On the Dielectric Properties of Poly(glutamic acid) As Studied by the Time Domain Reflectometry Technique

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The physical and chemical properties of synthetic polypeptides have been extensively studied as model systems for proteins. The dielectric properties of poly(glutamic acid) (PGA) are an example of such studies, where different experimental techniques have been used to cover a large frequency range. Takashima[1] used bridge techniques to investigate PGA solutions of different pHs in the kHz range. A strong dispersion was observed, the dielectric increment of which was pH dependent. Müller et al.[2] extended the frequency range to 100 MHz and found two relaxation processes with relaxation times of order 10 ms and 100 ns. Nakamura and Wada[3] employed a Fourier-synthesized pseudorandom noise technique to cover the frequency range < 10 kHz.

The time domain reflectometry (TDR) technique offers an attractive alternative in the measurement of permittivity spectra. Here the shape of a pulse being reflected from the cell filled with the sample is compared to that reflected from the cell filled with a reference substance. From the Fourier transforms of the line shapes, the spectrum can be obtained over a large frequency range. Mashimo et al.[4] applied the TDR technique to study the dielectric properties of PGA solutions in the frequency range 10 MHz to 10 GHz. Besides the high frequency dispersion due to water, a smaller pH-dependent dispersion was observed centered in the frequency range 50−100 MHz. This dispersion was attributed to the motion of side chain dipoles.

In an attempt to corroborate the existence of this dispersion, we applied the time domain spectroscopy technique based on transmitted pulse shapes as well as the TDR principle to the study of some PGA solutions of different pHs.[5] It was observed that the position of the dispersion in the 100 MHz range was strongly dependent on the time window used in the measurement. The longest time window available in that study was 50 ns. A shortening of the time window shifted the dispersion to higher frequencies. In view of the known presence of strong low frequency dispersions, a theoretical study was made of the consequences of premature truncation of time domain line shapes. It was found that a seeming dispersion was introduced, the position of which depended on the time window used. This raised the question whether the discussed dispersion was due to a truncation error in the TDR measurement or had a true molecular origin.

Bordi et al.[6] in a frequency domain measurement using an impedance analyzer working between 1 MHz and 1 GHz determined the permittivity spectra of PGA solutions of different molecular weights and concentrations. A dispersion centered in the range 10−100 MHz was observed. Mashimo et al.[7] in a renewed study again applied the TDR technique. Compared to previous measurements, a longer cell length was employed to increase sensitivity and longer time windows were used in order to avoid problems due to truncation of line shapes. A dispersion centered in the frequency range 10−100 MHz was found, the critical frequency being a fuction of pH.

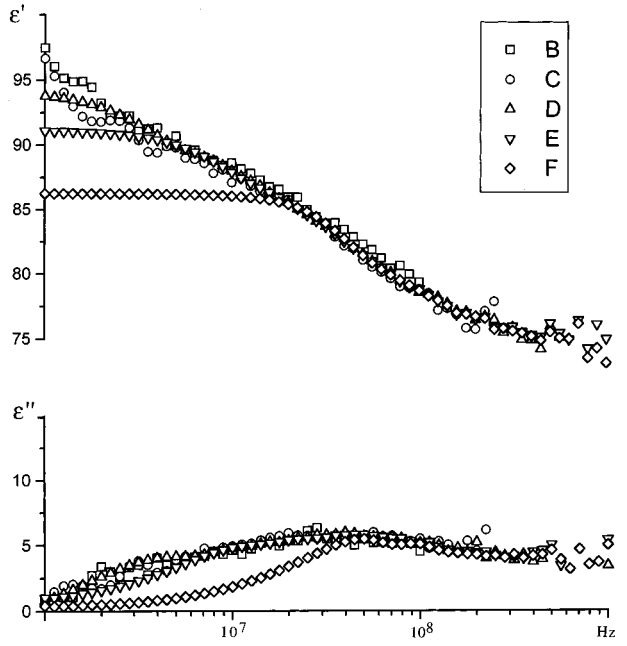

Figure 1. Permittivity spectra of a PGA solution as obtained with different time windows: B = 1 μs; C = 500 ns; D = 200 ns; E = 100 ns; F = 20 ns.

This indicates that the TDR method can be used on strongly conducting aqueous solutions to study dispersions also in the MHz range. As pointed out by Mashimo et al.[7] the reference sample should then be chosen to have nearly the same conductivity as that of the unknown. In order to confirm these results for PGA by an independent TDR measurement, the result of such a study is presented.

The total reflection method as previously[5] described was used with an effective cell length 6.3 mm. A HP54120B oscilloscope was used to monotor line shapes with time windows T = 20 ns, 100 ns, 200 ns, 500 ns, and 1 μs. Spectra were evaluated from 1 MHz to 1 GHz. The results for a 5 mg/mL PGA sodium salt solution of averge molecular weight 85 000 at pH 6 are presented in Figure 1. The ϵ'' spectra show the results after subtraction of a conductivity contribution, the conductivity adjusted to give ϵ'' near zero at 1 MHz.

As seen from the ϵ' spectra, the dispersion is strongly dependent on the time window used. A too short time window, e.g. 20 ns, gives a completely misleading estimate of the relaxation time if the whole calculated spectrum is retained. The dispersion is rather broad and extension of the time window adds to the dispersion on the low-frequency side. However, this feature becomes less pronounced at the longest time windows, and it appears that the major part of the dispersion is included at the longest time windows. This is also seen from the ϵ'' part of the spectrum. A too short time window, e.g. 20 ns, leads to a too short relaxation time. However, on extension of the time window, the maximum absorption is captured and the position of this is consistent for all time windows. The figure emphasizes the observation that for a certain time window T the spectrum should not be calculated for frequencies much lower than T^{-1}.

This result confirms the conclusions of Mashimo et al.[7] that the dispersion of PGA in the 10−100 MHz range observed by TDR is not due to the truncation of

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low frequency dispersions. The agreement between the frequency domain results of Bordi et al.[6] and the time domain results of Mashimo et al.[7] places confidence in the latter method as being accurate also for highly conducting systems. Caution should then be exercised in choosing observational time windows, to make sure that a sufficiently large frequency range is covered. The molecular interpretation of this dispersion is fully discussed in the paper of Mashimo et al.[7]

References and Notes

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