Electronic Supplementary Information to the paper

Ice-mediated coating of macroporous cryogels by carbon nanotubes: A concept towards electrically conducting nanocomposites

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1. *Synthesis of super-macroporous cryogels.*[1]

An appropriate amount of HEC was dissolved in distilled water under stirring to obtain homogeneous aqueous solution (1 wt.%). Initiator, H_2O_2, (5 wt% to polymer) was added under stirring at room temperature. The resulting homogeneous solution was poured into Teflon dishes forming a 4 mm thick layer, which was then kept in a freezer at minus 20 ^{o}C for 2 h. The frozen system was irradiated with full spectrum UV–vis light with a ''Dymax 5000-EC'' UV curing equipment with 400W metal halide flood lamp for 2 min (irradiation dose rate: 5.7 J/cm^2 min; input power: 93 mW/cm^2).

HEC/PAAm (wt. ration 1:0.5) and PNIPAAm cryogels were prepared from 1.5 and 2 wt% aqueous solution, respectively, using a cross-linking agent, N,N'-methylenebisacrylamide,(10 wt%) by the same procedure as described above.

2. *Preparation of stable aqueous dispersion of SWNTs.*

SWNTs (4 mg) and poly(ethylene oxide)$_{26}$-block-poly(propylene oxide)$_{40}$-block-poly(ethylene oxide)$_{26}$ ("Pluronic" P85 from BASF) triblock copolymer (40 mg) were added to 40 mL deionised water and gently dispersed by ultrasonication for 15 min.

3. *Preparation of stable aqueous dispersion of MWNTs.*

3.1. *Synthesis of PDMAAm-co-Py.*

Monomer, pyrene bearing acrylate (PyAc), were obtained by reacting 1-pyrenemethanol (2 g; 8.6 mmol) and acryloyl chloride (1.4 ml, 17.2 mmol) in the presence of triethylamine (2.4 ml, 17.2 mmol). 1-Pyrenemethanol was added to a solution of triethylamine in dry THF and, then, acryloyl chloride was added dropwise under stirring. The reaction was carried out overnight at room temperature. The reaction product was filtrated, THF evaporated and the solid residue was dissolved in dry dichloromethane. The solution was washed with an aqueous solution of sodium hydrogen carbonate and finally with water. After drying over magnesium sulphate the solution was filtered, and the organic solvent evaporated under vacuum. Finally, the collected solid was dissolved in 1,4 dioxane and freeze dried, providing 2.11 g yellow product. ^{1}H NMR($CDCl_3$, 600 MHz) δ : 7.99-8.19 (m, 9H, Py$\underline{H}$), δ : 6.4 (d, 1H, CHaHb=C$\underline{H}$), δ : 6.2 (d, 1H, C$\underline{Ha}$Hb=CH), δ : 5.92 (s, 2H, C$\underline{H_2}$O), δ : 5.8 (d, 1H, CHa$\underline{Hb}$=CH).

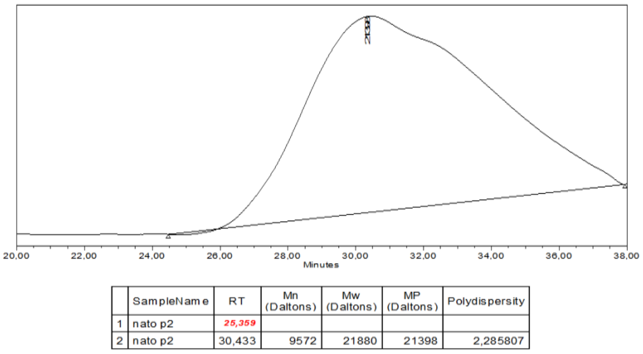
PDMAAm-*co*-Py copolymer was synthesized by free radical copolymerization of dimethylacrylamide (DMAAm) and PyAc using AIBN as initiator. In a typical experiment, 2,271 g (23 mmol) DMAAm and 0.73 g (2.55 mmol) PyAc were dissolved in 26 ml toluene into a glass reactor and degassed by purging with argon. Then, 0.15 g AIBN in 2 ml degassed toluene were added and the mixture was heated to 80 °C under stirring for 24 h. Finally, the polymer was recovered by precipitation in cold n-hexane (-20 °C). Yield: 2.36 g.

^{1}H NMR($CDCl_3$, 600 MHz): δ 7.99-8.19 (m, 9H, Py$\underline{H}$), δ 2.4-3 (m, 6H, N-(C$\underline{H_3}$)$_2$ + 1H, CH_2-C$\underline{H}$), δ 1.2-1.8 (m, 2H, C$\underline{H_2}$-C$\underline{H}$). The calculated molar ration of DMAAm:PyAc units was 0.94:0.06.

Molecular mass and polydispersity index of PDMAAm-*co*-Py were determined by size exclusion chromatography (Fig. S1).

3.2. Noncovalent side-wall functionalization of MWNTs.

1 mg MWNTs was sonicated in 25 ml DMF for 15 minutes until no visible particles were observed. Then, 20 mg of copolymer was added, and the mixture was sonicated for 15 additional minutes. The modified nanotubes were recovered by filtration and washed with DMF to eliminate the copolymer excess. The grafted copolymer estimated by TGA was ca.22 wt% (Fig.S2). Finally, MWNTs modified by PDMAAm-co-Py were re-dispersed in 10 mL water by ultrasonication.



	SampleName	RT	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Polydispersity
1	nato p2	25,359				
2	nato p2	30,433	9572	21880	21398	2,285807

Fig. S1 SEC traces of PDMAAm-*co*-Py at 70 °C obtained with a Waters chromatograph equipped with a UV detector (254 nm) and a Waters Styragel column eluted with 0.5 wt % LiBr containing dimethylformamide (DMF) at a flow rate of 1 mLmin^{-1}. PMMA standards were used for calibration.

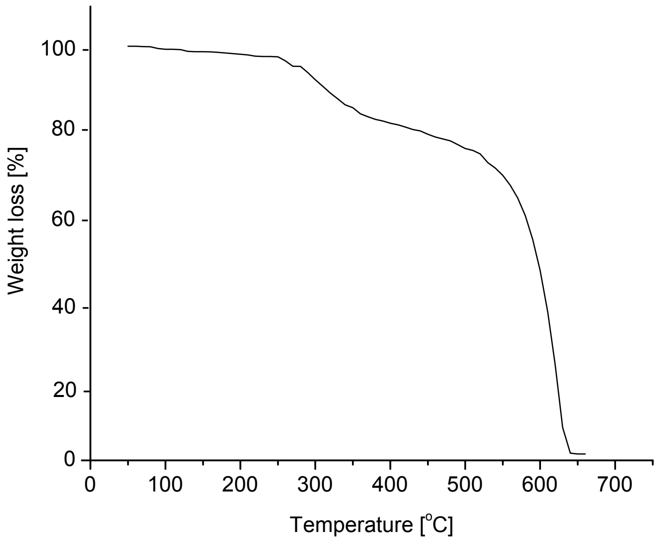


Fig. S2 TGA trace of MWNTs modified by PDMAAm-*co*-Py copolymer. Thermal Gravimetric Analysis was carried out with a SETSYS 2400 TGA thermal analyzer system in the 50-650 °C range, at a heating rate of 10 °C.min^{-1}, in air.

References

1. a) P. Petrov, E. Petrova, B. Tchorbanov, C.B. Tsvetanov, *Polymer* 2007, **48**, 4943; b) P. Petrov, E. Petrova, C.B. Tsvetanov Polymer 2009, **50**, 1118.