Supporting Documents

Table S-1 lists calculated interfacial surface tension ($\gamma_{(p\text{-}MMA/nBA//p\text{-}nBA/PFS)}$ of p-MMA/nBA/p-nBa/PFS particles as a function of nanoparticle composition.

Figure S-1 illustrates ^{13}C-NMR spectrum of specimen P60/40. The following NMR shifts were used to determine the monomer ratio after copolymerization: **C**H_3- at δ=18 ppm (g') of p-nBA and **C**H_3- at δ=51 ppm (d) of p-MMA. The resulting molar ratios were then converted to the w/w ratios. An experimental error is ~ 5w/w %.

Figure S-2,A shows AFM images on SiO_2 substrate and PTFE substrates. Colloidal nanoparticles of P100/0-S_2 (Figure S-2A, A_1, A_1', A_2, A_2') on SiO_2 show a softer phase p-nBA/PFS on the top of p-MMA. However, on PTFE, Figure S-2A, A_2-A_2', the low T_g p-nBA/PFS phase is coalesced. As seen a distinct p-nBA/PFS phase (light regions) is imbedded into a softer p-nBA/MMA matrix shown as dark regions for monolayer of P50/50-S_2 particles. . On a PTFE substrate, due to a higher degree of coalescence near the film-air (F-A) interface particle shapes are hard to differentiate. In terms of the core-shell particles P0/100-S_2 the resulting film morphologies are different. On the SiO_2 substrate Figure S-2A, C1 and C1', the phase image shows that the harder p-nBA/PFS phase is surrounded by a soft p-nBA phase, whereas on PTFE Figure S-2A, C_2 and C_2', substrate a homogenous morphology film, due to coalesced p-nBA phase is observed. The reported observations are supported by the recorded GATR spectra illustrated in Figure S-2B. For P0/100-S2 particles spectra S-2B, A, show a high intensity of 1500 and 1520 cm^{-1} bands corresponding to PFS (C-F) vibrations at the F-A interface on SiO_2 substrates. However, on PTFE the low T_g p-nBA/PFS phase is coalesced. A

strong decrease in the characteristic bands (1500 and 1520 cm^{-1}) of PFS is observed. Accordingly a higher band intensity of 1500 and 1520 cm^{-1} bands of PFS is observed in Figure S-2B, spectrum B, where as the 1165 and 1145 cm^{-1} bands attributed to C-O-C stretching vibrations of p-nBA and p-MMA decreased for colloidal particles of P50/50-S2 on SiO_2 substrate. On a PTFE substrate increasing intensities of the 2965, 2935, and 2875cm^{-1} bands attributable to CH_2 stretching vibrations 1165 and 1145 cm^{-1} bands attributed to C-O-C stretching vibrations of p-nBA and p-MMA is detected. Colloidal particles P100/0 which show no significant PFS bands at FA interface on the PTFE substrate spectra Figure 2 B,C,. For a monolayer on a SiO_2 substrate both p-nBA/PFS and p-nBA are detected.

Table S-1: Composition of core and 2-phase particles and their interfacial surface tension $\gamma_{(p\text{-}MMA/nBA//p\text{-}nBA/PFS)}$

Core Particle Description MMA/nBA ratio	Shell Particle Description PFA/nBA	2–Phase Particles	$\gamma_{(p\text{-}MMA/nBA//p\text{-}nBA/PFS)}$ [mN/m]
0/100	50/50	P0/100-S_2	1.7
20/80	50/50	P20/80-S_2	3.4
40/60	50/50	P40/60-S_2	6.7
45/55	50/50	P45/55-S_2	7.6
50/50	50/50	P50/50-S_2	8.7
55/45	50/50	P55/45-S_2	9.8
60/40	50/50	P60/40-S_2	10.6
80/20	50/50	P80/20-S_2	12.8
100/0	50/50	P100/0-S_2	15.2

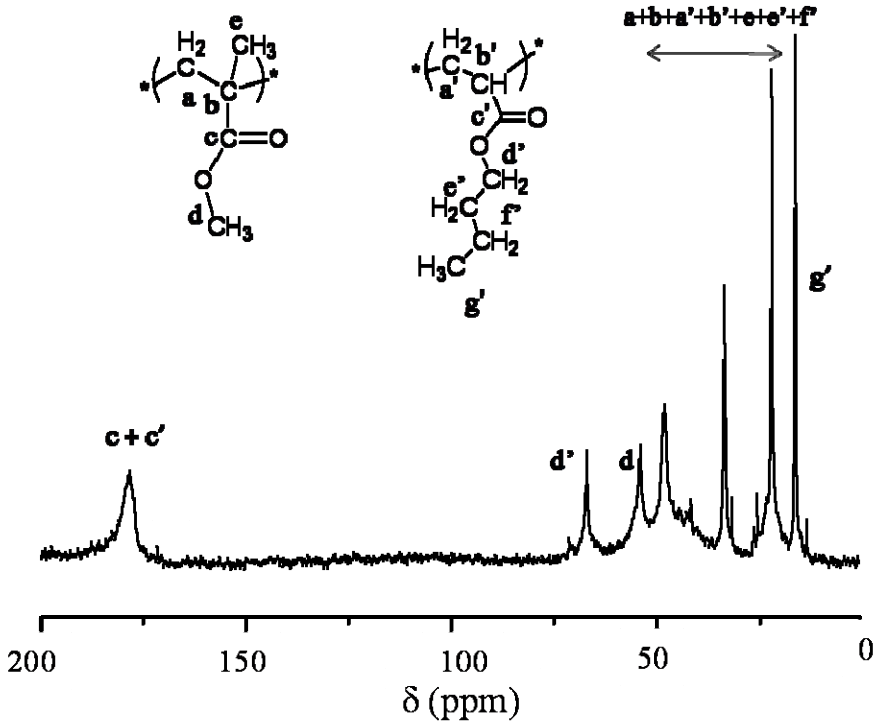

Figure S-1: ^{13}C-NMRspectra of specimen P60/40.

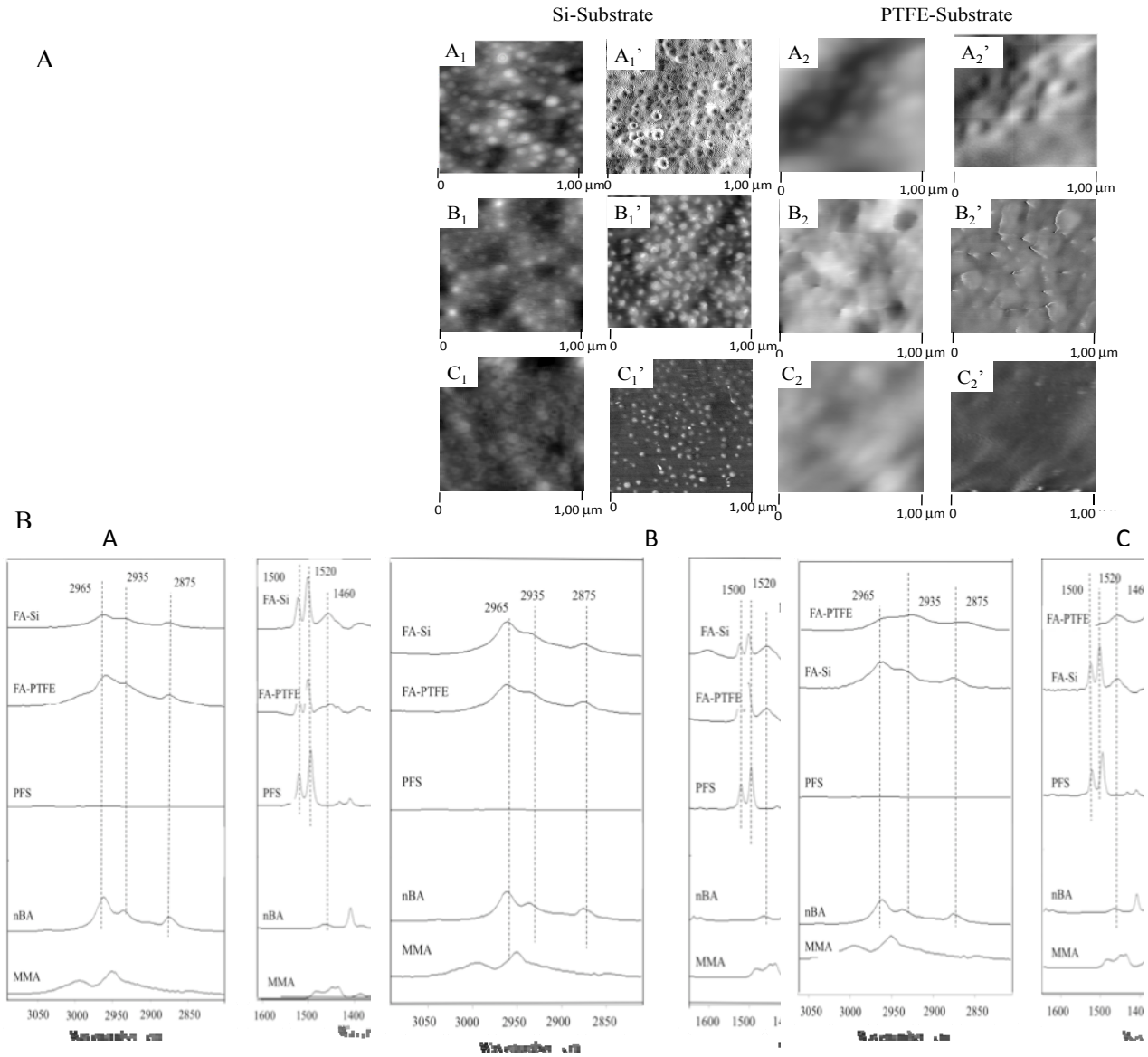

Figure S-2A: AFM phase images and height images of P100/0-S_2 (A_1, A_1',A_2,A_2'), P50/50-S_2 (B_1,B_1',B_2,B_2') and P0/100-S_2 (C_1,C_1',C_2.C_2') particles coalesced on SiO_2 and PTFE substrates. GATR-FTIR spectra recorded from the F-A interface of P100/0-S_2 (A), P50/50-S_2 (B) and P0/100-S_2 (C) in the 3050–2 850 cm^{-1} (1) and 1 550–1100 cm^{-1} (2) region of of P100/0-S_2 (A), P50/50-S_2 (B) and P0/100-S_2 (C) coalesced on Silica (trace a) and PTFE (trace b) substrates; and IR spectrum of c) PFS, d) nBA, and e) MMA monomers for reference purposes.