High-Frequency Dielectric Relaxation Measurements of Side-Chain Dynamics of Branched Chitosan Derivatives in Aqueous Solutions

F. Bordi

Sezione di Fisica Medica, Dipartimento di Medicina Interna, Università di Roma "Tor Vergata", Rome, Italy

C. Cametti*

Dipartimento di Fisica, Università di Roma "La Sapienza", Rome, Italy

G. Paradossi

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Rome, Italy

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ABSTRACT: The linear chain of polysaccharide chitosan has been derivatized by attaching different molecules to the 2-amino function of the backbone, namely lactose and ketoglutaric acid, therefore yielding branched comblike polymers. The dielectric behavior of aqueous solutions of these derivatives has been investigated in the frequency range from 1 MHz to 1 GHz, where pronounced dielectric dispersions occur. The deconvolution of both the permittivity and the dielectric loss spectrum into more than one dielectric mechanism shows that the high-frequency dielectric dispersion can be attributed to side-chain motions. The influence of pH and different species of counterions is investigated.

Introduction

Side-chain motions of aqueous solutions of polypeptides, in a picosecond time scale, have assumed a relevant role in the dynamics of biological macromolecules, involving catalytic reaction pathways, structural fluctuations, and chain conformations in protein molecules.[1] Theoretical and experimental approaches are currently receiving considerable attention, especially concerning their possible biophysical and biotechnological applications.

Dielectric dispersions caused by elementary processes in side-chain motions have been found in synthetic polymers in organic solvents, and a number of investigations have been recently reported. In particular, frequency relaxations with times of about 20 ps were found in different poly(α-amino acids) such as poly(γ-methyl L-glutamate), poly(γ-benzyl L-glutamate), and poly(γ-(p-chlorobenzyl) L-glutamate) in dioxane solutions.[2] On the other hand, the existence of a dielectric dispersion in aqueous solutions of poly(L-glutamic acid) in the region around 100 MHz, attributable to internal motions of the polar groups of the side chains, has been reported by Mashimo et al.[3] and more recently confirmed by Bordi et al.[4] on the basis of frequency domain dielectric spectroscopy measurements.

In this work, dielectric relaxation measurements have been carried out in aqueous solutions of two different chitosan derivatives over the frequency range from 1 MHz to 1 GHz by means of frequency domain dielectric spectroscopy methods.

Although several computational studies have been made to investigate the molecular dynamics of linear and branched polysaccharidic chains, the picture available from these works is not yet complete, particularly the role played by side chains in the interactions with the saccharidic backbone and with the solvent. Among other polymers, chitosan offers, by means of a simple synthetic route, the possibility of a systematic study of the dielectric behavior of the side chains as well as its correlation with the backbone. As a first approach to this line, we have comparatively investigated the behavior of two different types of branching that can be attached to the chitosan backbone. The choice was addressed to derivatives able to give stable solutions at concentrations suitable for dielectric spectroscopy measurements and the correlation between dielectric properties, and side-chain motion was studied by changing the degree of substitution by means of proper reaction conditions.

Chitosan is a polysaccharide obtained as the deacetylation product of chitin, the second most abundant biopolymer present in nature after cellulose. Both chitin and chitosan can be regarded as a copolymer of (1→4) linked 2-acetamido-2-deoxy-β-D-glucose. It is customary to call chitin the copolymer having a larger prevalence of acetamide-substituted glucose unit, while chitosan is related to the copolymer with a larger occurrence of the amine-substituted unit. Despite the large abundance and availability of these biopolymers, only in the last decade has a growing interest in the study of their structural properties, as well as of their potential applications, burst into the field.

At low pH, chitosan behaves in aqueous solution as a cationic polyelectrolyte.[5] Its rheological behavior has been analyzed in terms of intrinsic stiffness of the macromolecular chain and of the electrostatic contribution due to amine protonation.[6] This polymer is also capable of forming a cholesteric mesophase as a consequence of its chain stiffness.[7]

Dielectric behavior of chitosan in aqueous solution was recently studied in the frequency range from 1 kHz to 10 MHz.[8] A dielectric dispersion mechanism caused by counterion and proton fluctuation was evidenced and ascribed to the presence in the chain of both acid $-NH_3^+$ and basic NH_2 and $-OH$ groups, being able of exchanging and hosting protons. It must be noted, however, that the use of chitosan as a polyelectrolyte system is limited by its low solubility at neutral and high pH. One possible way to circumvent this difficulty was shown by Yalpani et al.[9] Taking advantage of the presence of the amino group born in position 2 in the glucosidic repeating unit of the backbone, these authors have shown the feasibility in derivatizing a chitosan chain by means of reductive amination. The derivatization reaction converts the linear polyglucosaminic backbone into branched-chain analogues, and, by changing the reaction conditions, it is sometimes possible to obtain products with different degrees of branching. Another advantage of this versatile reactive protocol is the variety of different types of branches attachable to the chitosan backbone. In this way, substituted chitosan with charges and/or hydrophobic groups on the side chain are obtained. Some of these derivatives are soluble in the whole pH range, owing to the flexibility of the side chains and/or the presence of charged groups, thus offering the possibility to study chain stiffness and metal ion chelating properties in pH conditions different from those allowed by the underivatized chitosan backbone.

Amino acid derivatives of chitosan have been recently studied; in particular, the chelating properties of the glutaryl derivative of chitosan toward metal ion transition[10] and the interactions between the glutaryl side chain and the backbone have been considered.[11]

As stated above, the dielectric behavior of branched-chain polypeptides recently appearing in the literature[3,4,12] evidenced the possibility to gain information about the side-chain dynamics. On the other hand, theoretical approaches to the modeling of the interactions occurring between backbone and side chains are a leading subject in the field of the conformational studies of comblike branched polysaccharides.[13]

On this basis, we have studied the high-frequency dielectric behavior of aqueous solutions of two comblike branched chitosan derivatives, the glutaryl and the 1-deoxylactit-1-yl derivatives, hereafter called CHK and CHL, respectively. This investigation was carried out at the temperature of 25 °C in the frequency range from 1 MHz to 1 GHz, the same frequency region where the polyglutamate sodium salt system showed a dielectric dispersion attributable to side-chain motions.

Moreover, the possible role of the high-frequency dielectric behavior of different cations (Na^+, K^+, NH_4^+) and anions (Cl^-, ClO_4^-) as counterions of the positively and negatively charged groups born on both the backbone and side chains of the polymers has been investigated. The experimental data have been analyzed and the dielectric parameters derived, on the basis of a simultaneous fit of the permittivity, ϵ', and the dielectric loss, ϵ'', of the Cole–Cole relaxation function. Evidences of a dielectric dispersion different from that generally occurring between 1 and 10 MHz and attributable to counterion diffusion mechanism or to the ordinary Maxwell–Wagner effect are reported. This dispersion is attributed to side-chain motions, and some implications on the physicochemical behavior of these compounds are reported.

Experimental Section

(a) Materials and Sample Preparation. All materials used in this study were analytical grade and used without further purification. CHK and CHL polymers were synthesized according to the procedures already published by Muzzarelli et al.[10] and by Yalpani et al.,[9] respectively. Characterization of the solution behavior of these Chitosan derivatives were already reported elsewhere in the literature.[11,14] The degree of deacetylation of the chitin used was about 0.95. The starting material was deacetylated according to the procedure reported by Paradossi et al.[11] The ^1H nuclear magnetic spectrum of the polymer after this procedure showed a peak around 1.8 ppm at pD = 2.0 attributed to acetyl groups and was estimated to be present in about 5% of the repeating units. A quantitative determination by means of potentiometric titration of the acetyl content in such low percentage was not possible since the end point of the titration for chitosan by Broussignac's method falls at about pH = 9.0, where the polymer solution is heterogeneous. The extent of branching on the backbone was obtained by potentiometric measurements, and the results are summarized in Table I. Polymer solutions were prepared by dissolving a known amount of freeze-dried sample in a given volume of water. The concentration ranged from 10 to 1 g/L, and the pH of CHK and of CHL solutions was 6.0 and 7.5, respectively. Solutions with different counterions were obtained by adding an amount of acid or base containing the anion or the cation needed for the measurement and fixing the pH at 3.0 or at 9.0, respectively. Samples prepared with this procedure did not show any difference in the dielectric behavior compared to samples in which the addition of titrant was followed by dialysis.

Table I. Molecular Weights and Degrees of Substitution of the (Different) Polymers Investigated Obtained from Different Experimental Techniques

polymer	M_w (g/monomol)	deg of substitution
chitosan	$\approx 160^a$	
CHK	238^a	0.43^a
	220^b	0.40^b
CHL	490^a	0.96^a
	500^b	0.98^b

[a] Potentiometric measurements. [b] Elemental analysis measurements. The molecular weight of the repeating unit of chitosan is estimated with an uncertainty of about 10%. This figure is consistent with a degree of deacetylation of about 95%.

(b) Dielectric Measurements. The dielectric properties (permittivity ϵ' and dielectric loss ϵ'') of the polymer solutions investigated were measured at a temperature of 25 °C, in the frequency range from 1 MHz to 1 GHz, by means of a radiofrequency impedance analyzer Hewlett-Packard Model 4191 A. The dielectric cell consists of section of a coaxial line, with a characteristic impedance of 50 Ω, terminated by a standard APC7 connector and directly connected to the meter.[15]

The dielectric parameters ϵ' and ϵ'' of the complex dielectric constant ϵ^* have been derived from the solution of a bilinear equation[16]

$$\frac{(\epsilon^* - \epsilon_1{}^*)(\epsilon_2{}^* - \epsilon_3{}^*)}{(\epsilon^* - \epsilon^*{}_2)(\epsilon^*{}_1 - \epsilon^*{}_3)} = \frac{(\rho^* - \rho^*{}_1)(\rho^*{}_2 - \rho^*{}_3)}{(\rho^* - \rho^*{}_2)(\rho^*{}_1 - \rho^*{}_3)} \tag{1}$$

where $\epsilon^*{}_j$ and $\rho^*{}_j = |\rho_j| e^{-i\phi j}$ (j = 1, 2, 3) are the complex dielectric constants and the measured input complex reflection coefficients (modulus $|\rho|$ and phase angle ϕ) of the coaxial line filled with known different standard liquids. As reference liquids, three NaCl solutions of different molarities with conductivities extending over the range of the samples investigated were used. For each electrolyte solution, the complex dielectric constant is written as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_\sigma - \epsilon_\infty}{1 + \iota\omega\tau} + \frac{\sigma_0}{\iota\omega\epsilon_0} \tag{2}$$

where the dielectric parameters ϵ_s, ϵ_∞, τ, σ_0, have been calculated for the different molarities, following Stogryn.[17] With the experimental arrangement used, it is difficult to evaluate how the uncertainties upon $|\rho|$ and ϕ reflect on the actual values of ϵ' and ϵ''. However, repeated measurements on reference liquids of known conductivity and dielectric constant show that the overall accuracy is within 2–3% on ϵ' and within 10% on ϵ'' for conductivity of the order of $10^{-3}\ \Omega^{-1}\ m^{-1}$. These values are further reduced as the electrical conductivity of the samples is lowered. The dielectric loss ϵ'' is calculated from the total loss ϵ''_{tot} subtracting the term due to the dc conductivity σ_0 according to the expression:

$$\epsilon'' = \epsilon''_{tot} - \frac{\sigma_0}{\epsilon\omega} \tag{3}$$

Results and Discussion

In the frequency range investigated, all the solutions employed show a more or less pronounced dielectric dispersion. It must be noted that, whereas at higher frequencies the measured permittivity is approximately that of the aqueous phase, at lower frequency these dispersions are not completely resolved, indicating that probably different molecular mechanisms concur to the observed behavior.

On the other hand, it is well known that polyion aqueous solutions display, from a dielectric point of view, a very complex phenomenology,[18] resulting in, at least, two different dielectric dispersions. The first one, occurring in the low-frequency region of the spectrum, approximately from 1 to 100 kHz, is due to the polarization of the ionic atmosphere[19] along the polymer chain and is governed by the counterion fluctuation in the neighboring of the charged groups. The origin of the dielectric dispersion at higher frequencies, in the range from 100 kHz to 10 MHz, is more questionable since different evidences for both the usual Maxwell–Wagner effect[20] and counterion fluctuation along a particular subunit of the polymer chain[21] can be provided. Moreover, the dielectric spectra, due to their dispersive nature, occur over several frequency decades, and frequently they overlap when different molecular mechanisms are simultaneously present. The deconvolution of a dielectric spectrum into its components is a very difficult problem, and depending on the particular system investigated, different procedures have been proposed.[22] This problem is especially evident in the present case, where the dispersion due to the Maxwell–Wagner effect or to the counterion fluctuation, extending up to the MHz region, can overlap with dispersions attributable to the dynamics of the side chains in linear charged polymers, when they occur.

We have made a 2-fold attempt to separate the high-frequency component from the whole spectrum. When the dc conductivity term $\sigma_0/\epsilon_0\omega$ is subtracted from the total dielectric loss, the resulting spectrum displays two interesting features. The first is an increase of the dielectric loss in the high-frequency region, indicating that a further dielectric dispersion should occur at higher frequencies. This dispersion must be attributed to the orientational polarization effect of the water molecule, whose relaxation frequency is about 17 GHz at 25 °C.[23] In the lower region of the spectrum, up to 5–10 MHz, the dielectric loss is poorly defined owing to the high dc ionic conductivity, but, in the intermediate frequency region, between 10 and 100 MHz, the dielectric loss spectra of all the different polymer solutions investigated display a maximum more or less broadened, showing that in this frequency range a dielectric dispersion should occur.

Consequently, the dielectric data have been analyzed on the basis of a Cole–Cole relaxation function,[23] according to the expressions

$$\epsilon'(\omega) = \epsilon_\infty + \frac{(\epsilon_s\text{-}\epsilon_\infty)\left(1 + (\omega\tau)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)\right)}{1 + (\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)} \tag{4}$$

$$\epsilon''(\omega) = \frac{(\epsilon_s\text{-}\epsilon_\infty)\left((\omega\tau)^{(1-\alpha)}\cos\left(\frac{\pi\alpha}{2}\right)\right)}{1 + (\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)} + \frac{(\epsilon_{sw} - \epsilon_{\infty w})\omega\tau_w}{(1 + (\omega\tau)^2)} \tag{5}$$

where the dielectric loss $\epsilon''(\omega)$ contains the term due to the contribution of the pure solvent. Here, ϵ_s and ϵ_∞ are the limiting values of the permittivity at low and high frequency, τ is the relaxation time, and α the Cole–Cole parameter governing the spread of the relaxation time around the mean value. The dielectric parameters of the pure solvent assume, at 25 °C, the following values: $\epsilon_{sw} = 78.5$, $\epsilon_{\infty w} = 4.5$, $\tau_w = 8.25$ ps.[24]

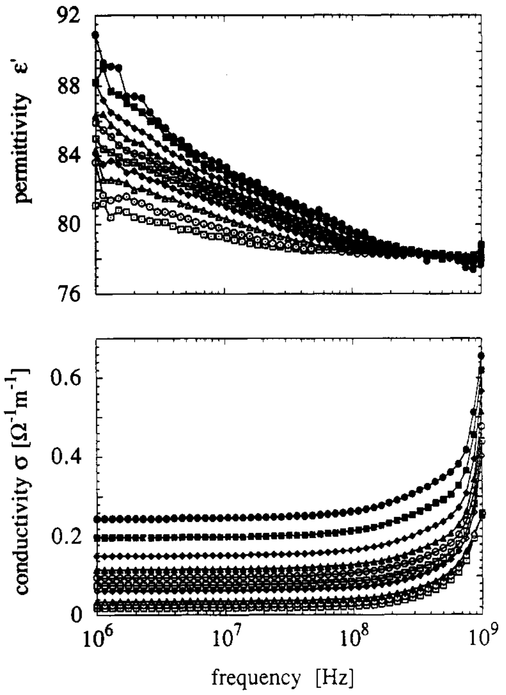

Figure 1. Permittivity ϵ' and the total electrical conductivity σ of CHK–aqueous solutions at pH = 3.0 as a function of frequency in the range from 1 MHz to 1 GHz, at a temperature of 25.0 ± 0.1 °C. The data refer to systems with Cl^- as counterion and to different polymer concentrations: (●) C = 15.5 mg/mL; (■) C = 11.8 mg/mL; (◆) C = 8.4 mg/mL; (▲) C = 5.9 mg/mL; (○) C = 4.6 mg/mL; (□) C = 3.3 mg/mL; (◇) C = 2.5 mg/mL; (△) C = 1.2 mg/mL; (⊙) C = 0.84 mg/mL; (⊡) C = 0.50 mg/mL.

The parameters of the dielectric dispersion $\Delta\epsilon = (\epsilon_s - \epsilon_\infty)$, $\nu = (1/2\pi\tau)$, and α have been determined by means of a nonlinear least-squares fitting procedure employing the Marquardt algorithm for complex function.[25] The method yields parameter evaluations based on the simultaneous fit of the real part, $\epsilon'(\omega)$, and the imaginary part $\epsilon''(\omega)$ of the complex dielectric constant $\epsilon^*(\omega)$. In particular, the presence of a maximum in the dielectric loss allows the relaxation frequency of the dispersion to be unambiguously determined.

A different fit procedure, considering separately the permittivity ϵ' and the dielectric loss ϵ'', does not allow the deconvolution of the spectra. In fact, the separate fit of ϵ' should result in a single broad dispersion since in the low-frequency limit no constant value is reached and the permittivity decreases continuously with the frequency. On the other hand, the maximum of ϵ'', with the localization of the relaxation frequency, implies the existence of a related dispersion on ϵ'.

To convince us of the presence of a high-frequency contribution to the observed dielectric behavior of the investigated polymer solutions, a further analysis has been carried out, plotting the data in the so-called Cole–Cole plot,[23] resulting in one or more overlapping semicircles according to the number of the dielectric dispersions present. This method provides a convenient "visual" approach, ensuring the existence of a dispersion falling in the frequency range investigated and differing from a contribution attributable to ionic polarization in the lower frequency limit and, in the higher frequency limit, to pure solvent polarization.

Finally, we have ascertained how the maximum of the dielectric loss ϵ'' might depend on the contribution due to dc conductivity, since the dielectric losses are evaluated

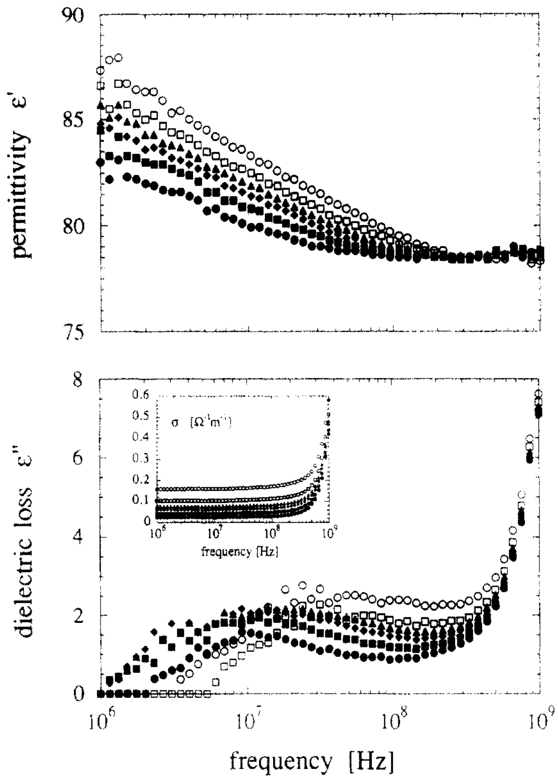

Figure 2. Permittivity ϵ' and the dielectric loss ϵ'' of CHK–aqueous solutions at pH = 3.0 as a function of frequency in the range from 1 MHz to 1 GHz, at a temperature of 25.0 ± 0.1 °C. The dielectric loss has been calculated from the conductivity σ by subtracting the ionic contribution $\sigma_0/\epsilon_0\omega$. The inset shows the measured electrical conductivity in the same frequency range. The data refer to systems with ClO_4^- as counterions and to different polymer concentrations: (○) C = 7.3 mg/mL; (□) C = 4.3 mg/mL; (▲) C = 3.0 mg/mL; (◆) C = 2.3 mg/mL; (■) C = 1.6 mg/mL; (●) C = 1.0 mg/mL.

from eq 3, by subtracting the ionic contribution. To verify if the maximum in the dielectric loss or the whole shape of the curves could markedly depend on losses of ionic origin, we have further analyzed our data considering either the dc conductivity σ_0 as a free parameter or we have varied it within ±10% of its measured value. In both cases, the curves of ϵ'' vs ν maintain the same shape, indicating the presence of a maximum around 10–50 MHz.

Some selected examples of the observed dielectric dispersions of the different polymer systems studied are shown in the following figures. Figure 1 shows the measured permittivity ϵ' and conductivity σ of CHK–aqueous solutions for polymer concentrations ranging from 15 to 0.5 g/L at pH = 3.0, over the entire frequency range investigated. Figure 2 shows again the measured permittivity ϵ' of the same system with, in this case, the dielectric loss ϵ'' obtained by subtracting the ionic loss $\sigma_0/\epsilon_0\omega$. As can be seen, the maximum of ϵ'' as a function of frequency clearly evidences the presence of a dielectric dispersion, almost completely resolved in the frequency range investigated. Finally, in Figure 3, the same data for two selected polymer concentrations are displayed as Cole–Cole plots. Also in this case, the data strongly support the existence of a dispersion in the frequency range 10–100 MHz.

Similar results, showing the appearance of well-defined dielectric dispersions, have been obtained for all the different polymer systems investigated. As above stated, the data have been analyzed by a simultaneous fit of the permittivity ϵ' and the dielectric loss ϵ'' to eqs 4 and 5. As an example of the overall consistency of the dielectric functions and the goodness of the fit procedure, typical results for CHL– and CHK–aqueous solutions are shown in Figures 4 and 5 for two different polymer systems at different concentrations and pH values.

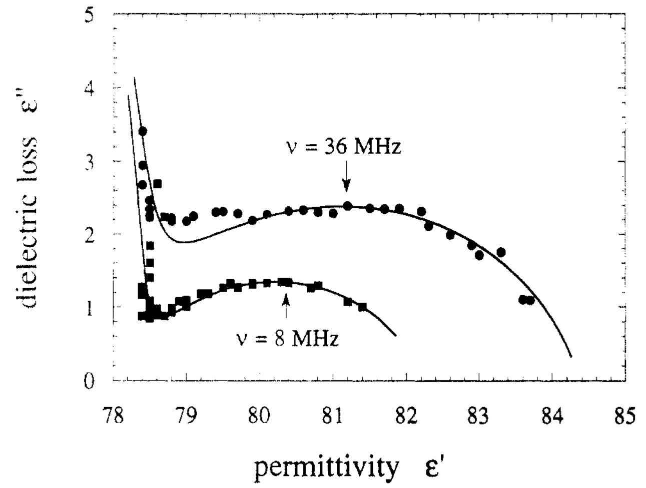

Figure 3. Cole–Cole plot of CHK–aqueous solutions at pH = 3.0 for two different polymer concentrations: (●) C = 7.3 mg/mL; (■) C = 1.0 mg/mL. This plot clearly evidences the presence of a dielectric dispersion in the 100-MHz region, resulting in a partial semicircle. The rapid increase at higher frequencies is due to the beginning of the orientational polarization of the aqueous phase.

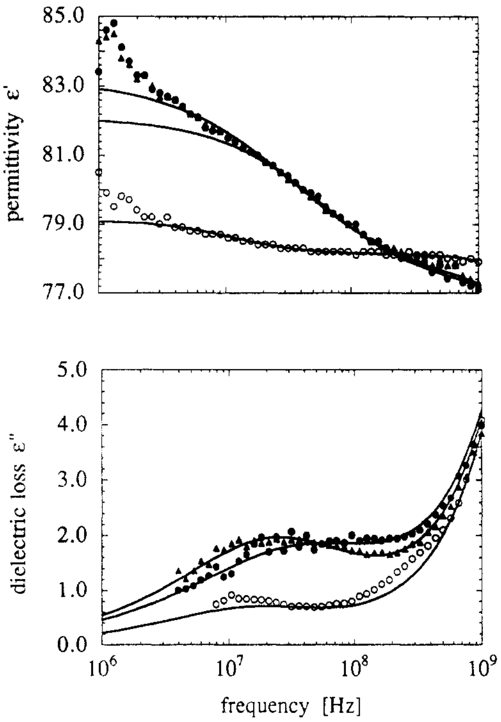

Figure 4. Permittivity ϵ' and the dielectric loss ϵ'' of CHL–aqueous solutions as a function of frequency in the range from 1 MHz to 1 GHz, at a temperature of 25.0 ± 0.1 °C and at different polymer concentrations: (○) pH = 7.0, C = 4.9 mg/mL; (▲) pH = 3.0, C = 13.0 mg/mL; (●) pH = 3.0, C = 8.6 mg/mL. The full lines are the calculated values on the basis of eqs 4 and 5. The dielectric parameters have been estimated by the simultaneous fit of the real, ϵ', and the imaginary part, ϵ'', of the complex dielectric constant, employing the Marquardt method for complex functions.

In some cases, the fitting procedure does not allow the dielectric parameters to be determined with a reasonable accuracy. Our analysis requires that the dielectric loss display a defined maximum in order to determine the relaxation frequency of the dispersion. The total dielectric

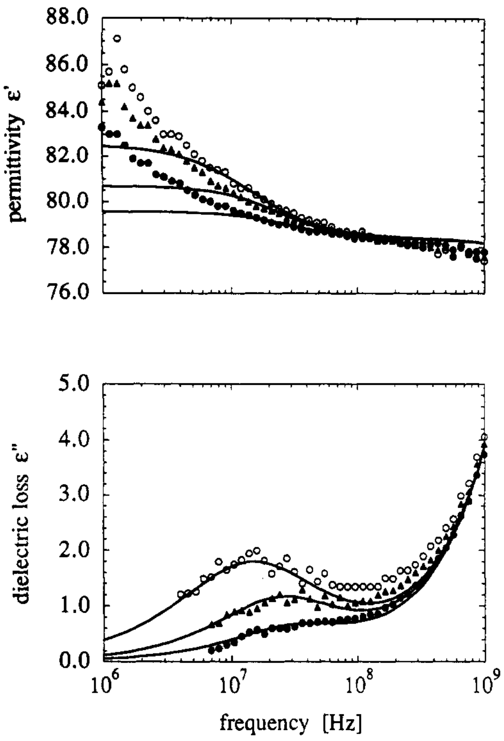

Figure 5. Permittivity ϵ' and the dielectric loss ϵ'' of CHK–aqueous solutions at pH = 9.0 as a function of frequency in the range from 1 MHz to 1 GHz, at a temperature of 25.0 ± 0.1 °C and at different polymer concentrations: (○) C = 9.3 mg/mL; (●) C = 6.9 mg/mL; (▲) C = 3.6 mg/mL. The full lines are the calculated values on the basis of eqs 4 and 5. The dielectric parameters have been estimated by the simultaneous fit of the real, ϵ', and the imaginary part, ϵ'', of the complex dielectric constant, employing the Marquardt method for complex functions.

loss $\epsilon'' = \sigma(\omega)/\epsilon_0\omega = \epsilon_{\text{diel}}'' - \sigma_0/\epsilon_0\omega$ will contain the contribution due to the dielectric loss ϵ_{diel}'' and the dc conductivity contribution $\sigma_0/\epsilon_0\omega$. At lower frequencies, this latter term dominates the first, especially in the case of high-conductivity samples, as those investigated here, and consequently the dielectric loss, when the frequency conductivity increment is small, cannot be correctly distinguished from the ionic losses. This implies that the dielectric dispersion cannot be separated from that occurring at lower frequencies.

A comment is in order. As can be seen, the calculated permittivity curves deviate from the measured values in the low-frequency limit of the spectrum, whereas the dielectric loss curves are able to account for the observed behavior over the entire frequency interval investigated. As above stated, this is due to the presence, at lower frequencies, of a further dispersion involving ionic mechanisms of polarization, whose existence is well established for charged polymeric systems.[18]

Finally, to surely attribute the observed dispersions to side-chain dynamics rather than to some mechanisms involving the ionic character of the polymer, we have carried out further measurements on the same systems but changing the counterions. Moreover, measurements have been made at two different values of pH; for CHK at pH = 3.0, the carboxyl groups on the side chain are uncharged, but a positive charge is beared on the backbone due to the presence of a protonated aminic group. On the other hand, at pH = 9.0, the charge distribution is reversed: the amine on the backbone is uncharged while the carboxyl groups on the side-chain are ionized. A scheme of the systems investigated together with the dielectric parameters derived from the adopted fitting procedure is shown in Table II.

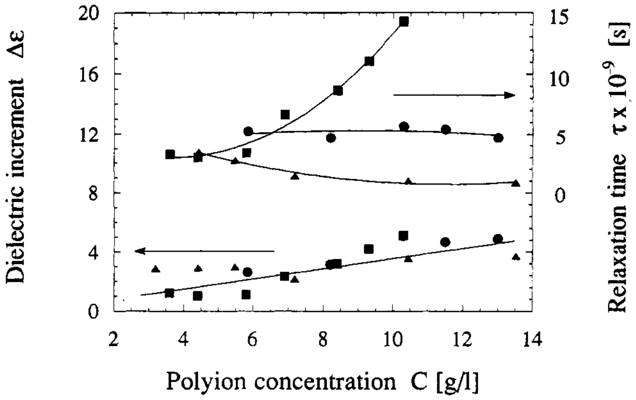

Figure 6. Dielectric increment $\Delta\epsilon$ and the relaxation time τ of the high-frequency dielectric dispersions of CHK–aqueous solutions as a function of the polymer concentrations, for different counterions, at a temperature of 25.0 ± 0.1 °C: (■) NH_4^+; (▲) Na^+; (●) K^+. The pH of the solutions is 9.0.

Table II. Dielectric Increment and the Relaxation Time of the Different Polyelectrolyte Solutions Investigated

system investigated	polyion concn (g/L)	dielectric increment $\Delta\epsilon$	relaxation time τ (ns)
CHL–HCl (pH = 3.0)	3.9		
	4.9		
	6.9	6.0	
	8.6	5.1	2.7
	11.3	6.1	4.4
	13	6.2	4.4
CHL (pH = 7.0)	4.9	1.8	
	7.8	1.9	10.6
	11.1	2.2	12.6
CHK–K^+ (pH = 9.0)	3.2	2.9	
	4.4	2.9	3.4
	5.5	3.0	2.7
	7.2	2.2	1.4
	10.5	3.6	1.0
	13.5	3.7	0.84
CHK–Na^+ (pH = 9.0)	5.8	2.6	5.2
	8.2	3.2	4.7
	10.3	5.1	5.7
	11.5	4.7	5.4
	13.0	4.9	4.7
CHK–NH_4^+ (pH = 9.0)	3.6	1.2	3.2
	4.4	1.0	3.0
	5.8	1.1	3.4
	6.9	2.3	6.6
	8.4	3.2	8.6
	9.3	4.2	11.0
	10.3	5.1	14.3
CHK–HCl (pH = 3.0)	2.5	3.9	3.0
	3.4	3.3	2.1
	4.6	4.3	1.7
	5.9	5.2	1.6
	8.4	5.2	1.2
	11.8	6.0	1.1
	15.0	6.2	0.9
CHK–$HClO_4$ (pH = 3.0)	2.3	4.8	
	3.0	5.1	7.7
	4.3	5.5	6.2
	7.3	6.1	4.8

For CHK in aqueous solution, we have studied the dielectric behavior at pH = 9.0 in the presence of different positive counterions, namely, K^+, NH_4^+, and Na^+, and at pH = 3.0 with Cl^- and ClO_4^- negative counterions. If the dispersion is attributed to side-chain motion rather than an overall effect due to fluctuation of counterions, the dielectric increment of this dispersion should be roughly independent of the ionic species. Figure 6 gives support to this hypothesis since the dielectric increment $\Delta\epsilon$ is, in a first approximation, independent of the ionic species.

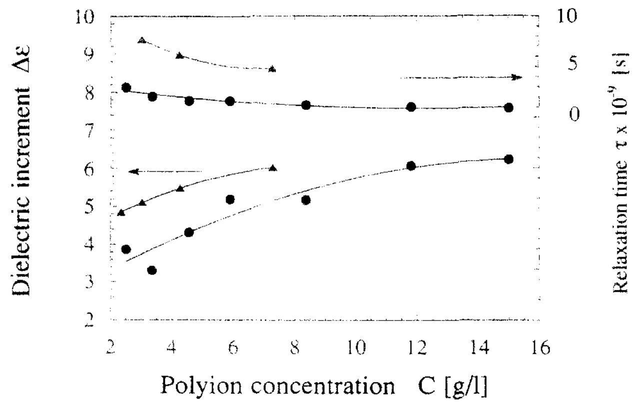

Figure 7. Dielectric increment $\Delta\epsilon$ and the relaxation time τ of the high-frequency dielectric dispersions of CHK–aqueous solutions as a function of the polymer concentrations, for different counterions, at a temperature of 25.0 ± 0.1 °C: (■) Cl^-; (▲) ClO_4^-. The pH of the solutions is 3.0.

Moreover, if the observed dispersion should be attributed to the tail of a lower frequency dispersion due to counterions, the relaxation times would be proportional to the ion mobilities and should lie in the order

$$\tau_{Na^+} > \tau_{K^+} > \tau_{NH_4^+}$$

The observed behavior of the relaxation times evidences a somewhat different order on the species of counterions, as is shown in Figure 6. This dependence can be accounted for if we assume that the relaxation time results from an orientation mechanism of the side chains besides a contribution due to the counterion association in the neighboring of the charged groups, according to the relation

$$\frac{1}{\tau} = \frac{1}{\tau_{rot}} + \frac{1}{\tau_c}$$

Since $\tau_c > \tau_{rot}$, it follows that $\tau < \tau_c$ and consequently the relaxation time should be inversely proportional to the association constants, that for the ions investigated are in the order

$$Na^+ \approx K^+ \gg NH_4^+$$

that follows from the affinity of the carboxylic group to the different monovalent cations. This is qualitatively found in the behavior shown in Figure 6. Moreover, it must be noted that at low pH, CHK and CHL polymers bear only positive charges in the same sites of the main chain, resulting in an approximately equal dielectric increment, in spite of the different counterions (Cl^- and ClO_4^-) investigated.

The relaxation times are a slightly different for the two polymers, but it must be considered that, in the case of CHL, the side chain consists of a lactose which is comparatively bulkier than the glutaryl branch of CHK. Moreover, as is shown in Table I, CHL polymer has a degree of substitution of about 1, while CHK has a substitution every other sugar ring of the backbone. This different structural situation makes the CHL side chain stiffer than that of CHK, and therefore a longer relaxation time for the more stretched chain has to be expected.

The existence of micro-Brownian motion in flexible polymer chains is an important property in the study of the polymer dynamics. In this note, we have provided further evidences that, also in aqueous systems, dielectric methods can furnish reliable informations on the internal dynamics of polymers. Work is in progress to obtain the microscopic parameters that describe the motion of side chains in branched polymers.

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