Ultrasonic Relaxation in *N*-Polyvinyl Pyrrolidone

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The ultrasonic relaxation technique has been applied to the investigation of the dynamic properties of biochemically important macromolecules, such as nucleic acids (calf thymus [1,2]), carbohydrates (dextran [3–5]), proteins (hemoglobin,[6,7] bovine serum albumine[8,9]) and polypeptides (polyglutamic acid,[10,12] polylysine [13,14]). The large number of plausible phenomena to which the observed relaxation may be attributed combined with the facts that the frequency range investigated generally is relatively small and that the systems are fairly badly defined have limited the kinetic interpretation of the ultrasonic relaxation spectra to qualitative considerations.

The ultrasonic relaxation observed in the megacycle region for a solution of a macromolecule may be attributed to macromolecule/solvent interactions, macromolecule/macromolecule interactions, or conformational changes of the polymer chain. Each of these phenomena which very often involves hydrogen bond formation is described by a reaction mechanism which consists of several coupled elementary reaction steps. This means that the frequency dependence of the ultrasonic absorption coefficient, α, is given by

$$\frac{\alpha}{\nu^2} = \sum_i^n \frac{A_i}{1+(2\pi\tau_i\nu)^2} + B \qquad (1)$$

where A_i is a relaxation strength, τ_i is a relaxation time, ν is the sound frequency, and B is the so-called background absorption. The summation goes over all n elementary reaction steps. The observed relaxation may also be attributed to dynamic shear viscosity. A linear viscoelastic theory predicts a spectrum of relaxation times for long chain flexible polymers in solution due to shear viscosity and it turns out that the frequency dependence of α for this phenomenon is given by an equation similar to eqn. (1) in which the summation now goes over all n segments of the polymer.[15] Thus a spectrum of relaxation times is expected for all of the above mentioned phenomena. Which of these or the extent to which the different phenomena contribute to the observed relaxation may be decided on the basis of numerical agreement between the measured data and the theoretical expressions for the relaxation spectra for the different phenomena. In order to construct these expressions, a knowledge of the detailed reaction mechanism for the phenomenon in question is required. Lack of information makes this way of interpretation impossible, however. An impression of the extent to which the different phenomena contribute to the relaxation spectra may be obtained by measuring the relaxation spectra for different macromolecules which assume similar configuration but which differ chemically.

This work presents the ultrasonic investigation of *N*-polyvinyl pyrrolidone, PVP, dissolved in dioxane. This system is a polymer system in which the possibility of hydrogen bonding is excluded.

PVP is a synthetic polymer which is commercially available with several molecular weights and was obtained from Fluka. Although PVP in some aspects behaves like serum albumine [16] no ultrasonic investigation is reported in the literature to our knowledge. Fig. 1 shows the relaxation spectra for different molecular weights at 20°C in the frequency range 1 – 40 Mc. The parameters computed for a single relaxation process ($i = 1$ in eqn. (1)) are given in Table 1 together with the sound velocity of the different solutions. The absorption coefficients at 1 and 4 Mc were obtained by means of a differential cell and the higher frequency points by means of the previously published pulse technique.[17] The sound velocity was measured by means of a sing around technique (NUS Corporation USA) using a differential cell at 3.5 Mc.

It is evident that although the possibility of hydrogen bonding is excluded a relaxation occurs. The reason why this relaxation may be described by one relaxation time only, even though a broad spectrum was to be expected, has been discussed.[18,19] The relaxation times given in Table 1 are presumably to be considered as average values of the smallest relaxation times involved in the mechanism. It appears that the relaxation times are relatively independent of the molecular weight while the relaxation strength at constant mass concentration increases with increasing molecular weight. These facts combined with

Table 1. Relaxation parameters and sound velocity for PVP/dioxane mixtures. U and U_0 are the sound velocity for the mixture and pure dioxane, respectively.

MW	$C \times 10^2$ g/ml	$A \times 10^{17}$ sec^{2}cm^{-1}	$\tau \times 10^8$ sec	$B \times 10^{17}$ sec^{2}cm^{-1}	$\frac{U-U_0}{U_0}$ ‰	$\frac{U-U_0}{U_0 C} 10^2$
Monomer	6.670	no relaxation			11.0	0.165
25 000	1.982	153	5.3	123	3.12	0.161
25 000	3.978	239	6.3	125	6.42	0.161
40 000	1.962				3.22	0.164
40 000	3.971	289	4.3	131	6.42	0.162
360 000	1.996				3.16	0.158
360 000	3.986	428	6.9	134	6.36	0.160

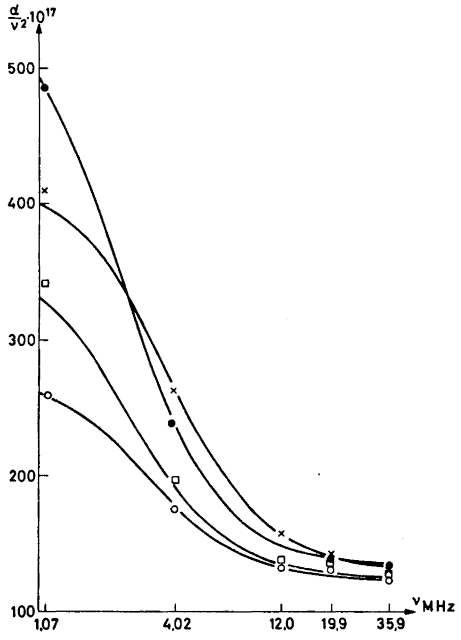

Fig. 1. Ultrasonic relaxation spectra for PVP dissolved in dioxane at 20°C. ○, MW 25 000, $C = 1.9824 \times 10^{-2}$ g/ml; □, MW 25 000, $C = 3.978 \times 10^{-2}$ g/ml: ×, MW 40 000, $C = 3.9718 \times 10^{-2}$ g/ml; ●, MW 360 000, $C = 3.9868 \times 10^{-2}$ g/ml.

the fact that the sound velocity depends on the mass concentration only, indicate that conformational changes of the polymer is the phenomenon which dominates. Further work to prove this assumption is in preparation.

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