data are discussed in the main manuscript.



Figure ESI 4. DSC thermogram of heat flow (a) and first derivative of heat flow (b) on cooling of blended sample: PMMA polymer **11** (2.5% PMMA-UIM) in blue, PS polymer **18** (1.5% PS-AIC) in red, and a 50/50 blend of these samples in purple.



Figure ESI 5. DSC thermogram of heat flow (a) and first derivative of heat flow (b) on cooling of blended sample: PMMA polymer **11** (2.5% PMMA-UIM) in blue, PS polymer **19** (2.0% PS-AIC) in red, and a 50/50 blend of these samples in purple.



Figure ESI 6. DSC thermogram of heat flow (a) and first derivative of heat flow (b) on cooling of blended sample: PMMA polymer **13** (5.5% PMMA-UIM) in blue, PS polymer **21** (5.5% PS-AIC) in red, and a 50/50 blend of these samples in purple.

Spectroscopic Analysis of Blend Formation



Figure ESI 7. ¹H NMR (500 MHz, CDCl₃) analyses of blending (a) 2.0% PMMA-UIM **12** (b) 5.0% PS-AIC **20** (c) samples – 2.0% PMMA-UIM **12** and 5.0% PS-AIC **20** were mixed in a 1:1 (wt) ratio. The NH resonances associated with the HBMs are extensively broadened in both cases, and are only observed for the 5.0% PS-AIC **20** sample; on mixing, a change in the NH resonances and the CH_2CO resonances are observed. Given the low field resonances for the NHs, it is likely that hydrogen-bonding occurs in unblended samples e.g. through intra-polymer interaction, however this changes on blending indicative of interpolymer heterodimierzation.



Figure ESI 8. IR analyses of blending. Polymers were drop cast as chloroform films onto Bruker Alpha Platinum ATR and allowed to evaporate then analysed (a) PMMA **10**, PS **17** and a 1:1 (wt) mixture, (b) 2.0% PMMA-UIM **12**, 5.0% PS-AIC **20** and a 1:1 (wt) mixture (c) 5.5% PMMA-UIM **13**, 5.5% PS-AIC **21** and a 1:1 (wt) mixture. The analyses illustrate that the C=O stretching bands for amide/urea groups in the HBMS of the co-polymers are of considerably lower intensity that the C=O of PMMA; differences are evident between unmixed and mixed samples, but a more meaningful interpretation is not feasible because stretches cannot be assigned, thus differences between different % incorporation of HBM are more difficult to discern.

Atomic Force Microscopy (AFM) Results



Figure ESI 9. Blend of PMMA (**10**) and PS (**17**): a) height, b) peak force error signal and c) modulus map, showing a high force (Approx. 500 nN) nanoindentation scratch across one domain, showing that the PF-QNM modulus contrast correlates perfectly with penetration of the sharp AFM tip, with a heavy 5.2 nm deep scratch on the lower modulus polystyrene (softer) matrix, and a light 0.3 nm deep scratch on the PMMA domain.



Figure ESI 10. a) Zoom-in of the 2.0 % PMMA-UIM **12** and 5.0 % PS-AIC **20** blend sample from the main Paper (Figure 3 panel d/e). Simultaneously acquired nanomechanical channels are shown in b) elastic DMT modulus, c) surface deformation and d) adhesion. Although the contrast in the modulus is very weak, deformation and adhesion show definite regions of contrast variation, with a maximum size of approximately 50 nm (and down to beyond resolution limits.



Figure ESI 11. AFM analyses of blended comprising 1:1 mixture of 5.0 % PMMA-UIM **13** and 5.5 % PS-AIC **21** (a,c) showing height images at 400 nm and 2.0 μ M and (b,d) showing rheological analysis at 400 nm and 2.0 μ M.

Monomer Characterization







ESI mass spectrum of **1** m/z found 289.1317 [M + H]⁺ C₁₄H₁₇N₄O₃ requires 289.1295.



ESI mass spectrum of **2** *m*/*z* found 356.1623 [M + H]⁺ C₁₉H₂₁N₃O₄ requires 356.1605.

Polymer Characterization

	Polymer	GPC Trace							
10	PMMA	Time (mins) 0 5 10 5 20 25 30							
11	2.5% UIM-PMMA								
		Time (mins) 0 5 10 15 20 25 30							
12	2.0% UIM PMMA	Time (mins) 0 5 10 5 20 25 30							
13	5.5% UIM PMMA	Time (mins) 0 5 10 15 20 25 30							

17	PS							
		Time (mins)						
		0 5 10 15 20 25 30						
18	1.5% AIC PS	Time (i)						
		0 5 10 15 20 25 30						
19	2.0% AIC PS							
		Time (mins)						
		0 5 10 15 20 25 30						
20	5.0% AIC PS							
		Time (mins)						
		0 5 10 15 20 25 30						
		V.						

21	5.5% AIC PS									
			Time (mins)							
		0	5	10	15	20	25	30		
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11 (c) 2.0% PMMA-UIM **13** (CDCl₃) (d) 5.5% PMMA-UIM **14**, (DMSO-d₆)



18 (c) 2% AIC-PS polymer 19 (d) 5% AIC-PS polymer 20, (e) 5.5% AIC-PS polymer 21

References

¹ Höhne, G. W. H., Hemminger, W. & Flammersheim, H.-J. in *Differential Scanning Calorimetry, An Introduction for Practitioners* (Springer-Verlag Berlin Heidelberg, 1996).