Electronic supplementary information

Instrumentation

Sedimentation velocity experiments.

The raw sedimentation data were evaluated by the program Sedfit using continuous c(s), which is based on the numerical resolution of the Lamm equation. It allows the least-squares boundary modeling ls – g*(s), which describes sedimentation of a non–diffusing species, and to determine the average frictional ratio (f/f_{sph}) of the particles.[1,2] The partial specific volume υ was determined by the density variation method, *i.e.*, by sedimentation velocity experiments on the nanoparticle suspensions, using in parallel H_2O and D_2O. The partial specific volume was found to be $\upsilon = (0.78 \pm 0.01)$ $cm^3 \cdot g^{-1}$. Molar masses of the particles were estimated applying the modified Svedberg equation:

$$M_s = 9\pi\sqrt{2}N_A\sqrt{[s]^3\upsilon}$$

where N_A is the Avogadro's number, υ the partial specific volume and [s] is the intrinsic sedimentation coefficient which is defined as:

$$[s] = \frac{s\eta_0}{(1-\upsilon\rho_0)}$$

where s_0 is the sedimentation coefficient at zero concentration, η_0 the dynamic viscosity of the solvent, and ρ_0 the density of the solvent. The diameters were calculated from the Stokes approximation for a sphere:

$$d = 3\sqrt{2}\sqrt{[s]\upsilon}$$

Notes and references

1. P. Schuck, *Biophys. J.*, 2000, **78**, 1606-1619.
2. P. Schuck, P. Rossmanith, *Biopol.*, 2000, **54**, 328-341.
3. W. G. Martin, W. H. Cook, C. A. Winkler, *Can. J. Chem.*, 1956, **34**, 809-814.
4. W. Maechtle, *Makromolekulare Chemie-Macromolecular Chemistry and Physics*, 1984, **185**, 1025-1039.

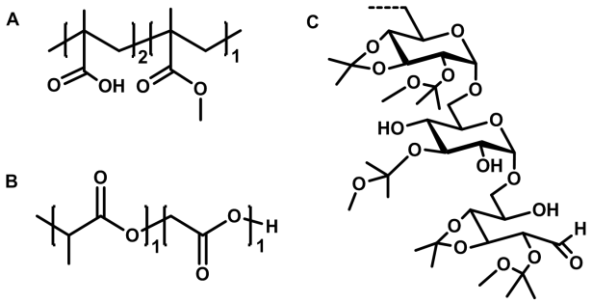

Fig. 1 Chemical structure of the polymers. A - p(MMA-*stat*-MAA)$_{2:1}$, B - poly(lactic-*co*-glycolic acid) (50:50), C - dextran acetal (DS = 2.17).

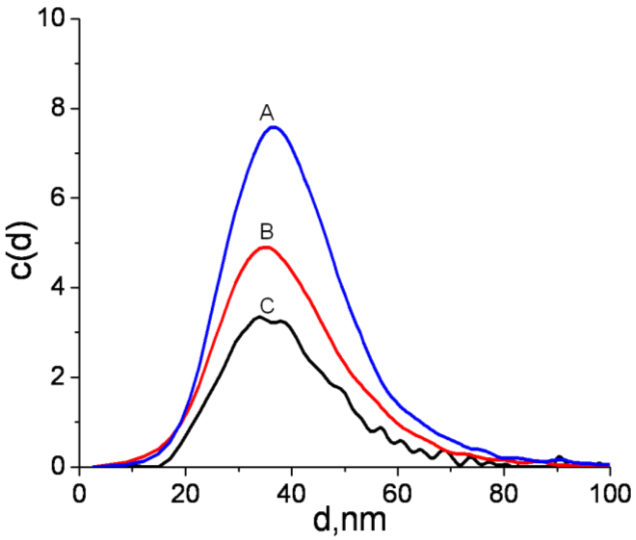

Fig. 2 Size distributions of the nanoparticles at different solvent/non-solvent ratios. The distributions were obtained by sedimentation velocity analysis. The values of the solvent/non-solvent ratio were 0.280 (A), 0.157 (B), and 0.099 (C). The polymer concentration was 3.57 mg·mL^{-1}. The particles were prepared by dropping the polymer solution into water.

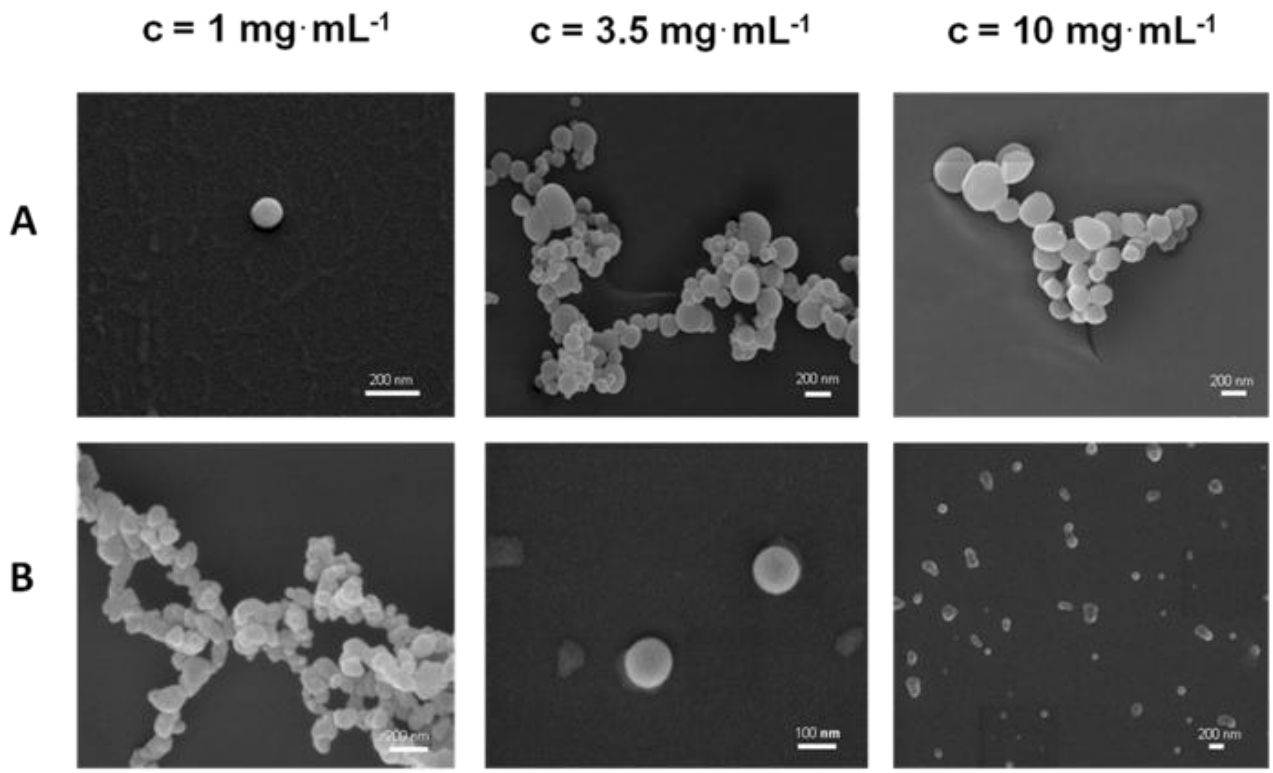

Fig. 3 SEM images of nanoparticles prepared from A) ac-dex and B) PLGA at different polymer concentrations. The particles were prepared by dropping the polymer solution into water.

Table 1 Summary of analytical data for p(MMA-*stat*-MAA)$_{2:1}$ particles

C, mg·mL^{-1}	sol/n-sol ratio	d_{DLS}, nm	d_{AUC}, nm	PDI_{AUC}	$\%Pd_{DLS}$	$M_s \times 10^{-6}$, g·mol^{-1}	ξ, mV	ρ, g·cm^{-3}	η, cP
	0.099	46	25	1.05	14.1		-(17±7)	0.9979	1.0218
1	0.157	44	25	1.06	16.0	6.2	-(22±4)	0.9978	1.0236
	0.280	42	25	1.04	15.1		-(31±7)	0.9978	1.0220
	0.099	71	43	1.12	25.6		-(44±5)	0.9979	1.0234
3.53	0.157	74	45	1.11	26.0	37	-(59±6)	0.9979	1.0238
	0.280	70	45	1.11	25.2		-(49±3)	0.9980	1.0230
	0.099	240	130	1.19	31.0		-(63±1)	0.9981	1.0292
9.67	0.157	240	130	1.18	35.4	1300	-(62±1)	0.9980	1.0312
	0.280	260	150	1.20	38.9		-(65±1)	0.9983	1.0468

* ρ denotes the density and η the viscosity of the nanoparticle suspensions

Table 2 Summary of analytical data for ac-dex and PLGA particles

Polymer	C, mg·mL^{-1}	d_{DLS}, Platereader nm	$\%Pd_{DLS}$ Platereader	d_{DLS}, Zetasizer nm	$\%Pd_{DLS}$ Zetasizer	ξ, mV
	1	78	14.3	112	22.5	-(16±11)
ac-dex	3.5	108	17.8	138	20.2	-(16±14)
	10	142	25.2	172	22.2	-(22±10)
	1	52	14.9	78	18.2	-(14±14)
PLGA	3.5	88	16.9	89	16.4	-(22±12)
	10	148	22.2	132	23.5	-(22±12)

Table 3 Slope and best fit coefficient obtained from the linear fit of the mean particle size vs initial concentration plots

Sample	slope*	slope**	slope***	r^2
p(MMA-*stat*-MAA)$_{2:1}$	0.44[a]	1.01[a]	0.66[b]	0.98[a] 0.94[b]
PLGA	–	–	0.44	0.99
ac-dex	–	–	0.21	0.93

*Linear fit for the data in the 1 – 6 mg·mL^{-1} range of concentration. **Linear fit for the data in the 6 – 10 mg·mL^{-1} range of concentration. Linear fit through all data points.