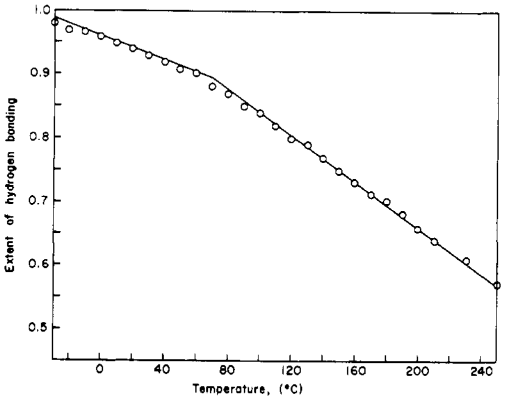

Figure 10. Extent of hydrogen bonding as a function of temperature in dilute solution when $\Delta H = 6$ kcal/mol and $\Delta S = 10$ eu.

one should be cautious in identifying the discontinuity displayed in this manner with a transition because even the equilibrium dissociation of hydrogen bonding in dilute solution can yield a similar discontinuity, depending on the values of ΔH and ΔS. For example, the dissociation of hydrogen bonding between hydroxyl and amine in dilute solution was represented by $\Delta H = 6$ kcal/mol and $\Delta S = 10$ eu.[9] When the fraction of hydrogen bonding is plotted as a function of temperature, Figure 10 is obtained, showing that an apparent discontinuity in slope occurs near 70 °C. Likewise, the discontinuity will be observed in the rubbery region of amorphous polymers if the values of ΔH and ΔS are in the range specified above. At the temperature where vitrification occurs, the hydrogen bond equilibrium is frozen in and the fraction of bonded NH should be in variance with temperature. Nonetheless, a distinct slope to the experimental data below the discontinuity is not uncommon.

One method of verifying the presence of a physical transition when evidence of a thermal transition by TMA or DSC is not applicable is to calculate the ratio $[C_B]/[C_f]^2$ from the absorption band using $\epsilon_f/\epsilon_B = 0.29^4$ to construct the normal plot of ln K vs. $1/T$ shown in Figure 4. The appearance of a discontinuity in the curve plotted in this fashion provides support for a physical transition. Furthermore, the values of ΔH and ΔS obtained for the high-temperature branch of the plot may be used to calculate the apparent absorbance so that the equilibrium and experimental data can be compared. It is of interest to note that Seymour and Cooper's data,[3] after correction for an assumed 85% bonded NH at room temperature and treated in the above fashion, lead to $\Delta H = 6.6$ kcal/mol and $\Delta S = -12.4$ eu.[10] The calculated curve for the fraction of bonded NH and the experimental data fit reasonably well above the discontinuity but separate sharply at lower temperatures confirming the physical origin of the discontinuity.

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Heats of Dissociation of Mixture of Poly(γ-benzyl L- and D-glutamate)

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ABSTRACT: The heats of dissociation of stacked side-chain benzyl groups in mixtures of various proportions of poly(γ-benzyl L- and D-glutamate) have been measured by a differential scanning calorimeter. In order to obtain further information about the dissociation, the heats of solution of poly(γ-benzyl L- and D-glutamate) were also measured by a twin micro calorimeter at 303 K. The agreement between the heat of dissociation obtained by DSC and that determined by the heat of dissolution is good. The average value of the heat of dissociation of stacking estimated by both methods is about 5 kJ/(mol of pairs of residue).

Complex formation in mixtures of poly(γ-benzyl L- and D-glutamate) (PBLG + PBDG) has been confirmed by several investigators,[1,2] and the physical properties of the complex have also been reported in a few papers.[3-5]

In order to obtain further information about the complex formation, we carried out thermal analysis for solid mixtures of various proportions of poly(γ-benzyl L- and D-glutamate) (PBLG + PBDG) and poly(γ-methyl L- and D-glutamate) (PMLG + PMDG) or poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-benzyl D-glutamate) (PBDG) by using a differential scanning calorimeter (DSC).

The DSC curve obtained for the (PBLG + PBDG) system had a transition peak which may be considered to correspond to the dissociation of a complex, whereas for the (PMLG + PMDG), PBLG, and PBDG systems no peak existed. From DSC curves of the former system, the heat of the transition was obtained.

To study the complex formation further and estimate the heat of dissociation, we measured the heats of dissolution of a (PBLG + PBDG) solid mixture and that of PBDG into the mixed solvents. The difference between these two heats of solution gave a value of the heat of dissociation which coin-

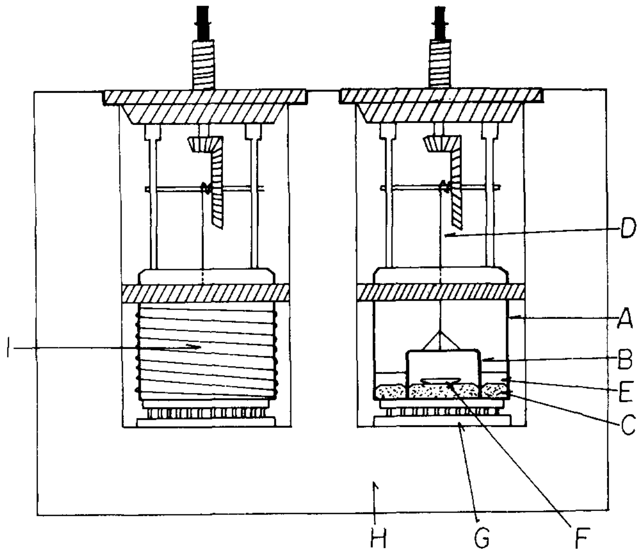

Figure 1. The twin microcalorimeter cell: (A) outer cell (stainless steel), (B) inner cell (glass), (C) mercury, (D) Stainless steel wire, (E) solvent, (F) sample, (G) thermomodule, (H) aluminum block, (I) heater (nichrome wire).

cides approximately with that estimated by the DSC method.

Experimental Section

Apparatus. The DSC apparatus used in this study was modified to enable us to measure the slight heat change in the phase transition of the polymer solution.[6]

The twin micro calorimeter used in this study was designed to measure the heat of solution of polypeptide into mixed solvents. It consists of two cell holders, mixing and reference cells. The mixing cell consists of an outer cell (A) made of stainless steel and an inner cell (B) made of glass. A standard heater (I) is wound around each cell and fixed with araldite, as shown in Figure 1. The outer cell is filled with the mixed solvents, and in the inner cell the polymer film is placed. The samples in each cell are separated with mercury (C). The polymer film and solvents are then mixed by pulling up the inner cell by manipulation of the stainless steel wire (D) from the outside of the calorimeter chamber.

Materials. The samples used were supplied by Ajinomoto Co. Ltd. The degrees of polymerization of PBLG and PBDG were about 1750 and 1320, and those of PMLG and PMDG were 1300 and 1600, respectively. The polypeptide films (about 0.01-cm thick) were prepared using a glass plate and dried at reduced pressure until the solvent was completely removed.

The solvents used are 1,2-dichloroethane (EDC) as the helicogenic solvent and dichloroacetic acid (DCA) as its opposite. The solvents were purified by ordinary methods described in the literature[7] and finally distilled by use of a long column.

Results and Discussion

DSC Method. The DSC measurements were carried out for the (PMLG + PMDG) and (PBLG + PBDG) systems in which the weight ratios of L to D were 4/1, 3/1, 2/1, 1/1, and vice versa, respectively. The heating rate was about 10 K/min.

For the (PMLG + PMDG), PBLG, and PBDG systems no peak of transition on the DSC curve was found in the temperature range from 300 to 393 K, indicating that there occurs no structural change for those systems. On the other hand, for each (PBLG + PBDG) system an endothermic peak on the DSC curve appeared, as shown in Figure 2. This peak may be reasonably considered to correspond to the dissociation of the complex. That the replacement of a methyl group by a benzyl group brings about the peak may suggest that the interaction between the benzyl group of L isomer and that of D isomer plays an important role in the complex formation.

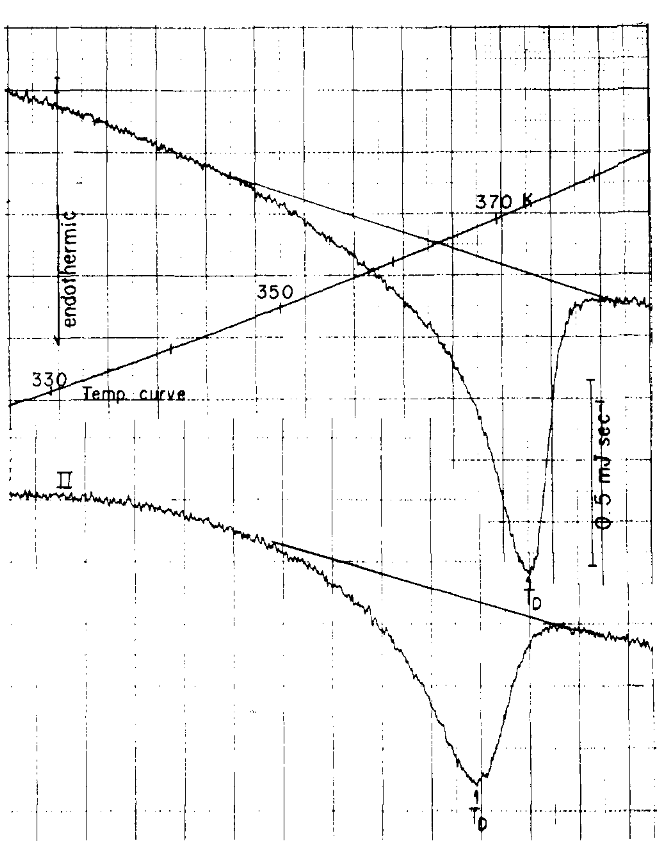

Figure 2. DSC curves of mixtures of PBLG and PBDG with various weight ratios of L to D: (I) L/D = 1/1, (II) L/D = 3/1. Dissociation temperature of L–D complex of PBG is T_D.

With the assumption that the peak is due to the dissociation of the complex, the heat of dissociation of the complex can be estimated from each peak area. The observed heats of dissociation (ΔH_{obsd}) per mole of residue for the mixtures of various weight ratios of L to D are shown in Table I. As seen in this table, ΔH_{obsd} for a 1/1 mixing ratio of L to D is larger than for other mixing ratios. Thus the complex formation in 1:n mixture may be expected to be $2/(1 + n)$ times that in 1:1 mixture and the value for 1:n mixture must be multiplied by $(1 + n)/2$ to obtain the corrected value per mol of pairs of residue. The corrected values of the heats of dissociation (ΔH_D) are tabu-

Table I[a]

D:L	T_D, K	ΔH_{obsd}, J(mol of res.)$^{-1}$	ΔH_D, kJ(mol of pairs of res.)$^{-1}$
4:1	366.0	700	3.5
3:1	368.2	1460	5.8
2:1	371.1	1820	5.4
1:1	373.2	2650	5.3
1:2	371.2	1960	5.9
1:3	368.0	1760	7.0
1:4	366.5	880	4.4
Av value			5.3 ± 1.8

[a] The temperature of dissociation (T_D) estimated from the peak temperature on DSC curve, the observed heat of dissociation (ΔH_{obsd}) per mole of residue estimated from the peak area on DSC curve, and the corrected heat of dissociation (ΔH_D) per mole of pairs of residue which converted the complex formation in 1:n complex into the 1:1 one of L and D isomers.

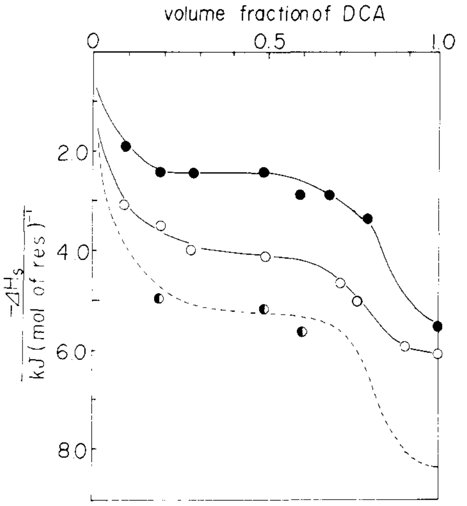

Figure 3. Plots of heats of solution (ΔH_s) against volume fraction of DCA: (●) PBG (D/L = 1/1), (○) PBG (D/L = 3/1), (◐) PBG (D/L = 1/0), (- - -) PBG (D/L = 0/1) (see ref 10).

lated in the last column of Table I, and their average value is 5.3 ± 1.8 kJ/(mol of pairs of residue).

Heat of Solution Method. In order to estimate further the heat of dissociation of the L–D complex, the heats of solution of PBG solid complex which consists of 1:3 and 1:1 mixtures of L and D isomers and those of solid PBDG were measured in the mixed solvents containing various volume ratios of DCA to EDC at 303 K. The reaction between DCA and mercury was not observed, as was found in our previous work.[8,9]

The results obtained are shown in Figure 3, as a plot of the heat of solution per mole of residue against the volume fraction of DCA. As seen in this figure, the heat of solution of solid D isomer coincides with that of solid L isomer, which was measured by Giacometti[10] over all the volume fraction range of DCA.

For the L–D complex, the curve of the heat of solution is similar to that for L and D isomers, except for the absolute magnitude, and the heat of the coil–helix transition is estimated from the sharp change of the heat of solution in the neighborhood of 0.7 of DCA in the volume fraction to be 3.0 and 2.2 kJ/(mol of residue) for 1:1 and 1:3 complexes, respectively, as compared with 2.7 kJ/(mol of residue) for L isomer according to Giacometti.[10]

The heat of solution of solid L–D complex may be divided into the following three hypothetical processes:

$$\text{solid L–D complex} \xrightarrow{\Delta H_1} \text{solid L isomer} + \text{solid D isomer} \quad (1)$$

$$\text{solid L isomer} + \text{solvent} \xrightarrow{\Delta H_2} \text{L isomer solution} \quad (2)$$

$$\text{solid D isomer} + \text{solvent} \xrightarrow{\Delta H_3} \text{D isomer solution} \quad (3)$$

overall

$$\text{solid L–D complex} + \text{solvent} \xrightarrow{\Delta H} \text{L isomer solution} + \text{D isomer solution}$$

where ΔH_1 is the heat of dissociation of L–D complex, ΔH_2 the heat of solution of L isomer, ΔH_3 the heat of solution of D isomer, and ΔH the heat of solution of L–D complex, respectively. From these three processes, the heat of dissociation, ΔH_1, of L–D complex may be estimated as the difference between ΔH and the sum of ΔH_2 and ΔH_3, assuming that the crystal structure of the L–D complex is the same as those of L and D isomers except for the complex formation. Then the complex formation in the 1:3 mixture may be expected to be half that in the 1:1 mixture and the value for the 1:3 mixture must be doubled to obtain the corrected value per mol of pairs of residue. For the 1:1 mixture at any given DCA concentration the difference between the observed heat of solution (ΔH_s) for the mixture and the individual isomers is doubled; for the 1:3 mixture the corresponding difference is quadrupled.

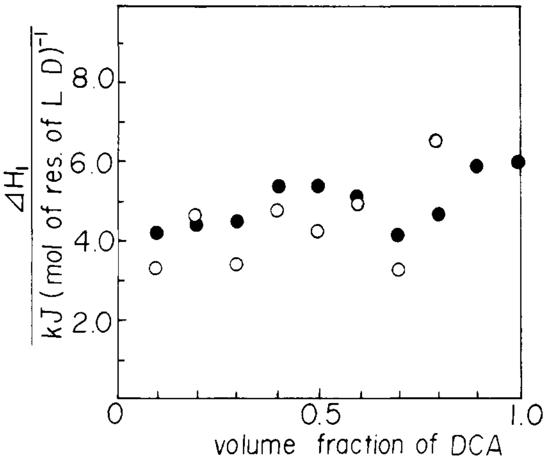

Figure 4. Plots of corrected heats of dissociation (ΔH_1) against volume fraction of DCA: (●) PBG (D/L = 1/1), (○) PBG (D/L = 3/1).

The values of ΔH_1 of L–D complex thus obtained are shown in Figure 4. In this figure, it will be seen that the values of ΔH_1 are scattered in the range of 4 to 6 kJ/(mol of pairs of residue) regardless of the composition of the mixed solvent, suggesting that ΔH_1 may be constant within experimental error.

The average value of ΔH_1 is 5.0 ± 1.3 kJ/mol and seems to be compatible with 5.3 ± 1.8 kJ/(mol of pairs of residue) obtained from the DSC method, indicating that the weak complex may be formed between L and D isomers by stacking of the benzyl side chains upon one another.

The value of 5 kJ obtained in this study is considerably less than 12–16 kJ estimated from the melting point depression of the polymer–solvent system[11] and 8 kJ determined from DTA method.[3] These differences may be ascribed in part to the annealing temperature of the sample film, but for a thorough explanation further study will be needed.

Acknowledgment. The authors wish to thank Dr. Shigeru Mori of the Ajinomoto Co., Ltd., for supplying them with the samples.

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