Electronic Supplementary Material

Spectrum of Hydrodynamic Volumes and Sizes of Macromolecules of Linear Polyelectrolytes *versus* their Charge Density in Salt-Free Aqueous Solutions

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The plots and tables showing the hydrodynamic results such as velocity sedimentation, translational diffusion, and intrinsic viscosity are presented.

Sedimentation data



Figure S1. Sedimentation data treatment using Sedfit software [1-3] and GUSSI interface [4].: (1) initial interference scans reflecting the integral distribution of MVAA–MVAH copolymer sample C11 at $c=1.7 \times 10^{-3}$ g/cm³ in the cell and calculated profiles, (2) residuals between experimental and calculated integral distributions, (3) sedimentation coefficients distribution (model: continuous c(s) distribution).





Figure S2. Sedimentation data treatment using Sedfit program: (1) initial interference scans reflecting the integral distribution of MVAA–MVAH copolymer sample C16 at $c = 0.8 \times 10^{-3}$ g/cm³ in the cell and calculated profiles, (2) residuals between experimental and calculated integral distributions, (3) sedimentation coefficients distribution (model: a - continuous c(s) distribution; b - least-squares l-s g*(s))



Figure S3. Differential distribution of MVAA–MVAH copolymer with respect to sedimentation coefficients *s*. Program: Sedfit, model- least-squares method $ls-g^*(s)$ with 1 discrete component. Polymer concentrations: C11 – c=0.855 \cdot 10^{-3} g/cm^3, C12 – c=0.940 $\cdot 10^{-3}$ g/cm³, C13 – c=0.860 \cdot 10^{-3} g/cm^3, C14 – c=0.890 $\cdot 10^{-3}$ g/cm³, C16 – c=0.895 \cdot 10^{-3} g/cm^3.



Figure S4. Concentration dependence of reverse sedimentation coefficient for copolymers MVAA– MVAH. The sedimentation coefficients at infinite dilution s_0 were determined from the linear approximations $s^{-1} = s_0^{-1}(1 + k_s c + ...)$.

Diffusion data

1



2





Figure S5. Diffusion interference diagrams obtained for MVAA– MVAH copolymer sample C11 after 1 hour (*1*), 10 hours (*2*), 24 hours (*3*) from the beginning of the boundary formation. Polymer concentration: $c = 0.521 \cdot 10^{-3} \text{ g/cm}^3$.



Figure S6. Dependence of diffusion boundary dispersion $\sigma^2 = \sigma_0^2 + 2Dt$ on time *t*. σ_0^2 is the initial dispersion which characterizes the quality of the boundary formation. The diffusion coefficients obtained at these concentrations were taken as the quantities extrapolated to zero concentration, $D_0 = kT/f_0$.

Viscometry data



Figure S7. Huggins plots for MVAA– MVAH copolymers and PMVAA homopolymer



Figure S8. Partial specific volume v of MVAA– MVAH copolymers and PMVAA homopolymer with respect to molar concentration of charge units.

N	%	[η], cm³/g	D ₀ ·10 ⁷ , cm ² /s	s ₀ ·10 ¹³ ,	A ₀ ·10 ¹⁰ , g·cm ² /(s ² ·mol ^{1/3} K)	M _{sD,} 10 ³ g/mol
C11	1.5	155	1.27	2.62	3.07	322
C12	4	132	1.70	2.65	3.54	242
C13	9	132	1.50	2.51	3.19	258
C14	11	129	1.75	2.63	3.55	230
C15	16	147	1.45	2.64	3.12	240
C16	17	129	1.69	2.32	3.30	204
C21	7	168	1.43	3.09	3.47	306
C22	11	181	1.34	2.72	3.35	311
C23	22	168	1.29	3.41	3.32	372
C24	30	190	1.20	3.44	3.31	383
C25	39	200	1.31	3.21	3.48	332
H1	0	165	1.16	2.97	3.07	400
H2	0	132	1.62	2.59	3.41	250

Table S1 – Hydrodynamic data for MVAA– MVAH copolymers in 0.2M NaCl at 25° C

The hydrodynamic invariants A_0 were calculated from the relationship $A_0 = (R[D]^2[s][\eta])^{1/3}$.

The low deviation of A_0 values about the average value indicate a correlation between molecular characteristics ([η], s_0 , and D_0), obtained in an independent experiments, which turns to the further interpretation of hydrodynamic data.

References

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