Dielectric Spectroscopy Study of Poly(methacrylic acid) Gels

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Summary: It was shown that swelling behavior of polyelectrolyte gels is determined by the state of network counterions. In nonpolar media the ionomer regime of swelling behavior can be realized, this regime is characterized by the formation of ion pairs and ion multiplets. Dielectric spectroscopy and conductivity measurements of the charged poly(methacrylic acid) gels in media rather low polarity in the frequency range from 10^2 to 10^5 Hz were made in order to detect the appearance of ionic multiplets. Extremely high values of dielectric dispersion for both swollen in methanol and dried gels at low frequencies can be explained by aggregation of ion pairs into multiplets with high polarizability. The appearance of resonance peak on the dielectric spectra of the samples under the study gives evidence of the existence of ionic aggregates mainly of the same size.

Introduction

The theoretical analysis has shown that in low polar media collapse of ion-containing gels may be induced by extra ionization of the gel[1]. The reason for the collapse is the formation of ion pairs and their subsequent aggregation to multiplets. The collapse should occur at some critical degree of ionization of the gel, when the gain in energy of electrostatic interaction from the formation of ion pairs and their subsequent aggregation into multiplets exceeds entropy and strain energy losses resulting from additional steric restrictions and deformation of polymer chains.

In the present work we confirmed the theoretical predictions experimentally by titration of poly(methacrylic acid) (PMAA) gels in media with different polarity from 78 to 2 and we established the presence an ionomer aggregates in these gels using a dielectric spectroscopy method.

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Experimental Section

The objects of the present study were PMAA gels prepared by free radical polymerization of methacrylic acid in DMF at a monomer concentration of 3.06 mol/L with 2,2′-azobis(isobutyronitrile) ($1.53 x 10^{-2}$ mol/L or 0.5 mol%) as initiator in the presence of cross-linking agent – N′N′-methylene-bis-acrylamide ($4.6 x 10^{-2}$ mol/L or 1.5 mol. %).

The PMAA gel samples swollen in methanol (approximately 0.15 g) were immersed in methanol solutions of sodium methoxide with definite concentration (3 mL of solution per 10^{-5} mol of network repeat units) at 25 °C until equilibrium was attained. The degree of swelling of the gel was characterised by swelling ratio m/m_o, where m and m_o - are masses of the swollen and dry gels, respectively.

The relative dielectric constant, ε, and electric conductivity, k, of the gel samples were obtained from the measured capacitance, C (Farad), and conductance, σ (Siemens), measured with the use of a.c. bridge equipped by two silver parallel contact cell in the audio-frequency range $f \sim 100$ - $10^5 Hz$ by using the relations:

$$\varepsilon = \frac{4\pi d(C - Co)}{S} \qquad \kappa = \frac{d}{S}\sigma$$

where d - thickness of the gel, S - the area of the electrode, C and C_0 - capacitance of the gel and cell, respectively.

Swelling Behavior

Typical swelling curves of PMAA gels as a function of degree of ionization, α, for water/methanol and methanol/dioxane mixtures are shown on Figs.1 (a) and (b). It is seen that at least three general regimes of the swelling behavior can be distinguished. In the first regime (in polar media $\varepsilon > 50$), the gel swells with increasing α. In the second regime (in less polar media $20 < \varepsilon < 50$) the gel swells at very low α and then collapses with increasing α. And finally, in the third regime, observed in media with low polarity ($\varepsilon < 20$), the increase of the degree of ionization results in a shrinkage of the gel. We can see that the collapse of the gel occurs when the critical α^* is reached and equilibrium between free ions and ion pairs is displaced toward the formation of ion pairs (Fig.1 (a), curves 4 -7 and Fig.1 (b), curves 1-2).

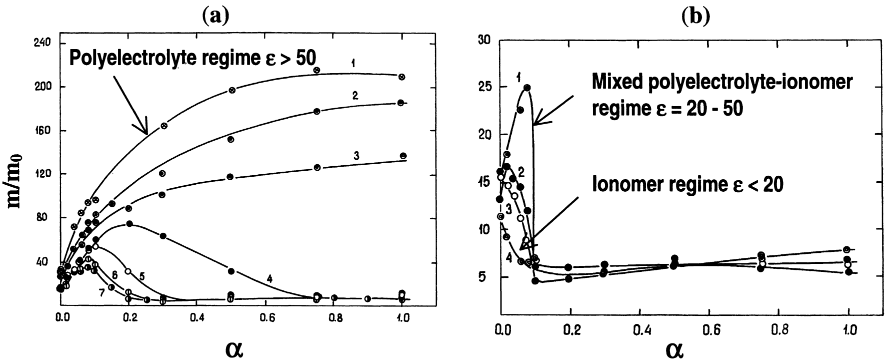

Fig. 1: Swelling curves of PMAA gels as a function of the degree of ionization α in media with different polarity: **(a)** ε =78.5 (1), ε =69 (2), ε =55 (3), ε =47.8 (4), ε =41.3 (5), ε =36.6 (6), ε =34.3 (7); **(b)** ε =29 (1), ε =24.5 (2), ε =21.5 (3), ε =8 (4).

To demonstrate an ion pair formation, conductivity measurements were performed. The typical dependence of the reduced conductivity (conductivity per carrier ion) of PMAA gel against α is presented on Fig.2.

In spite of the increase of the concentration of charged network units upon titration, the reduced conductivity increases only at low α and then dramatically falls, reaching the constant value unaffected by further increase of α. This confirms the formation of ion pairs in the system.

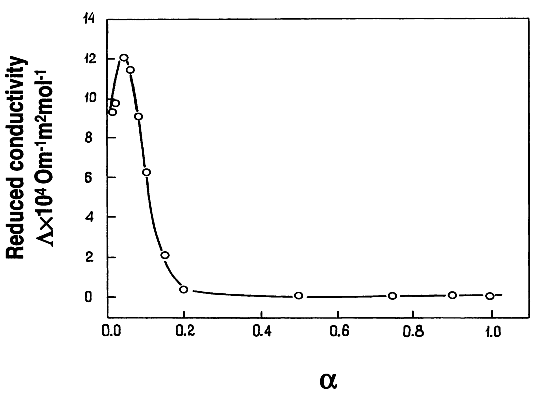

Fig. 2: Reduced conductivity of PMAA gel in methanol against α.

Dielectric Spectroscopy

There is another possibility to recognize a formation of ion pairs and their aggregation into multiplets - the method of dielectric spectroscopy. It is well known that dielectric spectroscopy is a powerful tool for studying morphology and ionic transport in charged polymers[2-4] . However, a little is known about dielectric properties of ion-containing gels[5-8].

The *log* permittivity against the alternating electric filed frequency for PMAA gels swollen in methanol is given on Fig. 3. These gels are characterized by high conductivity at the frequency *f* below 1 kHz that does not allow us to determine dielectric losses with a reasonable accuracy. So, only the real part of permittivity is given on Fig. 3.

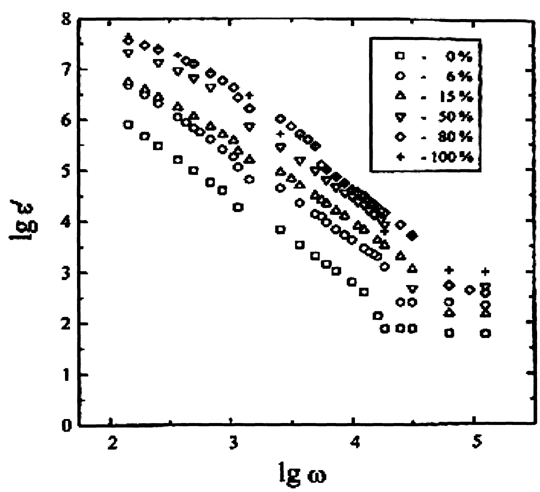

Fig. 3: Dielectric dispersion for PMAA gels swollen in methanol at 20 °C at different degree of ionization.

We can see that all PMAA gels under the study demonstrate a similar behavior. At high frequencies the permittivity value did not exceed 10^4 and it is independent from the frequency. This means that the dipole polarization of molecules is only a small part of their total polarization. But below 2 kHz the permittivity increases sharply to attain abnormally high values of 10^7 at low frequencies. According to the theory, so high permittivity values indicate aggregation of dipoles in a system and can be explained by high polarizability of dipole groups in multiplets[9]. Such high values of ε were earlier observed for polyacrylamide-co-sodium methacrylate gels[10].

Partially ionized PMAA gels can contain dipoles of at least two types $COO^{-}Na^{+}$ and $COO^{\delta-}H^{\delta+}$ differing in size of cation. First type is characterized by higher dipole moment and lower dissociation energy, while the second is less polarizable. The contribution of these dipoles to polarizability can be determined by comparison of the data of non-ionized and fully ionized PMAA gels. From Fig.3 it is seen that polarizability of fully ionized gels was almost by two orders of magnitude higher than that of a non-ionized one.

A comparison of permittivity values obtained for the gels with different degree of ionization showed that at low frequencies, *f ~ 100 Hz,* $\varepsilon'(\alpha)$, first, slowly depends on α and then rapidly increases (Fig.4, curve 1). A sharp increase of $\varepsilon'(\alpha)$ occurred simultaneously with the gel collapse caused by formation of ion pairs.

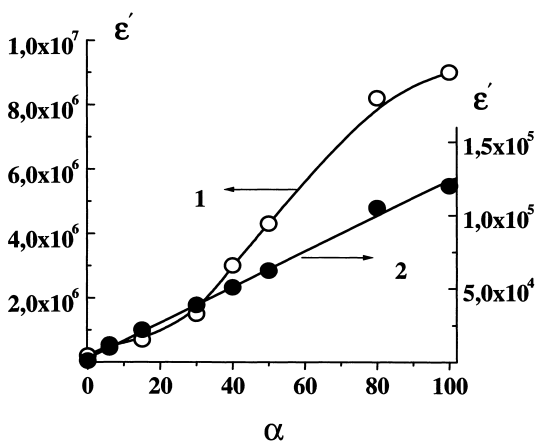

Fig. 4: Permittivity of PMAA gels swollen in methanol at different degree of ionization: curve 1 – at applied field frequency *f ~ 100 Hz, curve 2* - at applied field frequency *f ~ 1000 Hz.*

At high frequencies *f ~ 1000 Hz* (Fig. 4, curve 2*)* the $\varepsilon'(\alpha)$ increases linearly over the whole range of degree of ionization. Probably this frequency, which is far from the natural frequency of multiplet oscillations, was too high for the multiplets to respond on the electric field alternations. The dependence ε at high frequencies was therefore determined mainly by polarization of ion pairs, which was higher for COONa dipoles then for COOH.

Dried PMAA gels had substantially lower permittivities than swollen samples. In this case we were able to obtain frequency dependencies, $\varepsilon'(f)$, for both real and imaginary permittivity components. The *log* dependencies of dielectric dispersion and dielectric losses against frequency for PMAA gels containing 20 and 96 % of charged units are presented on Fig.5.

The removal of a solvent from a gel results in two effects: 1) gel vitrification because PMAA at room temperature is in the glassy state and 2) decreasing of medium permittivity because polymer itself is less polar than methanol. So, we can expect that the removal of the solvent results in the strengthening of aggregation of dipoles into multiplets. Both effects should decrease the mobility of ions within multiplets in the gel samples.

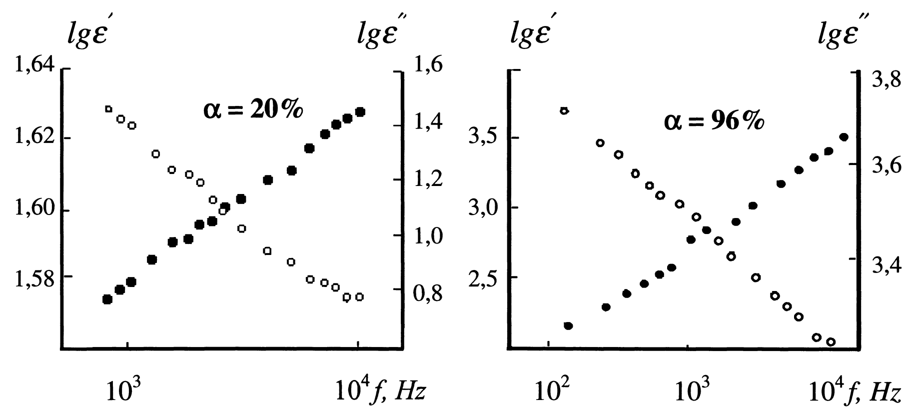

Fig. 5: Frequency dependencies of real $\varepsilon'(\alpha)$ and imaginary $\varepsilon''(\alpha)$ permittivity components for dried PMAA gels with ionization degrees of 20 and 96 %.

Indeed the removal of solvent significantly decreases the value of ε' but even dried fully ionized PMAA gels in glassy state exhibit rather high permittivity values ($\varepsilon' \sim 10^4$). This may be due to the retention of ion aggregates in the dried gels.

It is interesting to note that there were two specific features of all *log* $\varepsilon'(f)$ spectra for both swollen and dried ionized PMAA gels. The first feature is the presence of resonance peak, which results in subtraction of the line connecting the low- and the high-frequency linear segment from the total $\varepsilon'(f)$ spectrum (Fig.6). According to the theory[9] the appearance of this peak gives an evidence of the existence of ionic clusters mainly of the same size. A similar behavior of *log* $\varepsilon'(f)$ was observed in [6, 9].

Second feature is the presence of linear fragments with different slopes corresponding to the different exponents ***n*** and ***k.***

It is known that for majority of polymers, the universal law of dielectric dispersion is valid: $\varepsilon' \sim \omega^{-n}$ and $\varepsilon'' \sim \omega^{k}$, where ***n*** and ***k*** are constants whose values can be used to draw conclusions about character of conduction in the system. According to the theory [11], ordered systems with charged carriers are characterized by very low n values at low frequencies and by k values close to unity. Note that k = 0.5 corresponds to diffusion of ions, whereas k close to 1 corresponds to the free drift of ions.

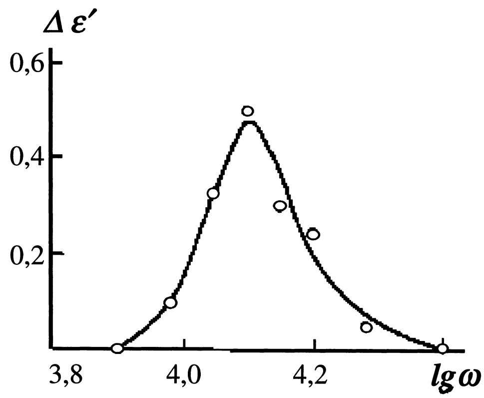

Fig. 6: Dependence of $\varepsilon'(f)$ for dried PMAA gel with the degree of ionization of 20 % after subtracting of the line connecting the low- and the high- frequency regions from the total spectra.

In our case dried ionized PMAA gels (20 %) have low ***n*** (0.04) and high ***k*** (0.75) values. This combination evidences the presence of a structural fragment with a high degree of ordering. At the same time a large number of interacting drifting ions in the PMAA gel containing 96 % of charged groups causes an increase in ***n*** (1.1) and decrease in ***k*** (0.3) values as a result of enhanced diffusion.

Conclusions

To summarize, the swelling behavior of ion-containing gels upon ionization depends on the dielectric constant of the medium. This dependence is determined by the state of network counterions: in polar media polyelectrolyte regime of swelling behavior is realized, but in nonpolar media the ionomer regime of swelling behavior is realized.

The method of dielectric spectroscopy allows us to establish the presence of ionic clusters and to evaluate the character of ionic transport in ionized PMAA gels. In the dried gels, the character of ion transport depends on the degree of ionization: ionic drift for weakly charged gels and diffusion for highly charged gels.

Acknowledgement

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