Solid State Side Chain Transitions of Poly(α-amino acids). I. Investigation by Differential Scanning Calorimetry

G. Pezzin,[1a] G. Ceccorulli,[1a] M. Pizzoli,[1a] and E. Peggion*[1b]

Center for the Study of Macromolecular Structure and Physics, University of Bologna, G. Ciamician Chemical Institute, Bologna, Italy, and the Institute of Organic Chemistry, University of Padua, Padua, Italy. *Received January 22, 1975*

ABSTRACT: The differential scanning calorimetric behavior of a series of α-amino acid homopolymers and copolymers was investigated in the range of temperature from −80 to +130°C. The following polymers have been examined: poly(N^ϵ-carbobenzoxy-L-lysine), poly(O-carbobenzoxy-L-tyrosine), random copolymers of O-carbobenzoxy-L-tyrosine and N^ϵ-carbobenzoxy-L-lysine, poly(N^γ-carbobenzoxy-L-diaminobutyric acid), and poly(N^δ-carbobenzoxy-L-ornithine). Each sample exhibited a prominent glass-like transition between +30 and +60°C with a specific heat increment Δc_p of the order of 0.03–0.11 cal/(g °C). Endothermal peaks, developed by annealing, have also been revealed. It is concluded that in poly(α-amino acids) side chain motions are capable of undergoing glass-like transition.

The solid state properties of poly(α-amino acids) have been recently investigated in several laboratories. Sugai et al.[2] reported the broad-line NMR and dielectric and dynamic mechanical behavior of several poly(γ-alkyl glutamates) and attributed the room-temperature transition of the samples to side-chain motions similar to that of the corresponding amorphous poly(alkyl methacrylates).

For a series of poly(γ-alkyl glutamates), extending to the decyl- and stearyl-substituted polymers, Yokomori et al.[3a] arrived recently at a similar interpretation of the dynamic mechanical transition.

The influence of conformational changes, induced by different casting techniques, on the dynamic mechanical, dielectric, and dilatometric properties of poly(γ-benzyl L-glutamate) and poly(γ-benzyl D-glutamate) and of their mixtures have also been reported[3b–6] together with X-ray data at different temperatures.[7]

Similar investigations have been carried out by Mohadger et al.[8] on poly(γ-methyl D-glutamate) and by Hiltner et al.[9] on poly(γ-methyl and γ-benzyl L-glutamates), poly(β-benzyl L-aspartate), poly(N^ϵ-carbobenzoxy L-lysine), poly(S-carbobenzoxymethyl-L-cysteine). The room-temperature transition, attributed to a side-chain motion, appears to be a common feature of all these polymers.

Recently, Tsutsumi et al.[11] investigated the relaxation phenomena of poly(γ-methyl and γ-benzyl L-glutamates) by means of dielectric, dynamic mechanical, NMR, dilatometric, and X-ray diffraction measurements. They observed a discontinuity in the slope of the specific volume–temperature plots near room temperature, with a thermal expansion coefficient change $\Delta\alpha$ close to the value normally associated to the glass transition of polymers. In addition, applying the time–temperature superposition principle to dielectric and mechanical data, they found that the transition is well described by the WLF equation.[12]

The main purpose of this paper is to investigate the nature of the room-temperature transition of poly(α-amino acids) by means of differential scanning calorimetry. We wish to report results obtained, in the range of temperature from −80 to +130°C, for the following samples: poly(N^ϵ-carbobenzoxy-L-lysine) (PCBL), poly(O-carbobenzoxy-L-tyrosine) (PCBT), a series of random copolymers of O-carbobenzoxy-L-tyrosine and N^ϵ-carbobenzoxy-L-lysine of various composition (mol % from 12.5 to 87.5), poly(N^γ-carbobenzoxy-L-diaminobutyric acid) (PCDBA), and poly(N^δ-carbobenzoxy-L-ornithine) (PCBO).

Experimental Section

The samples, in the form of white fibrous filaments, as obtained by precipitating the polymerization solution into methanol, were dried under vacuum at room temperature for 48 hr. The preparation and characterization of each sample are reported elsewhere.[13,14]

In the course of this work, the Perkin-Elmer DSC 1B differential scanning calorimeter was used. The instrument was calibrated daily with high-purity standards and whenever the heating rate was changed. Samples of 6 to 8 mg and a scanning rate of 32°C/min were normally used, unless otherwise specified. The transition temperature was measured from the midpoint of this step, on the DSC trace.[15]

Results and Discussion

Thermogravimetric measurements, carried out at 10°C/min in air, show that weight losses are less than 1% for all samples, below 130°C, the maximum temperature explored in the present work. This weight loss is probably due to methanol residual from the polymer isolation procedure. All samples have been investigated in the temperature range from −80 to +130°C. The most characteristic feature exhibited by the DSC thermograms is a step increase of the specific heat (of the order of 0.08 cal/(g °C) at about +40°C; such a transition is very similar to that shown by all presently known glasses at their glass temperature.[16] Examples are seen in Figure 1 for PCDBA, PCBO, and PCBL; the curves refer to results obtained on the second or successive rescan. In other words they are typical of samples cooled, from about 90 to −70°C, at the rate used during heating.

In the first scan, the thermograms normally show a more or less intense endothermal peak in the transition region; the peak, which disappears on the successive runs, can be attributed to relaxation effects analogous to that found by Illers,[15] Wolpert,[17] and Petrie[18] in the glass transition region for other polymers, and it is related to the thermal history of the samples.

The influence of annealing for different times at a fixed temperature lower than T_g' (where T_g' is the transition temperature) is shown in Figure 2 for the copolymer 7 (CBT 87.5 mol %) annealed at 22 ± 2°C. Before annealing, the sample was heated up to 90°C and cooled at the same rate (32°C/min), to cancel previous thermal effects. From the thermograms it can be seen that both the peak area and the transition temperature increase with increasing the annealing time, as found by others for amorphous commercial polymers in the glass transition region.[17–19] The apparent enthalpy increment, associated to the transition, was calculated from the peak area, by assuming as base line the extrapolation of the DSC line obtained at temperatures above the peak.[18] Both ΔH and T_g' values for copolymer 7, plotted in Figure 3, increase, at first rapidly, and then slowly, on increasing the annealing time.

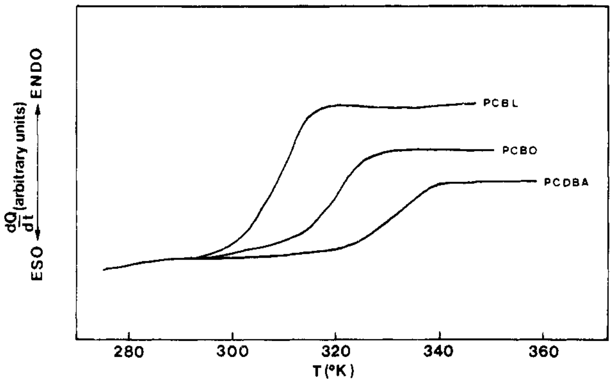

Figure 1. DSC scans of poly(α-amino acids) in the transition region. Traces refer to the same weight of samples and are displaced vertically to a unique base line.

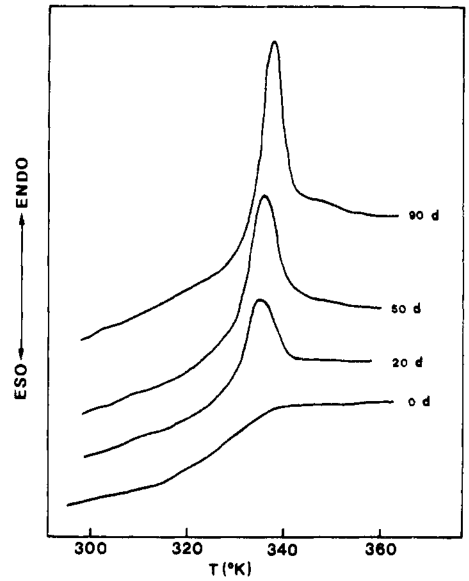

Figure 2. DSC scans of copolymer 7 annealed at 22°C for different times (days).

Table I
Transition Temperatures T_g' and Specific Heat Changes Δc_p of Poly(α-amino Acids) [-(NH-CHR-CO)$_n$-]

Sample	R	CBT, mol%	T_g', °C	Δc_p, cal/(g °C)
PCBL	$(CH_2)_4$-NHCOOCH$_2$C$_6$H$_5$		33	0.11
PCBO	$(CH_2)_3$-NHCOOCH$_2$C$_6$H$_5$		47	0.069
PCDBA	$(CH_2)_2$-NHCOOCH$_2$C$_6$H$_5$		57	0.053
PCBT	$(CH_2)C_6H_4$-OCOOCH$_2$C$_6$H$_5$		60	0.030
Copolymer 1[a]		12.5	33	0.089
2		25.0	35	0.087
3		37.5	37	0.083
4		50.0	38	0.083
5		62.5	41	0.071
6		75.0	45	0.069
7		87.5	51	0.062

[a] Copolymers of *O*-carbobenzoxy-L-tyrosine and *N*-carbobenzoxy-L-lysine. The amount of the first component in the peptide chain is indicated in the third column.

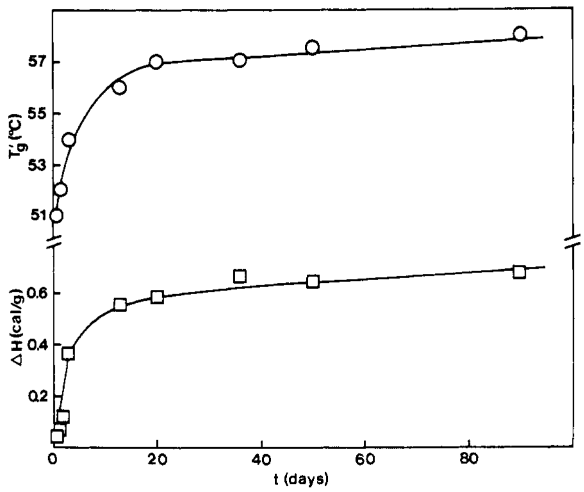

Figure 3. Transition temperature T_g' and relaxation enthalpy ΔH as a function of annealing (at 22°C) time for the copolymer 7.

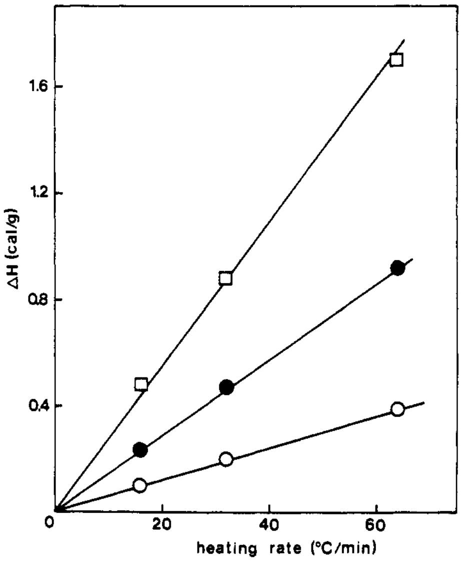

Figure 4. Influence of heating rate on the apparent ΔH of the transition of: CDBA annealed at 40°C for 15 hr (○); copolymer 7 annealed at room temperature for 500 days (□) and at 32°C for 70 hr (●).

The assignment of the endotherm to a first-order transition has to be ruled out also on the basis of the results obtained when investigating the phenomenon at different scanning rates. In fact, the apparent transition enthalpy ΔH, of samples annealed at the same temperature T (less than T_g') and for the same time, goes to zero when the rate is extrapolated to zero, as shown in Figure 4 for PCDBA and copolymer 7. Similar rate-dependent effects cannot be found in true phase transitions and are typical of relaxation processes taking place at the glass transition of amorphous or semicrystalline polymers.

In Table I the transition temperatures T_g' and the changes in specific heat Δc_p relative to the observed "glass-like" transition are collected for all the examined samples. The changes in specific heat were obtained by averaging the experimental values of several runs, and, within experimental errors, they are independent of scanning rate and relaxation effects. Furthermore, the Δc_p increment is perfectly reproducible, within experimental errors, after one or more heating cycles, up to 130°C.

From the table it is seen that, as far as the homologous series PCBL, PCBO, and PCDBA is concerned, the transi-

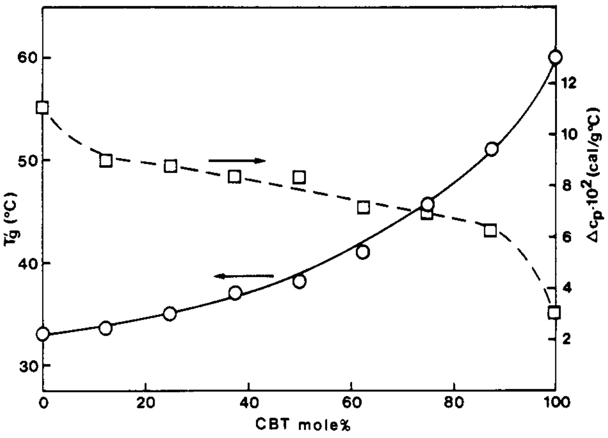

Figure 5. Dependence of T_g' (○) and Δc_p (□) on copolymer composition. Solid line refers to the Gordon–Taylor equation.

tion temperature increases and the Δc_p values decrease regularly with decreasing the number of methylene units in the side chain, i.e., with the side groups accounting for a smaller volume fraction of the polymer.

For the CBT–CBL copolymer series, the T_g' values increase at first slowly, with increasing CBT content up to 60%, and then rapidly, while the corresponding Δc_p values decrease almost linearly, as shown in Figure 5. The T_g' data could be tentatively fitted with the well-known Gordon–Taylor equation[20]

$$T_g = \frac{w_1 T_{g1} + w_2 T_{g2} \beta}{w_1 + w_2 \beta}$$

where w_1 and w_2 are the weight fractions of 1 and 2 monomers, T_{g1} and T_{g2} are the glass transition temperatures of the corresponding homopolymers, and β is the ratio of the thermal expansion coefficient differences $\Delta\alpha_1$ and $\Delta\alpha_2$ of the two homopolymers at their transition temperature, i.e., $\beta = \Delta\alpha_1/\Delta\alpha_2$. In this case, the calculation of the Gordon–Taylor curve (solid line in Figure 5) has been carried out by using the ratio of the specific heat increments $\Delta c_{p1}/\Delta c_{p2}$, instead of the unknown β value.

In order to interpret the nature of the transition, we have to consider the most peculiar features, i.e., the relatively high value of Δc_p and the relaxation effects developed by annealing, together with the dynamic mechanical and dielectric results obtained by other authors on similar poly(α-amino acids). It is well known that specific heat changes Δc_p of the order of 0.1 cal/(g °C) are characteristic of the glass transition of amorphous or slightly crystalline polymers. Furthermore, the appearance of endothermal peaks in the DSC trace of polymers which undergo peculiar thermal treatments is generally attributed to a relaxation process taking place in the glass transition region and is interpreted on the basis of the Hirai and Eyring hole theory for glasses.[21]

It is generally accepted that the glass-to-rubber transition of polymeric systems involves cooperative long-range motions of the main chain. For poly(α-amino acids), there seems to be little doubt that the "true" glass transition, i.e., that related to the main chain motion of their amorphous portion, should be found in proximity of 200°C, or at even higher temperatures. In fact, for the only two amorphous proteins for which data are available up to date, i.e., elastin and gelatin, the glass transition temperature is found at about 200°C, in the absence of diluent.[22] Investigation of our samples in this temperature range, on the other hand, was not possible due to thermal degradation.

Taking also into account that the transitions near room temperature, revealed by dynamic mechanical, dielectric, and NMR measurements, have been constantly attributed in literature to side-chain motions,[1-11] we may safely conclude that also in our case the observed transition must involve side-chain rather than main-chain motions, and that yet it exhibits all characteristics of a glass-to-rubber transition.

Interesting results have been obtained on applying the Wunderlich's rule[23] to the Δc_p data of Table I. According to Wunderlich, the glass transition of an amorphous polymer or of low molecular weight glasses is characterized by a constant heat capacity increment of about 2.7 ± 0.5 cal °K^{-1}, contributed by every mole of "beads" of the main chain. From the Δc_p data of Table I one obtains a number of "beads" ranging from 5 to 11, instead of 2 or 3, as one would expect for the polymer repeating unit (–NH–CHR–CO–). Surprisingly enough, these bead numbers are close to the number of chain atoms and rigid chain groups which constitute the relatively long side chains of the investigated poly(α-amino acids). On this basis and in the limits of validity of the Wunderlich rule, one arrives at the conclusion that the glass-like transition phenomenon takes place in the side chains, which behave as relaxing units independent of the main chain.

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