The Dielectric Behaviour of Poly-γ-benzyl-L-glutamate under the Influence of an Electric Field

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THE α-helical conformer of poly-(γ-benzyl-L-glutamate) (PBLG) exhibits dielectric relaxation ascribed to whole molecule rotation.[1,2] This relaxation occurring at low frequency (*ca.* 10^3Hz) is associated with a very large relaxing dipole (*ca.* 1500 D) and would therefore appear to lend itself to a study of the influence of the constraint of voltage gradient. Studies on the influence of electric fields on the electric permittivity of simple molecules have been reported[3] but, in general, very high voltage gradients are necessary to achieve the onset of dielectric saturation (decreases of permittivity due to dipolar constraint). With small, dipolar molecules it is generally not possible to apply fields large enough so that the energy available for constraint is of the order of kT per molecule. We report large dielectric saturation effects when solutions of PBLG are subject to constant electric fields of moderate magnitude. Observations extend into regions where the dielectric saturation effects become non-linear in the square of the voltage gradient.

solvent benzene was used as it had the required low permittivity and conductance. For this purpose either azepin-2-one (ε-caprolactam, CM) or benzyloxycarbonyl-L-glutamic acid diethyl ester (BGDE) were used. In the absence of the high electric field the system with CM as additive was found[2] to be substantially the same as reported by other observers;[1] with BGDE (10% w/v) however some polymer aggregation still appears to be present.

The constraint of high voltage reduces the real part of the permittivity up to and including the relaxation region but has little effect at higher frequencies. Values of the dielectric loss over the relaxation range are also reduced by a field (Figure 1). These observations are consistent with the concept that under the influence of a voltage gradient the incremental dielectric constant due to PBLG is reduced because constraints are imposed on the dipole associated with the α-helix. Buckingham has proposed a theory[5] for such effects which predicts that the extent of dielectric saturation can be described as a virial expansion in the
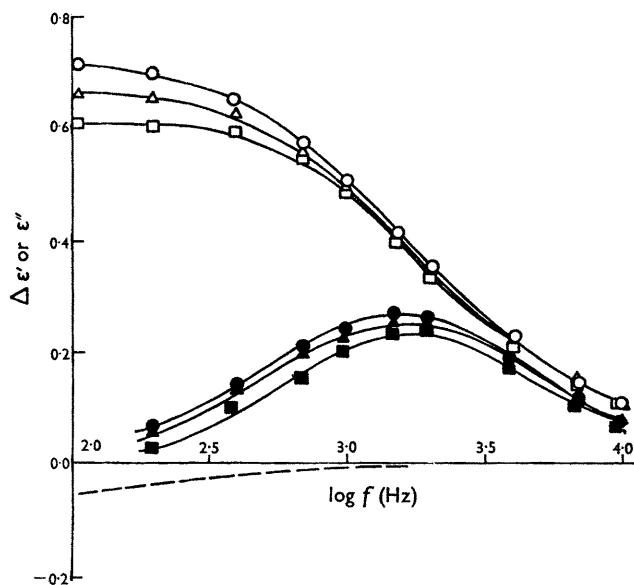

FIGURE 1. *The effect of voltage gradient on the frequency dependence of dielectric permittivity $\Delta\epsilon'$ and loss ϵ'' (both relative to solvent). PBLG (0.08%) in benzene + CM (10%). $\bigcirc = 0$ v cm.$^{-1}$; $\triangle = 2.35 \times 10^3$ v cm.$^{-1}$; $\square = 3.40 \times 10^3$ v cm.$^{-1}$. Open points $\Delta\epsilon'$, solid points ϵ''. The dashed curve represents the behaviour of benzene + CM at 8.0×10^3 v cm.$^{-1}$ in the absence of polymer.*

FIGURE 2. *The dependence of the change of dielectric saturation $\Delta\Delta\epsilon'$ (relative to solvent and additive) on the square of voltage gradient E^2 at 105 Hz. $\bigcirc = $ CM, $\triangle = $ BGDE. The dashed curve represents the change in permittivity of CM relative to benzene at 105 Hz as a function of E^2.*

Measurements were made in a rhodium-flashed cell with a 0.1 cm. annular gap to which combined high static and low alternating voltages were applied, only the latter serving to energise the capacitance–conductance bridges used. The polymer employed was one of viscosity-estimated (dichloroacetic acid)[4] molecular weight of 2.6×10^5 and measured[2] dipole moment of 1690 D. We found it necessary to add deaggregating substances to the solutions to inhibit the polymer self-association (*cf.* ref. 1), since the poor
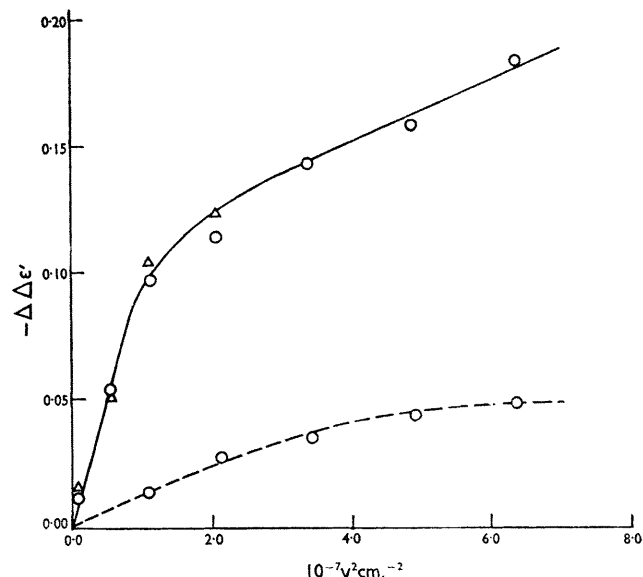
square of the voltage gradient. (Only even powers of voltage gradient can be involved since the dielectric constant of the bulk medium is isotropic.) Figure 2 shows that the behaviour is independent of the deaggregant used. We observed a voltage-induced decrease in the permittivity of CM in benzene (*c'*, Figure 1 and 2), which is most marked at low frequencies. The cause of this effect is unknown to us, although we have established that a molecular phenomenon rather than an experimental artifact is involved,

and that a number of other amides (but not BGDE) exhibit this effect. We have corrected all values of the CM–benzene–PBLG system for this effect.

Of particular interest in the PBLG systems is the experimental attainment of non-linearity which we believe has not previously been observed for any system. These effects become marked at voltage gradients of 4000 v cm.$^{-1}$ which corresponds to *ca.* $\frac{1}{2}kT$ per molecule at 25°. According to Buckingham[5] the gradient in regions of linear dependence between the dielectric saturation ($\Delta\Delta\epsilon'$) and a square of the voltage gradient (E^2) for small spherical molecules at infinite dilution is given by

$$\frac{\Delta\Delta\epsilon'}{E^2} = \frac{4\pi Nc\mu^2(\epsilon_s + 2)^4}{1215\,k^2T^2} \left\{ 6(\alpha_3 - \alpha) - \frac{\mu^2}{kT} \right\}$$

where μ is the dipole moment, ϵ_s the solvent dielectric constant, c the concentration and $(\alpha_3 - \alpha)$ the excess polarizability along the major axis. In the absence of a theory for long rigid molecules at the present time we have made use of this equation. The polarizability difference for PBLG has been estimated[6] to be of the order 10^{-19} cm.^{3}/molecule and may be neglected in relation to μ^2/kT. When $\mu = 1690$ D, $T = 298°$ K, and $c = 0.8$ g.l.$^{-1} = 3.1 \times 10^{-6}$M, the calculated slope is -14×10^{-9} cm.^{2} v^{-2}; this compares well with the experimental value of -9.4×10^{-9} cm.^{2} v^{-2}.

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