Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Detection and Evaluation of Polymer-Polymer Interactions in Dilute Solutions of Associating Polymers

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Determination of translational diffusion coefficient

Translational diffusion was studied in a Tsvetkov polarizing diffusometer by the classical method of forming a boundary between the solution and the solvent [1,2], which was created in a cell with a teflon interpiece of length h = 3 cm along the beam path. The diffusion process was registered by the digital camera. The diffusion interference scans obtained at different time are shown in (Figure ESI 1). Diffusion interferogramms were processed in Gaussian approach according to the method proposed in work [3]. The dispersion $\overline{\sigma^2}$ of the distribution $\partial c / \partial x$ of macromolecular displacements x was calculated by the method of maximum ordinate and area [1]:

$$\overline{\sigma^2} = (a^2/8)/[\arg erf(aH/Q)]^2 \qquad (1),$$

where H and Q are the maximum ordinate and the area under the interference curve, correspondingly; arg*erf* is the argument of probability integral, a is the spar twinning (0.11 cm). The dependence of $\overline{\sigma^2}$ on time t (Figure ESI 2) was approximated by the linear function and the diffusion coefficient was determined by its slope:

$$D = (1/2)\partial\overline{\sigma^2}/\partial t \qquad (2).$$

The mean concentration of the solution was $c < 3\cdot10^{-4}$ g·cm^{-3}. The concentration dependence of the translational diffusion coefficient was not observed in the investigated concentration range. The refractive index increment of the polymer-solvent system (dn / dc) was calculated on the basis of Q-values:

$$dn/dc = (\lambda / a\, b\, h)\, Q/c \qquad (3).$$

Here λ is the light wave length, b is the distance between the compensator interference fringes (b = 0.15 cm).

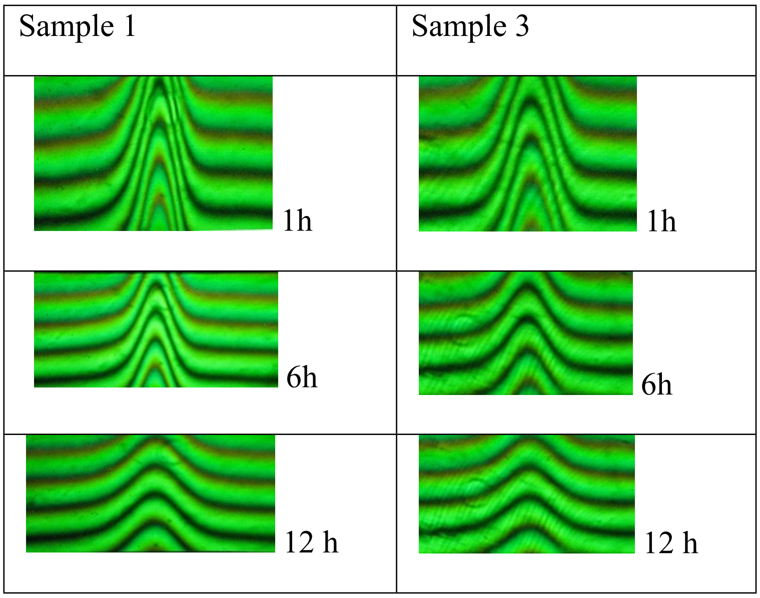


Figure ESI 1. The diffusion interference scans obtained for samples 1 and 3 after 1, 6, and 12 hours from the beginning of the formation of diffusion boundary.

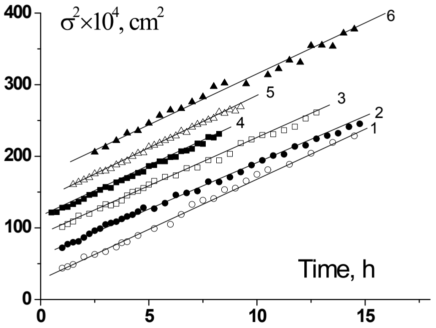


Figure ESI 2. The dependence of dispersion of the interference diffusion boundary on time. Curves numbers correspond to sample numbers in Table 1. Curves are shifted relative to each other.

Velocity sedimentation

The velocity sedimentation of the solutions in 0.1M NaCl solvent was studied with a Beckman XLI analytical ultracentrifuge (ProteomeLab XLI Protein Characterization System) in a two-sector cell with the optical path length of 12 mm at the rotor speed of 40 000 rpm. The sedimentation interference scans were processed with Sedfit program [4]. The Sedfit program allows obtaining the sample distribution with respect to sedimentation coefficients using Provencher's regularization procedure [5] (see Figure ESI 3). For the calculations, it is necessary to know the partial specific volume of polymer (υ), the solvent density (ρ_0) and viscosity (η_0). The sum of residuals is minimized on the basis of Contin program [6]. In addition, within the framework of Sedfit program was performed model-free least-squares estimation of the distribution of sample macromolecules with respect to sedimentation coefficients, [ls–$g^*(s)$] [4]. It should be noted that, although the distributions of sample macromolecules with respect to sedimentation coefficients, obtained using both models, may differ somewhat, the mean values of the velocity sedimentation coefficients practically coincide. The concentration dependences of sedimentation coefficients for all copolymers were studied at three concentrations of each sample ($c_{max}/c_{min} \geq 3.0$). Such conditions of dilution allow a reliable extrapolation of the experimental data to zero concentration. The sedimentation coefficients at infinite dilution s_0 were estimated from the linear approximations of the dependence of the reciprocal sedimentation coefficient on concentration (Figure ESI 4) using equation $s^{-1} = s_0^{-1}(1 + k_s c + \ldots)$, where is k_s Gralen parameter.

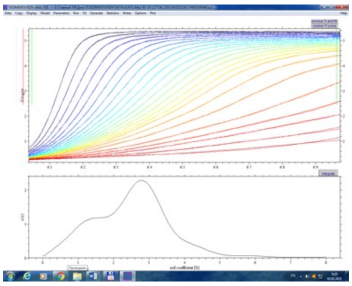
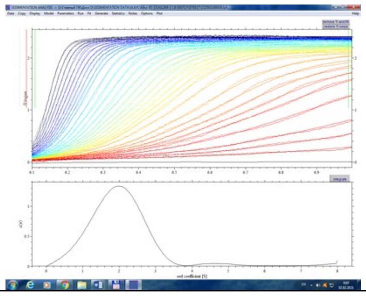
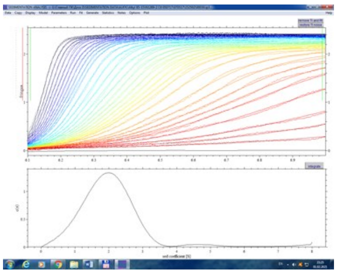
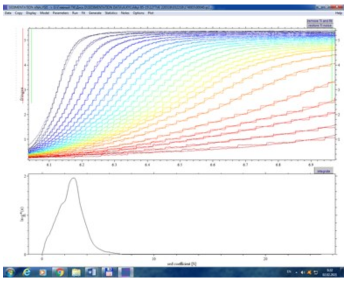
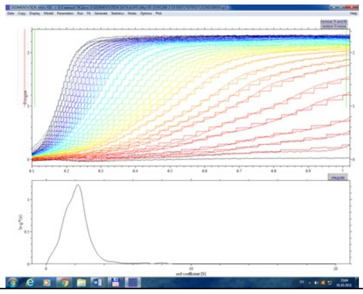
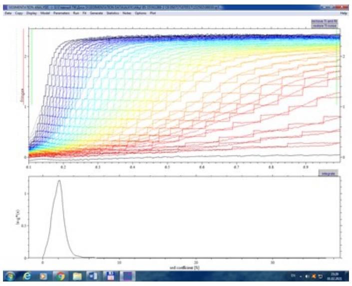
sample 1 c=0.195·10^{-2} g/cm^3	sample 4 c=0.102·10^{-2} g/cm^3	sample 6 c=0.086·10^{-2} g/cm^3
a 		
b 		

Figure ESI 3.
Sedimentation data treatment in the frame of Sedfit program: initial interference scans reflecting the integral distribution of sample and distribution of substance mass fraction vs. sedimentation coefficient using: (a) the model of continuous distribution $c(s)$ and (b) the model-free least-squares estimation of the distribution of sample macromolecules with respect to sedimentation coefficients, [ls–$g^*(s)$].

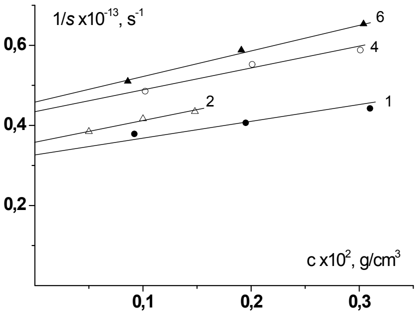


Figure ESI 4. Concentration dependences of sedimentation coefficients. Curves numbers correspond to sample numbers in Table 1.

Distribution of samples by intrinsic sedimentation coefficients obtained with the least-squares estimation ls–$g^*(s)$ is shown in Figure ESI5.

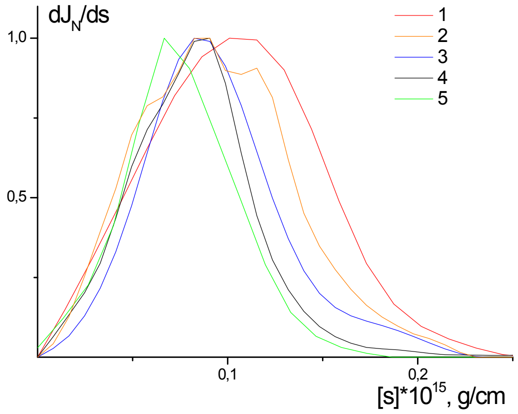


Figure ESI 5. Normalized distribution of substance mass fraction vs. intrinsic sedimentation coefficient $[s]=s_0{\cdot}\eta_0/(1-\upsilon\rho_0)$ expressed in the number of fringes J_N of interference curve. The curves numbers correspond to sample numbers in Table 1. Concentration of samples: Sample 1 $c = 0.0992 \cdot 10^{-2}$ g/cm^3; sample 2 $c = 0.0500 \cdot 10^{-2}$ g/cm^3; sample 3 $c = 0.0908 \cdot 10^{-2}$ g/cm^3; sample 4 $c = 0.102 \cdot 10^{-2}$ g/cm^3; sample 5 $c = 0.100 \cdot 10^{-2}$ g/cm^3.

Evaluation of the intrinsic viscosity from initial slops of lnη_r and/or η_{sp} dependencies on *c*

The definitions of the intrinsic viscosity [η] were given for the first time by Staudinger and then by Kraemer [7, 8] through the equations:

$$\lim(\eta_{sp}/c)_{c\to 0} \equiv [\eta] = \partial\eta_{sp}/\partial c_{\ c\to 0} \qquad (4)$$

$$\lim(\ln\eta_r/c)_{c\to 0} \equiv [\eta] = \partial\ln\eta_r/\partial c_{\ c\to 0} \qquad (5)$$

where $\eta_{sp} = \eta_r - 1$ is the specific viscosity of the solution and $\eta_r = (\eta/\eta_0)$ is its relative viscosity, η_0 and η are the dynamic viscosities of the solvent and solution, respectively; *c* is the concentration of polymer in solution. To determine the [η] value from Equations (4) and (5), it is necessary to plot the $\eta_{sp}=f_1(c)$ and/or $\ln\eta_r=f_2(c)$ dependencies and to measure their initial slopes at $c\to 0$ (Figures ESI 6 and ESI 7).

Table ESI 1. Values of Intrinsic viscosity and Huggins and Kraemer parameters for alkylated copolymer of N-methyl-N-vinyl acetamide and N-methyl-N-vinyl amine (MVAA-MVA$C_{12}H_{25}$), non alkylated copolymer of N-methyl-N-vinyl acetamide and N-methyl-N-vinyl amine hydrochloride, and Polystyrene.

Sample no.*	Solvent	$^{\#}[\eta]_{\eta sp/c}$, cm^3/g	*k'*	$^{\#}$ $[\eta]_{\ln\eta r/c}$, cm^3/g	*k''*	* $[\eta]_{\eta sp}$, cm^3/g	$^*[\eta]_{\ln\eta r}$, cm^3/g	** $[\eta]^{all}_{av}$, cm^3/g	Fig.
1	H_2O+NaCl 0.1M	69±1	0.88	69±1	+0.23	67±1	69±1	68.5±0.8	1, ESI1
	DMF+LiCl 0.1M	50±1	0.39	50.3±0.6	–0.15	46.4±0.4	44.6±0.4	48±3	4, ESI3
6	H_2O+NaCl 0.1M	166±1	0.35	165.4±0.7	–0.14	170±1	167±1	167±2	2, ESI2
Polystyrene (*M*=1.45×10^6 g/mol)	decalin at 20°C, θ–solvent	84	0.68	-	-	-	-	-	5, ESI4
	bromoform 25°C	240	0.29	-	-	-	-	-	
	decalin 80°C	161	0.48	-	-	-	-	-	

* Sample numbers correspond to numbers in Table 1.

Values obtained from intercepts of Huggins and Kraemer plots, see Eqs. (2) and (3) main text,

* Values obtained from initial slopes (Figures ESI 6 and ESI 7),

** Average of four estimations.

Table ESI 2. Results of Viscosity Measurements for alkylated Sample 1 in 0.1M NaCl. See Figure1 main text.

c, 10^{-2} g/cm^3	t, s	η_r	η_{sp}/c, 10^2 cm^3/g	$\ln\eta_r/c$, 10^2 cm^3/g	$\ln\eta_r$	η_{sp}
2.0102	865.3	10.350	4.652	1.163	2.337	9.350
1.7424	528.0	6.316	3.051	1.058	1.843	5.316
1.49	355.5	4.252	2.183	0.972	1.447	3.252
1.1939	240.25	2.874	1.569	0.884	1.056	1.874
0.9804	189.16	2.263	1.288	0.833	0.817	1.263
0.7398	149.88	1.793	1.072	0.789	0.584	0.793
0.5261	124.23	1.486	0.924	0.753	0.396	0.486
0.398	112.08	1.341	0.856	0.737	0.293	0.341
0.2997	104.03	1.244	0.815	0.730	0.219	0.244
0.1975	96.26	1.151	0.767	0.714	0.141	0.151
0.07006	87.82	1.050	0.720	0.703	0.049	0.050

Table ESI 3. Results of Viscosity Measurements for non alkylated sample 6 in 0.1M NaCl.

See Fig.2 main text.

c, 10^{-2} g/cm^3	t, s	η_r	η_{sp} /c, 10^2 cm^3/g	$\ln\eta_r$/c, 10^2 cm^3/g	$\ln\eta_r$	η_{sp}
1.3868	417.7	4.949	2.848	1.153	1.599	3.949
1.1882	356.**1**	4.219	2.709	1.212	1.440	3.219
0.9866	296.4	3.512	2.546	1.273	1.256	2.512
0.805	247.6	2.934	2.402	1.337	1.076	1.934
0.6684	213.7	2.532	2.292	1.390	0.929	1.532
0.5162	178.57	2.116	2.161	1.452	0.749	1.116
0.3978	153.5	1.819	2.058	1.504	0.598	0.819
0.2796	130.3	1.544	1.945	1.5539	0.434	0.544
0.1749	111.5	1.321	1.836	1.592	0.278	0.321
0.08979	97.5	1.155	1.729	1.607	0.144	0.155

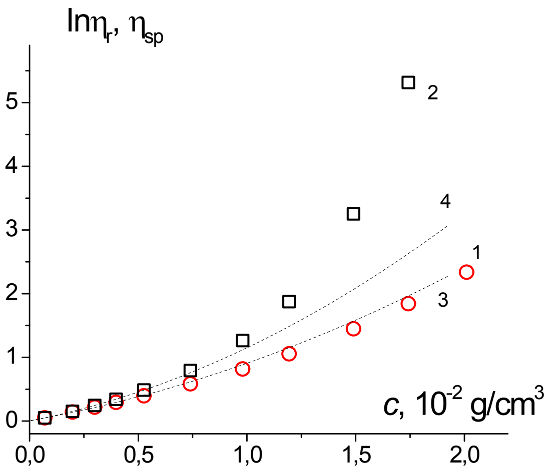


Figure ESI 6. Concentration dependences of $\ln\eta_r$ (1) and η_{sp} (2) for alkylated copolymer MVAA-MVAC$_{12}$H$_{25}$ (Sample 1 in Table 1) in 0.1 M NaCl. $[\eta]_{\ln\eta r}$=(69±1) cm^3/g, $[\eta]_{\eta sp}$= (67±1) cm^3/g, , (3) and (4) – approximations of $\ln\eta_r$ and η_{sp} dependences in the low concentration region, $c[\eta]< 0.5$, by second degree polynomials. The average meaning $[\eta]^{all}_{av}$=68.5±0.8 cm^3/g.

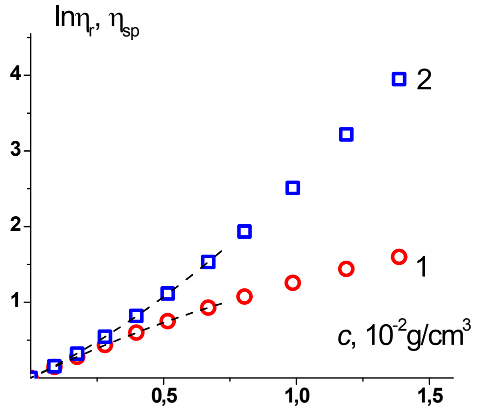


Figure ESI 7. Concentration dependences of lnη_r (1) and η_{sp} (2) for nonalkylated MVAA-MVAH copolymer (Sample 6 in Table 1) in 0.1 M NaCl. $[\eta]_{sp}$ =(170±1) cm^3/g, $[\eta]_{\ln\eta r}$=(167±1) cm^3/g. The average meaning $[\eta]^{all}_{av}$= (167±2) cm^3/g.

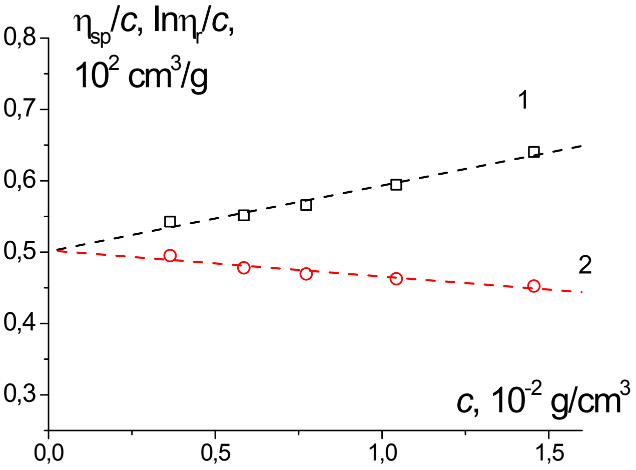


Figure ESI 8. Concentration dependences of η_{sp}/c (1) and lnη_r/c (2) for alkylated copolymer MVAA-MVAC$_{12}$H$_{25}$ (Sample 1 in Table 1) in DMF+0.1MLiCl. k'= 0.37, k''= –0.15.

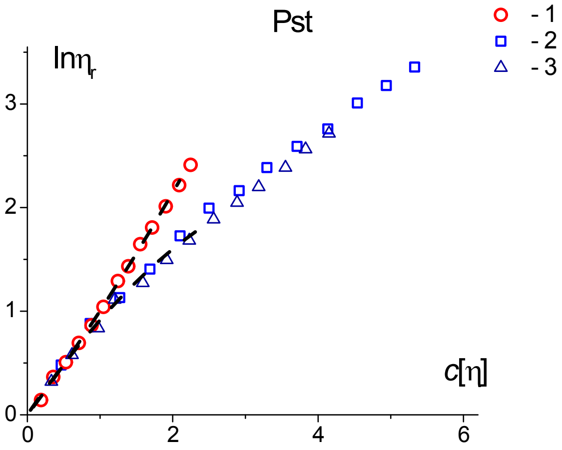


Figure ESI 9. Dependence of lnη$_r$ on degree of dilution c[η] for linear polystyrene (M = 1.45×10^6 g/mol) in vicinity of θ-condition (decalin at 20°C) (1) and in thermodynamically good solvents: bromoform (2) and decalin (at 80°C) (3). (1) Decalin 20^{o}C, θ-temperature [η]=84, k'=+0.68, lnη$_r$= 0.96c[η] + 0.054(c[η])^2 at c[η]<2; (2) bromoform 25^{o}C [η]=240, k'=+0.29, lnη$_r$= 0.96c[η] - 0.10(c[η])^2 at c[η]<2; (3) decalin 80^{o}C [η]=161, k'=+0.48, lnη$_r$= c[η] - 0.13(c[η])^2 at c[η]<2 [9].

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