

Polyelectrolyte Gel Swelling and Conductivity vs Counterion Type, Cross-Linking Density, and Solvent Polarity

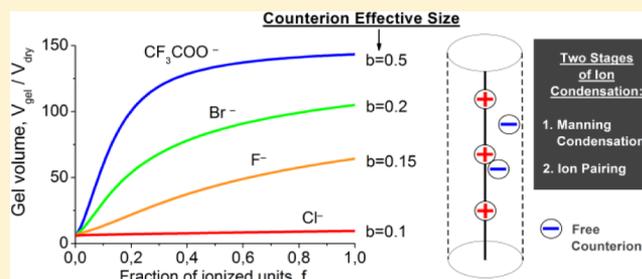
Artem M. Rumyantsev,[†] Abhishek Pan,[‡] Saswati Ghosh Roy,[‡] Priyadarsi De,[‡] and Elena Yu. Kramarenko^{*,†}

[†]Faculty of Physics, Lomonosov Moscow State University, Moscow 119991, Russia

[‡]Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, Nadia, West Bengal, India

S Supporting Information

ABSTRACT: A joint theoretical and experimental study is devoted to the swelling and electrical conductivity of highly charged polyelectrolyte (PE) gels in media of different polarity. Deprotected poly(*tert*-butyl carbamate L-alanine) gels provided with fluorine, bromine, chlorine, sulfate, and trifluoroacetic counteranions demonstrated different conductivity in aqueous medium as well as solvent uptake in water/methanol mixtures. Counterion specificity in PE gel properties was theoretically explained in the framework of the model which treats ion association within the network as a two-stage process. Manning-type condensation, being the first condensation stage not affected by counterion type, provides understanding of a gel maximal swelling at intermediate degrees of gel ionization f and a slight gel contraction at f tending to unity, which were earlier observed in experimental investigations. The second ion association stage is an ion pairing influenced by the kind of counterion. Since a considerable fraction of ions form pairs even in a swollen hydrogel, its properties are largely influenced by counterion type. Conductivity of the gel was calculated theoretically owing to the known fraction of free and condensed counterions. Developed theory containing no adjusting parameters allows for the first time to reach semiquantitative matching of experimental results on highly charged gel swelling and conductivity.



I. INTRODUCTION

High swelling of polyelectrolyte (PE) gels is conventionally ascribed to the osmotic pressure of counterions emerging within the gel under dissociation of ionic groups. A theoretical description of PE is known to be rather sophisticated, largely due to some difficulties of a proper account for ionic association/dissociation processes. These difficulties are absent in the case of low-molecular-weight counterparts, which are usually divided into two types: strong electrolytes and weak electrolytes. Strong electrolytes completely dissociate in solutions, while the degree of dissociation of weak ones is lower than unity; besides, it depends on their concentration and environmental conditions. For instance, in aqueous solutions almost all salts of alkali metals are known to be strong electrolytes while many organic acids are treated as weak electrolytes. However, in both cases the reversible association/dissociation process $AB \rightleftharpoons A^+ + B^-$ can be described by the law of mass action (LMA) connecting concentrations c_{A^+} , c_{B^-} , and c_{AB} of all the species via

$$\frac{c_{A^+}c_{B^-}}{c_{AB}} = \frac{1}{\nu}k$$

Here volume ν is of the order of molecule and ions volume, and the association constant $k = \exp(\Delta E/k_B T)$ depends on the energy gain ΔE of ion pairing but not on the state of other

neighboring ions because separate single processes do not directly affect each other (here we do not mean impact of ion concentration included through the structure of LMA itself). High and low values of k correspond to strong and weak electrolytes, respectively. Without any principal modification, LMA can be applied to the case of not only water but also organic solvent with a lower dielectric constant ϵ , where a higher energy gain due to enhancement of electrostatic interactions should result in a lower dissociation.

In polyelectrolyte gels the state of a polar group, whether dissociated or not, directly influences dissociation of other groups, especially close neighbors. We would mark three following aspects of this impact. (I) First, dissociation of ionic groups leads to the gel swelling accompanied by decreasing concentration of ionic groups within the gel, in turn promoting their further dissociation, and vice versa. (II) Second, considerable gel shrinking results in a change of the gel medium polarity: dielectric constant of the pure polymer is usually much lower than that of the solvent resulting in a more favorable ion pairing in a collapsed state. (III) Third, a gel counterion interacts electrostatically not only with a respective ion on the polymer

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chain but also with its spatial neighbors. In the collapsed state this leads to a multiplet formation, while in a swollen state the closest neighboring charges along the extended chain are at the same time the closest spatial neighbors. Thus, at some length scales exceeding the distance between nearest-neighboring ionic groups on the subchain, the counterion interacts with the collective electric field created by numerous charges of the subchain, and the latter can be treated as a uniformly charged cylinder. Cylindrical geometry of the charge distribution manifests itself in Manning condensation,^{1–4} i.e., trapping of some fraction of counterions in the vicinity of the stretched subchain, so that the linear charge density cannot exceed e/l_b , even at infinite dilution (infinitely long subchains in the case of a gel). As medium polarity decreases, the Bjerrum length $l_b = e^2/ekT$ grows favoring ion condensation, including both Manning condensation and ion pairing.

In pioneering theoretical works devoted to PE gel swelling all effects I–III were neglected as far as ionic groups were assumed to be completely dissociated (reasonable assumption if low-molecular-weight analogues are strong electrolytes), and their fraction in the gel subchains was considered to be low enough, $f \ll 1$.^{5,6} This approach allowed to explain a discrete character of volume transitions in PE gels induced by solvent quality changes. Since chain elasticity was supposed to be Gaussian, the gel degree of swelling defined as the ratio between equilibrated and dry gel volumes was predicted to equal (see Appendix)

$$V_{\text{gel}}/V_{\text{dry}} = N^2 f^{3/2} \quad (1)$$

The Manning condensation idea (aspect III for the swollen state), though known for several decades,^{1–4} has been applied to the theoretical treatment of gel swelling just in a very simple manner: it was proposed that at low degrees of ionization not exceeding $f^* = d/l_b$ all counterions are free, while above the threshold only the fraction $\beta = f^*/f = d/fl_b$ remains unbound, d being the length of a monomer unit.^{7–9} Then under assumption of Gaussian elasticity the gel swelling degree was found to equal

$$\frac{V_{\text{dry}}}{V_{\text{gel}}} = \begin{cases} N^2 f^{3/2}, & f \leq f^* \\ N^2 (f^*)^{3/2}, & f \geq f^* \end{cases}$$

In fact, the value of β depends substantially on PE chains concentration, i.e., on the gel degree of swelling,¹⁰ and the tendency of counterions to form ion pairs. Thus, the above results neglecting ion pairing and corresponding to the limiting case of infinite dilution are never valid in the case of gels. Another approach, striving to explain an experimentally observed lower gel swelling as compared to the theoretical prediction (1), took into consideration trapping of counterions by inhomogeneities of gel local cross-linking density: trapped counterions were called “osmotically passive” since they do not create exerting osmotic pressure within the gel similarly to Manning-condensed counterions.¹¹

As to the effect II, for the first time it was taken into account in refs 12 and 13 where a high importance of ion pairing and multiplet formation in dense gel states was emphasized; i.e., the effects I and III for collapsed gel were also taken into consideration. In order to avoid impact of Manning condensation (effect III in a swollen state), the developed theory was applied to the case of slightly charged PE gels, $f \ll 1$. Prediction of gel collapse in low polar media confirmed by experimental studies became a remarkable success of this concept.¹⁴ Later, the idea

of dielectric mismatch between solvent and pure polymer was widely used by other groups as well for theoretical treatment of different PE systems: gels,^{15,16} microgels,^{17,18} polymer micelles,^{19,20} single chains,^{21,22} and semidilute PE solutions.^{23,24}

Recently Borisov and coauthors have proposed a theory of weak pH-dependent PE (micro)gels swelling considering the effect I properly but avoiding the others (II, III).²⁵ They have revealed that not only pH but also salt concentration can shift the equilibrium in LMA and change the degree of gel ionization. Addition of salt causes two consequent phenomena: (i) gel swelling due to increasing number of dissociated groups and (ii) gel shrinking due to Donnan salting-out.²⁵ Here it should be noted that account for nonzero volume of salt ions and correlation effects would have resulted in a reentrant gel swelling at even higher salt concentrations, as it had been demonstrated by the Olvera de la Cruz group earlier.^{17,26}

This article is aimed to a thorough analysis of the swollen state of highly charged PE gels. Effects I and III are implicitly included into our consideration, and ion association is treated as a two-step process: the first step is Manning-type condensation while the second one is ion pairing between polymer charges and counterions trapped in the vicinity of the subchain backbone. These steps correspond to the interaction of counterions with the collective electric field created by numerous charges on polymer subchains and with separate ions at short distances, respectively (see Figure 1). At a fixed counterion

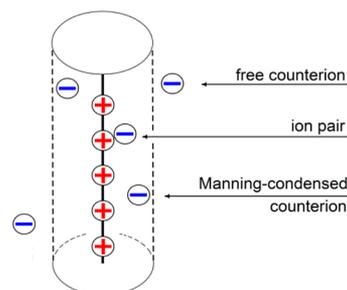


Figure 1. Schematic representation of two ion condensation steps: Manning condensation and ion pairing.

charge, Manning condensation is not affected by microscopic features of the counterion such as dimensions and charge distribution. On the contrary, it is the type of counterion that defines benefit of ion pairing. Thus, account for the second step of ion association is crucial in explaining effects of counterion specificity in PE gel swelling.

Another objective of this study is to reveal the effect of counterion type on the volume of a highly charged gel, especially in a swollen state. It is known from experimental investigations of both polycations^{27–30} and polyanions^{31–35} that the size of univalent counterions has a great influence on PE solution properties (conductivity, viscosity, correlation length, etc.) notable in both aqueous and low polar media. Satoh’s group has found that different polyanions in solution prefer binding of different cationic counterions: Na^+ and K^+ are preferable for poly(acrylic acid) (PAA), K^+ for poly(styrenesulfonate) (PSS), and Cs^+ for poly(vinyl sulfonate) (PVS). Moreover, a mixture of counterions of a smaller and a larger size than the optimal one, for instance Li^+ and tetrabutylammonium (TBA^+) for PVS chains, can provoke conductivity and viscosity drop only in combination of counterions close to half to half per charged subchain unit.^{33–35} Titration of poly(acrylic acid) gel with different bases in methanol providing gels with different

alkali and quaternary ammonium counterions (from small to bulky: Na⁺, Cs⁺, TMA⁺, TEA⁺, and TBA⁺) has lately been performed by us.¹⁶ Gel with the bulkiest TBA⁺ counterion is swollen at any value of f ; small counterions Na⁺ and Cs⁺ provoke gel collapse to ionomer state at relatively low degrees of ionization $f = 0.05$ – 0.15 ; gels with intermediate size ions (TMA⁺ and TEA⁺) undergo consequent collapse and reswelling in the region $f = 0.15$ – 0.25 . In ref 16, we have proposed a simple theoretical model being able to explain experimentally observed transitions in terms of benefit from ion pair formation: the smaller the counterion, the more favorable ion pairing and a broader the region of ionomer state stability. Reentrant swelling has been attributed to increasing dielectric constant of the collapsed gel upon titration. However, the theory developed for the case of relatively low content of ionic groups ($f < 0.3$) is unable to explain (i) absence of gel swelling or even slight gel contraction at f exceeding 0.5 and (ii) certain discrepancy of swollen gel volumes with TMA⁺, TEA⁺, and TBA⁺ counterions in the region of high f . The former effect has been earlier observed experimentally not merely in pure methanol but also in water–methanol mixtures and pure water for gels of sodium salt of PAA¹⁴ as well as in water for partially quaternized PVP gel.³⁰ Theoretical works by Bodrova and Potemkin³⁶ and by Muthukumar's group,¹⁵ also devoted to counterion specificity in polymer gel swelling and considering possible ion pairing, have either examined weakly charged PE gels or neglected Manning condensation at high f . Another publication³⁷ has focused solely on steric counterion impact on a gel swelling at low degrees of gel ionization entirely avoiding possible ion association. DPD computer simulations of a single highly charged chain have shown that not only counterion size but also the charge location (in the center of counterion or on its surface) defines chain dimensions as well as the region of collapsed ionomer state stability and even multiplet structure in it.³⁸ In the present investigation specificity of different counterions, such as F⁻, Cl⁻, Br⁻, HSO₄⁻, and CF₃COO⁻, to highly charged ($f = 1$) polycationic (deprotected Boc-Ala-HEMA) gel is investigated experimentally, and obtained results are comprehended theoretically. The proposed theoretical model predicts dependence of both gel swelling and conductivity on the PE gel degree of ionization, including the region of high f .

II. METHODS AND MATERIALS

II.A. Theoretical Model. We consider a polymer gel consisting of flexible subchains, each containing N statistical segments of length a . Suppose each statistical segment comprises n monomer units, $a = nd$. Let the fraction f of the monomer units is ionic. In order to calculate equilibrium degree of the gel swelling, one should construct free energy function taking into account (i) elasticity of network subchains, (ii) volume interactions, and (iii) contributions from the presence of charges, namely, (a) Manning condensation of counterions and (b) formation of ion pairs between counterions and charges on polymer chains (see Figure 1). All free energy terms below are given in $k_B T$ units.

Elastic contribution considers both chain elongation³⁹ and compression⁴⁰

$$F_{el} = N \left[\frac{R^2}{2N^2 a^2} - \ln \left(1 - \left(\frac{R}{Na} \right)^2 \right) \right] + \frac{3Na^2}{2R^2}$$

with R being the distance between nearest-neighbor cross-links. At low subchain elongation $R/Na \ll 1$ one gets the well-known Gaussian result $3R^2/2Na^2$ for the square brackets, while the term after brackets is responsible for entropy loss under chain compression.⁴⁰ This formula also allows for the finite chain extensibility^{39–42} since F_{el} diverges

at end-to-end distance close to the contour length, $R \rightarrow Na$ (see Appendix).

Volume interactions are written in the Flory–Huggins form^{40,43}

$$F_{FH} = \left(\frac{R}{a} \right)^3 [(1 - \Phi) \ln(1 - \Phi) - \chi \Phi^2]$$

and polymer volume fraction within the network is calculated as $\Phi = Na^3/R^3$. Two contributions F_{el} and F_{FH} describe the neutral gel swelling while the following terms take into consideration the presence of counterions and subchain charges within the PE network.

Let the fraction β of counterions is free and the $(1 - \beta)$ is Manning-condensed. To calculate the corresponding contribution, the gel volume per one subchain $V_{cell} = R^3$ is divided into two zones, the inner and the outer ones, with the volumes $V_{in} = Na^3$ and $V_{out} = R^3 - Na^3$, respectively. The inner zone is a cylinder with the radius $R_{in} = a/\sqrt{\pi}$ surrounding subchain backbone, while the outer zone is the coaxial cylinder with the radius $R_{out} = R^{3/2}/\sqrt{\pi Na}$. Translational entropy of counterions in the both zones is given by

$$F_{tr} = Nfn \left[(1 - \beta) \ln \left(\frac{nf(1 - \beta)}{a^3} \right) + \beta \ln \left(\frac{nfN\beta}{R^3 - Na^3} \right) \right]$$

while the excess electrostatic free energy of the coaxial cylinders reads

$$F_{el-st} = \frac{l_b^{solv}}{a} (nf\beta)^2 N \left[\frac{\ln(1/t) + \frac{t^2-1}{2}}{(1-t)^2} \right]$$

with $t = R_{in}/R_{out}$ being the ratio between the inner and the outer zone radii and l_b^{solv} being the solvent Bjerrum length.^{44,45} The next term is the aggregation free energy which allows to explicitly account for ion pairing^{19,20}

$$F_{agg} = Nfn \left[p + \ln(1 - p) + (1 - \beta) \ln \left(1 - \frac{p}{1 - \beta} \right) \right]$$

Since only counterions kept within the inner zone are supposed to be capable of ion pairing, the inequality $p \leq 1 - \beta$ is satisfied. The fraction of charges in polymer chains bounding counterions is defined from the LMA:

$$p = 1 - \frac{\beta}{2} + \frac{1}{2kfn} - \sqrt{\left(\frac{\beta}{2} - \frac{1}{2kfn} \right)^2 + \frac{1}{kfn}}$$

$$k = \exp \left(\frac{l_b^{pol}}{ab} \right)$$

Here l_b^{pol} is the Bjerrum length in the vicinity of the polymer backbone where ion pairing occurs. The parameter b is accounting for variations in the effective ion pair size: ab should be comprehended as a certain effective distance between the charges in the ion pair which depends not only on the types of the counterion and the charge on the polymer chain but also on solvating ability of solvent molecules. It reflects how favorable ion pairing is: the lower the efficient ion pair size ab , the more advantageous association of oppositely charged ions. The energy gain in the course of ion pairing of univalent ions is supposed to equal $\Delta E = -e^2/(\epsilon ab k_B T)$ with ϵ being the dielectric constant in the vicinity of polymer backbone. In fact, the energy gain from ion pairing is defined by three factors. The first one is the energy of Coulomb interaction of two charges within the ion pair, and this energy is inversely proportional to the geometrical dimensions of the counterion in a contact ion pair. The second factor is the energy loss under desolvation of both the counterion and the charged group on a polymer chain; it occurs to be essential for small enough counterions such as Li⁺ and F⁻ since they are known to be highly solvated. Indeed, Na⁺ and K⁺ counterions provide ion association in many polyanion systems more effectively than both bulky Cs⁺ and quaternary ammonium cations as well as small Li⁺ counterions. This fact proves that the second factor is comparable with the first one.^{16,33–35} Finally, the third factor is the

match of the counterion sizes and dimensions of charged groups on polymer subchain. It is known that 1:1 ionic salts with close ionic radii of cation and anion possess a higher melting temperature as compared to those with size mismatch. In the case of highly charged PEs, $f = 1$, the size of counterions should probably match not only the size of polymer charged group but also the distance along the chain between two nearest-neighboring charges. This hypothesis is also supported by enhanced ion pairing induced by mixing of counterions surpassing and ceding the size of the optimal ones.^{33–35}

Minimization of the total free energy

$$F_{\text{tot}} = F_{\text{el}} + F_{\text{FH}} + F_{\text{tr}} + F_{\text{el-st}} + F_{\text{agg}}$$

with respect to R and β allows to find the equilibrium gel volume. In order to reveal effects of ion association on the swelling of highly charged PE gel, we consider Θ -solvent conditions, $\chi = 0.5$, in most cases. For carbon-chain polymer $n = 3$ since its persistent length is known to be around 0.7 nm. Thus, dimensionless parameter $u = l_b^{\text{olv}}/a$ widely used in theories of PEs and defining solvent polarity equals to unity for water-swollen gels, while organic solvents such as e.g. methanol and ethanol approximately correspond to $u = 2.4$ and 3.3, respectively. Below we focus primarily on a proper swollen gel treatment and do not claim a precise description of the gel collapsed state. Hence, we neglect (i) multiplet formation (aspect III for the collapsed state) which could result just in ΔE renormalization and (ii) a dependence of the gel medium polarity on the gel volume (aspect II). For simplicity, gel local dielectric constant in the subchain vicinity and away from it is proposed to be the same, $u = l_b^{\text{olv}}/a = l_b^{\text{pol}}/a$.

II.B. Experimental Methods. Materials. *tert*-Butyl carbamate (Boc)-L-alanine (Boc-Ala-OH, 99%) and trifluoroacetic acid (TFA, 99.5%) were purchased from Sisco Research Laboratories Pvt. Ltd., India, and used without further purification. Hydrofluoric acid (HF, 99.9%), hydrochloric acid (HCl, 99.9%), hydrobromic acid (HBr, 99.9%), sulfuric acid (H₂SO₄, 99.9%), 4-(dimethylamino)pyridine (DMAP, 99%), anhydrous *N,N*-dimethylformamide (DMF, 99.9%), dicyclohexylcarbodiimide (DCC, 99%), and 2-hydroxyethyl methacrylate (HEMA, 97%) were obtained from Sigma and used as received. Diethylene glycol dimethacrylate (DEGDMA, 99%) was purchased from Sigma and purified by passing through an activated basic alumina column before use. 2,2-Azobis(isobutyronitrile) (AIBN, Sigma, 98%) was purified by recrystallization twice from methanol. Deuterated chloroform (CDCl₃, 99.8% D) and methanol (CD₃OD, 99.8% D) were purchased from Cambridge Isotope Laboratories Inc., USA, for NMR study. The chain transfer agent (CTA) 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDP) was synthesized following the procedure as mentioned elsewhere.⁴⁶ The Boc-alanine methacryloyloxyethyl ester (Boc-Ala-HEMA) monomer was synthesized from Boc-Ala-OH and HEMA following the procedure mentioned elsewhere.⁴⁷

General Procedure of Gel Synthesis. All cross-linked polymer gels were synthesized via reversible addition–fragmentation polymerization (RAFT) technique following the procedure describe elsewhere, using AIBN as radical source, CDP as CTA, and DEGDMA as cross-linker in a septa sealed 20 mL glass vial at 70 °C.⁴⁸ A typical example of gel synthesis is as follows: Boc-Ala-HEMA (1.00 g, 3.32 mmol), DEGDMA (16.08 mg, 0.0664 mmol), CDP (6.69 mg, 1.66 × 10⁻² mmol), AIBN (0.54 mg, 3.32 × 10⁻⁴ mmol; 0.1 g solution of 5.4 mg of AIBN in 1.0 mL of DMF), 0.15 g of anhydrous DMF, and a magnetic stir bar were taken in a 20 mL septa sealed glass vial. Then the reaction vial was purged with dry nitrogen for 20 min, and gelation reaction was carried out in a preheated reaction block at 70 °C. Stirring was stopped when the reaction mixture became viscous. Finally, the reaction was quenched by rapid cooling in ice–water bath and exposure to air after 24 h. Details of gel purification and characterization can be found in the Supporting Information.⁴⁹

Deprotection of Boc Protected Cross-Linked Gels. Confirmation of deprotection of P(Boc-Ala-HEMA) homopolymers led us to carry out the deprotection of cross-linked gels to obtain corresponding polyelectrolyte hydrogels with F⁻, Cl⁻, Br⁻, HSO₄⁻, and TFA⁻ counteranions. In a typical run, 100 mg of Ala50 organogel was soaked in the methanol/acid mixtures (1:2; v:v) for 48 h. Then, the swelled gel was

Table 1. Synthesis of Cross-Linked Polymer Gels via RAFT Polymerization of Boc-Ala-HEMA in DMF at 70 °C^a

gels	[monomer]/[DEGDMA]/ [CDP]/[AIBN]	gelation time ^b (min)	conv ^c (%)
Ala50	50/2/0.5/0.1	65	81
Ala100	100/2/0.5/0.1	75	78
Ala200	200/2/0.5/0.1	95	75

^aGels were synthesized for 24 h. ^bGelation time. ^cDetermined gravimetrically by comparing the weight of the dry gels with respect to the monomer.

washed six times with methanol and then with dichloromethane six times. In this process the gel collapsed to its original volumes. The modified gel was dried at room temperature for 1 day followed by drying under high vacuum at 45 °C for 2 days. Boc deprotection of polymer gels was confirmed by ¹³C CP/MAS NMR spectroscopy (Figure S2, Supporting Information).

Determination of Swelling Ratio (SR) by the Gravimetric Method. SR of synthesized cross-linked polyelectrolyte hydrogels was studied gravimetrically at room temperature. A measured amount of dry gel was kept in DI water overnight to reach equilibrium swelling. Then, the swelled hydrogel was taken out carefully from water, was wiped the surface water with moist tissue paper, and weighed. The SR of swelled gels was determined using eq 2:

$$\text{swelling ratio} = \frac{W_s - W_d}{W_d} \quad (2)$$

where W_d and W_s are the mass of the dried and swollen cross-linked polyelectrolyte samples, respectively.

Gel Conductivity Measurements. Ionic conductivity of polyelectrolyte hydrogels was measured at 25.2 °C by the Mettler Toledo SevenGo (8603 Schwerzenbach, Switzerland) portable conductivity meter. Measured amounts of gels were swelled in DI water (1.0 mg in 3.0 mL of water) for 24 h, water was removed, and swelled gels were put inside the probe of the conductivity meter.

NMR Studies. ¹H NMR spectroscopy was carried out in a Bruker Avance^{III} 500 spectrometer at 25 °C. Solid-state ¹³C CP/MAS NMR spectroscopy was also carried out in the same Bruker Avance^{III} 500 spectrometer, and details of the experimental procedure can be found elsewhere.⁵⁰

FT-IR Analysis. The FT-IR spectrum of cross-linked gels was recorded on KBr pellets using a PerkinElmer Spectrum 100 FT-IR spectrometer.

III. RESULTS AND DISCUSSION

III.A. Gel Swelling. A.1. Counterion Specificity. Theory.

To analyze the effect of counterion type on the gel swelling, the equilibrium gel parameters are calculated at various values of the parameter b corresponding to different efficiency of ion pairing. In Figure 2 we plot dependencies of (a) the gel volume normalized by the volume of a dry gel, $V_{\text{gel}}/V_{\text{dry}}$, (b) the fraction p of charges in polymer chains forming ion pairs with counterions, and (c) the fraction β of Manning-free counterions for different effective counterion sizes b .

First, the gel swelling ratio depends on the counterion effective size: the larger the counterion, the higher the swelling (Figure 2a). This tendency should be attributed to a stronger electrostatic attraction of small counterions to the charges on polymer chains resulting in a higher energy gain in the course of ion pairing:

$$\Delta E = -\frac{e^2}{\epsilon k_B T a b} = -\frac{l_b^{\text{pol}}}{a b} = -\frac{u}{b}$$

Values of p are higher and β values are smaller at low b (Figures 2b,c).

Scheme 1. Synthesis of Boc Protected Cross-Linked Organogels via RAFT Techniques, Followed by Boc Deprotection with HF, HBr, HCl, H₂SO₄, and TFA To Give Boc Deprotected Polyelectrolyte Hydrogels Containing Different Counterions

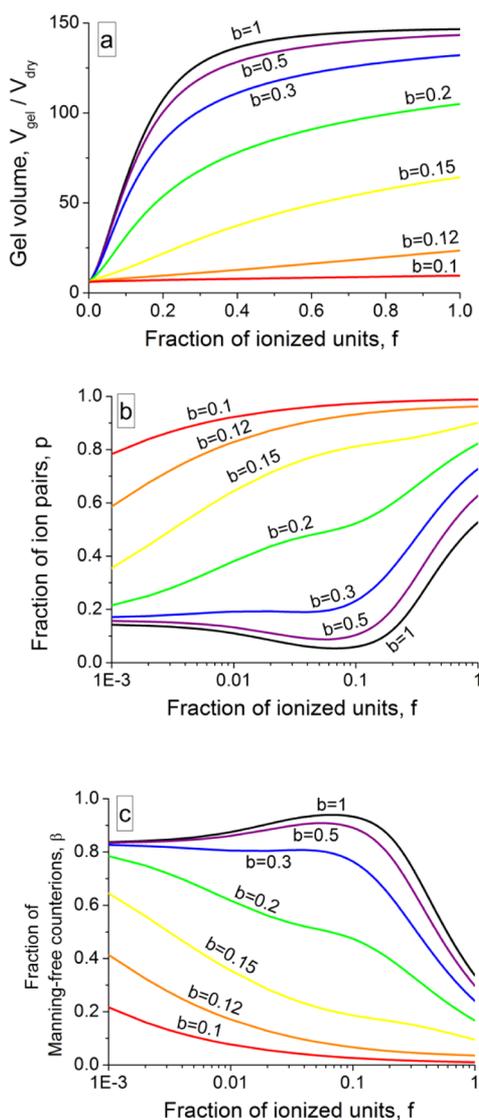
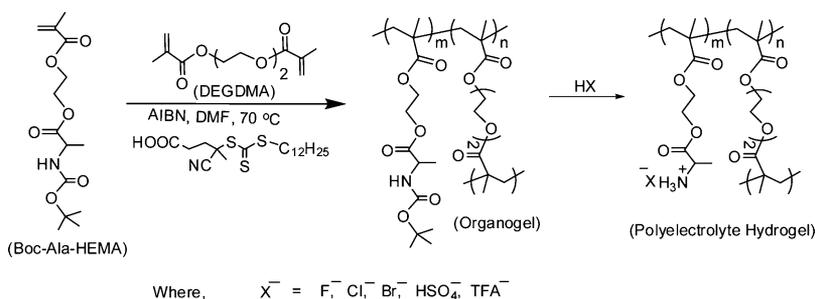


Figure 2. Effect of counterion type on gel swelling (a) and ion condensation (b, c): effective counterion size is varied from small ($b = 0.1$) to large ($b = 1.0$) at $N = 25$, $\chi = 0.5$, and $u = 1$.

Second, gel ionization causes a highly pronounced swelling only at relatively low values of f because at high f the Manning condensation sets in. At very low degrees of ionization ($f \ll 1/N$, i.e., much less than one counterion per subchain) the gel swells equally at any b since it is virtually neutral, and volume interactions dominating over effects caused by the presence of counterions govern gel swelling: e.g., in Θ -solvent

$V_{gel}/V_{dry} \approx \sqrt{N} \approx 5$. The characteristic threshold f^* of Manning condensation outset can be estimated from the equality between the solution Bjerrum length and the distance between nearest-neighbor charges along the chain: $f^* = a/nl_b^{sol}$. One can find $f^* = 0.33$ for parameter values chosen above, in accordance with the numerical calculations. At $f > f^*$ Manning condensation starts to manifest itself: appearance of additional counterions within the gel results not in increasing osmotic pressure but in their Manning condensation followed by ion pair formation. Thus, the gel retains approximately constant volume during further ionization (Figure 2a).

Third, the described above tendency is correct only for bulky enough counterions ($b > 0.3$) which almost do not form ion pairs at low degrees of gel ionization (Figure 2c). In contrast, small counterions are bound to charges on polymer chains even at low f so that the gel swelling occurs to be rather small, while the fraction of ion pairs p is high enough even below the threshold of Manning condensation $f^* = 0.33$. Note also that Manning condensation itself does not depend on the counterion size since it is caused by the interaction of the counterion with the collective electric field created by numerous charges on polymer chain. The former can be treated as point-like charges, and the parameter b is not required. Difference between swelling of the gels at $b = 1$ and $b = 0.5$ is small at low f when $p \approx 0$ and grows at higher f because of increasing ion pairing: for bulky counterions half of all counterions forms ion pairs in the completely ionized gel (Figures 2a,b).

Nonmonotonic dependence of p and β on f at relatively high counterion effective size, $b > 0.3$, is caused by the gel swelling due to osmotic pressure of free counterions. The higher the gel volume, the more favorable the escape of counterions into the outer zone due to entropic reasons. At low ionization degrees, $f < 0.1$, the average concentration of counterions within the gel goes down with f . Indeed, the gel volume can be estimated as $V_{gel} \sim N^3(nf)^{3/2}$ (see Appendix), and the concentration of counterions equals $Nnf/V_{gel} \sim N^{-2}(nf)^{-1/2}$. Therefore, ion binding diminishes: the fraction of ion pairs p is close to zero, and almost all counterions occupy the outer zone ($\beta \approx 1$) nearby $f = 0.1$ (Figures 2b,c; $b = 0.5$ and $b = 1$). At higher f gel swelling is lower than the estimate $V_{gel} \sim N^3(nf)^{3/2}$ because of decreasing extensibility of subchains (Langevin instead of Gaussian form of elasticity; see Appendix) and Manning condensation, so that the average counterion concentration grows at increasing f , resulting in enhanced ion association.

Finally, due to low entropy loss the vast majority of Manning-condensed counterions form ion pairs ($p \approx 1 - \beta$) at all ionization degrees except for the limit $f \approx 1$. Therefore, in subsequent consideration we plot only the fraction of free counterions β vs ionization degree f , which is enough to represent

Table 2. Swelling Ratio of Deprotected DGP($^{-}\text{XH}_3\text{N}^+\text{-Ala-HEMA}$) Polymer Gels of Various Cross-Linking Density (Ala50, Ala100, Ala200) with Different Counterions ($\text{X}^- = \text{Cl}^-$, HSO_4^- , F^- , Br^- , TFA^-) in DI Water

gel\counterion	Cl^-	HSO_4^-	F^-	Br^-	TFA^-
Ala50	4.1 ± 1.1	6.2 ± 1	34 ± 2.0	42 ± 2.5	87 ± 3.0
Ala100	5.4 ± 1.0	9.1 ± 1.5	50 ± 2.7	88 ± 3.5	94 ± 3.6
Ala200	8.5 ± 1.5	11.6 ± 1.7	58 ± 2.0	105 ± 3.5	136 ± 4.0
corresponding theoretical effective ion pair size b	0.1	0.12	0.15	0.2	0.5

ion association processes within the gel. Despite $p \approx 1 - \beta$, a separate account for the second ion association step is necessary to predict counterion specificity in gel swelling because the fraction of Manning-condensed counterions and fraction of ion pairs are interdependent values.

Experiment. Experimentally measured swelling ratios of deprotected gels are depicted in Table 2. One can see that swelling ratio of hydrogels increases in the order of $\text{Cl}^- < \text{HSO}_4^- < \text{F}^- < \text{Br}^- < \text{TFA}^-$ for any cross-linking density.

Since experimentally investigated gels are fully ionized and each of their monomer unit carries elementary charge, theoretical value $f = 1$ matches these gels well. Swelling ratios of Ala200 gels with different counterions approximately coincide with the theoretical ones calculated at $f = 1$ for different values of ion pair effective size (see the lower row of Table 2: $b = 0.5$ for TFA^- , 0.2 for Br^- , 0.15 for F^- , 0.12 for HSO_4^- , and 0.1 for Cl^-), i.e., for different values of the energy gain from ion pair formation. Note that this order of counterion affinity to charged primary amino group qualitatively coincides with the results known for the low molecular weight counterparts, i.e., affinity of counterions to the ammonium ion NH_4^+ which can be estimated from melting points and solubilities of the corresponding ammonium salts. Thus, NH_4Cl salt demonstrates the lowest solubility in water (29.4 g per 100 g of water at 273 K) and the highest melting temperature (793 K) among all, and it is reasonable that the hydrogel with Cl^- is the most shrunken. On the contrary, NH_4F and NH_4TFA salts are highly soluble in water (more than 100 g per 100 g of water for the both) and show relatively low melting temperatures (373 and 497 K, respectively) as compared to the other salts, so that a high swelling of the gels with F^- and TFA^- counterions is expected. Ammonium salt with Br^- counterion standing between F^- and TFA^- counterions in the gel swelling rank demonstrates only slightly higher melting temperature 508 K and a lower solubility, 60.6 g per 100 g of water (i.e., molar concentration is close to that of the NH_4Cl salt). This mismatch could be probably caused by different requirements to the counterions sizes providing the strongest ionic binding for low-molecular-weight and polymer salts, respectively. Close anion and cation ionic radii is known to be such a criterion in the former case, while in the latter case ionic counterion radius plus ionic radius of the charged group on polymer chain should be approximately equal to the distance between neighboring charged groups along the chain.^{33–35} As to rather bulky HSO_4^- counterions, most probably they exist in the solution in SO_4^{2-} form because $\text{pK}_a = 2$ for the second step of sulfuric acid dissociation $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$, and multivalent counterions are known to efficiently stabilize a collapsed state of PEs.^{15,26,51,52}

A.2. Effect of Solvent Polarity. Theory. Counterion size affects only the second step of ion association, i.e., ion pair formation, while solvent polarity influences Coulomb interactions within the gel at any length scales, and therefore both Manning condensation and ion pairing strengthen as solvent becomes less polar.

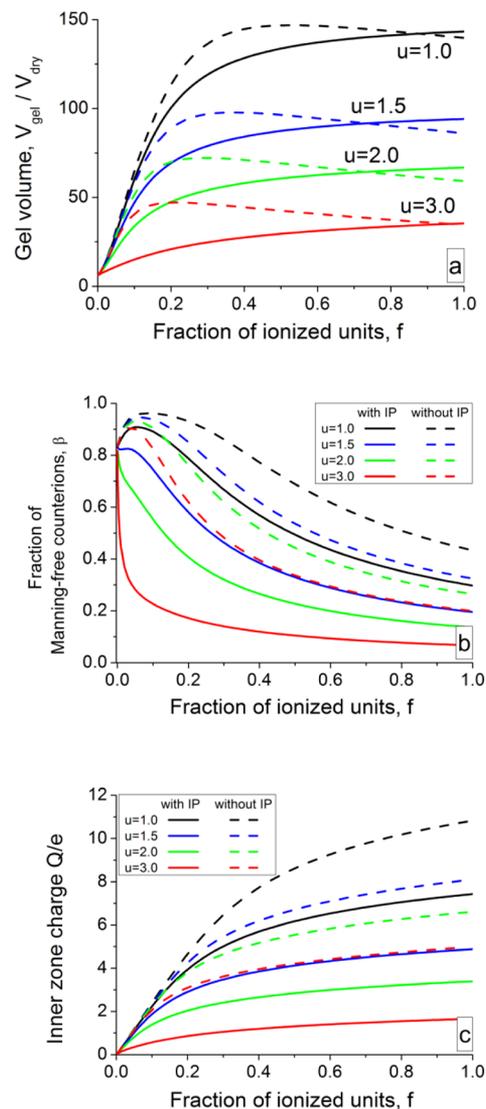


Figure 3. Gel swelling ratio (a), fraction of Manning-free counterions (b), and charge of the inner zone (c) vs fraction of charged monomers f at different solvent polarities $u = 1, 1.5, 2,$ and 3 ; $N = 25, \chi = 0.5$. Ion pairing is either considered (solid line, with IP) or neglected (dashed line, without IP); for solid curves $b = 0.5$; for dashed curves $F_{\text{agg}} = 0$.

A series of curves in Figure 3 are plotted for various values of the solvent polarity u . Solid lines were calculated with the account for ion pairing though counterions are assumed to be rather bulky and ion binding is weak, $b = 0.5$. The dashed curves are plotted for no ion pairing at all; i.e., aggregation free energy term was neglected, $F_{\text{agg}} = 0$. As mentioned above, $u > 1$ corresponds to the case of organic solvents being less polar than water. Since $u = l_b/a = e^2/\epsilon a k_B T$ and for water with dielectric constant $\epsilon = 80$ we get $u = 1$, one can easily find that the values $u \approx 2.4$ and $u \approx 3.3$ should be ascribed to methanol and ethanol with $\epsilon = 32$ and $\epsilon = 24$, respectively.

It is clearly seen from Figures 3a,b that decreasing solvent polarity favors ion condensation and results in a lower gel swelling. The threshold of Manning condensation given by $f^* = 1/nu$ equals 0.33, 0.22, 0.17, and 0.11 at $u = 1, 1.5, 2$ and 3 , respectively. Below $f^* = 0.11$ all dashed curves for both the gel volume (Figure 3a) and the fraction of Manning-free counterions β (Figure 3b) coincide with each other since counterion interaction with the charged polymer chain is weak because of its low charge density. At the same time, the solid curves considerably differ at any $f > 0$ (even $f < f^*$) because of ion pairing (Figures 3a,b). For any solvent polarity u gel ionization above the corresponding threshold of Manning condensation $f^* = 1/nu$ leads to a rather moderate gel swelling (Figure 2a, solid line), or even slight gel contraction if ion pair formation is omitted (Figure 3a, dashed line). Deswelling of the gel in the latter case is caused by a tendency to diminish an excess electrostatic energy of the gel interior: decreasing of the outer zone volume results in a higher neutralization of the excess inner zone charge Q due to redistribution of counterions with enhanced Manning condensation. At the same time, limiting values of the linear charge density at a high degree of ionization $f \rightarrow 1$ are much lower than the well-known Manning results $Q/Na\epsilon = 1/l_b$ owing to the outer zone finite volume. On the contrary, if ion pairing is possible providing additional energy gain ΔE , more counterions occupy the inner zone (Figure 3b) and its charge Q is much lower (Figure 3c, compare solid and dashed curves) so that gel shrinking is not required to ensure a higher degree of subchain neutralization.

Note gel volume at $f = 1$ even without ion pairing is almost 2 times lower than that calculated in the approximation when counterions are treated as an ideal gas (see Appendix and Figure 9). This discrepancy emphasizes the importance of Manning condensation in highly charged PE systems.

These results are supported by different experimental studies. PAA gel with bulky TBA counterions in methanol demonstrated remarkable swelling upon ionization only below $f \approx 0.3$. At higher content of charged groups its volume changed not more than by 20% against the maximum value slightly increasing in the range $0.3 < f < 0.5$ and decreasing at higher $f > 0.5$.¹⁶ Note that ion pairing between TBA⁺ counterions and carboxylic COO⁻ groups should be increasingly hindered upon gel ionization owing to strong steric repulsion of bulky counterions. The model neglecting ion pairing (dash curves) seems to be more appropriate in this case: theoretical prediction of slight gel deswelling ($\sim 20\%$) quantitatively coincides with experimental result. Probably, an additional reason for it is a dipole–dipole attraction between ion pairs^{53,54} and other correlation effects^{26,55,56} neglected in the above mean-field consideration. On the other hand, account for the inner and outer zone uncompensated charges, Q and $-Q$, seems to be a proper mean-field approximation, especially for highly charged swollen gels, and correlation effects should be a small correction. Swelling of the same PAA gel with Na⁺ counterions in water/methanol mixtures was considered in ref 14, and the gels in mixtures containing more than 35 vol % of water remained highly swollen under complete ionization, $f = 1$. In these mixtures gel volume versus fraction of ionized groups f increased in a monotonous manner; however, gel swelling above $f = 0.6$ in water ($\epsilon = 80, u = 1$) and above $f = 0.4$ in 35/65 vol % water/methanol mixture ($\epsilon = 49, u = 1.6$) was either very moderate (again less than 20%) or absent at all. Furthermore, the gel volume in pure water 1.5 times exceeded that in 35/65 vol % water/methanol mixture, in accordance

with our theoretical calculations (Figure 3a, solid curves for $u = 1$ and $u = 1.5$). In contrast to TBA⁺ ions, ion pairing with Na⁺ counterions is not sterically hindered, and the gel volume does not diminish even near complete gel ionization ($f \approx 1$), in coincidence with our analysis (solid curves go up in the whole range of ionization degrees, $0 \leq f \leq 1$).

Our theoretical model also predicts a diminution of the gel volume at decreasing solvent polarity, and influence of counterion type on this contraction is shown in Figure 4. Since solvent is

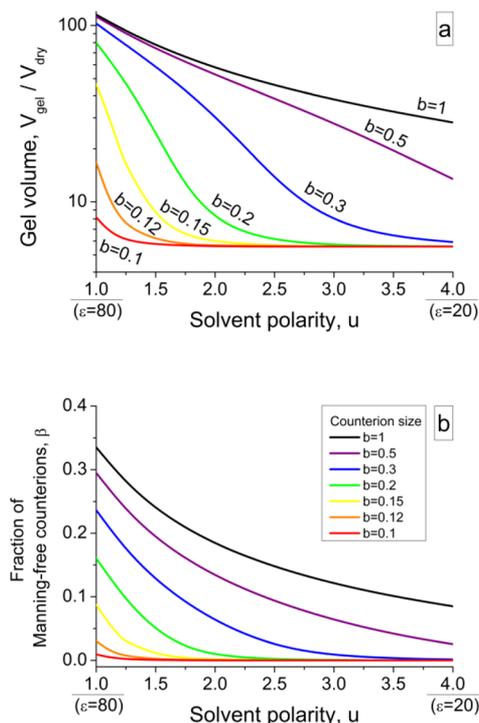


Figure 4. Gel swelling ratio (a) and fraction of free counterions (b) vs solvent polarity u at $N = 22, \chi = 0.5, f = 1$ and various values of counterion effective size in the range from $b = 0.1$ (small) to $b = 1.0$ (large). The range of parameter values $1 \leq u \leq 4$ approximately corresponds to that of a solvent dielectric constants $80 \geq \epsilon \geq 20$.

assumed to be Θ -solvent ($\chi = 0.5$), gel shrinking occurs continuously. In poor solvent this transition can be abrupt; see detailed discussion concerning effects of the solvent quality in the Supporting Information. For large counterions their specificity in gel swelling is well-defined in low polar medium, while volume of the gels with various small counterions differs higher in polar solvents. Gels with large counterions (effective size $b \geq 0.3$) demonstrate a higher swelling at any solvent polarity because of suppressed ion condensation (Figure 4b), and in the vicinity of $u = 1$ the smaller the counterion effective size b , the higher the rate of gel contraction at decreasing solvent polarity. In low polar solutions (high u) ion condensation processes are much stronger than in water, and in gels with small counterions almost all of them are bound with charges of the network (e.g., curves for $b \geq 0.2$ at $u > 3$). Since we neglect multiplet formation and effect of dielectric mismatch, gel volume under these conditions is mainly defined by volume interactions and coincides with that of a neutral gel, $f = 0$ (see Figure 2).

Experiment. Swelling of deprotected P(⁺H₃N-Ala-HEMA) gels with various cross-linking densities (Ala50 and Ala100) and different counterions was performed in aqueous methanol at

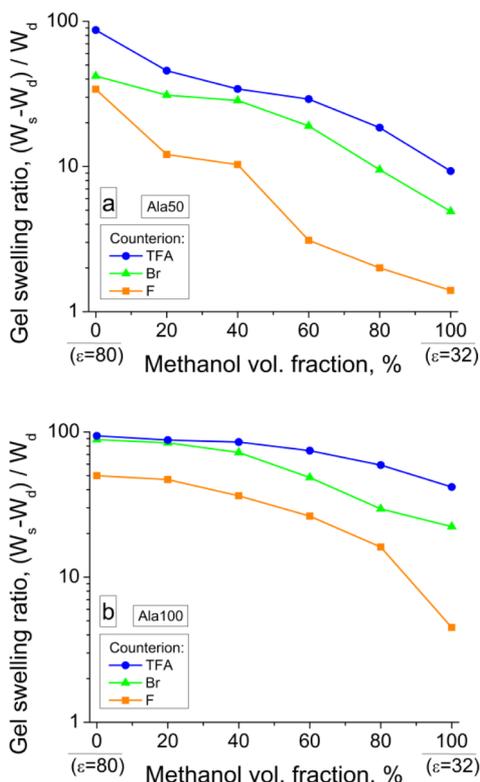


Figure 5. Swelling ratio of deprotected P(⁺H₃N-Ala-HEMA) gels in water/methanol mixtures with different types of counterions: TFA⁻, Br⁻, and F⁻. (a) and (b) correspond to the gels with different cross-linking density, Ala50 and Ala100, respectively.

different methanol volume fractions. As expected, gels with lower cross-linking densities demonstrate higher swelling (see detailed discussion in the next section). Counterions demonstrate affinity to the charges on polymer subchains in order $F^- > Br^- > TFA^-$ at any methanol content in the solution mixture. Decreasing gel volume upon methanol admixing supports our theoretical results on gel contraction induced by diminution of solvent polarity (see Figure 4). Direct comparison between theory and experiment can be found in Figure S5, where one-plot graphs of gel volume vs solvent polarity are shown.

A.3. Effect of Gel Cross-Linking Density. Theory. Our model allows to analyze the effect of the gel cross-linking density, i.e., subchain length N , as well (see Figure 6). Here we consider the case of a hydrogel ($u = 1$) in Θ -solvent ($\chi = 0.5$) with the counterion of intermediate size, $b = 0.2$.

Swelling of loosely cross-linked gel is considerably higher than that of densely cross-linked gel. However, a higher swelling should be attributed not only to the increasing length of subchains themselves but also to some changes in the state of the counterions (see Figure 6b and Figure S6). The higher the subchain length N , the higher the gel volume. Since $V(N)$ is much stronger than linear, concentration of counterions within the gel decreases at growing N . Therefore, ion condensation (both steps, Manning condensation and ion pairing) becomes less favorable because of higher entropy losses under counterion trapping and immobilization.

The gel volumes at $N = 10, 15, 25, 35, 50,$ and 100 equal to $V_{gel}/V_{dry} = 15, 35, 105, 215, 452,$ and 1900 . If one neglects Coulomb interactions at all, one would treat counterions as an ideal gas. Trapped within the network consisting of the subchains

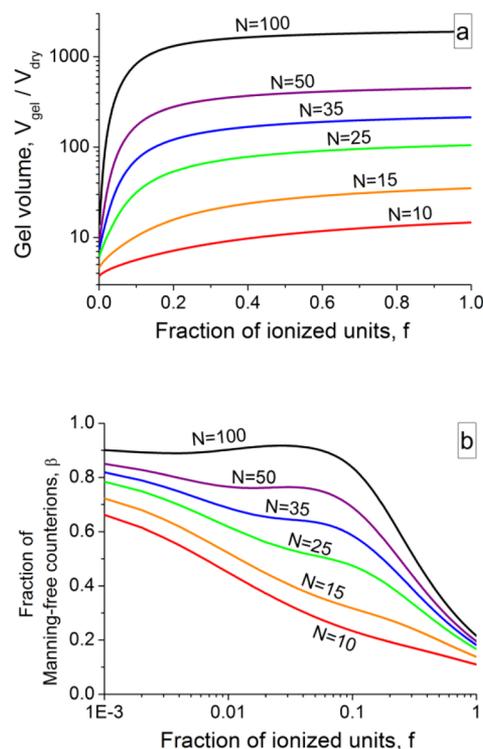


Figure 6. Gel swelling ratio (a) and fraction of Manning-free counterions (b) vs fraction of charged monomers f for $b = 0.2$, $u = 1$, and $\chi = 0.5$ at various subchain lengths expressed in the statistic segments number $N = 10, 15, 25, 35, 50,$ and 100 .

with the Gaussian elasticity, counterions create an exerting osmotic pressure and provide gel degree of swelling (signed below as $A \equiv V_{gel}/V_{dry}$) satisfying $A_{osm} \sim N^2$ (see Appendix). It should be emphasized that the Langevin form of subchain elasticity predicts the same values of exponents as the Gaussian one, $V_{gel} \sim N^3$ and $A_{osm} \sim N^2$.

Exact calculations (Figure 6a) show that $A(N = 25)/A(N = 10) \approx 7.0$ while in counterion ideal gas and Gaussian elasticity approximation the estimate $A(N = 25)/A(N = 10) = (25/10)^2 = 6.25$ should be satisfied. Similarly, $A(N = 50)/A(N = 25) \approx 4.3$ exceeds $2^2 = 4$ and $A(N = 100)/A(N = 50) \approx 4.2$ exceeds $2^2 = 4$. A higher swelling of slightly cross-linked gels predicted by theories omitting condensation processes is explained by Figures 6b,c: increasing N additionally promotes more counterions to locate in the outer zone and create exerting osmotic pressure. Plotting dependence of $\ln V_{gel}/V_{dry}$ on $\ln N$ at $f = 1$ in the range $10 < N < 100$, one can find linear dependence with a slope approximately equal to 2.11, so that $V_{gel}/V_{dry} \sim N^{2.11}$ and $V_{gel} \sim N^{3.11}$. In the power exponent 3.11 the contribution 3.0 should be referred to the subchain elongation itself, and the additional term 0.11 appears due to stronger dissociation of ionic groups in loosely cross-linked gels. Indeed, intensity of ion pairing is governed not only by counterion size but also by subchain length. Certainly, 0.11 is not a universal value, and it should vary with u and b values as well as N range, but here the power exponent was calculated in order to pictorially split it into two parts responsible for different effects, $3.11 = 3.0 + 0.11$.

Experiment. Comparing experimental results on the cross-linking density effect (Table 2), one can easily come to a conclusion that average efficient subchain lengths of Ala100 and Ala50 gels as well as Ala200 and Ala100 gels differ less than

twice because the volume differences of these gels is 2.1 times rather than $2^2 = 4$ or even $2^{2.11} \approx 4.3$ predicted by the above estimations. On the basis of our theory subchain lengths of Ala50, Ala100, and Ala200 gels can be approximately estimated (e.g., from the swelling of gels with Br^- counterions corresponding to $b = 0.2$) as $N = 15, 20,$ and 25 in statistical segment units (compare Table 2, gels with Br^- counterion, and Figure 6). More rigorous analysis of theoretical and experimental results on the gel swelling ratio based on comparison of gels with F^- , Br^- , and TFA^- counterions results in average values $N = 18, 22,$ and 25 (i.e., 54, 66, and 75 monomer units per subchain) for Ala50, Ala100, and Ala200 gels. Thus, the developed theory can serve as a tool for estimation of gel cross-linking density which generally differs from synthesis stoichiometry and depends on other synthesis conditions.

III.B. Gel Conductivity. In order to analyze theoretically the effect of the counterion type and the gel cross-linking density on the electric conductivity of the gels, the concentration of free counterions within the gel was found. Only counterions occupying the outer zone, i.e., neither involved in ion pairs nor Manning-condensed ones, were assumed to move freely within the gel and contribute to conductivity, so that their concentration was calculated as $c_{\text{free}} = Nf\beta/V_{\text{gel}}$. This assumption is supported by results of the von Klitzing and Mohvald groups on the conductivity of PE water solutions.⁵⁷ They found that below the threshold f^* of Manning condensation the solution conductivity increases linearly as the fraction f of ionic units goes up, while above f^* conductivity growth occurs to be approximately twice lower. It is natural to expect that the mobility of Manning counterions trapped within the charged cylinder of a subchain is restricted. Moreover, our model predicts that the most part of Manning-condensed counterions forms ion pairs thus being immobilized in the vicinity of subchain charges.

Here one could find an analogy to the case of solid crystalline materials where free mobile electrons of the conducting band contribute to conductivity while valence band electrons bound with the lattice sites do not. If all the electrons are bound and conducting band contains no charge carrier, sample represents dielectric rather than metal medium. In the case of PEs, the conducting band is analogous to the outer zone in our two-zone model, and the valence band is the inner zone. If there are no free counterions in PE gel, e.g., dense ionomer state is realized, gel conductivity is lower by far than that of a swollen gel.¹⁴ Similar conductivity drop at switching between PE and ionomer regimes was also observed for the case of PE solutions.^{58–61} Thus, if there are free counterions within the polymer system, PEs resembles metals, while in the absence of free charge carriers their electrical properties are alike with the ones of dielectrics. Analogy between PEs and metals/dielectrics occurs to be very wide and expands over the conductivity problem being useful for analysis of PEs conformational behavior as well⁴¹ (see Supporting Information). However, processes of charge carrier association in PEs and crystalline materials cardinal differ owing to different dimensionality of these problems: atoms in crystalline bodies are packed in 3D lattice while polymers at small length scales are 1D objects. Therefore, well-developed electron theory of metals cannot be directly applied to PEs.

It is known that conductivity is proportional to both concentration of mobile charges and their mobility μ . Thus, in order to compare gels with different cross-linking densities but the same type of counterions, it is enough to compare c_{free}

while comparison of conductivities of gels with different types of counterions Λ_i requires multiplying of c_{free} by μ , which is a microscopic characteristic of each counterion type, $\Lambda_i = \mu_i c_{\text{free}}$.

B.1. Effect of Cross-Linking Density. Theory. Dependencies of the relative gel volume $V_{\text{gel/dry}}$ and concentration of free counterions c_{free} (expressed in mol/L) vs degree of gel ionization f for various subchain lengths are plotted in Figure 7 in

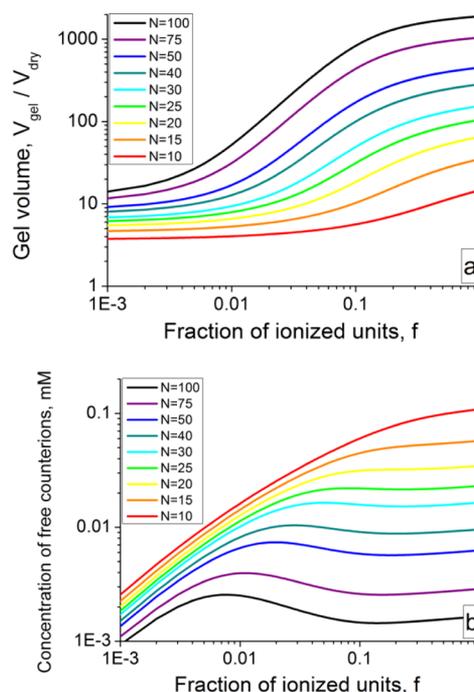


Figure 7. Effect of gel cross-linking density (different subchain length N) on the concentration of mobile counterions (i.e., gel conductivity) at $u = 1$ and $\chi = 0.5$.

double logarithmic coordinates. Three regimes of gel swelling and conductivity behavior can be distinguished.

Regime 1: $f \leq 1/Nn$. If the number of charges per one gel subchain is lower than unity (see Appendix), gel swelling is primarily defined by volume interactions and almost does not depend on f , $V(f) \approx \text{const}$ (see Figure 7a). At a constant gel volume (Θ -solvent case), ionization should lead to the linear growth of the free counterions concentration and conductivity, $c_{\text{free}} \sim Nf/N^{3/2} \sim f/\sqrt{N}$.

Regime 2: $1/Nn \leq f \leq f^*(N)$. $f^*(N)$ is a threshold of Manning condensation. Since the most part of counterions is free in this regime, they can be treated as an ideal gas which creates osmotic pressure striving gel subchains. Because of a moderate subchains stretching, the Langevin form of elastic energy coincides with chain elasticity in Gaussian approximation. Thus, the gel volume is given by $V_{\text{gel}} \sim f^{3/2}N^3$, and the gel conductivity goes down, $c_{\text{free}} \sim 1/(f^{1/2}N^2)$. This regime can be clearly distinguished for loosely cross-linked gels, $N \geq 40$ (Figures 7a,b). In the regime 2 the slopes of the curves $\ln V(\ln f)$ and $\ln c_{\text{free}}(\ln f)$ tend to $3/2$ and $-1/2$ with increasing N , respectively. Note that f^* depends considerably on N : at infinitely long gel subchains $N \rightarrow \infty$ the well-known result $f^* = 1/un$ is valid, and at the chosen $n = 3$ and $u = 1$ one gets $f^*(N \rightarrow \infty) = 0.33$. Entropy loss under counterions condensation is smaller for smaller N , $f^*(N)$ decreases, and hence condensation sets in at lower ionization degrees. For short subchains the value of the left regime border $1/Nn$ can be

equal to or even higher than the value of the right border $f^*(N)$, and this regime vanishes for densely cross-linked networks (e.g., $N = 10$ and $N = 15$, Figure 7). The curve for $N = 100$ reveals this regime in the ionization degree range 0.01–0.2, in approximate agreement with the above theoretical estimations.

Regime 3: $f \geq f^*(N)$. In this regime both the concentrations of free counterions and the gel volume hardly change, so that gel conductivity should be approximately constant (Figure 7b). However, in this regime our assumption that condensed counterions do not contribute to conductivity might lead to some inaccuracy. Increasing number of associated counterions upon gel ionization can result in a slight conductivity growth. Indeed, condensed counterions possess nonzero mobility along the backbone, though it is considerably limited.

It is clearly seen that the curves corresponding to various N being close at low values of f diverge upon gel ionization. This divergence is more pronounced in the second regime due to the strongest dependence of the conductivity on the subchain length, $\Lambda \sim c_{\text{free}} \sim 1/N^2$. As cross-linking density of the network decreases, the gel conductivity goes up at any f , though the dependence $c_{\text{free}}(N)$ shows different power exponents in different regions of gel ionization degree.

Experiment. The above theoretical result is qualitatively supported by experimental data on conductivity of gels with F^- , Br^- , and TFA^- counterions (see Table 3). As to quantitative

Table 3. Conductivity ($\mu\text{S cm}^{-1}$) of Deprotected DGP($^-\text{XH}_3\text{N}^+\text{-Ala-HEMA}$) Polymer Gels of Various Cross-Linking Density (Ala50, Ala100, Ala200) with Different Counterions ($\text{X}^- = \text{F}^-$, Br^- , TFA^-) in DI Water^a

gel\counterion	F^-	Br^-	TFA^-
Ala50	1780 ± 20	1210 ± 12	1122 ± 22
Ala100	1160 ± 16	1020 ± 13	756 ± 13
Ala200	750 ± 11	717 ± 18	555 ± 15
corresponding theoretical effective ion pair size b	0.15	0.2	0.5

^aAverage values from three measurements.

comparison, theory predicts approximately $\Lambda \sim N^{-2}$ for completely ionized network $f \approx 1$ (see Figure 7b); it follows from the crossover of regimes 2 and 3 and neglecting weak $f^*(N)$ dependence. Thus, analysis of experimental data on the gel conductivity in the framework of the developed theory also supports results of the previous part devoted to the gels swelling: difference in cross-linking density between Ala50 and Ala100 gels as well as between Ala100 and Ala200 gels is much lower than double.

Finally, nonmonotonous dependence of theoretically calculated conductivity Λ on the ionization degree f in gels, intricate as compared to monotonous one in PE solutions,^{63–65} should be attributed to the additional system degree of freedom, namely, variable gel volume. Polymer gel is able to change its volume in response to ionization while solution volume is fixed. Gel swelling/shrinking in turn suppresses/facilitates counterion condensation. In earlier attempts of theoretical comprehension of PE gel conductivity problem this fact was partly neglected. It was usually assumed that the fraction of Manning-condensed counterions depends solely on the subchain linear charge density but not on the gel volume,^{66–68} though network conductivity properties are known to resemble ones of the solution with the same concentration of polymer as within the gel.⁶⁷ We hope our

analysis could be useful for design of PE gels with desirable conducting properties since both fraction of ionized groups and network cross-linking density were shown experimentally to affect gel conductivity as well.^{70–73}

B.2. Effect of Counterion Type (Size). Theory. Concentrations c_{free} of free counterions within the gel vs the fraction f of ionized groups at various values of counterion effective size b are plotted in Figure 8a. In some ranges of b and f increasing b

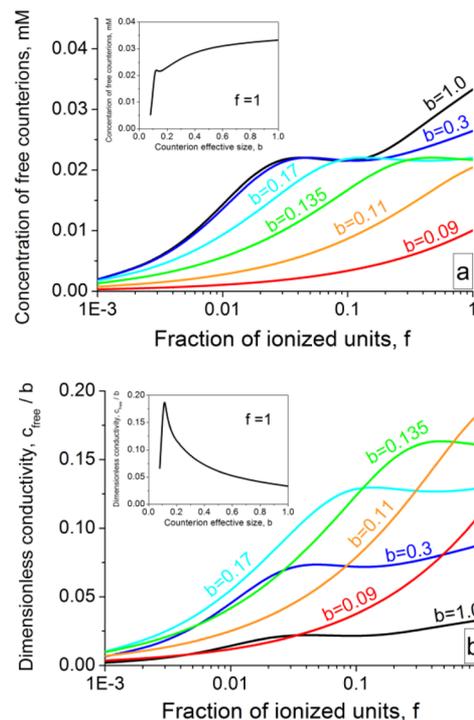


Figure 8. Effect of counterion effective size b on (a) the concentration of mobile counterions within the network c_{free} and (b) gel conductivity calculated as $\Lambda = c_{\text{free}}/b$ at $N = 25$, $u = 1$, and $\chi = 0.5$. Insets correspond to respective dependencies (c_{free} and $\Lambda = c_{\text{free}}/b$) on continuously varying b for fully ionized gel, $f = 1$.

results in c_{free} growth while in other ones c_{free} remains almost unchanged. To display this fact, we plot c_{free} as a function of b for completely ionized gel $f = 1$ (see inset in Figure 8a). Indeed, concentration of free counterions reveals a well-defined growth in the ranges $b < 0.1$ and $b \geq 1.5$ while it remains approximately constant (demonstrating even slight diminution) at $0.1 < b < 0.15$. At $f < 1$ the range of b with almost unchanged free counterions concentrations remains: for instance, at $f = 0.1$ concentration c_{free} is roughly the same at any b higher than 0.17 (see Figure 8a).

To calculate gel conductivity Λ , one should multiply concentration c_{free} by mobility μ_i of each counterion type. Mobility cannot be calculated theoretically since it is a function of not only counterions size but also counterion chemical structure (shape, charge distribution, hydrogen bonding with water molecules, etc.). For the set of rather large counterions with similar chemical structure like TMA^+ , TEA^+ , and TBA^+ mobility goes down as counterions dimensions grows,⁷⁴ and it is natural to propose $\mu_i \sim 1/b_i$. This assumption is hardly valid for small counterions even with similar chemical structure, e.g., alkali metals or halogens. For alkali metal ions limiting conductivity exhibits maximal value for the largest rubidium ion Rb^+ and goes down as ion dimensions decreases, so that lithium limiting

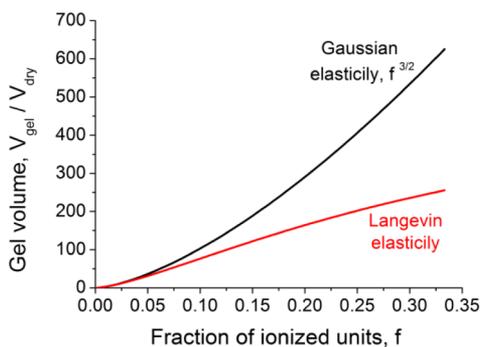


Figure 9. Gaussian vs Langevin elasticity; the gel volume vs fraction of ionized units at $N = 25$ and $n = 3$. Elastic energy is calculated in the framework of two approximations.

conductivity is the smallest in this set owing to the strongest solvation. Fluoride ion demonstrates the smallest mobility among halogens $\mu_{\text{F}^-} = 55.4 \times 10^{-4} \text{ S m}^2/\text{mol}$ because of strong solvation, while mobilities of other series terms are approximately equal, $\mu_{\text{Cl}^-} = 7.64$, $\mu_{\text{Br}^-} = 78.2$, and $\mu_{\text{I}^-} = 76.8$ in $10^{-4} \text{ S m}^2/\text{mol}$ units. Nevertheless, we plot dimensionless gel conductivity calculated as $\Lambda_i = c_{\text{free}}/b_i$ in the whole range of counterion effective sizes b (Figure 8b). Similarly to the case of free counterions concentration, dependencies of Λ_{free} on f demonstrate no common tendency with increasing b . The inset in Figure 8b demonstrates the curve c_{free}/b as a function of b at $f = 1$, and the maximum near $b = 0.135$ can be found. However, in this range of counterions effective size our assumption on ion mobility $\mu_i \sim 1/b_i$ is hardly valid. Prediction of conductivity diminution in the range $b > 0.3$ seems to be more reliable but also can be valid in the case of counterions with rather similar chemical structure.

Experiment. The developed approach allows to estimate theoretically numerical values of conductivity as well. It was demonstrated in the section A.1 that swelling of deprotected Ala200 gels with TFA^- , Br^- , and F^- counterions in water is approximately described by the theory at $N = 25$, $\chi = 0.5$, $u = 1$, and effective counterions sizes $b = 0.5$, 0.2 , and 0.15 (see Figures 2 and 8). Thus, our model predicts conductivity of these gels media equal to $\Lambda_{\text{F}^-} = 1191$, $\Lambda_{\text{Br}^-} = 1811$, and $\Lambda_{\text{TFA}^-} = 1231 \mu\text{S}/\text{cm}$. Here limiting ion conductivity for TFA^- ion was assumed to equal $\mu_{\text{CF}_3\text{COO}^-} = 42.6 \times 10^{-4} \text{ S m}^2/\text{mol}$, close to the one of acetate ion $\mu_{\text{CH}_3\text{COO}^-} = 40.9 \times 10^{-4} \text{ S m}^2/\text{mol}$ owing to their similar large sizes as compared to halogen ions.⁷⁵ Comparison between the obtained estimated values and experimental results shows that they differs approximately twice. Despite discrepancy between numerical experimental and numerical results which should be primarily attributed to numerous assumptions used in our theory, our approach seems to be rather advisable. It predicts correct qualitative results, and mismatch in numerical estimations is moderate. At that our model using minimal number of parameters (N , u , χ , b) should be rather clear and simple.

The present theory is aimed to a thorough consideration of a swollen gel state. It could be advanced by taking into account effect of polymer/solvent dielectric mismatch, i.e., combining with the one developed in refs 12, 13, and 16, in order to provide proper description of ionomer gel state. Both these theoretical approaches focus on ion association and contribute to comprehension of counterion specificity in PE gel swelling.

IV. CONCLUSION

The present combined theoretical and experimental investigation is aimed to development of a comprehensive understanding of ion condensation processes in highly charged PEs gels. In theoretical treatment applicable to the wide range of gel subchains linear charge density, two interdependent stages of ion association are considered: (i) interaction of counterions with charged cylinder of polymer subchain usually called “Manning condensation” and (ii) ion pairing, i.e., interaction of counterion directly with a separate chain charge. Accounting for ion pairing allows to explain experimentally observed counterion specificity of gel swelling. At the same time, it is account for Manning condensation which allows to correctly predict invariability of gel volume under ionization in the range of polymer linear charge densities exceeding Manning threshold which has many times been observed. With assumption that only free counterions are charge carriers, the developed model of ion association allows to explain the effect of counterion type and gel cross-linking density and on its conductivity. Since swelling and conformational transitions in PE gels are mainly defined by the state of counterions, free or associated, we hope our finding could be useful for design of highly responsive systems based on these gels.

APPENDIX

Consider counterions as an ideal gas trapped within the network volume. Since one subchain yields Nfn counterions and occupy the volume R^3 , the free energy of counterion translational motion equals

$$F_{\text{tr}} = Nfn \ln \left(\frac{Nfn}{R^3} \right)$$

Free energy of subchain stretching can be written either in Gaussian F_{el}^{G} or in Langevin F_{el}^{L} forms:

$$F_{\text{el}}^{\text{G}} = \frac{3R^2}{2Na^2}$$

$$F_{\text{el}}^{\text{L}} = N \left[\frac{R^2}{2N^2a^2} - \ln \left(1 - \left(\frac{R}{Na} \right)^2 \right) \right]$$

Note that at low deformations, $R \ll Na$, Langevin elastic free energy can be expanded into series, and the result exactly coincides with the Gaussian one.

Minimization of the total free energy including translational motion and elastic contribution can be done analytically, and the equilibrium end-to-end distance for gel subchains in Gaussian⁷⁶ and Langevin approximation equals

$$\frac{R_{\text{G}}}{aN} = \sqrt{fn} \quad (\text{A1})$$

$$\frac{R_{\text{L}}}{aN} = \sqrt{\frac{3}{2} \left(1 + fn - \sqrt{1 + \frac{2}{3}fn + (fn)^2} \right)} \quad (\text{A2})$$

Gel swelling degrees $V_{\text{gel}}/V_{\text{dry}} = R^3/Na^3$ vs the fraction of ionized units corresponding to these cases are plotted in Figure 9. If solvent is Θ -solvent for network subchains, un-ionized gel swells, and end-to-end subchain distance equals $R_{\Theta} = a\sqrt{N}$. The above results are correct when swelling induced by counterions osmotic pressure exceeds swelling caused by volume interactions, i.e., $R_{\text{G,L}} \gg R_{\Theta}$. Thus, formulas A1 and A2 are valid at $Nfn \gtrsim 1$, i.e.,

for a typical polymer gel with $n = 3$ (for instance, carbon-chain polymers) and $N = 25$ degree of ionization should exceed only 2–3%. Both approximations give cubic N dependence of the gel volume $V_{\text{gel}} \sim N^3$ and square N dependence of gel swelling degree $V_{\text{gel}}/V_{\text{dry}} \sim N^2$.

Above $f > 1/n$ Gaussian elasticity gives us unphysical result since end-to-end distance is higher than the contour length of the subchain, $R_G > aN$. Note that at $f = 1/n$ one can easily find $R_L/aN = 0.742$ while $R_G/aN = 1$, so that Gaussian approximation overestimates chain dimensions. Since gel volume is proportional to the cube of chain dimensions, $V_{\text{gel}} \sim R^3$, one can see that at $f = 1/n$ the ratio between gel volumes in Gaussian and Langevin approximations is $V_L/V_G = (R_L/R_G)^3 = 0.409$. Thus, for carbon-chain polymer gel ($n = 3$) at degree of ionization $f = 1/n = 0.33$ Gaussian approximation almost 2.5 times overestimates gel volume as compared to Langevin result. The latter in fact coincides much better with both experiment and computer simulations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b00911.

Details on gel synthesis and characterization, discussion of effect of the solvent quality on the polyelectrolyte gel swelling and collapse, direct one-plot comparison between theoretical and experimental results on gel volume vs solvent polarity, remarks on the analogy between polyelectrolytes and solid conductors/dielectrics (Figures S1–S6) (DOCX)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kram@polly.phys.msu.ru (E.Y.K.).

Notes

The authors declare no competing financial interest.

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