Polymer Bulletin 8, 269-274 (1982)

Polymer Bulletin

Ultrasonic Attenuation and Mobility in Polymer Solutions and Dispersions. Poly(Vinyl Alcohol) and Poly(Vinyl Acetate)

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Summary

To obtain informations about molecular processes, poly(vinyl alcohol) solutions and poly(vinyl acetate) solutions and dispersions have been studied by ultrasonic methods in the frequency range from 200 kHz to 150 MHz. The measured excess attenuations are qualitatively discussed in terms of cooperative and local mode motions of the macromolecules. In poly(vinyl alcohol) solutions with different residual vinyl acetate content a mixing of normal and local mode motions has been observed. In poly(vinyl acetate)/toluene solution two discrete relaxation processes have been detected which are probably related to a local mode and a coupling of local and normal mode motions, respectively. The frequency-temperature dependence of the absorption maximum of the poly(vinyl acetate) dispersion follows the WLF relation.

Introduction

The absorption of ultrasound in liquid polymer systems is connected with local modes of motion (segmental conformational change) and with cooperative whole molecule movements (normal or Rouse modes)(NOMURA et al. 1975; NORTH, PETHRICK, 1980). In view of the frequency range (100 kHz - 200 MHz) easily attainable, the advantage of the ultrasonic method is to cover the transition region between cooperative and local mode motions in concentrated polymer solutions.

0170-0839/82/0008/0269/$01.20

Until now, a quantitative relation between the absorption coefficient α and molecular parameters exists only in a phenomenological manner. Because of the stronger intermolecular interaction within the dispersion particle the mobility in a polymer dispersion is similar to that in a solid polymer, and the cooperative motion should be well detectable in the ultrasonic range. The character of the kinetic unit strongly influences the position of the absorption maximum on the temperature scale (ROTHE, 1980). The aim of our study is to probe the molecular motions via ultrasonic parameters.

Experimental

The ultrasonic attenuation has been measured as a function of temperature (0 ... 60 °C) and frequency using

(i) statistical reverberation method (200 kHz ...3 MHz)
(ii) pulse difference technique (1 MHz ... 20 MHz)
(iii) pulse method (20 MHz ... 150 MHz)

with accuracies of 5 - 10 %, 3 - 5 % and 3 - 6 %, respectively. Poly(vinyl alcohol) (PVA) of different residual vinyl acetate (VAc) content and molecular weight was dissolved in water. Poly(vinyl acetate) (PVAc) was dissolved in toluene, ethanol and xylene, respectively. In the case of the dispersion, PVAc was colloidally suspended in water.

Results

1. Poly(vinyl alcohol)/water solutions.

Figure 1 shows the ultrasonic absorption of various PVA/water solutions with different residual VAc content. These typical broad relaxation spectra can be described by normal mode processes leading to the dynamical viscosity

$$\eta(\omega) = \eta_s + nkT \sum_{i=1}^{N} \frac{\tau_i}{1 + (\omega\tau_i)^2} \qquad (1)$$

with η_s being the solvent viscosity, n the number of polymer molecules per unit volume, τ_i the relaxation time

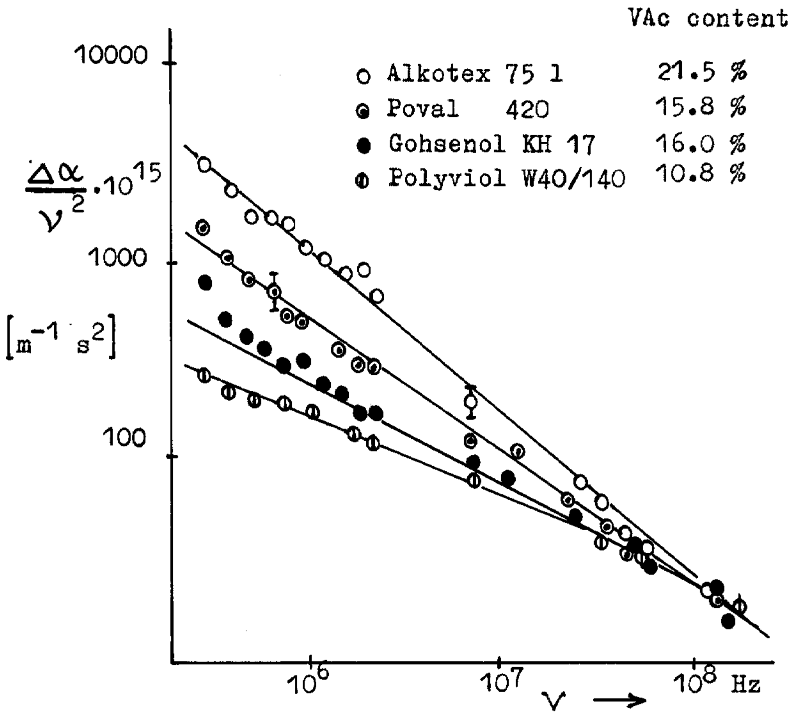

Figure 1: Frequency dependence of the ultrasonic excess absorption $\Delta\alpha/\nu^2$ of various PVA/water solutions with different residual VAc content (c = 10 g/ 100 ml, T = 20 °C)

of the ith mode, ν the frequency and $\omega = 2\pi\nu$. The excess attenuation $\Delta\alpha$ is given by

$$\frac{\Delta\alpha}{\nu^2} = \frac{4\pi^2}{\varrho c^2}(\eta - \eta_s) \qquad (2)$$

where c is the sound velocity and ϱ is the density of the solution. With increasing VAc content of the PVA, the slope of the curve $\Delta\alpha/\nu^2 \sim \nu^{-n}$ changes from n = 0.5 to n = 0.7. This behaviour reflects that the local mode of motion mechanism has become more pronounced, and therefore, a mixing of normal and local mode motions becomes apparent.

2. Poly(vinyl acetate) solutions.

In polymers with big side groups one would expect to observe the local mode process characterized by a single relaxation time

$$\frac{\Delta\alpha}{\nu^2} = \frac{A}{1 + (\omega\tau)^2} + B \qquad (3)$$

where A and B are constants. However, the $\Delta\alpha/\nu^2$ curve of the PVAc/toluene solution (Figure 2) indicates two discrete relaxation processes. The process at 80 MHz involves a pure local mode which is related to conformational changes with an activation energy of a few kJ/mol. The second relaxation process in the range of a few MHz can be related to a coupling of local and normal mode motion. It is possible that the molecular mechanism is a trans - gauche transition, where the number of involved bonds determines the relaxation frequency.

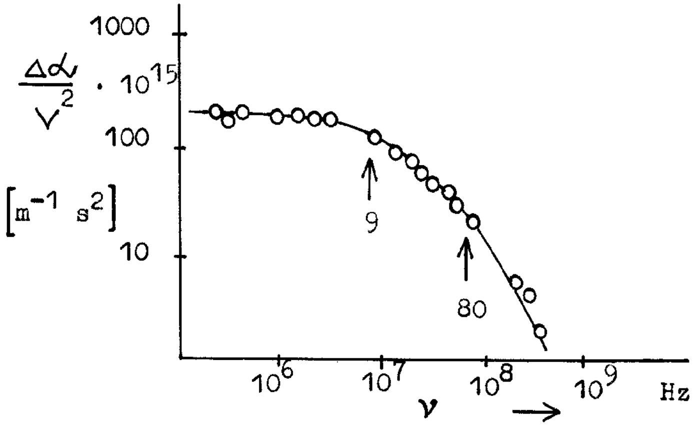

Figure 2: Frequency dependence of $\Delta\alpha/\nu^2$ of a PVAc/toluene solution (c = 54 g/100 ml, T = 20 °C)

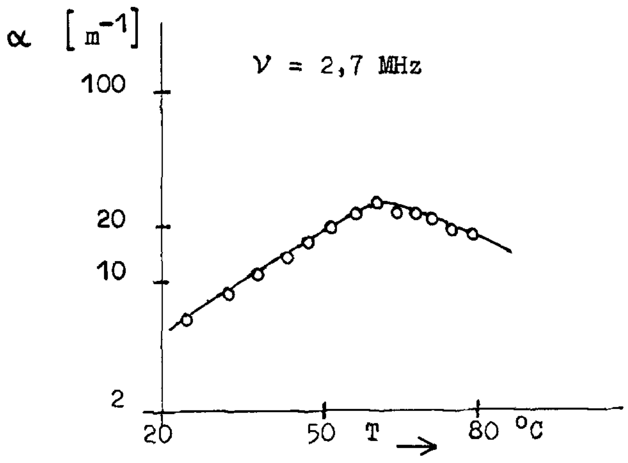

Figure 3: Ultrasonic absorption of a PVAc dispersion as a function of temperature; polymer content is 5 %, measuring frequency ν = 2.7 MHz

In the case of other solvents, e. g. ethanol, a relaxation spectrum is observed at frequencies below 10 MHz instead of the discrete relaxation. This indicates a change in the molecular properties due to the influence of the solvent.

3. Poly(vinyl acetate) dispersion.

In the case of the PVAc dispersion, we found that the excess absorption $\Delta\alpha/\nu^2$ at room temperature is proportional to ν^{-1} which can be mainly explained by viscous and thermal losses within the dispersion. With increasing temperature a deviation from the ν^{-1} behaviour was observed at frequencies below 10 MHz. This indicates additional losses due to relaxation processes (GRIGORJEW et al. 1980). The temperature dependence of the absorption at a fixed frequency shows a maximum (Figure 3). The frequency - temperature dependence of the absorption maximum, α_{max}, follows the WLF relation (FERRY 1969). Local mode motions could not be detected in the frequency range given. The position of the attenuation maximum responds very sensitively to modifications of the backbone. The increase of the mobility in the polymer chain causes a shift of the maximum to lower temperatures; a stiffening of the chain causes a shift to higher temperatures. We conclude this additional ultrasonic attenuation is connected with the α-relaxation process within the PVAc particle.

Conclusions

The experimental results on the frequency dependence of the ultrasonic excess attenuation of PVA and PVAc solutions indicate normal mode and local mode motions. The ultrasonic absorption behaviour of the PVAc dispersion can be related to the α-relaxation process within the polymer particle. The measurements illustrate that the ultrasonic methods provide a good means to study the motional behaviour of both very dilute and concentrated polymer solutions. The experimental determined relaxation times are directly correlated to molecular transition processes. But at present, it is difficult to infer a particular molecular mechanism, since a molecular model for the description of the acoustic parameters is not available. It is also necessary to take the results of other methods into consideration. Future improvement in the interpretation of ultrasonic results on polymer systems could be expected from a more extensive use of conformational energy calculation and their relation to ultrasonic attenuation.

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Received June 21, accepted after revision August 31, 1982
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