

# Conductometric properties of linear polyelectrolytes in poor-solvent condition: The necklace model

F. Bordi, C. Cametti,<sup>a)</sup> T. Gili, S. Sennato, and S. Zuzzi

*Dipartimento di Fisica, Universita' di Roma "La Sapienza," Piazzale A. Moro 5, I-00185 Rome, Italy  
and Istituto Nazionale per la Fisica della Materia (INFN) CRS-SOFT Unita' di Roma 1, "La Sapienza,"  
Piazzale A. Moro 5, I-00185 Rome, Italy*

S. Dou and R. H. Colby

*Department of Materials Science and Engineering, The Pennsylvania State University, University Park,  
Pennsylvania 16802*

(Received 10 March 2005; accepted 13 April 2005; published online 20 June 2005)

We present a set of low-frequency electrical conductivity measurements of solutions of differently charged, salt-free polyelectrolytes in poor- and in good-solvent conditions, in the semidilute concentration regime. The data have been analyzed and discussed in light of the necklace model for hydrophobic polyelectrolytes recently proposed by Dobrynin *et al.* [Macromolecules **29**, 2974 (1996)] that predicts the chains to collapse into spheroidal cores connected by narrow strings. By varying the quality of the solvent, we have measured the polyion equivalent conductance  $\lambda_p$  in an extended concentration range in the semidilute regime and have demonstrated that this parameter is influenced by the polyion chain conformation, giving further support, when the poor-solvent condition prevails, to the picture of a string of electrostatic blobs. On the contrary, in good-solvent condition, the electrical conductivity data are in reasonable good agreement with the picture of an extended chain consisting of a collection of electrostatic blobs. These electrical conductivity measurements, in light of scaling theory, furnish new experimental support for the necklace model for hydrophobic polyions in poor solvents. © 2005 American Institute of Physics.  
[DOI: 10.1063/1.1931607]

## I. INTRODUCTION

Polyelectrolytes are polymers containing many ionizable groups, whose behavior in aqueous solution deeply differs from that of uncharged polymers and from that of simple electrolytes. The charges along the polymer chains and the associated counterions, being partially correlated, impart to these systems some peculiar characteristics which make them of central importance in many fields of soft-matter physics. Although in the last few years a notable progress has been done in the understanding of the behavior of polyelectrolytes in good solvents, considerably less attention has been paid to the behavior of polyelectrolytes in poor-solvent condition, in spite of the practical relevance, considering that most systems have organic nonpolar backbones in polar aqueous solvents, so that poor-solvent condition appears to be more appropriate. Although the solvent quality can be properly defined for uncharged polymers, by "poor solvent," in simple models for polyelectrolyte solutions, it is meant that the solvent does not dissolve the uncharged chain.<sup>1</sup>

From the point of view of statistical physics, the problem is interesting because of the balance between the long-range repulsive Coulomb interactions and the short-range attraction, the sign of which depends on the quality of the solvent. This balance introduces new length scales that make the polymer behavior very complicated.

Dobrynin *et al.*<sup>2</sup> have suggested that a charged chain in

poor solvent will collapse in a "pearl-necklace" conformation due to the balance between short-range attraction and long-range Coulomb repulsion between monomers along the polymer chain. This idea goes back to Rayleigh<sup>3</sup> who predicted that, as the charge density increases, a globular aggregate becomes unstable and starts to split into smaller droplets which tend to maximize their distance.

The pearl-necklace picture was supported by Monte Carlo simulation<sup>4-6</sup> that showed a cascade from one to more globules with the increase of the electrostatic interactions. The chain assumes a typical pearl-necklace conformation where small globules are connected by thin bridges.

Experimental evidence for the necklace model thus far is sketchy and in some cases controversial.<sup>7,8</sup> The most convincing of them are reported by Aseyev *et al.*<sup>9</sup> who interpreted dynamic light scattering<sup>10</sup> and small-angle neutron scattering (SANS) data<sup>9</sup> of poly(methacryloyl ethyltrimethylammonium methyl sulfate) (PMETMMS) in water-methanol mixtures as indicating the presence of compact globules connected by flexible chain segments. Similar conclusions have been reached by Lee *et al.*<sup>11</sup> on the basis of NMR spectra comparing the spectral intensity of three charged polyions [poly(styrene sulfonic acid) (PSS), poly(acrylic acid) (PAA), and poly(methacrylic acid) (PMA)]. However, these experiments provide some indications but not a direct proof for the existence of a pearl-necklace chain structure. In order to offer further experimental support on this interesting issue, we expect that electrical conductivity

<sup>a)</sup>Electronic mail: cesare.cametti@roma1.infn.it

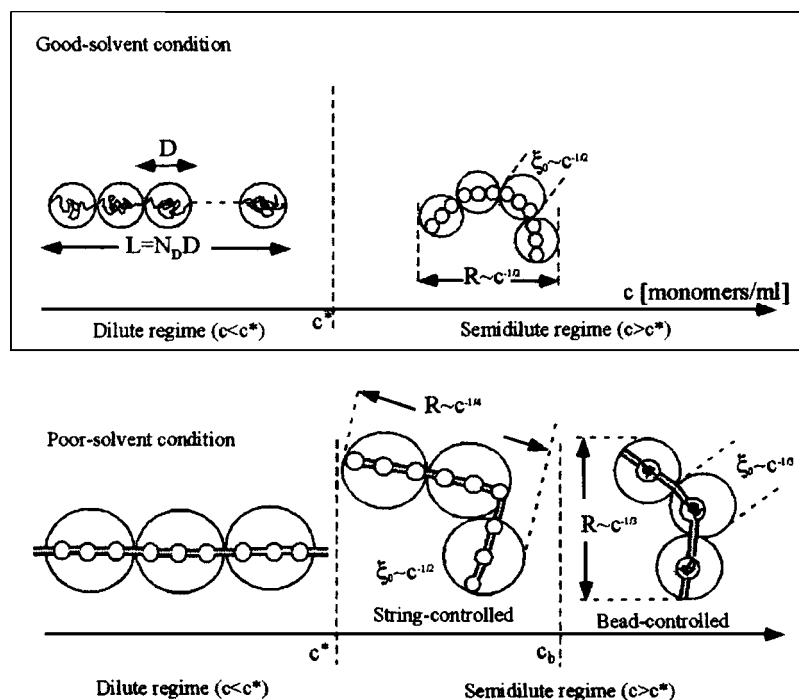


FIG. 1. A sketch of the different conformations assumed by the polymer chain in good- and poor-solvent conditions. Upper panel: dilute and semidilute concentration regimes in good-solvent condition. The polyion assumes an extended conformation of electrostatic blobs and a random walk of correlation blobs, respectively. Bottom panel: dilute and semidilute (string-controlled and bead-controlled) concentration regimes in poor-solvent condition. In the string-controlled regime, the chain is assumed to be a random walk of correlation segment  $\xi_0$ ; in the bead-controlled regime, only one bead per each correlation volume  $\xi_0^3$  is expected.

measurements could provide a useful tool for investigating the different polymer conformations and could offer insight for the plausibility of the model.

We have investigated the electrical conductometric properties of poly(*N*-methyl-2-vinyl pyridinium chloride) (PMVP-Cl), at two different charge densities, in different mixed solvents, ranging from pure water (poor solvent) to pure ethylene glycol (good solvent). The conductometric behavior of this polymer has been compared to the one of poly(2-vinyl pyridine) (P2VP), the uncharged linear polymer from which the polyelectrolytes were made by partial random quaternization.

These polymers, the uncharged P2VP and the two partially charged PMVP-Cl polymers, modified with pendant ionic groups to impart solubility in water, possess a carbon-based backbone for which water is a poor solvent and, on the contrary, for all of them, ethylene glycol (EG) behaves as a good solvent.<sup>12,13</sup>

The use of a range of solvents allows us to test separately the influence of the solvent quality on the polyelectrolyte behavior in a variety of different experimental conditions. In this article, we will present electrical conductivity measurements of polyelectrolyte solutions with the solvent quality changing from good- to poor-solvent condition. Five different mixed solvents (ethylene glycol-water mixtures at different molar ratios) of varying quality were studied for various polymer contents, in the semidilute concentration regime, by means of low-frequency electrical conductivity measurements.

Even though the solvent is poor, the polyelectrolyte chain may be soluble in water if the electrostatic repulsion between monomers is sufficiently strong. This happens, at different degrees, for the two partially charged polyions investigated, where the degree of ionization imparts the necessary charges along the chain and for the uncharged polymer in a water-ethylene glycol mixture. Our results are in reason-

able good agreement with the predictions of the scaling theory of polyelectrolyte solutions, once the appropriate quantities describing the electrical behavior of the polyion are derived within the Manning counterion condensation model.

The paper is organized as follows. In Sec. II, we summarize the pearl-necklace chain model and we report the main relationships for the electrical conductivity as a function of the polymer concentration, according to the appropriate solvent condition. In Sec. III, we characterize the polymer systems investigated and the experimental procedures employed. In Sec. IV we compare the model predictions to our experimental data and, finally, in Sec. V we discuss our results in light of the necklace model for poor-solvent condition and we suggest for further experiments. A conclusion follows.

## II. THEORETICAL BACKGROUND

Recently, we have discussed<sup>14,15</sup> the conductometric behavior of polyelectrolyte solutions in good- and poor-solvent conditions, in the absence of added salt, in light of the scaling approach proposed by Dobrynin *et al.*<sup>16</sup> A sketch of the different chain conformations assumed by the polyion in different concentration regimes for both poor- and good-solvent conditions is shown in Fig. 1. Here, we will confine ourselves to analyze the necklace model and we will summarize the relevant equations defining the conductometric behavior of the polymer solution in different concentration regimes, in poor-solvent condition.

We consider a polyelectrolyte solution containing polyions at a numerical concentration  $N_p$ , with each polyion having  $N$  monomers of size  $b$  and a contour length  $L = Nb$ . Counterion condensation reduces the effective charge of each polyion to  $Q_p = fNz_p e$ , with  $fNz_p/z_1$  counterions of charge  $z_1 e$  released in the solvent, where  $f$  is the fraction of mono-

mers on the chain that bears an effective charge. The electroneutrality condition implies  $z_p = z_1 \nu_1$ , with  $z_p$  and  $z_1$  valences of the charged groups on the polyion chain and counterions and  $\nu_1$  is the counterion stoichiometric coefficient, respectively.

According to the Manning counterion condensation theory,<sup>17,18</sup> counterion condensation is governed by the charge-density parameter defined as the ratio of the Bjerrum length  $l_B$  ( $\sim 7 \text{ \AA}$  at  $25^\circ \text{C}$  in water) and the distance between effective charges along the chain  $b/f$

$$\frac{fl_B}{b} = \frac{fe^2}{\epsilon k_B T b}. \quad (1)$$

Here  $e$  is the elementary charge,  $\epsilon$  the dielectric constant of the solvent, and  $k_B T$  is the thermal energy. For strongly charged polyions in a high dielectric constant medium,  $l_B/b > 1$  and  $f$  is lowered by counterion condensation until  $f = b/l_B$ . The charge on the polyion and the release of counterions into solution drive the polyion to dissolve in solvents of high dielectric constant, even if the energetic interaction between uncharged monomer and solvent is unfavorable. Such solvents are referred to as “poor solvents” and the conformation of the chain on the scale of a few monomers is collapsed into interesting conformations (discussed below in Sec. II B). This conformation is governed by the solvent quality parameter in poor solvent (the Flory parameter), which is effectively a reduced temperature  $\tau = (\theta - T)/\theta$ , where  $T$  is the absolute solvent temperature and  $\theta$  the temperature at which the net-excluded volume for uncharged monomers is zero. The solvent quality parameter is  $\tau = 0$  at  $T = \theta$  and  $\tau$  increases towards unity as the solvent becomes poorer ( $T < \theta$ ). It must be noted that for a polyelectrolyte, since the  $\theta$  temperature refers to the uncharged chain, this quantity is not experimentally accessible. On the other hand, separating the contributions of pure electrostatic interactions from polymer-solvent interactions favors the understanding of polymer conformation in different solvents and radiowave dielectric relaxation measurements could provide useful hints to this problem.<sup>19</sup>

### A. Electrical conductivity of a polyelectrolyte solution

With no added salt, the electrical conductivity of a polyelectrolyte solution is the sum of contributions from polyions and counterions and can be written as

$$\sigma = Q_p N_p u_p + z_1 e N_1 u_1, \quad (2)$$

where  $N_p$  and  $N_1$  are the numeric concentrations of the polyion and counterions deriving from the charge group ionization and  $u_p$  and  $u_1$  their mobilities, respectively. In the present case ( $z_p = z_1 = \nu_1 = 1$ ), Eq. (2) can be rearranged, as usually, to give

$$\sigma = \frac{fc}{\mathcal{N}} [\lambda_p + \lambda_1], \quad (3)$$

where  $\lambda_p$  and  $\lambda_1$  are the equivalent conductance of polyions and free counterions, respectively,  $c$  the polyion concentration expressed in number of monomers per unit volume, and  $\mathcal{N}$  the Avogadro number.

### B. The equivalent polyion conductance

The equivalent conductance  $\lambda_p$  of the polymer chain is given by the ratio of the total effective charge  $Q_p$  and the “effective” electrophoretic coefficient  $f_{\text{eff}}$

$$\lambda_p \equiv F u_p = F \frac{Q_p}{f_{\text{eff}}}, \quad (4)$$

where  $F = e\mathcal{N}$  the Faraday number with  $e$  the elementary charge. Manning<sup>20</sup> has derived an expression for the “effective” electrophoretic coefficient  $f_{\text{eff}}$  that takes into account the “asymmetry field effect” as

$$f_{\text{eff}} = \frac{f_E + \frac{Q_p}{u_1^0} \left(1 - \frac{D_1}{D_1^0}\right)}{D_1/D_1^0}, \quad (5)$$

where  $f_E$  is the usual electrophoretic coefficient,  $u_1^0$  the counterion mobility in the solvent (without polyions), and  $D_1/D_1^0$  the ratio of the diffusion coefficients of the counterions in the presence of polyion and in the limit of infinite dilution, respectively.

### C. The necklace model

Within the so-called necklace model, in poor-solvent condition, a hydrophobic chain will split into a set of smaller charged globules (beads) connected by long and narrow sections (strings). In the dilute regime ( $c < c^*$ ), the necklace chain of length  $L_n = N_b l_s$  is composed of  $N_b$  beads of size  $D_b$ , each of them containing  $g_b$  monomers, joining  $(N_b - 1)$  strings of length  $l_s$  ( $l_s \gg D_b$ ). According to the scaling approach for the electrical conductivity,<sup>14,15</sup> the electrophoretic coefficient  $f_E$  can be written assuming that the mass and any condensed counterions are primarily associated with the beads as

$$f_E = \frac{3\pi\eta N_b D_b}{1 + \frac{D_b}{l_s} |\ln(N_b)|}. \quad (6)$$

The characteristic quantities scale as<sup>2</sup>

$$N_b \sim N/g_b \sim N(l_B/b)\tau^{-1}f^2, \quad (7)$$

$$D_b = b(l_B/b)^{-1/3}f^{-2/3}, \quad (8)$$

$$l_s = b(l_B/b)^{-1/2}\tau^{1/2}f^{-1}. \quad (9)$$

The number of monomers in a bead is  $m_b \sim \tau(l_B/b)^{-1}f^{-2}$  and, in the present case, this value is of the order of  $m_b \sim 10$ . On average, among them, a fraction  $f$  is charged and  $f m_b N_b$  counterions per chain are released into the solution.

In the semidilute regime ( $c > c^*$ ), two different concentration intervals appear, defining a string-controlled regime ( $c^* < c < c_b$ ) and a bead-controlled regime ( $c_b < c < c_D$ ). The two characteristic concentrations,  $c^*$  and  $c_D$ , identify two concentration regimes, where the distance between chains equals their extended length and where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size, i.e., where chains and electrostatic blobs overlap, respectively.

In the semidilute regime ( $c > c^*$ ), the polyion conformation is described by a single correlation length  $\xi_0$ . When  $\xi_0$  is larger than the average distance between beads, a string-controlled regime dominates and  $\xi_0$  has the same  $c^{-1/2}$  concentration dependence as it happens in a good solvent. As the polymer concentration increases,  $\xi_0$  equals the distance between pearls at  $c_b$  and a bead-controlled regime holds with a less usual  $c^{-1/3}$  concentration dependence of the correlation length. In the semidilute regime, the electrophoretic coefficient  $f_E$  for a random-walk chain of  $N_{\xi_0}$  correlation blobs of size  $\xi_0$  each containing  $g_\xi$  monomers is given by

$$f_E = \frac{N_{\xi_0} \zeta_{\xi_0}}{1 + 8 \sqrt{N_{\xi_0} \zeta_{\xi_0}} / 3 \sqrt{6 \pi^3 \eta \xi_0}}, \quad (10)$$

where the friction coefficient  $\zeta_{\xi_0}$  can be written as

$$\zeta_{\xi_0} = \frac{3 \pi \eta N_b D_b}{1 + \frac{D_b}{l_s} \left| \ln \left( \frac{l_s}{\xi_0} \right) \right|}, \quad (11)$$

in the string-controlled regime ( $c^* < c < c_b$ ) and as

$$\zeta_\xi = 3 \pi \eta D_b, \quad (12)$$

in the bead-controlled regime ( $c_b < c < c_D$ ), respectively. The basic assumptions in deriving the electrophoretic coefficient  $f_E$  are discussed in Ref. 14, considering the elementary unit as the electrostatic blob with a cutoff function  $\exp(-r_{ij})/N_D D$  in the dilute regime and the elementary unit as the bead with a cutoff function  $\exp(-r_{ij})/N_b l_s$  in the semidilute regime. According to Dobrynin and Rubinstein,<sup>21</sup> the characteristic quantities scale as

$$\xi_0 = b^{-1/2} c^{-1/2} \tau^{1/4} (l_B/b)^{-1/4} f^{-1/2}, \quad (13)$$

$$N_{\xi_0} = (N/g_\xi) = N \tau^{-3/4} (l_B/b)^{3/4} f^{3/2} c^{1/2} b^{3/2}, \quad (14)$$

for  $c^* < c < c_b$  and as

$$\xi_0 = c^{-1/3} \tau^{1/3} (l_B/b)^{-1/3} f^{-2/3}, \quad (15)$$

$$N_{\xi_0} = (N/g_\xi) = N \tau^{-1} (l_B/b) f^2, \quad (16)$$

for  $c_b < c < c_D$ . In the above dependences and throughout the paper, numerical coefficients (of the order of unity) have been dropped, to keep the discussion at scaling level and consistently, the comparison with the experimental results has been carried out assuming unity for the prefactors in all the scaling laws.

The polyion concentrations that define the different concentration regimes, from the dilute to the semidilute (string-controlled and bead-controlled regimes) are given by

$$c^* \sim b^{-3} N^{-2} f^{-3} (l_B/b)^{-3/2} \tau^{3/2}, \quad (17)$$

for poor-solvent condition and

$$c^* \sim b^{-3} N^{-2} f^{-12/7} (l_B/b)^{-6/7}, \quad (18)$$

for good-solvent condition, respectively, and by

$$c_b \sim b^{-3} f (l_B/b)^{1/2} \tau^{-1/2}, \quad (19)$$

$$c_D \sim b^{-3} \tau. \quad (20)$$

The number of beads, passing from the dilute to the semidilute regime, changes progressively. Whereas in the dilute regime, the number  $N_b$  of beads is independent of  $c$  [Eq. (7)], the number  $N_{\xi_0}$  of correlation segments  $\xi_0$  in the semidilute (string-controlled) regime increases as  $c^{1/2}$  [Eq. (14)]. At the overlap concentration  $c^*$ ,  $N_{\xi_0}(c^*) \sim 1$ , i.e., a chain gives rise to a single correlation blob and from that point on, the number of correlation segments increases as  $c^{1/2}$  (in the  $c^* < c < c_b$  regime).

### III. EXPERIMENT

#### A. Materials

Poly(2-vinyl pyridine) (P2VP) ( $M_w=364$  kD) was purchased from Polymer Source Inc. and was used without further purification. The samples of poly(*N*-methyl-2-vinyl pyridinium chloride) (PMVP-Cl) were prepared from the neutral parent dry polymer P2VP by means of a quaternization procedure, resulting in various charge-density polymers. Poly(2-vinyl pyridine) dissolved in *N*-dimethyl formamide (DMF) was quaternized with dimethyl-sulfate (on the pyridine nitrogen) and the methyl sulfate counter-anion was then substituted by  $\text{Cl}^-$  upon addition of NaCl. Two different samples with two different degrees of quaternization ( $Q=0.17$  and  $Q=0.55$ ) were prepared. The polydispersity index of the samples is estimated to be  $M_w/M_n=1.06$ . The degree of quaternization of the partially quaternized polymers was determined by using sodium chloride and silver nitrate based on the standard counterion titration technique.

Experiments were performed using mixed ethylene glycol-water solutions at five different mole fractions  $X = [\text{EG}]/([\text{EG}]+[\text{water}])$  ( $X=0, 0.25, 0.5, 0.75, 1$ ). Solutions with varying polymer concentrations were prepared by consecutive dilution and the range covered was from 0.01 to 10 mg/ml. All the dilutions were prepared using deionized  $Q$ -quality water (electrical conductivity less than  $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature) and commercially available highly purified grade ethylene glycol (Sigma Chem. Co.). All measurements were done at the temperature  $T=25.0 \pm 0.1$  °C.

#### B. Electrical conductivity measurements

The electrical conductivity of the three polymer solutions investigated in solvents of different qualities has been measured by means of a frequency domain dielectric spectroscopy technique using two Hewlett-Packard impedance analyzers, model 4294A in the frequency range from 40 kHz to 100 MHz and model 4291A in the frequency range from 1 MHz to 2 GHz. Details of the conversion from the measured electrical impedance of the conductivity cell filled with the sample to be investigated and its electrical conductivity  $\sigma$  have been given elsewhere.<sup>22,23</sup> The conductivity spectra extend over an extremely large frequency range showing different dispersion regions, associated with the different conductive mechanisms, at a molecular level, occurring in the solutions. In the low-frequency tail, an electrode polarization appears due to the polarization of the ionic



double layer at the electrode-solution interface. This effect, resulting in a more and more considerable decrease of the conductivity as the ionic strength of the solution is increased, has been corrected following the procedure discussed in Ref. 23. In the intermediate frequency range, the dispersion associated with the polymer predominates. This dispersion depends essentially on the counterion fluctuation along some typical polymer lengths and, therefore, reflects the polymer conformation. Finally, in the high-frequency range, approximately from 100 MHz to 2 GHz, the conductivity increase is due to the orientational polarization of the aqueous phase, whose relaxation time falls at about 10 ps ( $\nu_0 \approx 17$  GHz),<sup>24</sup> at room temperature. Our experimental setup allows the frequency to be investigated up to 2 GHz, approximately a decade before the relaxation frequency and, consequently, only the beginning of this dispersion region is detectable.

In this paper, we will consider only the low-frequency limit of the electrical conductivity (once corrected for the electrode polarization), and we postpone to a further paper the analysis of the dielectric behavior of the polymer solutions.

## IV. RESULTS

### A. Comparison with experiments

The overall electrical conductivity behavior of the P2VP (uncharged) and 55%PMVP-Cl and 17%PMVP-Cl (partially charged) polymers in different solvent mixtures, over the whole concentration range investigated, is shown in Fig. 2. The different solvent composition, ranging from pure water to pure ethylene glycol, allows the quality of the solvent to be tuned from poor to good conditions.

Before going on with the comparison between the model prediction and the experimental results, we must determine the concentration regime that the system experiences. Recently, two of us (Dou and Colby) have measured the charge-density effect in the rheology behavior of these polymers in ethylene glycol solution.<sup>25</sup> On the basis of this study, the overlap concentration  $c^*$  can be defined as the concentration at which the specific viscosity  $\eta_{sp} = (\eta - \eta_s) / \eta_s$ , where  $\eta$  and  $\eta_s$  are the zero shear rate viscosity of the solution and the solvent, respectively, is approximately unity. For the samples in ethylene glycol, i.e., P2VP, 17%PMVP-Cl and 55%PMVP-Cl, the concentrations  $c^*$  are 0.057, 0.0017, and 0.0017 moles of monomers per liter of solution, respectively, corresponding to concentrations of about 5.6, 0.23, and 0.23 mg/ml. For the same sample 17%PMVP-Cl and 55%PMVP-Cl in water, the concentration  $c^*$  are 0.0015 and 0.0004 moles of monomers per liter of solution, respectively, corresponding to about 0.17 and 0.05 mg/ml. The concentrations defining the different regimes can be also estimated, to a first approximation, from the above-stated scaling laws. For example, from relationships (17)–(20), assuming a solvent quality factor  $\tau = 0.6$  (poor solvent), we obtain that  $c^*$  varies between  $6.8 \times 10^{16}$  and  $9.0 \times 10^{14}$  monomer/ml, for  $f$  varying from  $f = 0.2$  to  $f = 0.8$ . Within the same interval of values of the parameter  $f$ , we find that  $c_b$  varies between  $1.0 \times 10^{21}$  and  $7.0 \times 10^{21}$  monomer/ml. Finally,  $c_D$  is of the order of  $1.0 \times 10^{22}$  monomer/ml. These values, based on the

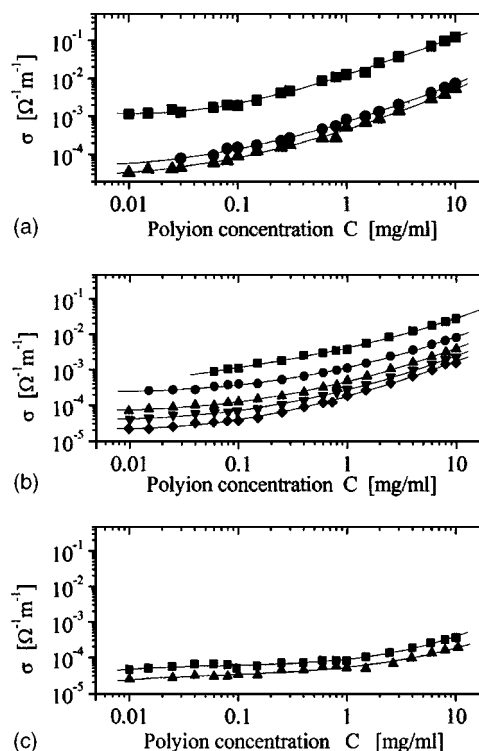


FIG. 2. The electrical conductivity of the different polyions investigated as a function of the polymer concentration expressed as mg/ml. (a) 55%PMVP-Cl in different solvents: (■):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0$ , pure water; (●):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0.75$ ; (▲):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 1$ , pure ethylene glycol. (b) 17%PMVP-Cl in different solvents: (■):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0$ , pure water; (●):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0.25$ ; (▲):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0.5$ ; (▼):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0.75$ ; (◆):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 1$ , pure ethylene glycol. (c) P2VM, uncharged polymer, in different solvents: (■):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 0.5$ ; (▲):  $X = [\text{EG}] / ([\text{EG}] + [\text{H}_2\text{O}]) = 1$ , pure ethylene glycol. The full lines are third-order polynomial fits of the data to guide the eye only.

scaling laws (17)–(20), are in reasonable agreement with those derived on the basis of the rheology properties of these polymers.<sup>25</sup>

This means that the range of polymer concentrations where the semidilute, string-controlled regime holds occurs at concentrations higher than  $C = 0.2$  mg/ml for 17%PMVP-Cl and higher than  $C = 0.3$  mg/ml for 55%PMVP-Cl, up to the highest concentration investigated ( $C = 10$  mg/ml). Consequently, we will discuss in detail this concentration regime within the above-stated necklace model and we will compare the expected behavior to the one that should occur if the necklace model was unable to take into account the observed electrical conductivity. The behavior in the dilute regime, for concentration below  $c^*$ , and the overlap with the semidilute one will be considered in a forthcoming paper.

As can be seen from Eq. (3) together with Eqs. (10) and (11), the electrical conductivity depends, for a fixed value  $\tau$  of the solvent quality, on a single free parameter, the fraction  $f$  of monomers bearing an effective charge (and hence, for uni-univalent charges, the fraction of free counterions), once the appropriate dependence for the characteristic quantities of the model given by the scaling laws [Eqs. (7)–(9) and Eqs. (13)–(16)] are considered. As far as the viscosity of the solvent is concerned, we used the value  $\eta = 16.1$  cP for ethylene

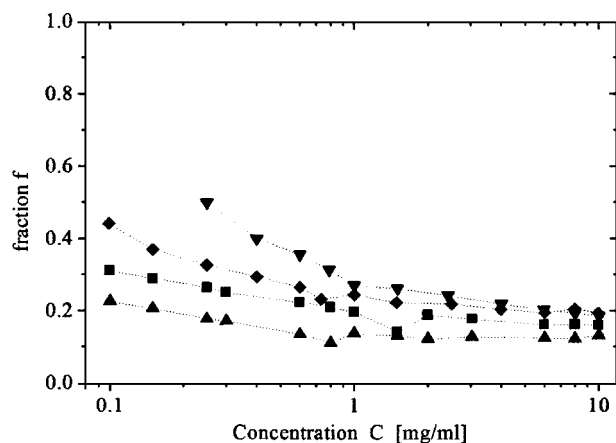


FIG. 3. The fraction  $f$  of monomers bearing an effective charge derived from the electrical conductivity measurements for the charged polymers in good- and poor-solvent conditions. (■): 55%PMVP-Cl in water (poor solvent); (▲): 55%PMVP-Cl in ethylene glycol (good solvent); (▼): 17%PMVP-Cl in water (poor solvent); (◆): 17%PMVP-Cl in ethylene glycol (good solvent). The dotted lines are drawn for visual purpose only.

glycol and  $\eta=0.89$  cP for water at 25 °C. For mixed solvents, an interpolation relationship was employed. In the following analysis, for all the ethylene glycol-water mixtures investigated, we have assumed for the solvent quality a value  $\tau=0.6$ , close to the one used by Lyulin *et al.*<sup>26</sup> in computer simulation of a single polyelectrolyte chain in poor solvent. We have also verified that in the vicinity of this value the result of our analysis does not change appreciably. For some typical polymer solutions, in pure water or in pure ethylene glycol, Fig. 3 shows the parameter  $f$  as a function of the polymer concentration  $C$  derived from Eqs. (4) and (5), with Eq. (10) (poor solvent, semidilute string-controlled regime, assuming for  $\tau$  the value  $\tau=0.6$ ), or from Eq. (4) (good solvent, semidilute regime). In the water-ethylene glycol mixtures, the behavior of  $f$  as a function of  $C$  is similar. In the evaluation of the “effective” electrophoretic coefficient  $f_{\text{eff}}$ , the ratio  $D_1/D_1^0$  has been calculated from Eqs. (46) and (47) of Ref. 15 and the counterion mobility  $u_1^0$  in the different solvents has been obtained from the appropriate value in water, taking into account the different viscosities of the different mixtures employed. However, changes in the value of the counterion mobility reflect in a relatively small variation of the fraction  $f$  of free counterions (within 2%–3%).

For all the systems investigated, the fraction  $f$  decreases with the polymer concentration, both in poor-solvent and in good-solvent conditions. This dependence, although unexpected within the Manning model,<sup>20</sup> is in qualitative agreement with the one observed in aqueous solutions of sodium polyacrylate salt both in the presence and in the absence of added salt<sup>14,15</sup> and with molecular-dynamic simulation<sup>27</sup> that suggests an increase of the counterion condensation when the chain assumes a more compact conformation, as it happens for hydrophobic polyelectrolytes, when concentration increases, as predicted by the necklace model.<sup>21</sup>

The electrostatic interactions governed by the Bjerrum length vary with the solvent permittivity. We have measured the permittivity of the water-ethylene glycol mixtures at different mole fractions  $X$  that changes from  $\epsilon'=78.5$  for  $X=0$

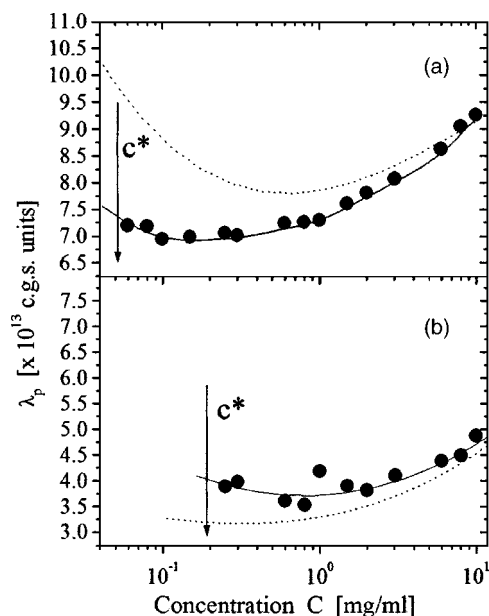


FIG. 4. The equivalent polyion conductance  $\lambda_p$  as a function of the polyion concentration  $C$  for 55%PMVP-Cl ( $Q=0.55$ ); (a) polyion in water solvent (poor-solvent condition) (●): values derived from the measured values of the electrical conductivity; the full line represents the values calculated according to the necklace model in semidilute, string-controlled condition [Eqs. (4), (10), and (11)], assuming  $\tau=0.6$ . The dotted line represents the calculated values in the semidilute, good-solvent condition. (b) polyion in ethylene glycol solvent (good-solvent condition) (●): values derived from the measured values of the electrical conductivity; the full line represents the values calculated according to the semidilute, good-solvent condition. The dotted line represents the calculated values in the necklace model in semidilute, string-controlled condition [Eqs. (4), (10), and (11)].

(pure water) to  $\epsilon'=37.7$  for  $X=1$  (pure ethylene glycol), at the temperature of 25 °C. We have considered the solvent phase as a continuous phase with an effective permittivity, neglecting the possible effects of a preferential solvation of the polymer, i.e., a different concentration for water and ethylene glycol close to the polymer chain.

In the following, we will present the polyion equivalent conductance  $\lambda_p$  derived from the electrical conductivity measurements using the values of  $f$  shown in Fig. 3 and will compare its behavior with the one expected on the basis of the necklace model in the semidilute, string-controlled regime. We will discuss the results concerning the three systems investigated separately.

### 1. Degree of quaternization $Q=0.55$

This polyelectrolyte chain is relatively strongly charged. A monomer extends over roughly 3 Å and, at a degree of quaternization  $Q=0.55$ , there is one charge per about two monomers, the average distance between adjacent charges being about  $b=5.4$  Å. The polymer chain of molecular weight 364 kD contains 3460 monomers, meaning about 1900 charges. In this case, the Manning parameter  $\xi$  is close to  $\xi=l_B/b \approx 1.3$  for pure water solvent and  $\xi=l_B/b \approx 2.7$  for pure ethylene glycol solvent. This means that counterion condensation is expected to set in for all the pure and mixed solvents investigated, with a “nominal” fraction of condensed counterions ranging from  $f=0.75$  in water to  $f=0.4$  in ethylene glycol. Figure 4 shows the equivalent conduc-

tance  $\lambda_p$  in two limiting cases, i.e., polyions in water (poor solvent) and in ethylene glycol (good solvent) together with the values calculated on the basis of the appropriate models (necklace model for poor solvent and blob model for good solvent). As can be seen, the agreement is quite good over the whole concentration range where the semidilute regime holds. Moreover, as expected, large deviations occur if the values of  $\lambda_p$  for water solution (poor solvent) are compared with those calculated for good-solvent condition [dotted line, Fig. 4(a)] and conversely if values of  $\lambda_p$  for ethylene glycol (good solvent) are compared with the ones calculated for poor-solvent condition [dotted line, Fig. 4(b)]. This finding strongly supports the necklace model for hydrophobic polyions and represents a well-documented experimental evidence of the influence of the solvent quality on the polyion conformation.

Finally, to complete our analysis, we can evaluate the prediction of the electrostatic blob model<sup>16</sup> in poor-solvent condition. According to Dobrynin *et al.*,<sup>16</sup> the characteristic parameters are the contour length  $N_{\xi_0}\xi_0$  of the random-walk chain of correlation blobs, the number  $N_{\xi_0}$  of correlation blobs within each polyion chain, and the ratio ( $g/g_e$ ) of the monomers inside a correlation blob to that inside an electrostatic blob. These quantities, in the semidilute regime and poor-solvent condition, scale as

$$N_{\xi_0}\xi_0 \sim Nb(l_B/b)^{2/3}\tau^{-1}f^{4/3}, \quad (21)$$

$$N_{\xi_0} \sim Nc^{1/2}b^{3/2}(l_B/b)\tau^{-3/2}f^2, \quad (22)$$

$$(g/g_e) \sim c^{-1/2}b^{-3/2}\tau^{1/2}. \quad (23)$$

In this case, the electrophoretic coefficient  $f_E$  of Eq. (10) holds with the friction coefficient  $\zeta_{\xi_0}$  given by

$$\zeta_{\xi_0} = \frac{3\pi\eta\xi_0}{\ln(g/g_e)}. \quad (24)$$

Once the appropriate values of the parameters are considered, we obtain, for 55%PMVP-Cl polymer in water (poor solvent), an equivalent polyion conductance  $\lambda_p$  with a very small dependence on the polyion concentration and values close to 1.9, 2.0, and  $2.2 \times 10^{13}$  cgs unit for  $\tau=0.4, 0.6, 0.8$ , respectively. These values are well below those derived from the measured conductivity (Fig. 4). This rules out the applicability of the electrostatic blob model in poor-solvent condition and gives further support to the necklace model. The polyions in water-ethylene glycol mixtures behave consistently with the above-stated picture.

## 2. Degree of quaternization $Q=0.17$

In this case, the chain is less charged and there is one charge per about 5.8 monomers, the average distance between charges being about 17.6 Å. In these conditions, the charge-density parameter  $\xi$  is always less than unity (for monovalent counterions) and counterion condensation, within the Manning theory, should not occur for all the polymers investigated. On the contrary, also in these systems, we observe, from the values of the electrical conductivity, that a fraction of counterions continues to condense both in water

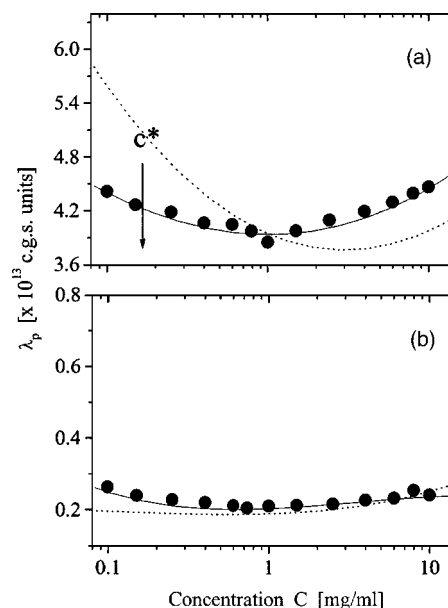


FIG. 5. The equivalent polyion conductance  $\lambda_p$  as a function of the polyion concentration  $C$  for 17%PMVC-Cl ( $Q=0.17$ ). (a) polyion in water solvent (poor-solvent condition); (●): values derived from the measured values of the electrical conductivity; the full line represents the values calculated according to the necklace model in semidilute, string-controlled condition [Eqs. (4), (10), and (11)]. The dotted line represents the calculated values in the semidilute, good-solvent condition. (b) polyion in ethylene glycol solvent (good solvent condition); (●): values derived from the measured values of the electrical conductivity; the full line represents the values calculated according to the semidilute, good-solvent condition. The dotted line represents the calculated values in the necklace model in semidilute, string-controlled condition [Eqs. (4), (10), and (11)].

and in ethylene glycol, despite the weaker electrostatic interactions along the chain (Fig. 3). Also in this case, for polymers in water solvent, the necklace model is able to take into account for the equivalent polyion conductance  $\lambda_p$  over the whole semidilute concentration range [Fig. 5(a) full line]. Conversely, if good-solvent condition should be applied, marked deviations appeared both at low- and high-concentration values [Fig. 5(a), dotted line]. On the contrary, polymers in good-solvent condition are well accounted for by the blob semidilute model [Fig. 5(b) full lines] and moreover, necklace model fails in the description of the experimental data [Fig. 5(b), dotted line].

## 3. Uncharged polymers

For uncharged polymers, the above-stated models do not apply and the electrical conductivity of uncharged polymer must be analyzed in a completely different context. In this case, the parameter associated to with the polymer chain conformation is the polyion equivalent conductivity  $\Lambda$ . This quantity can be calculated from the measured conductivity of the solution,  $\sigma$ , and the solvent,  $\sigma_0$ , according to the usual relationship

$$\Lambda = (\sigma - \sigma_0)/C_p, \quad (25)$$

where  $C_p$  is the polymer concentration expressed in monomol/l.

Figure 6 shows the values of  $\Lambda$  for the uncharged P2VP polymer in good solvent (ethylene glycol) as a function of

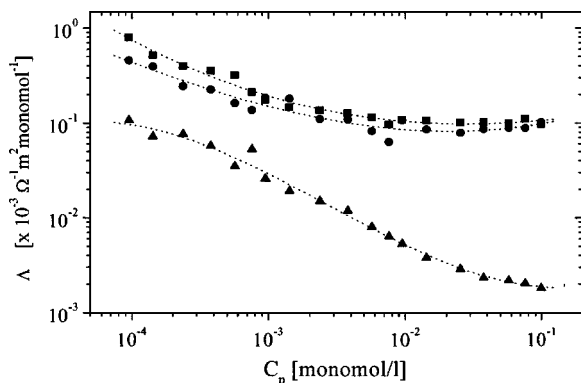


FIG. 6. Concentration dependence of the equivalent conductivity  $\Lambda$  for the different polymers investigated in ethylene glycol solution. ( $\blacktriangle$ ): P2VP, uncharged polymers; the behavior of  $\Lambda$  for the charged polymers is shown for comparison: ( $\blacksquare$ ): 55%PMVC-Cl ( $Q=0.55$ ); ( $\bullet$ ): 17%PMVC-Cl ( $Q=0.17$ ). The dotted lines are to guide the eye only.

concentration, compared with the corresponding values of the other two charged polymers investigated (55%PMVC-Cl and 17%PMVC-Cl). As can be seen, while the two charged polymers behave similarly, as expected on the basis of the same basic conformation of the chain, the uncharged polymer differs both in the observed values and in the concentration dependence.

## B. Frequency dependence of the electrical conductivity spectra

Before concluding, we want to underline an interesting issue deriving from the high-frequency tail of the frequency dependence of the electrical conductivity. Typical conductivity spectra of charged and uncharged polymers in solvents of different qualities, changing from poor- to good-solvent conditions, display an increase as a function of frequency, basically due to two concomitant effects, the biggest associated with the dipolar orientation effect of the solvent molecules and the smallest which takes into account the polymer-solvent interactions. This latter effect should depend on the quality of the solvent and consequently it can be considered as an appropriate probe to investigate, even if only qualitatively, the influence of the solvent on the conformation of the polymer chain. We have analyzed the high-frequency region of the conductivity dispersion to support furtherly the different polyion-solvent interactions when the solvent quality is progressively changed from poor to good condition.

The frequency dependence of the electrical conductivity can generally be described by a power law, terminated by a dc conductivity  $\sigma_{\omega=0}$  at low-frequency

$$\sigma(\omega) = \sigma_{\omega=0} + A\omega^\beta. \quad (26)$$

Any change in the value of the parameter  $\beta$  is indicative of a change in the polyion-solvent interactions. When the dielectric or conductometric relaxation process is described by a Cole-Cole relaxation function, the dependence of the electrical conductivity on the frequency can be given, to a first approximation, as

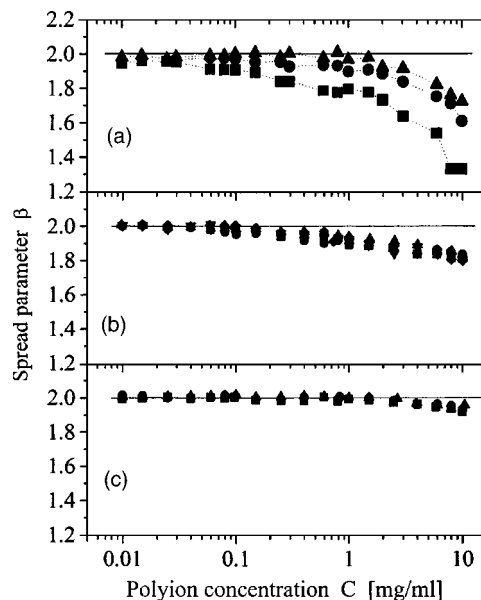


FIG. 7. The spread parameter  $\beta$  of the power law of the frequency dependence of the electrical conductivity as a function of the polymer concentration  $C$  (expressed as mg/ml). (a) 55%PMVP-Cl in different solvents: ( $\blacksquare$ ):  $X=[EG]/([EG]+[H_2O])=0$ , pure water; ( $\bullet$ ):  $X=[EG]/([EG]+[H_2O])=0.75$ ; ( $\blacktriangle$ ):  $X=[EG]/([EG]+[H_2O])=1$ , pure ethylene glycol. (b) 17%PMVP-Cl in different solvents: ( $\blacksquare$ ):  $X=[EG]/([EG]+[H_2O])=0$ , pure water; ( $\bullet$ ):  $X=[EG]/([EG]+[H_2O])=0.25$ ; ( $\blacktriangle$ ):  $X=[EG]/([EG]+[H_2O])=0.5$ ; ( $\blacktriangledown$ ):  $X=[EG]/([EG]+[H_2O])=0.75$ ; ( $\blacklozenge$ ):  $X=[EG]/([EG]+[H_2O])=1$ , pure ethylene glycol. (c) P2VM, uncharged polymer, in different solvents: ( $\blacksquare$ ):  $X=[EG]/([EG]+[H_2O])=0.5$ ; ( $\blacktriangle$ ):  $X=[EG]/([EG]+[H_2O])=1$ , pure ethylene glycol. The continuous line at  $\beta=2.0$  marks the value expected for a single Debye-type relaxation function.

$$\sigma(\omega) = \sigma_{\omega=0} + \omega\epsilon_0\epsilon''_{\text{diel}} \approx \omega^{2-\alpha}, \quad (27)$$

where  $\epsilon''_{\text{diel}}$  is the dielectric loss and  $\alpha$  the Cole-Cole parameter associated with the spread of the relaxation times. Equation (27) reduces to the power law of Eq. (26) with  $\beta=2$  ( $\alpha=0$ ) for a process described by a single exponential decay (Debye-type relaxation) and to a power law with an exponent smaller than 2 for a process described by a superposition of exponential decays (Cole-Cole-type relaxation).

In the high-frequency tail of the electrical conductivity spectrum (approximately from 5–10 MHz to 2 GHz, the highest frequency employed in this work), the data follow the power law of Eq. (26) and from a fitting procedure, the exponent  $\beta$  can be appropriately evaluated. This value is shown in Fig. 7, as a function of the polymer concentration, for the three differently charged polymers, for all the different solvents investigated. As can be seen in Fig. 7, the dependences of  $\beta$  show, as expected, deviations from the value  $\beta=2$ , corresponding to a single Debye-type relaxation, as the polymer concentration is increased, but, moreover, these deviations are progressively more marked as the quality of the solvent changes, passing from good solvent to poor solvent. While  $\beta$  is approximately around 2 in the case of P2VP polymer, indicating an absence of polymer-solvent interaction, this parameter reaches values as low as 1.4–1.5 in the case of 55%PMVP-Cl in poor solvent (water) at the highest concentration investigated.



## V. DISCUSSION

We have presented the electrical conductometric properties of moderately charged polyelectrolytes under poor- and good-solvent conditions within a unique consistent approach based on the scaling theories proposed by Dobrynin *et al.*,<sup>16</sup> and Dobrynin and Rubinstein.<sup>21</sup> Whereas for good solvents, the polymer chain, because of the electrostatic interactions between monomers, assumes a rodlike conformation of electrostatic blobs, for poor solvents this structure is abandoned in favor of a necklace configuration, consisting of highly stretched segments (strings) alternated with more collapsed globules (beads). The aim of this paper is to explore the possibility to offer experimental evidence for this model by means of electrical conductivity measurements. Since this technique probes the movements of any charged object in the solution, it should be able in principle to provide an unambiguous proof of the influence of the polymer chain conformation on the ion distribution or, conversely, to evidence the conformational changes produced by counterion release. Moreover, this transport property can be used as a very simple parameter to separate different concentration regimes and to show the conformational changes induced by polyion concentration. This can be investigated since the equivalent polyion conductance  $\lambda_p$ , which is the key parameter of the problem, depends on the chain conformation and moreover on the different models proposed.

The relevant parameter to explain the experimental results is the fraction  $f$  of free counterions. Figure 3 shows, for all the systems investigated, the fraction  $f$  as a function of the polymer concentration, both in poor- and in good-solvent conditions. Although for systems for which the Manning parameter exceeds the critical value, a fixed charge density is expected, on the contrary a marked dependence both on the solvent quality and on the concentration was observed. This is a clear hint that the more or less compact conformation assumed by the chain in the semidilute regime play an important role on the condensation effect. In the necklace model, the counterion condensation has been discussed in detail by Dobrynin and Rubinstein,<sup>21</sup> who considered the effects of condensation on the whole necklace conformation, in addition to the ones on the strings and on the spherical beads, controlled by the charge density of the strings and charge and size of the beads, respectively. By minimizing the free energy of the necklace, considering the translational entropy of the counterions, these authors derived the following relationship between the fraction  $f$  of free counterions and the numerical concentration  $c$  of monomers

$$c = \frac{\tau}{b^3} \frac{1-f}{1+f[\exp(2/3v_c f^{-1/3})]-1}, \quad (28)$$

where  $v_c$  is the electrostatic interaction between a bead and a counterion at its surface in terms of the thermal energy  $k_B T$ . Although Eq. (28) strongly depends on the value of the parameter  $v_c$ , the overall behavior confirms a decrease of the values of  $f$  as the monomer concentration  $c$  increases, as derived from the electrical conductivity measurements (Fig. 3). However, this dependence could not be peculiar to the necklace model since, as pointed out by Dobrynin and

Rubinstein,<sup>21</sup> in very dilute solutions, almost all counterions reside far from the polyion. As the polymer concentration increases, the balance between electrostatic and entropic interactions results in a continuous decrease of free counterions, also for polyion solutions in good solvent. Therefore, on the basis of this ambiguity (also confirmed by the observed dependence of  $f$  on the polymer concentration  $C$ ), we will consider the fraction  $f$  of free counterions as a free parameter to be adjusted on the basis of the experimental values of the electrical conductivity, in the different experimental conditions investigated. On the basis of this approach, the polyion equivalent conductance  $\lambda_p$  can be derived, within the appropriate model depending on the quality of the solvent. All the other quantities involved are known or they can be derived directly from the model adopted. The comparison of the two different behaviors of  $\lambda_p$  for the two charged polymers, derived for good- or poor-solvent conditions, strongly supports the necklace model when the experimental conditions allow its applicability. It is worth noting that if one considers good-solvent conditions when poor-solvent condition applies, or conversely, poor-solvent condition when good-solvent condition applies, even if the agreement is forced by finding the best set of values for the fraction  $f$  of free counterions, a notable disagreement is observed, which rules out the possibility of applying a model based on the assumptions of the wrong solvent quality. In other words, the necklace model accounts for the electrical behavior of PMVP-Cl in water (poor solvent) and fails for its electrical behavior in ethylene glycol (good solvent). Moreover, we have progressively changed the solvent quality, passing from good to poor solvent, modifying the solvent composition and considering ethylene glycol-water mixtures at different molar fractions. Even if the analysis of the results is not reported in detail here, we observe that the agreement becomes more and more weak, as the quality of the solvent differs from that for which the model applies.

This analysis is confined to the semidilute string-controlled regime since the polymer concentration investigated falls in this interval. In order to have a more strong support to the necklace model for hydrophobic polyelectrolytes and a more meaningful comparison with the experimental data, the semidilute bead-controlled regime should be investigated. In these conditions, the chain should assume a different conformation that the polyion equivalent conductance  $\lambda_p$  should reflect. A somewhat different approach has been proposed by Schiessel and Pincus<sup>28</sup> and Schiessel<sup>29</sup> who provided a scaling picture where counterion condensation is considered the “driving force” to induce attraction between different parts of the polyelectrolyte chain. This effect results in a shrinkage of the chain and, in appropriate conditions, in a collapse towards a globule conformation. Moreover, a phase separation triggered by concentration-induced counterion condensation has been described by Dobrynin and Rubinstein<sup>21</sup> and Lia *et al.*<sup>30</sup> who showed that solutions of polyelectrolytes in necklace configuration (poor solvent) can be unstable with respect to phase separation. All these effects should reflect in changes of the equivalent polyion conductance and, ultimately, in the dependence of the observed

electrical conductivity on the polyion concentration. This work is in progress and will be the subject of a forthcoming paper.

## VI. CONCLUSIONS

We presented a set of electrical conductivity measurements of polyelectrolyte solutions with the aim to investigate the influence of poor-solvent condition on the conformation of a moderately charged flexible polyion chain in salt-free solution. We have analyzed our results on the basis of the model proposed by Dobrynin *et al.*, considering appropriate expressions for the equivalent polyion conductance  $\lambda_p$  derived within the Manning approach.

We find that this model is adequate to describe the semidilute string-controlled regime of a hydrophobic polyelectrolyte under poor-solvent conditions. This finding is further supported by the comparison of the behavior of the same polymer system in two different solvents, which act as good and poor solvents, respectively. The necklace model applies only in the case of poor-solvent condition, when, for not too high charged polyelectrolytes, the short-range attraction induces a collapse with the formation of globules which try to separate, giving rise to the so-called pearl-necklace structure. In good-solvent condition, when the polyion is predicted to form a rodlike electrostatic blob structure, the conductivity data are well accounted for by the polyelectrolyte scaling theory.

<sup>1</sup>A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP, New York, 1994).

<sup>2</sup>A. V. Dobrynin, M. Rubinstein, and S. R. Obukhov, *Macromolecules* **29**, 2974 (1996).

- <sup>3</sup>L. Rayleigh, *Philos. Mag.* **14**, 184 (1882).
- <sup>4</sup>H. J. Limbach, C. Holm, and K. Kremer, *Europhys. Lett.* **60**, 566 (2002).
- <sup>5</sup>U. Micka and K. Kremer, *Europhys. Lett.* **49**, 189 (2000).
- <sup>6</sup>U. Micka, C. Holm, and K. Kremer, *Langmuir* **15**, 4033 (1999).
- <sup>7</sup>M. D. Carbajal-Tinoco and C. E. Williams, *Europhys. Lett.* **52**, 284 (2000).
- <sup>8</sup>M. Heinrich, M. Rawiso, J. G. Zilliox, P. Lesieur, and J. P. Simon, *Eur. Phys. J. E* **4**, 131 (2001).
- <sup>9</sup>V. D. Aseyev, S. I. Klenin, H. Tenau, I. Grillo, and E. Geissler, *Macromolecules* **34**, 3706 (2001).
- <sup>10</sup>V. D. Aseyev, H. Tenau, and S. I. Klenin, *Macromolecules* **32**, 1838 (1999).
- <sup>11</sup>M. J. Lee, M. M. Green, F. Mikes, and H. Morawetz, *Macromolecules* **35**, 4216 (2002).
- <sup>12</sup>B. Ermi and E. Amis, *Macromolecules* **30**, 6937 (1997).
- <sup>13</sup>D. Hodgson and E. Amis, *J. Chem. Phys.* **91**, 2635 (1989).
- <sup>14</sup>F. Bordi, C. Cametti, and T. Gili, *Phys. Rev. E* **66**, 021803 (2002).
- <sup>15</sup>F. Bordi, C. Cametti, and T. Gili, *Phys. Rev. E* **68**, 011805 (2003).
- <sup>16</sup>A. V. Dobrynin, R. H. Colby, and M. Rubinstein, *Macromolecules* **28**, 1859 (1995).
- <sup>17</sup>G. S. Manning, *J. Chem. Phys.* **51**, 924 (1969).
- <sup>18</sup>G. S. Manning, *J. Chem. Phys.* **51**, 934 (1969).
- <sup>19</sup>F. Bordi, C. Cametti, W. E. K. N. P. J. S. Tan, D. C. Boris, and R. H. Colby, *Macromolecules* **35**, 7031 (2002).
- <sup>20</sup>G. S. Manning, *J. Chem. Phys.* **85**, 1506 (1981).
- <sup>21</sup>A. V. Dobrynin and M. Rubinstein, *Macromolecules* **34**, 1964 (2001).
- <sup>22</sup>F. Bordi, C. Cametti, and G. Paradossi, *Biopolymers* **40**, 485 (1997).
- <sup>23</sup>F. Bordi, C. Cametti, and T. Gili, *Bioelectrochemistry* **54**, 53 (2001).
- <sup>24</sup>J. B. Hasted, *Aqueous Dielectric* (Chapman and Hall, New York, 1973).
- <sup>25</sup>S. Dou and R. Colby, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **45**, 261 (2004).
- <sup>26</sup>A. Lyulin, B. Dunweg, O. Borisov, and A. Darinskii, *Macromolecules* **32**, 3264 (1999).
- <sup>27</sup>U. Micka, C. Holm, and K. Kremer, *Langmuir* **15**, 4033 (1999).
- <sup>28</sup>H. Schiessel and P. Pincus, *Macromolecules* **31**, 7953 (1998).
- <sup>29</sup>H. Schiessel, *Macromolecules* **32**, 5673 (1999).
- <sup>30</sup>Q. Liao, A. V. Dobrynin, and M. Rubinstein, *Macromolecules* **36**, 3399 (2003).