Polyacrylamide Hydrogels with Trapped Polyelectrolyte Rods

Olga E. Philippova,*,† Rudy Rulkens,‡ Boris I. Kovtunenko,† Sergei S. Abramchuk,§ Alexei R. Khokhlov,† and Gerhard Wegner‡

Physics Department, Moscow State University, Moscow 117234, Russia, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, Mainz D-55128, Germany, and Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilova 28, Moscow 117813, Russia

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ABSTRACT: A new type of intermacromolecular system consisting of a flexible polymer gel with embedded synthetic rigid-rod linear polyelectrolyte has been investigated for polyacrylamide hydrogel and linear poly(4,4″-(disodium 2,5-dimethyl-1,1′:4′,1″-terphenyl-3′,2″-disulfonate)). It has been shown that the incorporation of stiff-chain polyelectrolyte inside the uncharged network improves both the ability to absorb water and the mechanical strength of the gel. This makes such systems potentially promising as superabsorbent materials. Study of the kinetics of the release of polyelectrolyte rods has shown that the rods are effectively retained by the gel although they are not covalently attached to the network chains. This is apparently due to the formation of aggregates of rods including some of the network chains. The release can be completely suppressed by the addition of low-molecular-weight salt, which favors the self-aggregation of similarly charged rods. An interpenetrating network consisting of a physical network of anionic rods cross-linked by bivalent cations and of chemically cross-linked polyacrylamide has been synthesized. It has been shown that the binding of the polyelectrolyte by bivalent cations in a physical network prevents very effectively its release to the solution. The quantitative theory of the kinetics of gel swelling coupled with the release of rods from the gel has been developed. The main results of the theory are in good agreement with the experimental data.

Introduction

In the present paper we study a new type of intermacromolecular system consisting of a three-dimensional network of a flexible polymer with embedded synthetic rigid-rod linear polyelectrolyte. Synthetic water-soluble polyelectrolytes with a rigid-rod backbone were prepared only recently.[1−13] The study of these substances gives a further refinement of our knowledge of the chemistry and physics of polyelectrolytes.

Here it is of particular interest to investigate the behavior of charged rods inside the hydrogels and their influence on the gel properties. The incorporation of polyelectrolyte rods in a flexible network can impart some useful properties to the hydrogel. In particular, it may enhance the gel swelling due to the exerting osmotic pressure of counterions of the rods; at the same time it can mechanically reinforce the hydrogel, which is potentially promising for the creation of superabsorbent materials with optimized properties. For such a purpose previously different substances were proposed, for example clay minerals.[14]

With this application in mind the rigid rods should be held tightly in the gel. As the stiff-chain polyelectrolyte is not covalently attached to the network, we should find out the conditions under which the release of the rods from the gel becomes negligibly slow. In addition, a study of the kinetics of release of the stiff-chain polyelectrolyte could provide useful information about the interaction of the gel with charged rods during their reptational diffusion as well as about the structure of the gel.

The aim of the present paper is to study the properties of a rodlike polyelectrolyte/flexible hydrogel system on the basis of a neutral polyacrylamide (PAA) gel and a rigid-rod linear polyelectrolyte [poly(4,4″-(disodium 2,5-dimethyl-1,1′:4′,1″-terphenyl-3′,2″-disulfonate)) (PPP3) shown in Figure 1]. We will study the swelling behavior and the mechanical characteristics of PAA hydrogels with incorporated PPP3 rods as well as the factors influencing the release of the polyelectrolyte from the network.

Experimental Section

Synthesis and Characterization of the Rigid-Rod Polyelectrolyte PPP3. The synthesis of PPP3 (polymer 3 in ref 11) has been described previously.[11] Characterization of the precursor polymer which had sulphonate groups protected as 3,5-di-*tert*-butylphenolate, which allowed the characterization of the material by conventional methods, has been presented elsewhere.[12] The following values of the degrees of polymerization have been determined: $P_n = 86$, $P_w = 204$ (size exclusion chromatography, universal calibration technique); $P_n = 105$ (osmometry), $P_w = 239$ (light scattering). The persistence length of the precursor polymer was 14.4 nm. This value comes from the comparison of intrinsic viscosity, size exclusion chromatography, osmometry, and light-scattering data. It is evaluated according to the procedure described in ref 13. The obtained value of persistent length when compared with the contour length assumes that the polymer behaves as a wormlike persistent chain. The chain in its protected form contains approximately five Kuhn segments. In the present work PPP3 is used in a sodium salt form. The sodium salt is made by titration with 0.1 M NaOH in a water/ethanol (1:1 v/v) mixture.[11]

Synthesis and Characterization of Linear Polyacrylamide. Linear PAA was prepared by free-radical polymerization of acrylamide in solution. Ammonium persulfate (4.4×10^{-3} mol/L) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (4.4×10^{-3} mol/L) were used as initiator and accelerator, respectively. The concentration of the monomer was 80 g/L. A mixture of water and ethanol (4:1 v/v) was used as solvent. The polymerization was carried out at room temperature for 22 h. PAA was then precipitated from the reaction mixture

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* To whom correspondence should be addressed.

† Moscow State University.

‡ Max-Planck-Institut fuer Polymerforschung.

§ Russian Academy of Sciences.

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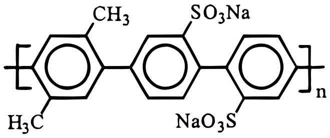

Figure 1. Chemical structure of rigid-rod polyelectrolyte PPP3.

into a 7−10-fold excess of ethanol.

The molecular weight of PAA (340 000) was calculated using intrinsic viscosity data in 1 M $NaNO_3$ aqueous solution at 30 °C according to $[\eta] = (3.73 \times 10^{-4})M_{\eta}^{-0.66}$. The absence of COOH groups in PAA was confirmed by IR spectroscopy.

Gel Preparation. (A) Polyacrylamide Gels with Trapped PPP3. The gels were prepared by free-radical copolymerization of acrylamide in aqueous solutions of PPP3 with *N*,*N*′-methylenebis(acrylamide) (BAA) as the cross-linker. Ammonium persulfate (2.1×10^{-3} mol/L) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (2.1×10^{-3} mol/L) were used as initiator and accelerator. The initial concentrations of monomer, linear polyelectrolyte PPP3, and BAA for different gel samples are listed in Table 1. The gel synthesis was carried out in cylindrical glass tubes with an inner diameter of 0.40 cm at room temperature for 18 h.

In the following, the polyacrylamide gels which are synthesized in aqueous solutions of stiff-chain polyelectrolyte PPP3 are marked with an asterisk (PAA1*−PAA5*). The reference polyacrylamide gels, which are prepared under similar conditions but without a polyelectrolyte, are designated as PAA1−PAA4.

Two gel samples were further prepared in aqueous solutions of PPP3 in the presence of low-molecular-weight salt. The gel PAA2*−NaCl was synthesized in a solution of PPP3 in 0.05 M NaCl, and the gel PAA2*−$CaCl_2$ was obtained in a solution of PPP3 in 0.016 M $CaCl_2$ (Table 1).

(B) Polyacrylamide Gels with Trapped Poly(sodium *p*-styrenesulfonate). The gels were prepared under the same conditions as for PAA1*−PAA5* gels but with poly(sodium *p*-styrenesulfonate) (PSS) instead of PPP3. PSS (M_w = 70 000) from Aldrich was used as received. For the sake of comparison the molar concentration of charged groups of PSS in the polymerization mixtures was kept the same as in the corresponding PPP3-containing samples. The conditions of preparation of PAA−PSS gels are given in Table 1.

(C) Poly(acrylamido-*co*-sodium 2-acrylamido-2-methylpropanesulfonate) Gel. The gel designated further as PAA−AMPSA gel was prepared by copolymerization of acrylamide with sodium 2-acrylamido-2-methylpropanesulfonate (in 97.45/2.55 molar ratio) under the same conditions as for the PAA4* gel.

Gel Swelling. The degree of swelling of the gel samples was characterized by the ratio m/m_0, where m is the mass of the gel sample swollen in aqueous solution and m_0 is the mass of the dry gel. The values of the degree of swelling of the gels in water and in 0.2 M NaCl are compiled in Table 2.

Kinetic Studies. To study the release of rods from the gel, the gel samples just after the preparation were put to swell in water or in sodium chloride solution. Unless otherwise specified, the volume of solution was 2.50 mL per 1 mg of the dried gel. During the experiment the solution with a gel specimen was agitated by a shaker (Edmund Bühler 7400 Tubingen "KL2"). At certain intervals the mass of the gel and the concentration of PPP3 in the surrounding solution were measured until constant values of these parameters were attained. In all the experiments water purified by a Milli-Q system (Millipore) was used.

The concentration of the rigid-rod polyelectrolyte PPP3 in the solution was measured by UV spectroscopy using the optical density at $\lambda_{max} = 272.7$ nm ($\epsilon = 2.32 \times 10^4$ L/(mol cm)). UV spectra were recorded on Perkin Elmer Lambda 9 UV/vis spectrophotometer. The content of PPP3 in the gel phase was evaluated by subtraction of the amount of polyelectrolyte in the surrounding solution from the initial amount of polyelectrolyte. The fraction of the polyelectrolyte in the gel was characterized by the molar ratio between PPP3 and PAA repeat units in the gel θ. The initial molar ratio of PPP3 and PAA repeat units in the system is designated as θ_0. The efficiency of the retaining of stiff-chain polyelectrolyte by the gel was characterized by the ratio C_g/C between the concentrations of PPP3 in the gel, C_g, and in the surrounding solution, C.

The analogous measurements were made for PAA-PSS gel using the absorption band at $\lambda_{max} = 262.0$ nm ($\epsilon = 550$ L/(mol cm)).

SAXS Measurements. The SAXS data were obtained with a Kratky camera using a slit collimation. A Cu *K*α X-ray source was used. The scattering rays were counted by a wire counter in the range $0.2\ \text{nm}^{-1} < q < 3.2\ \text{nm}^{-1}$, where q is the scattering vector. The data were desmeared as described in ref 15.

Mechanical Measurements. Evaluation of the Young E and shear G moduli of the gel samples was carried out by means of a resonance technique. The upper side of the cylinder gel sample was attached to a surface of a massive steel plate. A very small thin ferromagnetic steel plate was attached to the bottom of the sample and was subjected to the influence of a low-frequency electromagnetic field. As a result a periodic mechanical force was acting on the gel at a given frequency. The amplitude of the sample deformation was measured optically with the accuracy 0.001 mm. The vibration frequency was measured with the accuracy 0.1 Hz. Damping of the oscillations was negligible. An additional check of the validity of the measurements was performed, verifying the well-known expression $E = 3G$. This equality was always valid within an accuracy of ±5%.

Results and Discussion

Properties of Gels with Trapped Stiff-Chain Polyelectrolyte. To incorporate charged rods in a polyacrylamide gel, the polymerization of acrylamide together with a cross-linking agent was performed in a solution of the linear rigid-rod polyelectrolyte. As a result of the network formation, most of the polyelectrolyte rods became trapped by the gel. The characteristic data of the gels prepared in this way and swollen to equilibrium in water or in 0.2 M NaCl solution are presented in Table 2. For the sake of comparison, the data for reference PAA gels are given as well.

Gels Swollen in Water. Examination of the values of the equilibrium degree of swelling of the gels in water shows that the incorporation of the linear stiff-chain polyelectrolyte into the uncharged gel results in a gel swelling (Table 2). This is a consequence of the osmotic pressure exerted by counterions of the rigid-rod polyelectrolyte.[16,17]

As one might expect, the swelling of PAA* gels increases also with lowering of the cross-link density (cf. PAA1*, PAA2*, PAA3*).

Usually the swelling of the gels results in a deterioration of their mechanical characteristics, in particular, lowering of the modulus of elasticity E. The values of E of the gels swollen in water are presented in Table 2. It is seen that the gels with trapped polyelectrolyte rods possess significantly higher moduli of elasticity than the corresponding reference gels in spite of the fact that the incorporated polyelectrolyte rods induce a considerable swelling of the gel and hence a decrease of the concentration of elastically active chains. Thus, the introduction of linear rigid-rod polyelectrolyte improves both the ability to absorb water and the mechanical strength of the gel.

Gels Swollen in Aqueous Salt Solutions. Figure 2 shows the equilibrium degrees of swelling of the gels in NaCl solutions of different concentrations. It is seen

Table 1. Conditions of Preparation of the Gels

N	sample	solvent	C_M°,[a] g/L	C_{BAA}°,[b] mol %	C_{PPP3}°,[c] g/L	C_{PSS}°,[d] g/L
1	PAA1*	water	47	0.0033	9.0	0
2	PAA2*	water	47	0.0050	9.0	0
3	PAA2*−NaCl	0.05 M NaCl	47	0.0050	9.0	0
4	PAA2*−CaCl$_2$	0.016 M CaCl$_2$	47	0.0050	9.0	0
5	PAA3*	water	47	0.0100	9.0	0
6	PAA4*	water	90	0.0050	9.0	0
7	PAA5*	water	90	0.0050	20.0	0
8	PAA1	water	47	0.0033	0	0
9	PAA2	water	47	0.0050	0	0
10	PAA3	water	47	0.0100	0	0
11	PAA4	water	90	0.0050	0	0
12	PAA2−PSS	water	47	0.0050	0	8.0
13	PAA4−PSS	water	90	0.0050	0	8.0
14	PAA5−PSS	water	90	0.0050	0	18.2

[a] C_M° is the initial concentration of acrylamide in the polymerization mixture. [b] C_{BAA}° is molar fraction of cross-linker with respect to acrylamide in the polymerization mixture. [c] C_{PPP3}° is the concetrantion of PPP3 in the polymerization mixture. [d] C_{PSS}° is the concentration of PSS in the polymerization mixture.

Table 2. Characteristic Data of the Gels Swollen to Equilibrium in Water and in 0.2 M NaCl Solution

		water			0.2 M NaCl		
N	sample	m/m_0[a]	C_{PPP3},[b] g/L	*E*,[c] kPa	m/m_0	C_{PPP3}, g/L	*E*, kPa
1	PAA1*	130	1.0	1.94			
2	PAA2*	99	1.1	2.73	78	1.1	3.58
3	PAA3*	64	1.8	7.22			
4	PAA4*	31	2.7		19	4.8	17.50
5	PAA5*	56	2.8		16	11.1	27.00
6	PAA1	56	0	0.90		0	
7	PAA2	48	0	1.57	50	0	
8	PAA3	38	0	3.88		0	
9	PAA4	23	0		22	0	11.95
10	PAA2−PSS	66	0	0.52	52	0	0.68
11	PAA4−PSS	31	0		23	0	4.5
12	PAA5−PSS	32	0		22	0	4.3

[a] m/m_0 is the ratio of mass of the swollen and dry gels. [b] C_{PPP3} is the concentration of PPP3 in the swollen gel. [c] *E* is the modulus of elasticity of the gel.

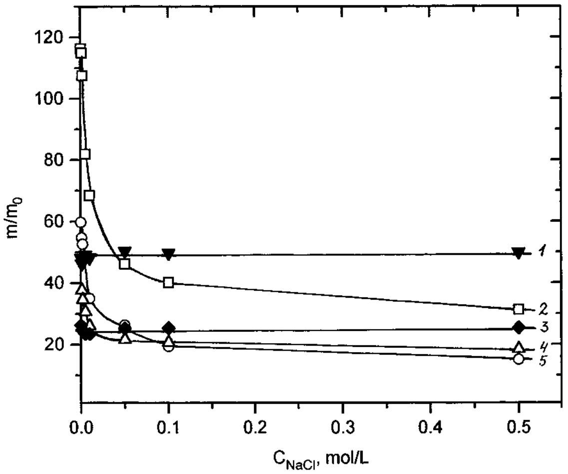

Figure 2. Degree of swelling of the gels PAA2 (1), PAA2* (2), PAA4 (3), PAA4* (4), and PAA5* (5) as a function of the concentration of NaCl.

that for uncharged reference gels the degree of swelling is the same in water and in aqueous salt solutions. The situation is different for PAA* gels containing stiff-chain polyelectrolyte. The degree of swelling of these gels decreases with increasing concentration of NaCl and then levels off (Figure 2). This reminds us of the usual deswelling of polyelectrolyte gels in salt solution.[18,19]

The limiting values of the degrees of swelling of PAA* gels at high salt concentrations are lower than those of the uncharged PAA gels. The extra contraction of PAA* gels may be caused by the hydrophobic aggregation of the charged rods entangled in the network chains. Low-molecular-weight salt favors the aggregation of similarly charged macroions because of the screening of electrostatic repulsion. The additional evidence for the polyelectrolyte aggregation in the gel will be provided later.

The moduli of elasticity *E* of the gels swollen in 0.2 M NaCl are given in Table 2. For PAA2* gel it is seen that the value of *E* for the gel swollen in 0.2 M NaCl is higher than that for the gel swollen in water. This is mainly due to the deswelling of PAA* gel in salt solution, which leads to the increase of the concentration of elastically active chains. At the same time the elastic moduli increase for the PAA* gels with higher content of charged rods (cf. PAA4, PAA4*, and PAA5* gels). Thus, the stiff-chain polyelectrolyte behaves as a reinforcing filler agent for the hydrogel. It should be pointed out that, to influence the moduli of elasticity of the gel, the polyelectrolyte rods should interact strongly with elastically active network chains.

Aggregation of Rods. As was shown above, the incorporation of charged rods in the uncharged gel leads to the gel swelling. It is of interest to compare the degree of swelling of the PAA* gels with trapped PPP3 with that of the model PAA−AMPSA gel containing the same amount of charged groups attached to the network chains.

Such a comparison was made for the PAA4* gel with 2.55 mol % of charged groups of PPP3 with respect to network chain units. The equilibrium degree of swelling of this gel in pure water ($m/m_0 = 31$) is substantially lower than that of the model PAA-AMPSA gel ($m/m_0 = 103$). This discrepancy can be due to the partial

Table 3. Interaggregate Distances in Aqueous Solutions of PPP3 at Concentrations of Rigid-Rod Polyelectrolyte Used at the Network Preparation

$C_{PPP3}°$, g/L	d_B,[a] nm	d,[b] nm
9.8	12.5	14.5
20.0	8.7	10.1

[a] d_B is the Bragg distance representing interference between layers of columns. [b] d is the distance between the columns with $d_B = {}^1/_2\sqrt{3}d$.

condensation of PPP3 counterions in the PAA4* gel.

According to Manning's theory,[20] the condensation of counterions in water at room temperature begins when the distance between charged groups is lower than approximately 7.0 Å. In a PPP3 chain the average distance between charged groups is approximately 6.4 Å. Thus, in a single PPP3 chain all the counterions should be free. The condensation may be due to the aggregation of several PPP3 molecules in a rod. In this case the charge density increases by a factor of N_{agr} (where N_{agr} is the average number of molecules in one aggregate) and a certain fraction of counterions becomes condensed in the vicinity of the rod by a strong electric field. Thus, the reduced swelling of the PAA4* gel can be connected with the aggregation of PPP3 chains inside the gel.

Such aggregation of PPP3 chains in solution is evidenced by SAXS measurements. Experimental investigation of PPP3 as a sodium salt in an otherwise salt-free solution by SAXS showed that at room temperature the aggregation between the chains takes place at concentrations as small as 8 g/L. Analysis of the SAXS data revealed that the radial aggregation number is approximately 3, independent of the concentration up to the bulk state. This value follows from the structure factor, which can be interpreted as a Bragg peak and is clearly prevalent at a concentration higher than 8 g/L up to the solid state. These threefold strand aggregates are arranged in a hexagonal columnar fashion, the lattice parameters being dependent on the overall concentration. The interaggregate distances at concentrations where the gels were synthesized are presented in Table 3. No definite information concerning the aggregation number along the columnar axis is available yet. However, viscosity data indicate that it may be much larger than the contour length of the parent polymer. Further information concerning the type of lateral aggregation has been obtained from crystal structure analysis of model oligomers.[10] The salient feature is contained in Figure 3, showing a projection of the structure of the aggregate along the columnar axis and on a plane normal to the columnar axis.

Thus, the PPP3 rods are aggregated even in a salt-free solution. SAXS data show that in NaCl solutions the radial aggregation number of the rods (equal to approximately 3) remains the same as that in the salt-free solution. At the same time it is reasonable to suppose that low-molecular-weight salt should facilitate the self-aggregation of anionic rods. This assumption is supported by viscosity measurements.[11] It was shown that in the presence of NaCl the reduced viscosity of aqueous solutions of PPP3 increases exponentially with increasing concentration of PPP3, while in the absence of NaCl it drops slightly. Bearing in mind the constant value of radial aggregation number of the rods in water and in NaCl solutions, this fact could be explained, in particular, by the increase of the number of rods along the columnar axis. Alternatively, one can suppose that single PPP3 chains can cross over from one aggregate to another acting as cross-links.

The growth of the aggregates of rods may be responsible for the extra contraction of PAA* gel at high salt concentrations (Figure 2). At the same time, SAXS of PAA* gels swollen in 0.1 M and 0.5 M NaCl did not reveal any Bragg maxima. This fact does not exclude the self-aggregation of PPP3, but it indicates that such aggregates inside the gel are not arranged periodically with respect to each other like they do in solution. Probably, the statistically disordered network interferes with a possible periodic order among the aggregates. The disturbance of the spatial order of rodlike molecules incorporated in a gel was described previously.[21−23] Also, we can suppose that the scattering intensity caused by PAA network levels off the differences in scattering intensity caused by PPP3 aggregates.

Release of Polyelectrolyte Rods by the Gel. Being immersed in aqueous solutions, the PAA* gels lose a part of the polyelectrolyte rods because of their diffusion in the surrounding solution. Many factors are found to influence this process: the cross-linking density of the gel, the concentration of monomer (acrylamide) and of polyelectrolyte rods at the network preparation, and the presence of low-molecular-weight salt.

(A) Release in Water. The fraction of PPP3 released in water, q, and the ratio of concentrations C_g/C of the polyelectrolyte in the gel and in the solution (after final equilibration) are presented in Table 4. From this table it is seen that the gel retains a major part of the polyelectrolyte rods. The fact that most of the rods do not diffuse to the external solution but become trapped in the gel can be explained by partial aggregation of rods in the gel medium. Since the average length of the rods (∼150 nm) is more than 10 times larger than the mesh size of the gel (∼12 nm), such aggregation should involve the gel chains, leading to the effective immobilization of the aggregates.

The increase of both the degree of cross-linking and the concentration of monomer (acrylamide) at the network formation reduces the release of stiff-chain polyelectrolyte, the effect of the concentration of the monomer being much more pronounced. For instance, a twofold increase of the concentration of monomer (cf. PAA2* and PAA4* gels) leads to a fall of q by a factor of 2.5, while a twofold increase of the cross-linking density results only in a slight lowering of q by 10%. A decrease of the initial molar ratio between PPP3 and PAA gel repeat units θ_0 also reduces the release of PPP3. These data may indicate interactions between the gel chains and polyelectrolyte rods.

A priori it could be suggested that the release of polyelectrolyte should depend on the volume of the surrounding solution. The data presented in Table 4 show that the increase of the volume of the surrounding solution affects mainly the C_g/C values, which directly depend on the volume ratio between the gel and the solution, while the fraction of the released polyelectrolyte changes insignificantly.

(B) Release in Aqueous Salt Solutions. The influence of the addition of sodium chloride on the release of rigid-rod polyelectrolyte is illustrated in Figure 4. It is seen that the fraction of PPP3 expelled from the gel (after final equilibration) decreases with increasing concentration of sodium chloride and reaches a limiting value at $C_{NaCl} > 0.01−0.05$ mol/L. The fact that low-molecular-weight salt prevents the release of

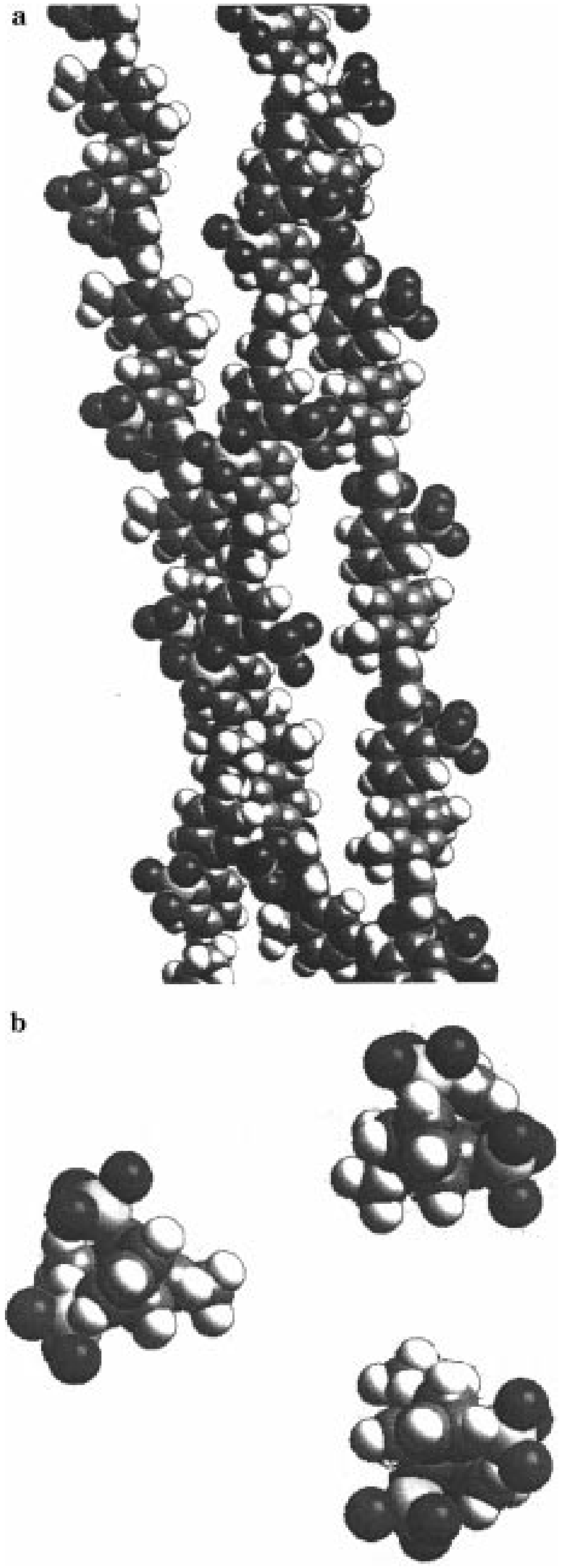

Figure 3. Schematic representation of the aggregate of PPP3 along the columnar axis (a) and projection of the aggregate on a plane normal to the columnar axis (b).

polyelectrolyte rods from the gel can be related to the additional aggregation of the polyelectrolyte in salt solution. The rods in the aggregates are effectively immobilized; hence, the fraction of the released rods decreases at higher salt concentrations. Also, the addition of NaCl makes the entropic effect of the release of polyelectrolyte to the external solution less important.

The release of PPP3 is more significant for PAA2* and PAA5* gels. This implies that the fraction of the released PPP3 depends on the initial molar ratio between PPP3 and PAA gel repeat units θ_0.

The ratios of concentrations of polyelectrolyte rods in the gel and in the solution C_g/C (after final equilibration) as a function of salt concentration in the external solution are presented in Figure 5. This figure clearly demonstrates that most of the polyelectrolyte rods are retained in the gel. In addition, the values of C_g/C increase as the concentration of sodium chloride increases. The highest values of C_g/C are obtained for the PAA4* gel with the lowest θ_0 among the studied PAA* gels. This may be the consequence of the interaction of the network chains with the charged rods, preventing their release.

Figures 2, 4, and 5 show that the most significant changes of the degree of swelling of PAA* gels, as well as of the fraction of the released polyelectrolyte and the C_g/C ratio, take place at salt concentrations lower than 0.01 mol/L, which is less than or close to the concentration of charged groups of PPP3 inside the gel. Thus, the addition of low-molecular-weight salt to the external solution reduces the release of PPP3; at the same time it causes the osmotic deswelling of the gel.

To check whether the final degree of swelling of the gel m/m_0 and the fraction of released polyelectrolyte, q, correspond to the equilibrium in the system, the following experiment was performed. The PAA2* gel was swollen in water until m/m_0 and q values no longer changed. The swollen gel thus obtained, designated further as PAA2**, was cut into two parts. One of them was dried at room temperature; the other one was left intact, that is in the swollen state. Then the both PAA2** gels were immersed in pure water. Figure 6 shows that after final equilibration in a new solution the degree of swelling of the initially dried gel is lower than that of the initially swollen gel. This shows that in this system the equilibrium is not reached. As to the release of the stiff-chain polyelectrolyte, the low-molecular-weight salt prevents almost completely the release of PPP3 from both PAA2** gel samples at $C_{NaCl} > 0.01$ mol/L. At lower salt concentrations the fraction of the released PPP3 is higher for the initially swollen gel; for example, in water the final q values are equal to 0.103 and 0.067 for the initially swollen and dry gels, respectively.

The results obtained can be explained as follows. Upon drying, the concentration of rods within the gel essentially increases, inducing the additional aggregation of rods. This aggregation may be not reversible when the dry gel is further immersed in a solution; therefore, the reswelling of the gel is not complete. So, the aggregation of rigid rods inside the gel can be responsible for the emergence of the nonequilibrium state of the PAA* gels.

If we take a flexible polymer, PSS, instead of rigid rod one (PPP3), the behavior of the PAA gel with incorporated linear chains becomes quite different. In this case the gel looses almost all the polyelectrolyte. The gels with extracted PSS (PAA−PSS gels) possess elastic moduli even lower than those of the correspond-

Table 4. Fraction of Rigid-Rod Polyelectrolyte PPP3 Released in Water, q, and the Ratio of Concentrations of PPP3 in the Gel and in Solution C_g/C

N	sample	m/m_0	θ_0[a]	θ[b]	q[c]	C^g/C^c	q[d]	C^g/C^d
1	PAA1*	130	0.030	0.020	0.34	34	0.31	
2	PAA2*	99	0.030	0.021	0.31	50	0.29	5.5
3	PAA3*	64	0.030	0.022	0.28	90	0.22	9.9
4	PAA4*	31	0.015	0.013	0.13	660		
5	PAA5*	56	0.034	0.026	0.24	150		

[a] θ_0 is the initial molar ratio between PPP3 and polyacrylamide repeat units in the system. [b] θ is the molar ratio between PPP3 and polyacrylamide repeat units in the gel. [c] Initial volume ratio between the solution and the gel: 137.6. [d] Initial volume ratio between the solution and the gel: 12.2.

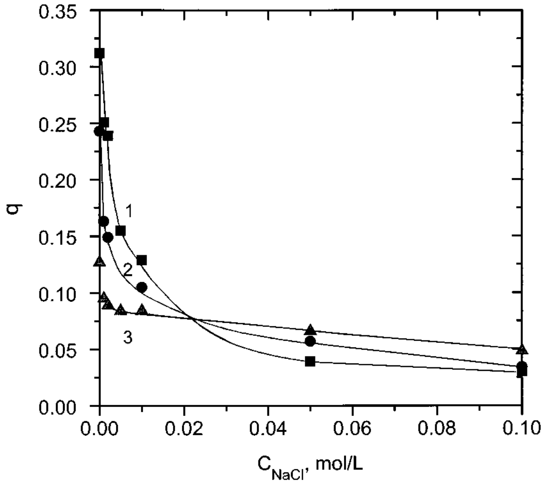

Figure 4. Fraction of PPP3 released from the gel, q, as a function of concentration of NaCl for PAA2* (1), PAA5* (2), and PAA4* (3) gels.

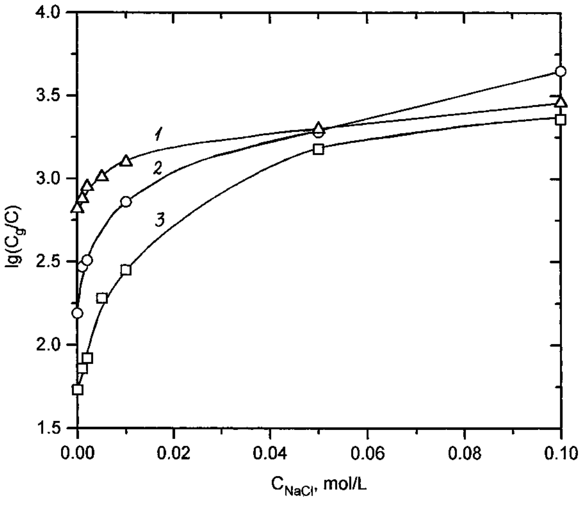

Figure 5. Final ratio C_g/C between the concentration of PPP3 in the gel and in the solution as a function of concentration of NaCl for PAA4* (1), PAA5* (2), and PAA2* (3) gels.

ing reference PAA gels (Table 2). This may be due to the fact that PSS chains hinder the formation of a more dense polyacrylamide network. A rather high degree of swelling of PAA−PSS gels (Table 2) counts in favor of this supposition.

Kinetics of the Release of Polyelectrolyte Rods from the Gel. The kinetic curves of the release of polyelectrolyte from the gels are presented in Figures 7a and 8a. From these data we can see that the initial rate of the release decreases with the increase of salt concentration. As was discussed above, the low-molecular-weight salt favors the aggregation of similarly charged rods, thus preventing their release to the external solution. In addition, NaCl lowers the gain in entropy due the release of PPP3.

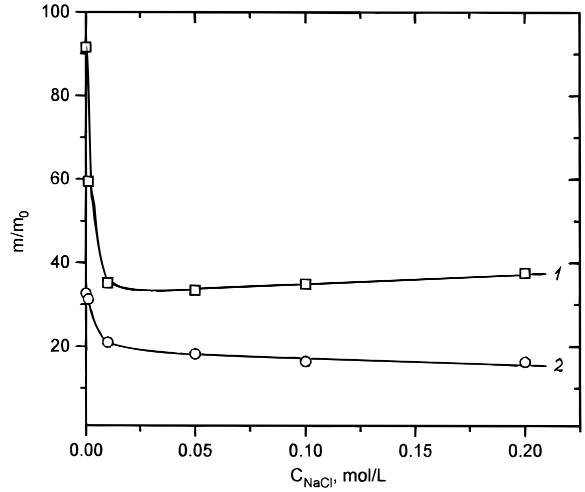

Figure 6. Final degree of swelling of PAA2** gel as a function of the concentration of NaCl for initially swollen (1) and initially dry gel (2).

The kinetic curves of the change of the degrees of swelling of the gels are shown in Figures 7b and 8b. From these figures we notice that in water the gels at first swell and then shrink with time. What can be the reason for such a nonmonotonous kinetic dependence of the degree of swelling? In water the kinetic curves of the change of the degree of swelling of the gel reflect at least three processes: first, the swelling of the uncharged gel in a good solvent; second, the swelling due to the osmotic pressure of counterions of PPP3 entrapped by the gel; third, the contraction due to the release of PPP3 by the gel. The comparison of the curves for PAA* gels with those for the corresponding reference PAA gels allows us to estimate the contribution of the first process to the overall gel swelling (Figures 7b and 8b). It can be seen that for PAA* gels swelling in water the role of this first process is relatively small. Thus, the main effect causing the gel swelling at the initial stage of kinetic measurements is the osmotic pressure generated inside the gel by mobile counterions of entrapped PPP3. When stiff-chain polyelectrolyte with its counterions leaves the gel, the swelling pressure becomes lower, which forces the gel to shrink.

The rate of the gel shrinking can be influenced by a number of different processes, including stimulus rate (defined by the nonequilibrium diffusion of PPP3 from the gel due to the concentration gradient) and polymer network relaxation to a more contracted configuration. To identify the rate-limiting steps, the kinetic curves of the gel swelling and the PPP3 release by the gel should be compared. From Figures 7 and 8 it is clear that the rate of PPP3 release in water is somewhat

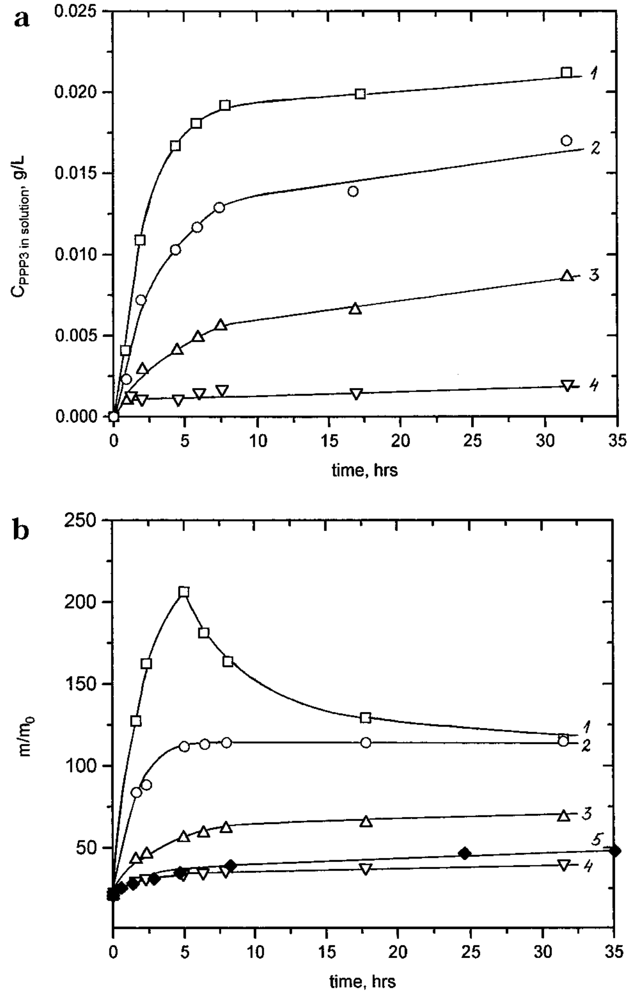

Figure 7. (a) Kinetics of release of PPP3 from the gel PAA2* in water (1), 0.001 M NaCl (2), 0.01 M NaCl (3), and 0.1 M NaCl (4). (b) Kinetics of swelling of the gel PAA2* in water (1), 0.001 M NaCl (2), 0.01 M NaCl (3), and 0.1 M NaCl (4) and kinetics of the corresponding reference gel PAA2 in water (5).

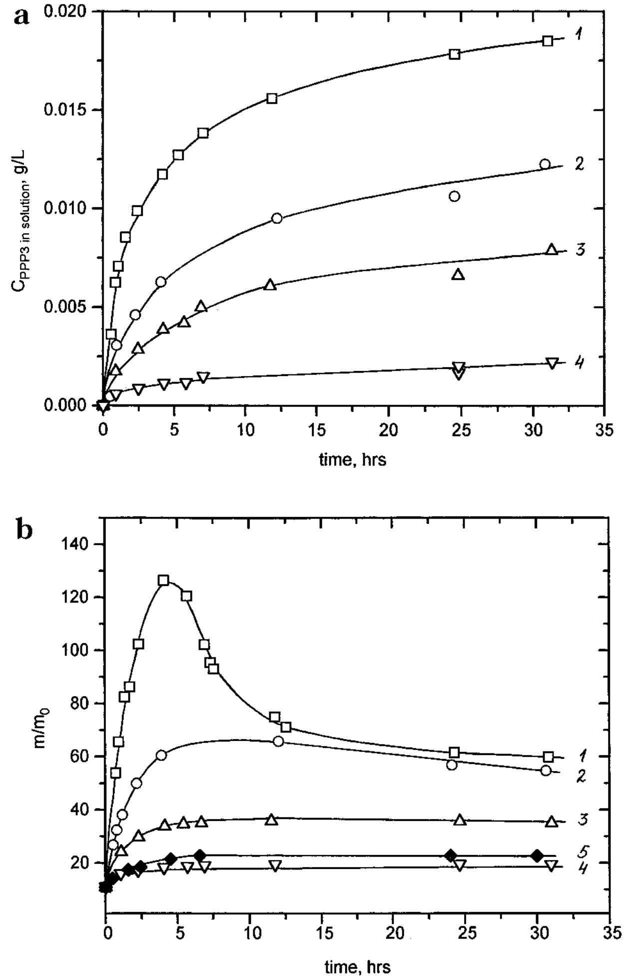

Figure 8. (a) Kinetics of release of PPP3 from the gel PAA5* in water (1), 0.001 M NaCl (2), 0.01 M NaCl (3), and 0.1 M NaCl (4). (b) Kinetics of swelling of the gel PAA5* in water (1), 0.001 M NaCl (2), 0.01 M NaCl (3), and 0.1 M NaCl (4) and kinetics of the corresponding reference gel PAA4 in water (5).

faster than the rate of change of the degree of swelling of the gel. Thus, it is the rate of network conformational changes that determines the rate of the gel volume change. So, the different character of kinetic curves of the gel swelling and of PPP3 release in water (Figures 7 and 8) can be related with slow processes of the contraction of the gel, leading to a significant retardation of the network deswelling in response to the release of rigid-rod polyelectrolyte.

In the presence of low-molecular-weight salt a maximum on the swelling curve disappears (Figures 7b and 8b), probably because the salt prevents the release of PPP3, which is responsible for the gel shrinking. From Figures 7b and 8b we also notice that the rate of gel expansion falls off with increasing concentration of sodium chloride. This effect is due to the osmotic deswelling of the gel with trapped charged rods in salt solution. It seems reasonable to assume that small salt ions can rapidly redistribute between the solution and the gel, so that the rate of salt ion exchange itself does not influence the kinetics of swelling.

The quantitative theory of the kinetics of gel swelling coupled with the release of rods from the gel is presented in the Appendix. The main results of this theory support the conclusions presented in this section, and the theoretical plots of Figure 13 agree well with the experimental curves in Figure 8.

Effect of the Addition of Salt at the Network Formation. When a bivalent salt is added to an aqueous solution of PPP3 of high enough concentration, the system gelifies, apparently due to the ionic cross-linking of different anionic rods by bivalent cations. This property of the linear polyelectrolyte was used to obtain a "physical" network of charged rods inside the covalently cross-linked PAA gel. For this purpose calcium chloride was added to the polymerization mixture just before the initiator. The addition of this salt leads to the instantaneous gelification of the polymerization mixture. The subsequent three-dimensional polymerization of acrylamide inside the "physical" gel results in a formation of some kind of interpenetrating network (IPN). It was observed that the binding of the polyelectrolyte in a physical network prevents effectively its release in the solution (Figure 9). Besides, the obtained IPN has a degree of swelling in water twofold higher than that of the network prepared in the absence of salt (Figure 10). This results from the osmotic pressure of counterions of polyelectrolyte rods retained inside the gel. The detailed study of the properties of such IPNs is in progress. The results will be published in a separate paper.

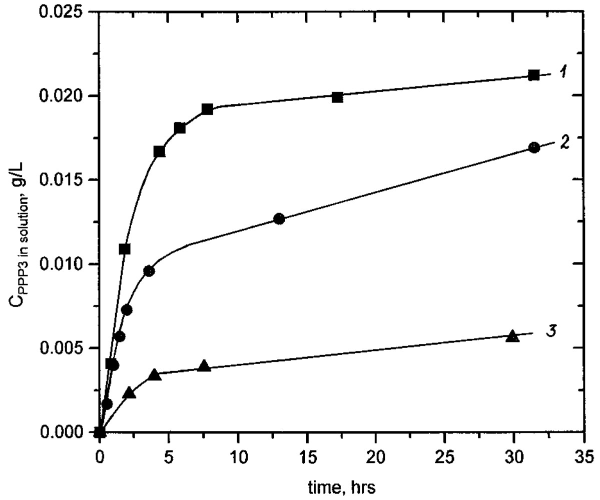

Figure 9. Kinetics of release of PPP3 from the gels PAA2* (1), PAA2*−NaCl (2), and PAA2*−$CaCl_2$ (3) in water.

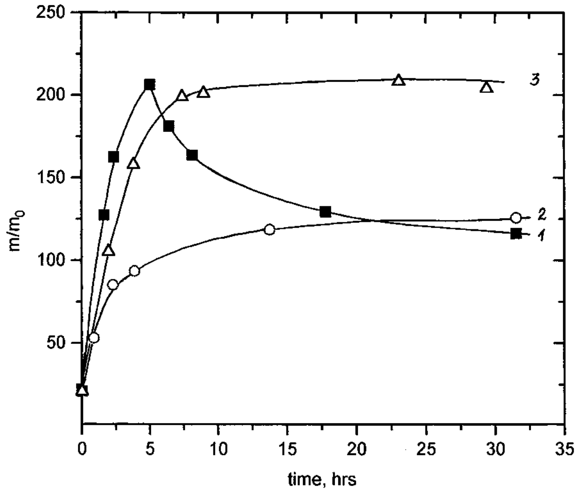

Figure 10. Kinetics of swelling of the gels PAA2* (1), PAA2*−NaCl (2), and PAA2*−$CaCl_2$ (3) in water.

The polymerization was also performed in the presence of monovalent salt (sodium chloride), which cannot cross-link the charged rods. Sodium chloride was shown to reduce the fraction of the released polyelectrolyte, but to a much smaller extent than $CaCl_2$ (Figure 9). In addition, the final degree of swelling of PAA2*−NaCl gel upon immersion in water is close to that of the PAA2* gel prepared without any salt (Figure 10). The comparison of the kinetic curves (Figures 7b and 10) shows that the gel PAA2*−NaCl swells in water similarly to the PAA2* gel immersed in 0.001 M NaCl. The calculation shows that in both these cases the overall concentration of NaCl in the system (gel + solution) is the same. The obtained results imply that the PAA*−NaCl gel immersed in water expels first the low-molecular-weight salt and then the less mobile polyelectrolyte macromolecules. Thus, the introduction of NaCl in the gel during the polymerization produces the same effect as the immersion of the PAA* gel synthesized without salt in the solution of sodium chloride.

Absorption of Polyelectrolyte Rods by a Gel. Most of the properties of PAA gels with trapped PPP3 could be explained if we assume strong specific interactions between polyelectrolyte rods and network chains. If these interactions do exist, we can expect that the reference PAA network being immersed in PPP3 solution will effectively absorb the rods. Alternatively, as the length of polyelectrolyte rods is much higher than the mesh size of the gel, the polyelectrolyte should not penetrate the gel because the confinement energy of a chain trapped in a gel is very large.

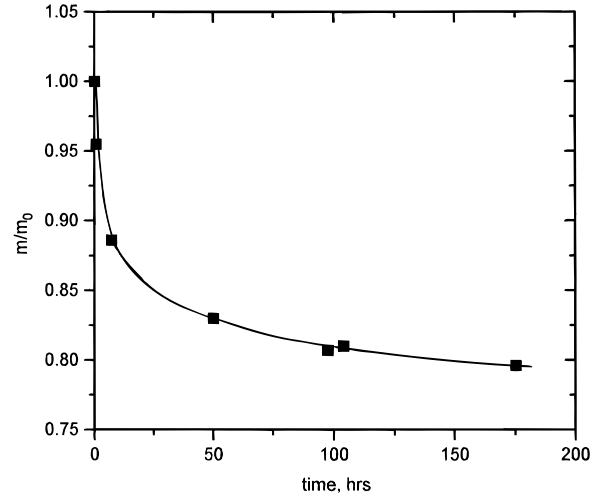

Figure 11. Deswelling of reference gel PAA2 in an aqueous solution of PPP3 (C_{PPP3} = 0.185 g/L).

To study the absorption of polyelectrolyte rods, the reference PAA2 gel was immersed in an aqueous solution of linear polyelectrolyte. The obtained experimental results show that the polyelectrolyte rods do not penetrate the PAA gel at all. At the same time, the gel equilibrated in water deswells when put in an aqueous solution of rigid-rod polyelectrolyte (Figure 11) due to the external compressing osmotic pressure of the rod counterions.

Thus, on the one hand, the PAA gel does not absorb the polyelectrolyte rods from solution; on the other hand, the PAA* gel with charged rods incorporated at the network formation retains most of the rigid polyelectrolyte chains. This discrepancy may be related with the formation of nonequilibrium aggregates of polyelectrolyte rods inside the gel at the stage of its preparation, which include some of the network chains. As the length of the charged rods is much higher than the mesh size of the gel, the rods approaching each other cannot expel completely the gel chains. The additional aggregation of stiff chains in the course of the network preparation can result from the well-known effect of the microphase separation transition in polyelectrolyte systems.[24−26] For the present case the segregation tendency may be due to the incompatibility of polymer rods and flexible network chains,[27] while the stabilizing tendency is as usual due to the counterions; a similar effect was considered in ref 28. Indeed, we have shown that the mixtures of linear PAA and PPP3 at the same monomolar concentrations, as in the gel just after the preparation, do not exhibit a macrophase separation. Therefore, the incompatibility of rigid-rod and flexible polymer probably manifests only in the formation of microdomains enriched with one of the polymer components. These microdomains should be of small enough size, because they do not prevent considerably the free motion of counterions, inducing the gel swelling. The absence of opacity or transluscence in the gels containing rigid rods also counts in favor of the relatively small size of such aggregates.

Conclusion

In the present paper we have investigated the flexible polymer gel synthesized in the presence of stiff-chain polyelectrolyte. We have shown that, due to the formation of aggregates of stiff macromolecules involving gel chains, most of the polyelectrolyte rods are immobilized within the gel. The counterions of these charged rods are responsible for the enhancement of the absorption capacity of the gel, while the presence of stiff elements in the gel structure gives rise to the increase of the modulus of elasticity. Both these effects make such systems potentially promising as superabsorbent materials.

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Appendix: Theory of the Swelling of Gels with Embedded Polyelectrolyte Stiff Chains

A1. Model and Main Notations. Let us consider a gel sample with embedded polyelectrolyte stiff chains freely swelling in a large amount of solvent. Let us assume that the neutral gel contains N monomer units and that the average number of monomer units in the subchain between two cross-links is equal to m. The interaction of the gel with the solvent (water) will be described within the framework of the Flory−Huggins lattice model with the interaction parameter χ_g and the characteristic cell size a. The gel chains are assumed to be flexible; therefore, a is the only microscopic size. For example, the length of the Kuhn segment of the chain is assumed to be of order a, while the volume of monomer units is $v = a^3$.

Let us also suppose that the charged stiff chains have N_p monomer units of size a_p and volume $v_p = a_p{}^3$. Each of these units can in principle be charged with two negative elementary charges e. If we assume that polyelectrolytes are highly charged and take into account Manning's condensation of counterions, the effective charge of the monomer unit should be e/u_p, where

$$u_p = \frac{e^2}{\epsilon a_p k T} \tag{1}$$

and ϵ is the dielectric constant of the solvent, k is the Boltzmann constant, and T is the temperature. The total number of the stiff chains in the system will be denoted as $n_p°$. To describe the experimental results, it is necessary to assume that some of the stiff chains within the gel form aggregates; the number of stiff chains in one aggregate will be designated as N_{agr}. For simplicity we will assume that only aggregates of size N_{agr} and single stiff chains exist inside the gel. The number of stiff chains in the aggregates is assumed to be fixed for the present simplest theory. Since we introduce a second polymeric component, we should also introduce two new Flory−Huggins parameters χ_p and χ_{gp} to describe the interaction of the stiff chains with the solvent and with the gel chains, respectively.

To describe the release of the stiff chains to the external solution, we should make some assumptions on the type of diffusive motion of nonaggregated stiff chains inside the gel. Since for the case described in the present paper the length of the stiff macromolecules is much larger than the mesh size of the gel, it is natural to assume that the stiff chains move inside the gel via a reptation type of motion in an effective tube formed by the surrounding gel chains. We will denote the diffusion constant of the stiff chains along the tube as D_p. We will also assume that only nonaggregated stiff chains can be released from the gel to the external solution, while the aggregated stiff chains are effectively trapped by the gel chains.

A2. Free Energy for the Gel with Embedded Stiff Chains. Following the general theory of swelling of polyelectrolyte gels,[17] the free energy of the network can be written as a sum of three terms

$$F_n = F_{el} + F_{int} + F_0 \tag{2}$$

where F_{el} is the free energy of elastic deformation of the network, F_{int} is the free energy of the volume interaction of monomeric units, and F_0 is the free energy of the translational motion of the free stiff chains and of the ions within the network.

The first term, F_{el}, can be written in the Flory form[29] modified by Birshtein and Pryamitsyn[30,31]

$$F_{el} = \frac{3}{2} kT \frac{N}{m}\left[\alpha^2 + \frac{1}{\alpha^2}\right] \tag{3}$$

where $\alpha = (V_g/V_o)^{1/3}$ is the swelling ratio of the network, V_g is the volume of the network, and V_o is the volume of the network in its reference state, in which the network chains are most close to the Gaussian coils[32]

$$V_0 \sim N m^{1/2} v \tag{4}$$

The free energy of interaction of monomeric links, F_{int}, can be written within the framework of the Flory−Huggins approximation[29]

$$F_{int} = kT\frac{V_g}{v}[(1 - \Phi - \Phi_p)\ln(1 - \Phi - \Phi_p) - \chi_g\Phi^2 - \chi_p\Phi_p{}^2 + \chi_{gp}\Phi\Phi_p] \tag{5}$$

where Φ and Φ_p are the volume fractions of monomeric units of the gel and of the stiff chains, respectively, inside the gel

$$\Phi = \frac{Nv}{V_g}, \quad \Phi_p = \frac{N_p(n_p° - n_p)v_p}{V_g}$$

and n_p is the number of stiff chains outside the gel.

The translational entropy, F_0, of stiff chains and ions can be written as

$$F_0 = kT\left\{(n_p° - n_p - n_{pb})\ln\frac{(n_p° - n_p - n_{pb})}{V_g} + \left[N_p°\left(n_p° - n_p - n_{pb} + \frac{n_{pb}}{N_{agr}}\right) + N_s\right] \times \ln\frac{\left[N_p°\left(n_p° - n_p - n_{pb} + \frac{n_{pb}}{N_{agr}}\right) + N_s\right]}{V_g} + N_s\ln\frac{N_s}{V_g}\right\} \tag{6}$$

where n_{pb} is the number of stiff chains in the aggregates

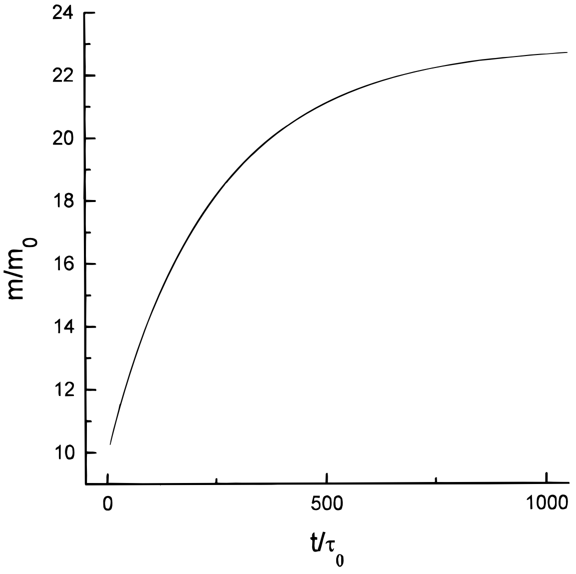

Figure 12. Calculated kinetic curve of swelling of the reference gel PAA4 in water.

within the gel and N_s is the number of molecules of low-molecular-weight salt (in our case NaCl) inside the network.

It is also necessary to write the expression for the free energy of the external solution. Here the terms in the free energy connected with the interaction between stiff chains and all the translational entropy contributions have to be taken into account:

$$F_{\text{out}} = kT\left\{-\frac{V-V_g}{v}\chi_p\left(\frac{N_p n_p v_p}{V-V_g}\right)^2 + n_p \ln\frac{N_p n_p v_p}{V-V_g} + (N_p^\circ n_p + N_s^\circ - N_s)\ln\frac{N_p^\circ n_p + N_s^\circ - N_s}{V-V_g} + (N_s^\circ - N_s)\ln\frac{N_s^\circ - N_s}{V-V_g}\right\} \quad (7)$$

where V is the total volume of the solution and N_s° is the total amount of molecules of NaCl in the solution.

A3. Kinetics of the Gel Swelling and of the Release of Stiff Chains. Since we cannot describe the change of the amount of the stiff chains in the aggregates with the gel swelling without additional assumptions for the aggregates, let us assume for simplicity that the amount of the stiff chains in the aggregates is fixed and does not depend on the gel volume. However, it does depend on the salt concentration, and we will take this amount from the experimental data for the equilibrium swelling of the gel at different concentrations of NaCl (Figure 8a).

It is also important to mention that there are two different scales of time in the described process: the time of swelling of the gel and release of the stiff chains and the time of redistribution of salt between the gel and the external solution. It is obvious that the latter time scale is much smaller than the first one because the diffusion time of a counterion is much less than that for a stiff chain, as well as the time of the gel swelling. So let us assume that at any moment the amount of the salt within the gel corresponds to the equilibrium amount for the fixed values of V_g and n_p. This amount can be determined from the condition of equality of the chemical potentials for the salt molecules inside and outside the network[30]

$$\frac{\partial(F_{\text{in}} + F_{\text{out}})}{\partial N_{\text{in}}}(V_g, n_p, N_s) = 0 \quad (8)$$

So we have only two dynamic variables: the swelling ratio of the gel α and the amount of the stiff chains outside the gel n_p.

(a) Dynamics of Gel Swelling. Let us consider the simplest theory of gel swelling. The force per unit of surface of the gel (pressure) which causes the swelling is equal to

$$p = -\frac{\partial(F_{\text{in}} + F_{\text{out}})}{\partial V_g} \quad (9)$$

The friction force per unit volume of the gel is

$$f = c\xi\tilde{v} \quad (10)$$

where $c = N/V_g$ is the concentration of the gel monomer units, $\tilde{v} \sim 1/V_g^{2/3}\, dV_g/dt$ is the average velocity of collective motion of the gel monomer units, and ξ is playing the role of the friction coefficient for a monomer unit.

$$fV_g = pV_g^{2/3} \quad (11)$$

From eqs 9, 10, and 11 we finally have

$$\frac{N\xi}{V_g^{4/3}}\frac{dV_g}{dt} = -\frac{\partial(F_{\text{in}} + F_{\text{out}})}{dV_g} \quad (12)$$

(b) Release of Stiff Chains from the Gel. Each of the stiff chains moves within the gel in an effective tube formed by the surrounding gel chains. The diffusion equation is

$$\frac{dn_p}{dt} = -D_p S\frac{dC_p}{dl} \quad (13)$$

where C_p is the concentration of the free stiff chains, S is the square of the tube, and l is the length through the tube. Let us assume that

$$\frac{dC_p}{dl} \approx \frac{C_p^{\text{out}} - C_p^{\text{in}}}{L} \quad (14)$$

where L is an effective length of the tube and C_p^{out} and C_p^{in} are the concentrations of the free stiff chains outside and inside the gel, correspondingly.

$$S \sim \left(\frac{V_g}{N}\right)^{2/3};\quad L \sim \left(\frac{V_g}{N}\right)^{1/3} \quad (15)$$

From eqs 13, 14, and 15 we have

$$\frac{dn_p}{dt} = D_p\left(\frac{V_g}{N}\right)^{1/3}(C_p^{\text{in}} - C_p^{\text{out}}) \quad (16)$$

Substituting eqs 2–7 into eqs 8, 12, and 16 we finally obtain

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{1}{\tau_0}\frac{X^{4/3}}{\Phi_0}\Bigg\{-\frac{\Phi_0}{mX}\left[\left(\frac{X}{\Phi_0 m^{1/2}}\right)^{2/3} - \left(\frac{\Phi_0 m^{1/2}}{X}\right)^{2/3}\right] - \ln\left[1 - \frac{\Phi_0}{X}(1+\delta_\mathrm{p}(1-\tilde{n}_\mathrm{p}))\right] - \Phi_0\frac{1+\delta_\mathrm{p}(1-\tilde{n}_\mathrm{p})}{X} - \frac{{\Phi_0}^2}{X^2}(\chi_\mathrm{g} - \chi_\mathrm{gp}\delta_\mathrm{p}(1-\tilde{n}_\mathrm{p})) + \chi_\mathrm{p}{\Phi_0}^2{\delta_\mathrm{p}}^2\left[\left(\frac{\tilde{n}_\mathrm{p}}{\beta - X}\right)^2 - \left(\frac{1-\tilde{n}_\mathrm{p}}{X}\right)^2\right] + \Phi_0\left[\frac{\delta\left(1 - \tilde{n}_\mathrm{p} - \tilde{n}_\mathrm{pb} + \frac{\tilde{n}_\mathrm{pb}}{N_\mathrm{agr}}\right) + 2\delta_\mathrm{s}n_\mathrm{s}}{X} - \frac{\delta\tilde{n}_\mathrm{p} + 2\delta_\mathrm{s}(1-n_\mathrm{s})}{\beta - X}\right]\Bigg\} \quad (17)$$

$$X(t{=}0) = 1 \quad (18)$$

$$\frac{\mathrm{d}\tilde{n}_\mathrm{p}}{\mathrm{d}t} = \frac{1}{\tau_1}\frac{1}{\Phi_0}\left(\frac{X}{\Phi_0}\right)^{1/3}\left[\frac{1-\tilde{n}_\mathrm{p}-\tilde{n}_\mathrm{pb}}{X} - \frac{\tilde{n}_\mathrm{p}}{\beta - X}\right] \quad (19)$$

$$\tilde{n}_\mathrm{p}(t{=}0) = 0 \quad (20)$$

$$\ln\frac{\left[\delta\left(1 - \tilde{n}_\mathrm{p} - \tilde{n}_\mathrm{pb} + \frac{\tilde{n}_\mathrm{pb}}{N_\mathrm{agr}}\right) + \delta_\mathrm{s}n_\mathrm{s}\right]n_\mathrm{s}}{[\delta\tilde{n}_\mathrm{p} + \delta_\mathrm{s}(1-n_\mathrm{s})](1-n_\mathrm{s})} + 2\ln\frac{\beta - X}{X} = 0 \quad (21)$$

where $X = V_\mathrm{g}/V_\mathrm{g}° \approx (1/10)m/m_\mathrm{o}$ is the parameter of swelling of the gel, $\tilde{n}_\mathrm{p} = n_\mathrm{p}/n_\mathrm{p}°$ is the fraction of stiff chains outside the gel, $\tilde{n}_\mathrm{pb} = n_\mathrm{pb}/n_\mathrm{p}°$ is the fraction of stiff chains in the aggregates inside the gel, $n_\mathrm{s} = N_\mathrm{s}/N_\mathrm{s}°$ is the fraction of salt molecules inside the gel, and the constants δ_p, δ, δ_s, and β are defined as follows:

$$\delta_\mathrm{p} \equiv \frac{N_\mathrm{p}n_\mathrm{p}°v_\mathrm{p}}{Nv},\quad \delta \equiv \frac{N_\mathrm{p}°n_\mathrm{p}°}{N},\quad \delta_\mathrm{s} = \frac{N_\mathrm{s}}{N},\quad \beta = \frac{V}{V_\mathrm{g}°}$$

Φ_0 is the initial volume fraction of gel chains, $\tau_0 = \xi V_\mathrm{g}°^{2/3}/kT$ is the characteristic time of the gel swelling, and $\tau_1 = V_\mathrm{g}°/D_\mathrm{p}V^{1/3}$is the characteristic time of the stiff chains release out of the gel.

For polyacrylamide in water at room temperature we use the value $\chi_\mathrm{g} = 0.44$ according to ref 33. We also assume $\chi_\mathrm{p} = 1$ and $\chi_\mathrm{gp} = 1$, since the stiff chains with compensated charges should be fairly hydrophobic.

We took the sample PAA5* for our calculations. Therefore $\Phi_0 = 0.1$ and $C_\mathrm{p}^\mathrm{in}(t{=}0) = 20$ g/L. The parameter m was determined from the calculation for the gel swelling in water without embedded stiff chains (Figure 12). We can see that if $m = 200$, there is a good connection with the experimental results (Figure 8b). The parameter N_agr can be determined from the equilibrium swelling ratio X for the gel with embedded stiff polyelectrolyte chains swollen in water. The greater is the value N_agr the less is the amount of free counterions defining the gel swelling. We obtain the best fit with the results of Figure 8b for $N_\mathrm{agr} = 8$.

A4. Results and Discussion. From the system in eqs 17−21 we can calculate the dependences $m/m_0(t/\tau_0)$ and $C_\mathrm{p}^\mathrm{out}(t/\tau_0)$ for different concentrations of NaCl in solution. The results are shown in Figure 13. At the beginning of the process the osmotic pressure of counterions within the gel leads to the gel swelling. At the same time nonaggregated stiff chains with their counterions are released from the gel. The latter effect leads to the decrease of the osmotic pressure of counterions and, consequently, to the decrease of the degree of swelling of the gel. As a result the maximum in Figure 13b appears. The more salt we have in the solution the less pronounced is the maximum because the salt reduces the effect of the osmotic pressure of counterions (both because the salt is distributed between the gel and the external solution and because the amount of nonaggregated stiff chains in the gel decreases).

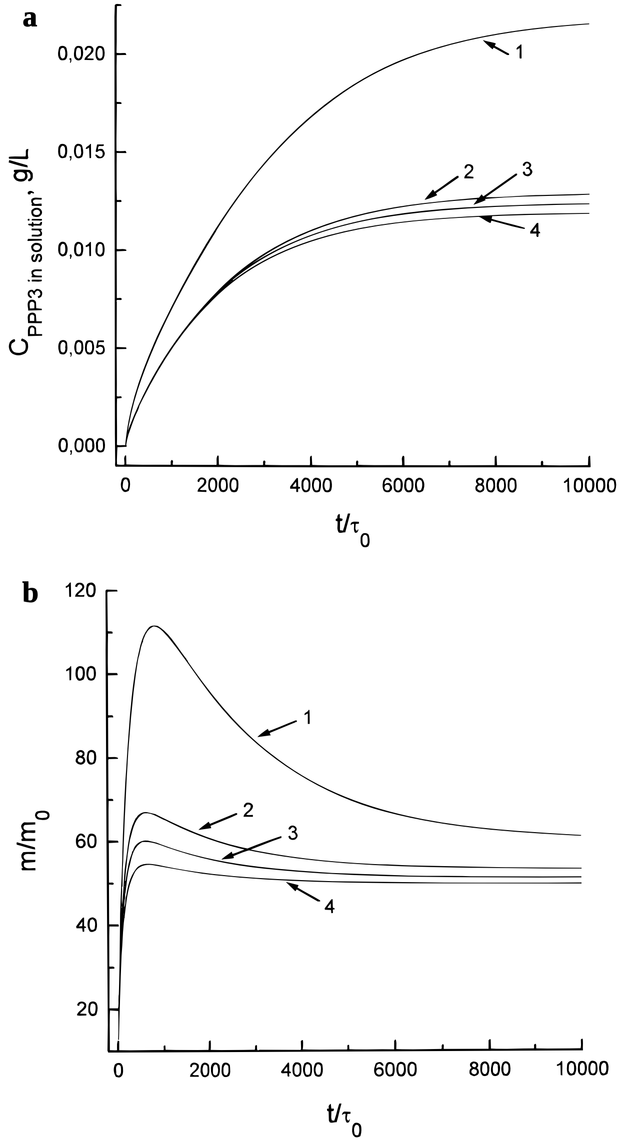

Figure 13. (a) Calculated kinetic curves of release of PPP3 from the gel PAA5* in water (1), 0.001 M NaCl (2), 0.002 M NaCl (3), and 0.005 M NaCl (4). (b) Calculated kinetic curves of swelling of the gel PAA5* in water (1), 0.001 M NaCl (2), 0.002 M NaCl (3), and 0.005 M NaCl (4).

From the comparison of experimental Figure 8 and theoretical Figure 13 it can be seen that even such a simple theory gives a rather good connection with the experimental results for the concentrations of the salt from 0 to 0.005 M. But there is still some theory−experiment discrepancy which should be discussed. SAXS experiments on PPP3 solution with added salt evidence the existence of aggregates of predominantly one size with $N_\mathrm{agr} = 3$. On the other hand, it is clear

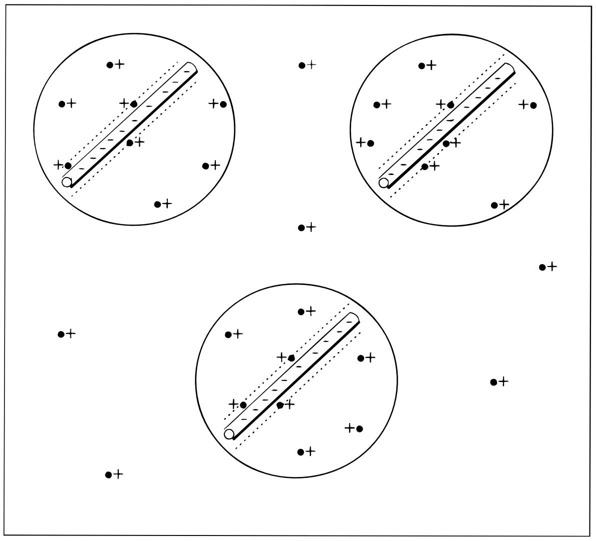

Figure 14. Schematic representation of uneven distribution of counterions in a system with inhomogeneously arranged polyelectrolyte molecules.

that N_{agr} in the gel cannot be much larger than the corresponding value in the solution, since the fraction of water within the gel is dominant. However, from our calculations we obtained the best fit for $N_{agr} = 8$. To explain this contradiction, let us consider the rough picture of the structure of polymer gel with embedded polyelectrolyte rods (Figure 14). The counterions which are brought to the gel together with polyelectrolyte rods can be either "condensed" (in the Manning sense) or "free". However, for the case of a highly inhomogeneous distribution of negative charges within the gel (as it is for the case of Figure 14, when we have highly negatively charged areas, where the aggregates are located, and regions with no negative charge available) the "free" counterions can be further roughly subdivided in two classes. The first of these classes corresponds to counterions, which are "free" in the Manning sense; however, they are located near the aggregates, since they are "trapped" by the potential well formed by the oppositely charged aggregates. Therefore, these "free trapped" counterions do not contribute to the osmotic pressure. The second subclass is formed by "truly free" counterions, which can overcome not only the attraction of the aggregate at close distances (from which the aggregate is seen as a cylindrical object and therefore Manning consideration is valid) but also the attraction at larger distances (from where the aggregate is seen as closer to spherical object). It is clear that only these "truly free" counterions contribute to the osmotic pressure. Therefore, they can be called "osmotic free counterions". By analyzing the theoretical derivation presented above, it is possible to conclude that the value of $1/N_{agr}$ enters in all the expressions only as the value proportional to the number of "osmotic free" counterions per one chain of the aggregate. If now we assume that not all the "free" counterions are in fact "osmotic free", that is contribute to the osmotic pressure, the above-mentioned contradiction is effectively resolved. The result that $N_{agr} = 8$ instead of the expected value $N_{agr} = 3$ means simply that $^3/_8$ths of the "free" counterions contribute to the osmotic pressure, while $^5/_8$ths of all the "free" counterions are trapped by the aggregates.

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