

## Ultrasonic Properties of Poly( $\gamma$ -methyl D-glutamate) Film in the $\alpha$ -Helical Conformation under Pressure

Tsuneto YOSHIKUMI, Tisato KAJIYAMA, and Motowo TAKAYANAGI

*Department of Applied Chemistry, Faculty of Engineering,  
Kyushu University, Fukuoka 812, Japan.*

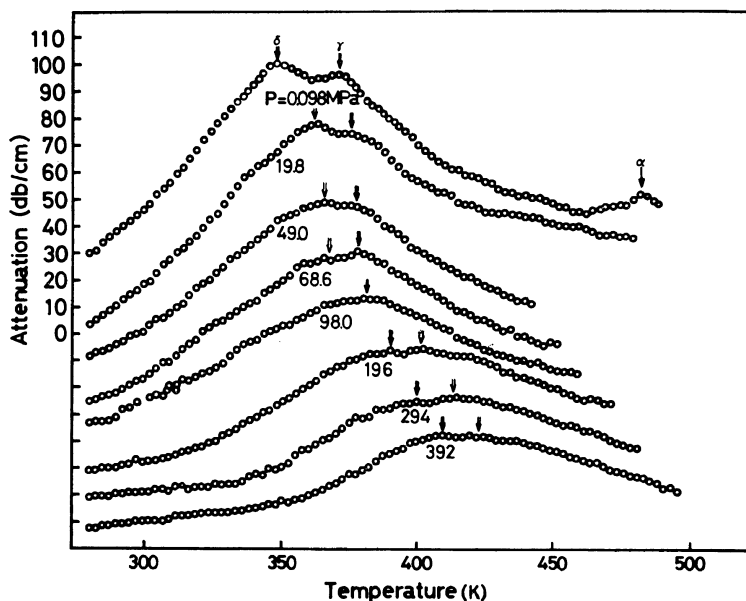
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A few detailed investigations concerning the ultrasonic relaxation behavior of polyethylene<sup>1,2</sup> and polytetrafluoroethylene<sup>3</sup> have been reported; however, there has hardly been any study on the ultrasonic relaxation in bio-related synthetic polymers such as poly(amino acid)s or poly(amino acid) esters. In order to obtain detailed information on ultrasonic relaxation behavior and the Grüneisen parameter of poly( $\gamma$ -methyl D-glutamate) (PMDG) films in the form of the  $\alpha$ -helical conformation, the temperature depend-

ences of specific volume, sound velocity and attenuation were measured at various pressures up to 392 MPa (4000 kg/cm<sup>2</sup>).

The PMDG films were cast from a solution in the  $\alpha$ -helix forming solvent of 1,2-dichloroethane (DCE) at room temperature. It was confirmed from the X-ray diffraction study that the films were composed of the  $\alpha$ -helical molecular chains. The PMDG films were annealed at 488 K for 1 hr *in vacuo*. Using a provisionally set up device, longitudinal ultrasonic measure-



**Figure 1.** The isobaric measurements of ultrasonic attenuation for the PMDG film cast from a solution in DCE. The curve for 19.8 MPa is shifted downward by 20 db/cm, and the others by 10 db/cm, successively.

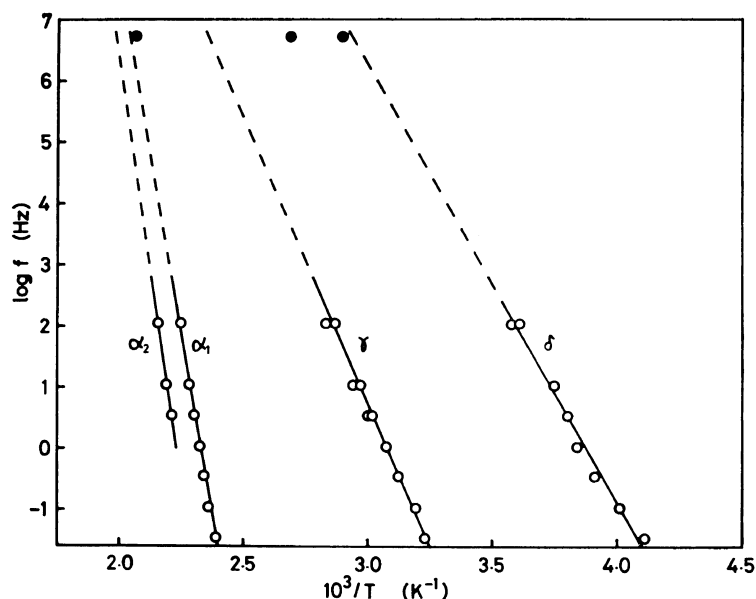


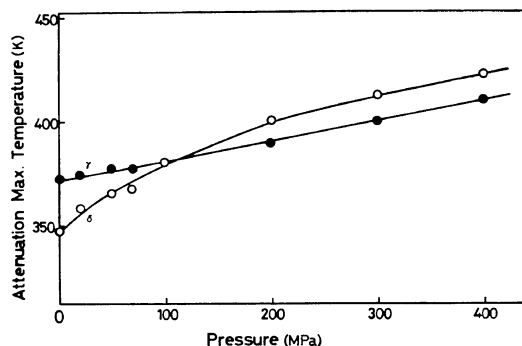
Figure 2. The frequency-temperature locations of the  $\delta$ ,  $\gamma$ ,  $\alpha_1$ , and  $\alpha_2$  relaxations, which were obtained by viscoelastic measurement ( $\circ$ ) and ultrasonic measurement ( $\bullet$ ).

ments were carried out by the pulse technique at 5 MHz, over a temperature range from 283 to 503 K under various hydrostatic pressures below 392 MPa. The sound velocity and the attenuation were calculated as the delay time and the attenuation per unit thickness of the PMDG film in the disk shape.

Figure 1 shows the isobaric measurements of the ultrasonic attenuation for the PMDG film. The values on the ordinate are for the normal pressure curve. The curve for 19.8 MPa shifted downward by 20 db/cm, and the other isobaric attenuation curves shifted by 10 db/cm, successively. For calculation of the sound velocity and the attenuation, the thickness of the PMDG disk under pressure was evaluated from the dilatometric data on the specific volume at various pressures. The three attenuation maxima were observed at 348, 368, and 483 K under normal pressure. On the basis of the transition map obtained from the dynamic viscoelastic measurements from 0.035 to 110 Hz, the attenuation maxima at 348, 368, and 483 K may be assigned the  $\delta$ -,  $\gamma$ -, and  $\alpha$ -relaxation processes, respectively,<sup>5,6</sup> as shown in Figure 2. The  $\alpha$ -relaxation associates with the thermal molecular motions of the  $\alpha$ -helical chains in the crystalline region.

The  $\alpha$ -viscoelastic crystalline relaxation was composed of two mechanisms: the shear deformation in the interhelix region (the  $\alpha_1$ -mechanism) and the tensile or bending deformation of the  $\alpha$ -helix core itself (the  $\alpha_2$ -mechanism).<sup>5</sup> Also, the  $\gamma$ - and  $\delta$ -relaxations arise from motions of the entire side chain groups in the crystalline- and the disordered-regions, respectively.<sup>6</sup>

The temperature locations of the  $\alpha$ - and  $\gamma$ -attenuation maxima shifted to higher temperature range with increasing pressure as shown in Figure 1. It seems that the transition curves intersect at about 98 MPa, as shown in Figure 3 when the shapes of attenuation curves of Figure 1 are surveyed in detail. The pressure coefficients of the peak temperature of the ultrasonic attenuation maxima at normal pressure are 29.6 and 9.7 K/100 MPa (29.0 and 9.5°C/1000 kg/cm<sup>2</sup>) for the  $\delta$ - and  $\gamma$ -absorptions, respectively. In general, the pressure dependence of the molecular motions in the crystalline region is smaller than that in the amorphous region.<sup>7</sup> Consequently, the pressure coefficients of the ultrasonic attenuation peak temperature are consistent with the assignments of the  $\gamma$ - and  $\delta$ -absorptions associated with the motions of the entire side-chain groups in the crystalline and the disordered-regions, re-



**Figure 3.** The pressure dependence of the peak temperature of the ultrasonic attenuation maxima, for the  $\gamma$  and  $\delta$  relaxations.

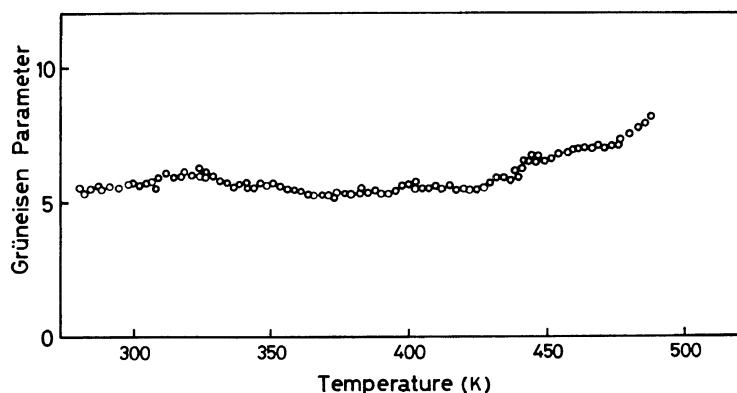
spectively. Thus, it seems reasonable to conclude that the two attenuation maxima of 348 and 368 K at normal pressure are attributable to the  $\delta$ - and  $\gamma$ -relaxation processes, respectively. The coefficient of the pressure dependence of the  $\delta$ -relaxation process is actually comparable to that of the primary dispersion for many amorphous polymers.<sup>7</sup> Kaneko, *et al.*,<sup>8</sup> have reported that the side chain relaxation of poly(glutamic acid) esters is somewhat different from that of poly(alkyl methacrylate)s and is, to some degree, similar to the primary relaxation related to the glass transition. Accordingly, the pressure dependence of 29.6 K/100 MPa for the  $\delta$ -relaxation is consistent with Kaneko's results.

The Grüneisen constant,  $\gamma_s$  is a measure of the anharmonicity of the molecular vibrations in the crystal lattice.  $\gamma_s$  is ordinarily defined in terms of the lattice frequency, but it can be also

represented indirectly in terms of some other physical properties as described by eq 1.<sup>2</sup>

$$\gamma_s = \frac{1}{c} \left( \frac{\partial c}{\partial P} \right)_T \frac{1}{\kappa} + \frac{1}{3} \quad (1)$$

where  $c$ ,  $\kappa$ , and  $P$  are the sound velocity, the compressibility and pressure, respectively. Figure 4 shows the temperature dependence of  $\gamma_s$  for the PMDG film under normal pressure. For calculation of the  $\gamma_s$  value, the pressure coefficient of the isothermal compressibility and the sound velocity of the PMDG film were evaluated by using the temperature dependence of the specific volume and also, sound velocity at various pressures, respectively. Since the specimen used in this study is a partially crystalline material, the  $\gamma_s$  value represents an average one. In a lower temperature range, the  $\gamma_s$  value changes considerably, but in a higher temperature range above about 425 K,  $\gamma_s$  exhibits a tendency of abrupt increase. It was reported that the temperature dependence of the distance between neighboring  $\alpha$ -helices in the crystal region by means of X-ray study revealed a distinct break from around 420 K.<sup>5,6</sup> This phenomenon is caused by an increased contribution from the anharmonicity on the intermolecular potential well, and is consistent with the abrupt increase of the Grüneisen constant at about 425 K. Also, the abrupt increase of  $\gamma_s$  at 425 K may be closely related to the viscoelastic crystalline  $\alpha$ -relaxation process, which is associated with the thermal molecular motion of  $\alpha$ -helices in the crystalline region. This is easily under-



**Figure 4.** The temperature dependence of Grüneisen parameter for the PMDG film under normal pressure.

stood considering that the onset of thermal molecular motions of the  $\alpha$ -helices in the crystalline region may become possible due to large amplitude molecular chain vibration or rotation activated upon heating, and this will be accompanied by the remarkable break in the thermal expansion of the distance between the  $\alpha$ -helices in the crystalline region.

From the temperature dependence of the sound velocity and the attenuation at various hydrostatic pressures, the following experimental results were found; (1) the ultrasonic attenuations corresponding to the mechanical  $\alpha$ -,  $\gamma$ -, and  $\delta$ -relaxation processes were observed and (2) the Grüneisen constant begins to increase at around 425 K and this corresponds to the viscoelastic crystalline relaxation and also, to the abrupt increase of the inter- $\alpha$ -helical distance observed at about 420 K by the X-ray study.

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