

# Dielectric Polarization of a Partially Neutralized Poly(methacrylic acid) in Dilute Aqueous Solutions: Conformational Transition

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**Abstract**—Dielectric permittivity  $\epsilon'$  (at a frequency of 1 MHz) of aqueous solutions of a partially neutralized poly(methacrylic acid) Na-PMAA was studied with varying the degree of ionization  $\alpha_i$  from 0 to 0.78 and concentrations  $w_2$  (g/g) from  $1.25 \times 10^{-4}$  to  $6 \times 10^{-3}$  at 25°C. It was shown that the concentration dependence of  $\epsilon'$  for Na-PMAA aqueous solutions at all  $\alpha_i$  values contains two regions corresponding to different changes in  $\epsilon'$ , and the above regions are separated by the crossover point  $w_2^*$ . In the first region,  $\epsilon'$  increases with the increasing concentration  $\Delta\epsilon'/\Delta w_2 > 0$ ; in the second region,  $\epsilon'$  decreases with the increasing concentration  $\Delta\epsilon'/\Delta w_2 < 0$ . The sign inversion of  $\Delta\epsilon'/\Delta w_2$  is explained by different structures of water and mechanisms of hydration in regions I and II. In the region corresponding to the ascending branch of the  $\epsilon'$ – $w_2$  curve, the dipole moments of macromolecules per repeating unit,  $\mu = (\langle M^2 \rangle / N)^{1/2}$ , were calculated according to the Buckingham theory. The  $\mu$  value is high; as a macromolecule is saturated with ionized units, this value nonmonotonically changes from ~10 D at  $\alpha_i = 0$  to ~18 D at  $\alpha_i \sim 0.24$ . This dependence peaks at ~30 D at  $\alpha_i \sim 0.1$ . As is assumed,  $(\langle M^2 \rangle / N)^{1/2}$  depends on the vector sum of partial dipole moments of hydrated nonionized monomer units ( $\mu \sim 10$  D) and fluctuation-induced dipole moments of ionized monomer units. The profile of  $\mu$  as a function of the degree of ionization of Na-PMAA indicates the occurrence of the conformational transition in an individual macromolecule. This transition takes place at the degree of ionization  $\alpha_i \sim 0.1$ . An analysis of molecular interactions in the (ionized coil)–solvent system explains the conformational transition in Na-PMAA.

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## INTRODUCTION

Poly(methacrylic acid) (PMAA) is one of the best known polyelectrolytes. Numerous studies have been devoted to studying the conformational properties of PMAA in aqueous solutions by various physical methods, such as viscometry, birefringence, etc. (see references cited in [1]). As was shown, partially neutralized Na-PMAA undergoes intramolecular conformational transition (for example, Okamoto and Wada [2]) within a narrow interval of neutralization degree  $\alpha_i$ . However, many problems concerning quantitative and qualitative features of the mechanism behind conformational changes in Na-PMAA during conformational transition are still open. Furthermore, on the whole, molecular interactions taking place in the system, comprising a dilute solution of charged Gaussian coils in a structured polar liquid, is far from being well studied. For such systems composed of polar components, the method of dielectric polymerization seems to be advantageous as

this method makes it possible to identify changes in the degree of mutual polarization of the components.

In this study, to gain a deeper insight into mechanisms behind molecular interactions in isolated coils of polyelectrolytes, when both macromolecules and solvent contain hydrogen bonds, the dielectric behavior of aqueous solutions of partially neutralized Na-PMAA was studied as a function of the degree of neutralization.

This investigation presents the follow-up study on molecular interactions in dilute solutions by the dielectric method for systems that involve a polar compound in a polar solvent and both components contain hydrogen bonds: isobutyric acid in methanol [3], nonionized poly(methacrylic acid) (PMAA) in methanol and water [4], and the sodium salt of poly(methacrylic acid) in methanol [1]. As was shown, the dielectric method is highly sensitive for studying the molecular interactions between oth similar and different molecules of constituent components in the solution. The above interactions

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are reflected by changes in the dielectric permittivity  $\epsilon'$  of solution and dipole moments of acid with varying concentration, temperature, or degree of ionization of molecular coils (hereinafter,  $\epsilon'$  defining the real part of dielectric permittivity is denoted as  $\epsilon$ ). In particular, the dielectric method allowed us to gain valuable information concerning the mechanism of intramolecular conformational transition in Na-PMAA solutions in methanol under infinite dilution conditions. As was shown, with the increasing degree of neutralization, the Na-PMAA chains tend to collapse and produce contact  $\text{COO}^- \dots \text{Na}^+$  ion pairs; this process is also accompanied by a partial release of solvated solvent molecules. In this study, we used the dielectric method to study conformational changes with the increasing degree of neutralization of Na-PMAA in water.

### EXPERIMENTAL

In this study, we used the same PMAA samples (Polyscience) with  $M \sim 10^5$  as in our earlier publications [1, 4]. PMAA was neutralized by an aqueous solution of sodium hydroxide. The samples were prepared using fresh bidistilled water with a specific resistivity of  $\sim 5 \times 10^6$  Ohm cm.

The dielectric measuring device and the testing procedure have been described in our recent publications [3–5]. To prevent the effect of near-electrode polarization on the dielectric parameters of the polar systems under study, the measurements were performed at a frequency of 1 MHz by using an E7-12 bridge.

Dielectric permittivity of solutions at 25°C was estimated by the interpolation of the linear temperature dependences of electric capacity of a capacitor with a solution at temperatures ranging from 20 to 30°C. The experimental error in temperature measurements was no higher than  $\pm 0.1^\circ\text{C}$ . Concentrations  $w_2$  of aqueous Na-PMAA solutions did not exceed  $6 \times 10^{-3}$  g/g.

The effective dipole moment of Na-PMAA molecules per repeating unit in the polar solvent (water) was estimated through the Buckingham–Fröhlich formula [6]; this formula takes the following form for a system composed of two polar components:

$$\begin{aligned} & [(\epsilon_{12} - 1)(2\epsilon_{12} + 1)/3\epsilon_{12}]V_{12} \\ & - [(n_1^2 - 1)(2\epsilon_{12} + 1)/(2\epsilon_{12} + n_1^2)]V_1x_1 \\ & - [(n_2^2 - 1)(2\epsilon_{12} + 1)/(2\epsilon_{12} + n_2^2)]V_2x_2 \\ & = (4\pi N_A/3kT)[(\mu_{1\text{eff}})^2x_1 + (\mu_{2\text{eff}})^2x_2], \end{aligned} \quad (1)$$

where  $\epsilon$  is the dielectric permittivity,  $n$  is the refractive index,  $V$  is the molar volume,  $V = Mv_{\text{sp}}$  ( $v_{\text{sp}}$  is the specific volume),  $M$  is the molecular mass,  $x$  is the molar fraction,  $T$  is the absolute temperature,  $N_A$  is Avogadro's number,  $k$  is the Boltzmann constant, and  $\mu_{\text{eff}}$  is the effective dipole moment; subscripts 1 and 2

refer to the solvent and dissolved component, respectively.

Molecular masses  $M_2$  and refractive indices  $n_2$  of the second component (Na-PMAA) should be introduced with account for the molar content  $\alpha$  of neutralized MAA units.

With use of the additivity principle, the molecular mass  $M_2$  and the molar refraction  $R_2$  for a Na-PMAA unit are estimated according to the following relationships:

$$M_2 = \alpha_i M_{\text{Na-MAA}} + (1 - \alpha_i) M_{\text{MAA}}, \quad (1a)$$

$$(R_D)_2 = \alpha_i (R_D)_{\text{Na-MAA}} + (1 - \alpha_i) (R_D)_{\text{MAA}}, \quad (1b)$$

where  $M_{\text{Na-MAA}}$  and  $(R_D)_{\text{Na-MAA}}$  stand for the molecular mass and molar refraction of the Na-MAA repeating unit, respectively.

In this case,  $\mu_{2\text{eff}}$  in Eq. (1) characterizes the mean-square dipole moment of the Na-PMAA macromolecule per repeating unit  $(\langle M^2 \rangle / N)^{1/2}$ , where  $N$  is the sum of neutralized  $\alpha_i N$  and nonneutralized  $(1 - \alpha_i) N$  units.

According to the statistical theory of dielectric polarization,

$$(\mu_{\text{eff}})^2 = (\mu_{\text{app}})^2 g. \quad (2)$$

Here,  $g$  is the correlation parameter for orientations of dipole moments, which characterizes the short-range interaction, and  $\mu_{\text{app}}$  is the apparent dipole moment of a polar molecule, which is related to its dipole moment in vacuum,  $\mu_0$ , by the following relationship:

$$\mu_{\text{app}} = [(n^2 + 2)(2\epsilon + 1)/3(2\epsilon + n^2)]\mu_0. \quad (3)$$

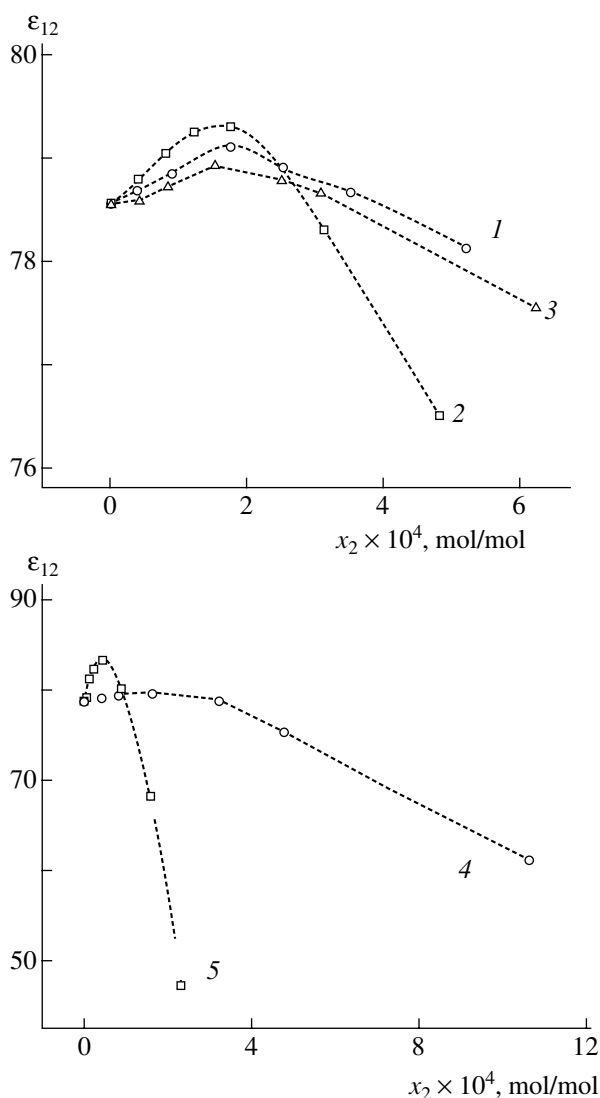
To estimate  $\mu_{2\text{app}} = [(\mu_{02})^2 g_2]^{1/2}$  under the infinite dilution conditions, the orientation polarization of the components are calculated according to formulas (1)–(3):

$$\begin{aligned} S_{12} &= [(\mu_{1\text{eff}})^2(1 - x_2) + (\mu_{2\text{eff}})^2x_2] \\ &= \{(\mu_{1\text{eff}})^2 + [(\mu_{2\text{eff}})^2 - (\mu_{1\text{eff}})^2]x_2\} \\ &= (3kT/4\pi N_A)[(\epsilon_{12} - 1)(2\epsilon_{12} + 1)/3\epsilon_{12}]V_{12} \\ &\quad - [(n_1^2 - 1)(2\epsilon_{12} + 1)/(2\epsilon_{12} + n_1^2)]V_1x_1 \\ &\quad - [(n_2^2 - 1)(2\epsilon_{12} + 1)/(2\epsilon_{12} + n_2^2)]V_2x_2. \end{aligned} \quad (4)$$

The corresponding dependences of  $S_{12}$  on concentration  $x_2$  are plotted. As is seen, such dependences should consist linear functions  $S_{12} = a + bx_2$ . With the knowledge of coefficients  $a$  and  $b$ , dipole moments of both components under infinite dilution conditions are estimated as:

$$(\mu_{1\text{eff}})^2|_{x_2=0} = (S_{12})|_{x_2=0} = a, \quad (5)$$

$$(\mu_{2\text{eff}})^2|_{x_2=0} = (\mu_{1\text{eff}})^2|_{x_2=0} + b. \quad (6)$$



**Fig. 1.** Dielectric permittivity  $\epsilon_{12}$  vs. concentration  $x_2$  of aqueous solutions of Na-PMAA at  $\alpha_i = (1)$  0.05, (2) 0.1, (3) 0.24, (4) 0.5, and (5) 0.78. Temperature is 25°C.

Finally, taking into account the fact that, under the infinite dilution conditions, the extrapolation of  $\epsilon_{12}$  to  $x_2 = 0$  leads to  $\epsilon_{1\text{extr}}^2$  and using relationships (2) and (3), one can calculate the dipole moments of water (1) and Na-PMAA (2):

$$\begin{aligned} \mu_{1\text{app}} &= [(\mu_{10})^2 g_1]^{1/2} \\ &= [(\mu_{1\text{eff}})|_{x_2=0}] / [(n_1^2 + 2)(2\epsilon_1 + 1)/3(2\epsilon_1 + n_1^2)], \end{aligned} \quad (7)$$

$$\begin{aligned} \mu_{2\text{app}} &= [(\mu_{20})^2 g_2]^{1/2} \\ &= [(\mu_{2\text{eff}})|_{x_2=0}] / [(n_2^2 + 2)(2\epsilon_{1\text{extr}} + 1)/3(2\epsilon_{1\text{extr}} + n_2^2)]. \end{aligned} \quad (8)$$

<sup>2</sup> Owing to polarization of a continuum of water by charged Na-PMAA coils,  $\epsilon_{1\text{extr}}$  may not coincide with  $\epsilon_1$  of pure water.

Refractive indices  $n$  are calculated from the molar refraction  $R_D$  at fixed temperatures through the following formula:

$$R_D = [(n^2 - 1)/(n^2 + 2)]/(M/\rho). \quad (9)$$

The molar refraction  $R_D$  is estimated from the molar refractions of bonds. The refraction of the  $\text{Na}^+$  ion is assumed equal to  $\sim 0.400 \text{ cm}^3$  [7].

The density  $\rho_2 = 1/\bar{v}_2$  for Na-PMAA is taken equal to the density of nonneutralized linear Na-PMAA (in bulk) [2]. Specific volumes  $v_{12}$  of aqueous Na-PMAA solutions are taken equal to the specific volume  $v_1$  of a pure solvent (water) because polymer concentrations in the solution are very small.

The overall error in the estimation of dipole moment was  $\pm 0.02 \text{ D}$ .

## RESULTS AND DISCUSSION

Figure 1 presents the dielectric permittivity  $\epsilon_{12}$  plotted against the molar fraction  $x_2$  of polymer in solution; the curves correspond to the aqueous solutions of Na-PMAA with different degrees of neutralization  $\alpha_i$  (0.05, 0.1, 0.5, and 0.78) at 25°C. As is seen, for all Na-PMAA–water systems under study, the resultant concentration dependences of dielectric permittivity appear to be virtually the same. All curves clearly show two regions with different changes in  $\epsilon_{12}$  with increasing the polymer concentration in the solution: regions with positive ( $\Delta\epsilon/\Delta x_2 > 0$ ) and negative ( $\Delta\epsilon/\Delta x_2 < 0$ ) increments of dielectric permittivity. In [4], aqueous solutions of nonneutralized PMAA were studied; as was shown, the sign inversion of  $\Delta\epsilon/\Delta x_2$  is provided by the specific interaction of PMAA molecules with water and this interaction is different for isolated coils at  $x_2 < x_2^*$  and for coils with overlapped hydration spheres at  $x_2 > x_2^*$ .

As was mentioned in our previous publication [4], water is known to be a specific solvent. According to the models of liquid water and ice [8, 9], water molecules are grouped via hydrogen bonding into a lacelike three-dimensional structure; this structure is composed of flat pentagonal or hexagonal cycles, which are assembled into polyhedrons of different dimensions [10]. It is worth mentioning that water molecules in flat cycles are arranged so that the resulting dipole moment is different from zero, whereas bent cycles in icelike structures are nonpolar. Furthermore, singular water molecules are usually located inside a polyhedron in liquid water (in the general case, polyhedrons are open), and this is the reason for a denser packing of water molecules in liquid water as compared with ice. When a certain molecule with hydrophilic groups is placed into the continuum of water, it replaces a central water molecule in a polyhedron, and hydrogen bonds between different molecules are formed. In this way, a

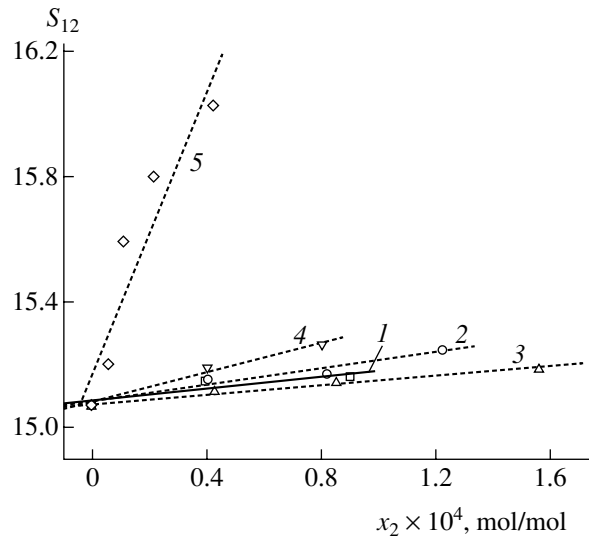
three-dimensional network of polyhedrons can accommodate monomer units of a macromolecule. Under infinite dilution conditions (an isolated macromolecule), local order excitations in the water continuum may be neglected within the first approximation. In this case, the mutual orientation of polar monomer units of PMAA and the nearest surroundings of water molecules in the polyhedral structure increase the dielectric permittivity of solution and  $\Delta\epsilon/\Delta x_2 > 0$ . Above a certain concentration  $x_2^*$  of macromolecules, the above behavior becomes impossible. The structure of polyhedrons based on water molecules breaks down and, on the whole, the dielectric permittivity of solution decreases ( $\Delta\epsilon/\Delta x_2 < 0$ ).

As follows from Fig. 1, the polymer concentration  $x_2^*$  corresponding to the point between ascending and descending branches of the concentration dependence of  $\epsilon_{12}$  decreases with increasing the content of neutralized units in a macromolecule. The  $x_2^*$  value changes by almost an order of magnitude, from  $1 \times 10^{-3}$  g/g at  $\alpha_i = 0.05$  to  $1.25 \times 10^{-4}$  at  $\alpha_i = 0.78$ . This behavior is related to the fact that strong electrostatic fields of ionized units break down the local order of water molecules inside the continuum sphere of a bigger radius.

Let us consider in more detail the dielectric behavior of the Na-PMAA aqueous solutions at the concentration  $x_2 < x_2^*$ , where  $\Delta\epsilon/\Delta x_2 > 0$ . The values involved in Eq. (1) are listed in the table:  $M_2$ ,  $n_2^2$ , and  $\epsilon_{1\text{extr}}$  at 25°C. As is seen, a gain in  $\epsilon_{1\text{extr}}$  over  $\epsilon_1$  grows with increasing the degree of neutralization  $\alpha_i$ . This behavior is related to an enhanced polarization of the water continuum by charged polyacid units.

Increments of the dielectric permittivity  $\Delta\epsilon/\Delta w_2$  and  $\Delta\epsilon/\Delta Q_2$  are also presented in the table. The values of the above increments are high and change on passing from solutions of non-neutralized acid to Na-PMAA solutions. The order of the  $\Delta\epsilon/\Delta Q_2$  values agree with the literature data for Na-PMAA solutions in water [11, p. 2168; Table 3].

According to Eq. (1) and the tabulated data, the orientation polarization of the components of Na-PMAA



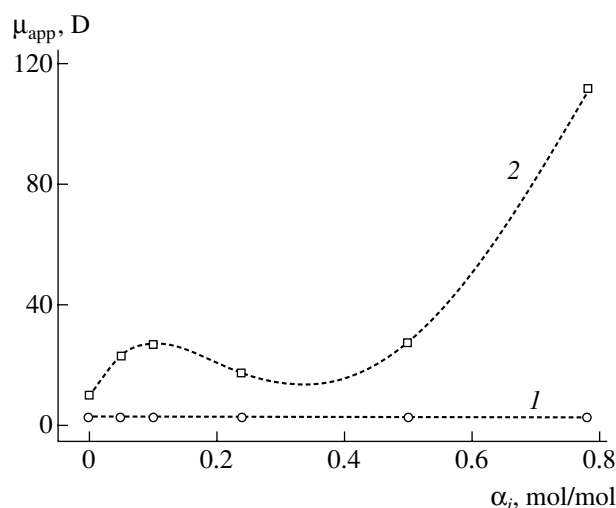
**Fig. 2.** Orientation polarization  $S_{12}$  of aqueous solutions of Na-PMAA vs. concentration  $x_2$  at  $\alpha_i = (1) 0.05, (2) 0.1, (3) 0.24, (4) 0.5, \text{ and } (5) 0.78$ . Temperature is 25°C.

aqueous solutions are calculated:  $S_{12} = x_1 \mu_{1\text{eff}}^2 + x_2 \mu_{2\text{eff}}^2$ . Figure 2 presents  $S_{12}$  plotted against the molar fraction  $x_2$  of the Na-PMAA component in aqueous solution. The linear character of such dependences makes it possible to use Eqs. (2)–(9) in order to estimate the apparent dipole moments  $\mu_{2\text{app}}$  and  $\mu_{1\text{app}}$  under infinite dilution conditions for a Na-PMAA macromolecule and water, respectively. In Fig. 3, the above values are plotted against the degree of neutralization of Na-PMAA. As is seen, the values of  $\mu_{1\text{app}}$  are slightly different from the dipole moment of water molecules (3.1 D), which was calculated for a continuum in [4]. This fact demonstrates the infinite dilute conditions in polymer solutions.

As follows from Fig. 3, changes in the dipole moment  $\mu_{2\text{app}}$  of Na-PMAA with increasing the degree of neutralization  $\alpha_i$  show a complex character and the  $\mu_{2\text{app}} = f(\alpha_i)$  curve can be divided into three regions.

Characteristics of Na-PMAA and aqueous solutions of Na-PMAA at different degrees of neutralization  $\alpha_i$  and at  $T = 25^\circ\text{C}$

$\alpha_i$ , mol/mol	$M_2$	$n_2^2$	$\epsilon_{1\text{extr}}$	$\Delta\epsilon/\Delta w_2$ , g/g	$\Delta\epsilon/\Delta Q$ , g-mol/l
0	86	2.107281431	78.54	489	40
0.05	87.1	2.082845981	78.56	638	54.81
0.1	88.2	2.059298377	78.56	1215	104
0.24	91.28	1.897810169	78.68	563	48.4
0.5	97	1.997696479	78.70	1008	87
0.78	103.16	1.807164557	78.98	19739	1698



**Fig. 3.** Dipole moments  $\mu_{app}$  for aqueous solutions vs. the degree of neutralization  $\alpha_i$  of (1) water molecules and (2) Na-PMAA under infinite dilution conditions. Temperature is 25°C.

**Region I ( $0 \leq \alpha_i \leq \sim 0.1$ ).** In region I, the dipole moment  $\mu_{2app}$  of Na-PMAA macromolecules increases from  $\sim 10$  D at  $\alpha_i = 0$  to  $\sim 30$  D at  $\alpha_i = 0.1$ . According to [12], the intrinsic viscosity of solutions in this region remains unchanged; that is, macromolecules preserve their dense compact structure even though the concentration of ionogenic salt units increases. The constancy of the intrinsic viscosity may attest to the absence of any dissociation between such units; namely, it indicates the formation of the  $-\text{COO}^- \dots \text{Na}^+$  ion pairs. The fact that the dipole moment increases when neutralized units with a high dipole moment appear in the structure of a macromolecule is not unexpected. The dipole moment of the  $-\text{COO}^- \dots \text{Na}^+$  ion pair is equal to  $\sim 7$  D, whereas the dipole moment of the non-neutralized fragment in gaseous state is  $\sim 1.9$  D [13]. However, an increased polarity of the neutralized units in the Na-PMAA macromolecule cannot explain high dipole moments  $\mu_{2app}$ . In the case under study, one should take into account the specific character of conformational changes in the Na-PMAA macromolecule with increasing the content of neutralized units in the chain, the content of the  $-\text{COO}^- \dots \text{Na}^+$  ion pairs, and the mutual orientational polarization of macromolecular units and clusters of water molecules surrounding the units and connected with them via hydrogen bonds.

In this study,<sup>3</sup> for the analysis of neutralized polyacid coils under infinite dilution conditions, we assume

<sup>3</sup> Measurements of the dielectric permittivity  $\epsilon_{12}$  of Na-PMAA aqueous solutions were performed at 1 MHz; hence, it seems expedient to consider only the motions of counterions that are perpendicular to the backbone of the macromolecule. As was shown in [14, Scheme], in this case, a nonalternating component of the induced dipole moment of the ionized monomer unit arises.

that  $(\langle M^2 \rangle / N)^{1/2}$  depends on the vector sum of partial dipole moments of hydrated nonneutralized units ( $\mu \sim 10$  D) and fluctuation dipole moments of segments that contain neutralized units. Fluctuation dipole moments of segments are the sum of alternating projections onto the direction of segments of dipole moments of neutralized units induced in the external electric field (see Scheme in [14]).

The resultant effect of the vector summation of dipole moments in the macromolecule with allowance made for conformation and specific hydration of both types of units is responsible for a high dipole moment of the Na-PMAA macromolecule in its aqueous solutions.

**Region II ( $0.1 \leq \alpha_i \leq \sim 0.3$ ).** In region II, the dipole moment  $\mu_{2app}$  of Na-PMAA macromolecules abruptly decreases with increasing the degree of neutralization  $\alpha_i$ . According to [12], the intrinsic viscosity in this region is somewhat increased. This fact indicates a partial breakdown of a compact macromolecular conformation. The reason for the unfolding of polyelectrolyte chains in the salt-free infinitely diluted solution is likely related to the electrostatic repulsion between similarly charged units that are formed owing to dissociation of ionogenic  $\text{COO}^- \text{Na}^+$  salt groups. This process involves conformational rearrangements in chains and proceeds cooperatively with abrupt changes in molecular parameters, such as intrinsic birefringence [15], the diffusion coefficient [16], and the relaxation time of polarized luminescence [17]; in the case under study, it concerns dipole moments. As follows from Fig. 3, owing to the conformational transition of a macromolecule from its dense compact state to a more unfolded state, the dipole moment decreases from  $\sim 30$  D at  $\alpha_i = 0.1$  to  $\sim 18$  D at  $\alpha_i = 0.24$ . This behavior can be related to the fact that, as a result of coil unfolding, conformers with the *trans* arrangement of side polar groups with respect to the macromolecular backbone are predominant, and dipole moments of units appear to be directed so that they partially compensate each other. Another reason for the reduced values of dipole moments concerns the dissociation of ionogenic salt units and formation of free counterions (the main contribution to dielectric permittivity is provided by associated counterions).

**Region III ( $\alpha_i > 0.24$ ).** In this interval of the degrees of neutralization  $\alpha_i$ , the dipole moment  $\mu_2$  of Na-PMAA macromolecules markedly increases. This dramatic increase in  $\mu_2$  is related to the condensation of dissociated counterions on a strongly charged polyelectrolyte chain [18]. According to the Onsager–Manning theory [19], one can estimate the linear charge density of the Na-PMAA chain corresponding to the onset of condensation of counterions or the related degree of neutralization of PMAA, equal to  $\alpha_c \sim 0.3$ . This fact implies that, at higher degrees of neutralization ( $\alpha_i > 0.3$ ), all newly formed counterions appear to be “locally” attached to a polymer chain and partially

compensate its charge [19]. With increasing the degree of neutralization, more counterions appear to be condensed on a chain; hence, the dipole moment of NaPMAA polyelectrolyte macromolecules increases. As follows from Fig. 3,  $\mu_2$  comes to  $\sim 140$  D at  $\alpha_i = 0.78$ . To provide such high values of the dipole moment, the macromolecules should possess a strong asymmetry of electron density.

Therefore, an analysis of dielectric permittivity and dipole moments of nonneutralized and neutralized PMAA in infinitely diluted solutions and polar associated liquids (methanol and water) performed in this study and in our earlier studies [1, 4] makes it possible to gain important information concerning the correlation of solvation and association processes (at intramolecular and intermolecular levels) with conformational properties of macromolecules (intramolecular interactions). Isolated nonneutralized PMAA macromolecules are shown to experience conformational transition depending on temperature, and this transition in NaPMAA macromolecules depends on their degree of neutralization.

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