

NOTE

## The Electric Conduction of Poly( $\gamma$ -benzyl L-glutamate)

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Several mechanisms have been proposed for electric conduction in biopolymers, especially proteins and DNA. Eley and Spively,<sup>1</sup> and Rosenberg<sup>2</sup> proposed electronic conduction in proteins. However, calculations of the band energy of the hydrogen-bonded polypeptides revealed that polypeptides are good insulators.<sup>3</sup>

Electric conduction of poly( $\gamma$ -benzyl L-glutamate) (PBLG), one of the well-known synthetic polypeptides, was previously investigated by Miyoshi and Saito,<sup>4</sup> who maintained there was no possibility of an ionic and protonic conduction mechanisms in PBLG. They suggested the electronic conduction mechanism, in which a hole is assumed to be trapped on the impurity level at about 2 eV higher from the top of the valence band.

Sasabe<sup>5</sup> and Sasabe, Oosugi, and Saito<sup>6</sup> investigated the conduction of poly( $\gamma$ -methyl D-glutamate) and poly( $\gamma$ -ethyl D-glutamate), and concluded that the conduction process is ionic. Thus, the conduction mechanism in polypeptides does not seem conclusive. In this paper, electric conductivity of PBLG is reexamined and discussed in terms of molecular motions.

### EXPERIMENTAL

The PBLG used in this work was prepared by the polymerization of *N*-carboxy anhydride of  $\gamma$ -benzyl L-glutamate in dioxane. The PBLG as polymerized in dioxane was precipitated in ethanol. The polymer was dissolved again in chloroform

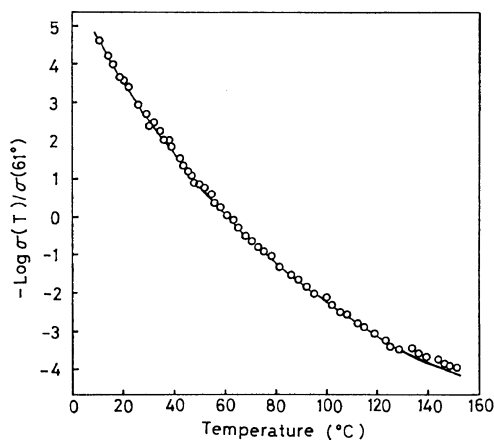
and precipitated in ethanol repeatedly to eliminate any trace of hexamethylenediamine used as an initiator. The sample for conductivity measurements was a film of 0.05-mm thickness, cast from concentrated chloroform solution. The sample was heat-treated at a temperature above 150°C for several hours in the atmosphere. Circular electrodes were painted on both sides of the film by silver paste (Dotite). The guard ring was employed to reduce the effect of the surface current. Conductivity measurements were performed with a vibrating reed electrometer of Takeda TR-84B type. Various voltages up to 70V were applied across the sample from batteries. Measurements were made after more than three hours, from the beginning of application of voltage to avoid the effect of the absorption current. Temperature was raised from room temperature to 150°C and was measured by a Cu-constantan thermocouple.

### RESULTS AND DISCUSSION

It was found that the Ohm law holds in the whole range of temperatures and voltages used for this study. This is in agreement with the results obtained by Miyoshi and Saito.<sup>4</sup> There is, however, a remarkable difference between their results and ours. Our results show that the temperature dependence of the dc conductivity  $\sigma$  of PBLG does not follow the Arrhenius-type equation in contrast with their results.

Figure 1 shows the logarithm of the dc conductivity of PBLG as a function of temperature. The data are represented in units of the value of conductivity at 61°C which is  $2.3 \times 10^{-15} \Omega\text{cm}^{-1}$ .

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**Figure 1.** The logarithm of ratio of dc conductivities  $\sigma(T)$  at temperature  $T$  and  $\sigma(61^\circ)$  at  $61^\circ\text{C}$  of PBLG as a function of temperature.  $\sigma(61^\circ)$  is  $2.3 \times 10^{-10} \text{ } \Omega \text{ cm}^{-1}$ . The solid line represents eq 1 (see text).

The data are better described by the following WLF-type equation

$$-\log \sigma(T)/\sigma(61^\circ) = -13.3(T-61)/(196.0 + T-61) \quad (1)$$

which is shown as a solid line in the figure. The parameters of the WLF equation,  $C_1$  and  $C_2$ , were determined by plots of  $(T-T_s)/\log(\sigma(T)/\sigma(T_s))$  vs.  $(T-T_s)$ , where  $T_s=61^\circ\text{C}$ . Values of  $C_1$  and  $C_2$  seem to be within the range of values obtained for various polymers.

PBLG shows a mechanical dispersion as well as a dielectric dispersion at around room temperature, and is attributed to side-chain motions. In previous papers<sup>7,8</sup> we reported that the temperature dependence of the relaxation time of these mechanical and dielectric dispersions is well described by the WLF equation. It is of interest to note that the dc conductivity of PBLG also follows

the WLF equation in the temperature range where side-chains of PBLG undergo motions, but the main back-bone chain does not.

Sasabe and Saito<sup>9</sup> noted that the temperature dependence of  $\sigma$  for a number of polymers in the glass transition region follows the WLF-type equation, and suggested that the dc conduction mechanism in these polymers is ionic. Thus, it is reasonable that the conduction mechanism in PBLG is ionic. An acceptable model for PBLG in the solid state is that the  $\alpha$ -helical back-bone is embedded in the matrix of side-chains which seem to be arranged randomly. It is probable that the conduction process takes place in the matrix of side-chains.

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