Supporting Information

Colloidal stabilization of graphene sheets by ionizable amphiphilic block copolymers in various media

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Determination of the apparent absorption coefficients of G/P hybrids ($\alpha_{G,P}$)

Estimation of graphene/polymer hybrid concentration in various media was performed by adopting a weighting approach. 100 mg of synthetic graphite was mixed with 50 ml of polymer solution and was tip sonicated for three cycles of 30 min. The samples were left to stand overnight. Afterwards, the upper phase (~ 45 mL) was pipetted away and transferred to a different vial. The samples were centrifuged at 2000 rpm for 30 min. The supernatant volumes (~ 40 mL) were filtered through a preweighted PTFE membrane (Millipore, pore size 0.45 µm). After vacuum drying each membrane which contained the graphitic material on top, they were weighted again yielding the hybrid concentration. Further on, these suspensions were measured by UV-vis spectroscopy at a wavelength of 660 nm with a Shimadzu UV 2500 absorption spectrophotometer. For this purpose, the samples were controllably diluted such that the measured absorbance never exceeded unity. The apparent absorption coefficients of graphene/polymer hybrids ($\alpha_{G/P}$) in various solvents were determined by the formula $\alpha_{G/P} = A/l c_{G/P}$, which obeys the Lambert–Beer law (Figures S1 and S2). Since the light absorbance of the dispersions was measured at 660 nm, this is correlated to the transmitting light through the dispersion without any energy variation (turbidimetry). For safety, all measurements were performed against a blank of the appropriate polymer/solvent mixture as to avoid any secondary source of absorption (i.e. scattering effects). However, the same values were obtained against solvent when the polymer solutions were transparent. Thus, by plotting A (at 660 nm) against the concentration c (as determined by the vacuum filtration method described above), the $\alpha_{G/P}$ (in mL/mg/m) were determined by fitting straight lines through the data. The results are collected in Tables S1 and S2.



Figure S1. Absorbance spectra of G/P hybrids in $CHCl_3$ for linear (L) PS-P2VP and star (S) PS_nP2VP_n at different concentrations as determined by gravimetric analysis. Inset: Linear fit of the absorbance at 660 nm vs concentration used to extract the absorption coefficient.

Sample	C _{pol} (g/L)	α (L g ⁻¹ m ⁻¹)
linear (B55)	0.1	2055
linear (B55)	1.5	2688
star (A34)	0.1	2481
star (A34)	1.5	1991

Table S1. The apparent absorption coefficients, $\alpha_{G/P}$, of the GP hybrid dispersions in CHCl₃.





Figure S2. Absorbance spectra of G/P hybrids in H_2O (pH 2) for linear (L) PS-P2VP and star (S) PS_nP2VP_n at different concentrations as determined by gravimetric analysis. Inset: Linear fit of the absorbance at 660 nm vs concentration used to extract the absorption coefficient.

Sample	Polymer <i>conc</i> (mg/mL)	α (L g ⁻¹ m ⁻¹)
linear (B55)	0.1	1330
linear (B55)	1.5	1782
star (A34)	0.1	1542
star (A34)	1.5	2115

Table S2. The apparent absorption coefficients, $\alpha_{G/P}$, of the G/P hybrid dispersions in H₂O pH 2.

Dynamic Light Scattering (DLS)



Figure S3. DLS of the aqueous polymer solutions of 0.1 mg/ml in aqueous medium at pH 2.

G/P dispersions in various media



Figure S4. Digital photographs of G/P hybrids dispersed in CHCl₃. Initial graphene concentration 2 mg/mL.



Figure S5. Digital photographs of pH responsive behavior of GR/block copolymer composites at 0.1 mg/ml, prepared by film hydration.



Figure S6. Digital images of the aqueous phase at different pH values after 72 h of phase transfer from CHCl₃.

Table	S3 .	Initial	values	of	graphite	and	polymer	quantities	in	ethanol-based
suspen	sions									

Starting graphite quantity	Star copolymer quantity	Graphite to polymer mass
(mg)	(mg)	ratio
20	1	20
10	1	10
20	5	4
10	5	2

Electron microscopy images



Figure S7 Representative TEM images from direct exfoliation in acidic water (a); ethanol (b); and CHCl₃ (linear: c, star: d) (Scale bar is $0.5 \mu m$)



Figure S8. Left: SEM image after casting a centrifuged graphene suspension in EtOH; Right: TEM image of the very same sample.



Figure S9. TEM images of G/L hybrids after phase transfer from the organic (CHCl₃) to the aqueous phase (pH 2).



Figure S10. TEM images of G/S hybrids after phase transfer from the organic $(CHCl_3)$ to the aqueous phase (pH 2).

Fabrication of graphene/PVA nanocomposites

The preparation procedure for a well-dispersed graphene/PVA nanocomposite (0.1 wt%) was as follows: graphite powder (2mg/mL) was well-dispersed in CHCl₃ (30 mL) in the presence of $(PS_{35})_{22}$ - $(P2VP_{136})_{22}$ star copolymer (1.5 mg/mL) using a bath sonicator (Branson 1200-E1, 30W) for 10 hours, by adding ice cubes to keep the temperature below 25 °C. After centrifugation, a grey-colored dispersion (20 mL) of graphene sheets was obtained. In a following step, the phase transfer of the graphene/star copolymer dispersion from CHCl₃ to an equal volume acidic water (pH 1) was attempted after agitation (100 rpm) for more than 72 hours. The concentration of graphene was measured by UV-Vis absorbance spectroscopy at 660 nm, according to Lambert-Beer equation, taking α =3620 L/g m [19]. Further, PVA (500 mg) was well-dissolved in distilled water (10 mL) at 90 °C and the graphene/star copolymer hybrid was gradually added to the PVA solution and sonicated for an additional 30 min at room temperature. This homogeneous PVA/graphene/star copolymer solution was stirred at 80 °C for several minutes for condensing the suspension and subsequently was poured into a glass Petri dish and dried firstly at 50°C for ~24 hours in an oven for film formation and then at 70°C in a vacuum oven for ~48 hours until its weight equilibrated. The film was peeled off from the substrate carefully and was cut into strips for mechanical characterization by dynamic mechanical analysis (DMA). The composite contained 0.1 wt% graphene nanosheets. A film of neat PVA was prepared as a reference sample, using 0.5 g of PVA in 10 ml of distilled water.



Figure S11. SEM image of cryo-fractured PVA /G(Star) hybrid nanocomposite.



Figure S12. DSC curves of neat PVA (-) and the corresponding PVA/G(Star) hybrid nanocomposite (-): T_g regime (a), T_m regime (b).

Gel Permeation Chromatography (GPC)

GPC measurements were carried out to investigate whether the polymer chains retain their integrity after the sonication procedure by using a Polymer Lab chromatographer equipped with two Plgel 5 mm mixed columns, a UV detector (254 nm), and using CHCl₃ as eluent with a flow rate of 1 mL/min at 25 °C. Figure S13 clearly shows that the peaks corresponding to the sample before and after sonication coincide, suggesting that the polymer chains remain intact after sonication.



Figure S13. GPC measurements of the PS-b-P2VP linear block copolymer before and after tip sonication at 10% amplitude for 90 minutes.