Thermomechanical Behavior of a Systematic Series of Poly(L-alpha-alkylamino Acids) in Dry and Moist Nitrogen

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Synopsis

The solid-state thermomechanical behavior of polyglycine, poly-L-alanine, poly-L-valine, and poly-L-leucine was investigated throughout the temperature range $-180°$ to 500°C in dry and moist nitrogen atmospheres at about 1 cps using torsional braid analysis. Transitions of the dry polymers and complexities introduced by the presence of water were investigated by temperature cycling.

INTRODUCTION

This preliminary communication reports the thermomechanical behavior of a systematic series of polypeptides in dry and moist nitrogen atmospheres using a torsional pendulum. The number of carbon atoms in the α-substituent of the polypeptides is varied from 0 to 4 (excluding 2) in the series polyglycine, poly-L-alanine, poly-L-valine, and poly-L-leucine.

EXPERIMENTAL

Thermomechanical spectra (Figs. 1, 2, and 3) were obtained at about 1 cps using the technique of torsional braid analysis (TBA),[1] and complementary thermogravimetric data (Figs. 1 and 2) were obtained using a du Pont 950 thermogravimetric analyzer. The polymers were obtained from commercial sources (poly-L-glycine: lot no. V1302, cat no. 1288, Mann Research Laboratories, New York, N.Y.; poly-L-alanine: lot no. 69111, cat. no. PAA-001, New England Nuclear Co., Pilot Chemicals Division, Boston, Mass.; poly-L-valine: lot no. W3506, cat. no. 904635, Schwarz/Mann Co., Orangeburg, N.Y.; poly-L-leucine: lot no. S3756, cat. no. 1701, Mann Research Laboratories, New York, N.Y.). Three sets of thermomechanical spectra were obtained in a nitrogen atmosphere. The first set (Fig. 1) displays the thermomechanical behavior for a temperature scan of 170° to $-180°$ to 500°C. The second set (Fig. 2) shows the effect of thermal cycling about a high-temperature damping peak, and the third set (Fig. 3) shows the influence of water vapor in the ambient at-
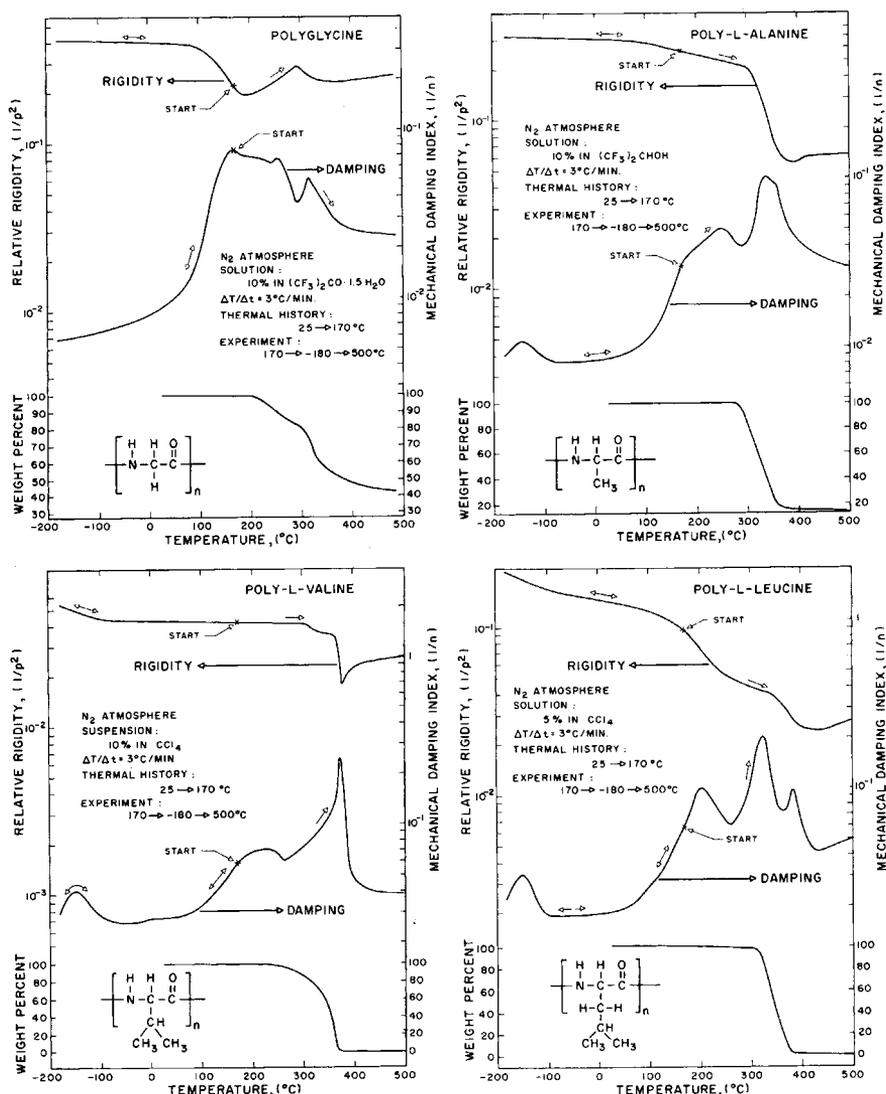
Fig. 1. Thermomechanical behavior of the polypeptides in dried nitrogen.

mosphere (saturated at room temperature) on the thermomechanical behavior.

Composite specimens for the thermomechanical experiments were prepared by depositing the polymers on heat-cleaned glass braids from solutions (see Table I). Ten per cent (g/ml) solutions were easily made with polyglycine and poly-L-alanine in hexafluoroacetone sesquihydrate[2] and hexafluoroisopropanol,[3] respectively, at room temperature. Poly-L-valine only swelled in carbon tetrachloride at room temperature, and so an impregnated substrate was made by using a suspension of the
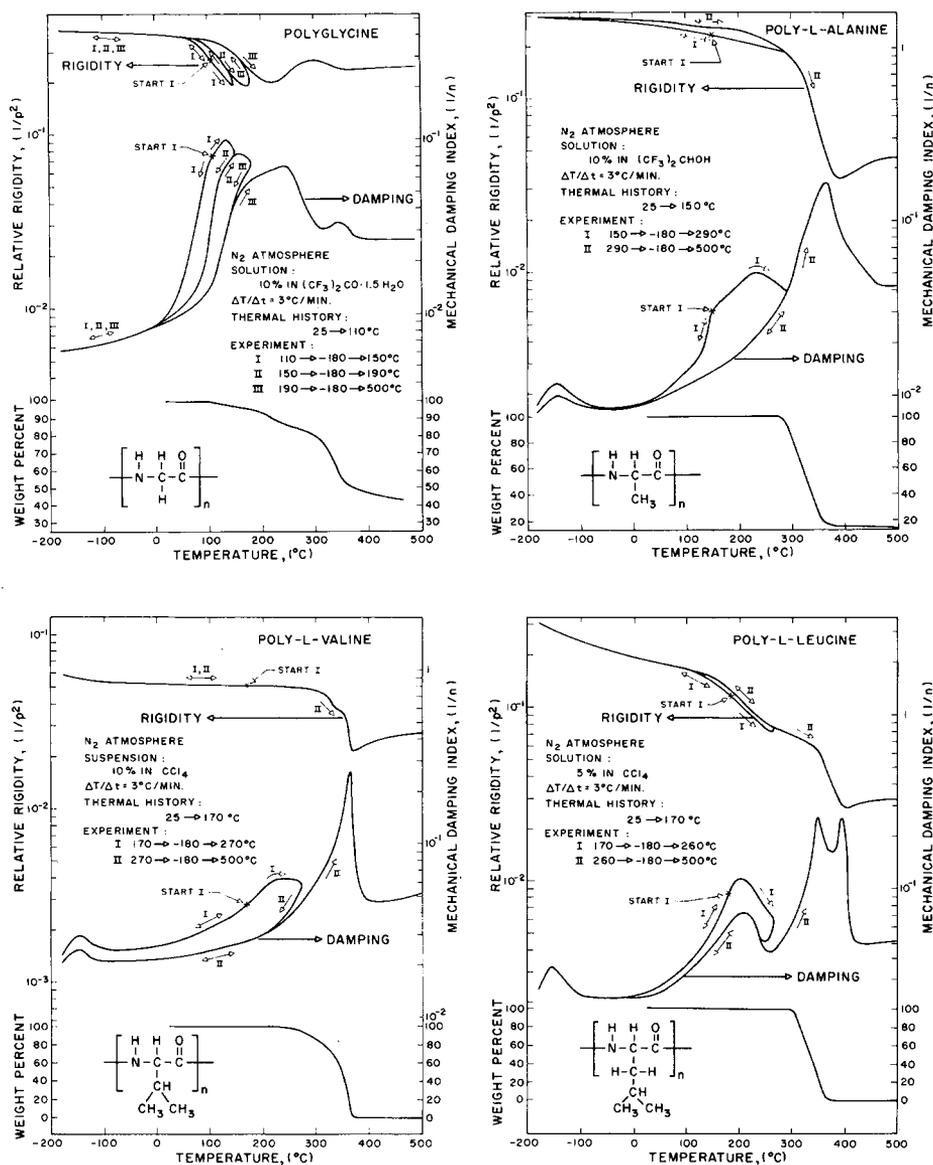
Fig. 2. Effect of temperature cycling on the thermomechanical behavior of the poly-peptides in dried nitrogen.

polymer in carbon tetrachloride.   Poly-L-leucine formed a dilute solution (about 1%) in carbon tetrachloride at room temperature and, at higher concentrations, formed a gel.   Solvent was removed from a poly-L-leucine solution over a period of 3 hr by slow heating until the concentration increased to about 5%.   The braid was impregnated in this warm solution. Thermogravimetric analyses indicated that, with the exception of polygly-

TABLE I
The Polypeptide Series

Polymer	Side group	Molecular weight[a]	Solvent	Boiling point, °C
				dissociates
Polyglycine	—H	11,000	$(CF_3)_2CO \cdot 1.5H_2O$	<100
Poly-L-alanine	—CH_3	40,000	$(CF_3)_2CHOH$	58.2
Poly-L-valine	—$CH(CH_3)_2$	50,000–100,000	CCl_4 (swells)	76.8
Poly-L-leucine	—$CH_2CH(CH_3)_2$	69,000	CCl_4	76.8

[a] Dilute solution viscosity (manufacturer's estimate).
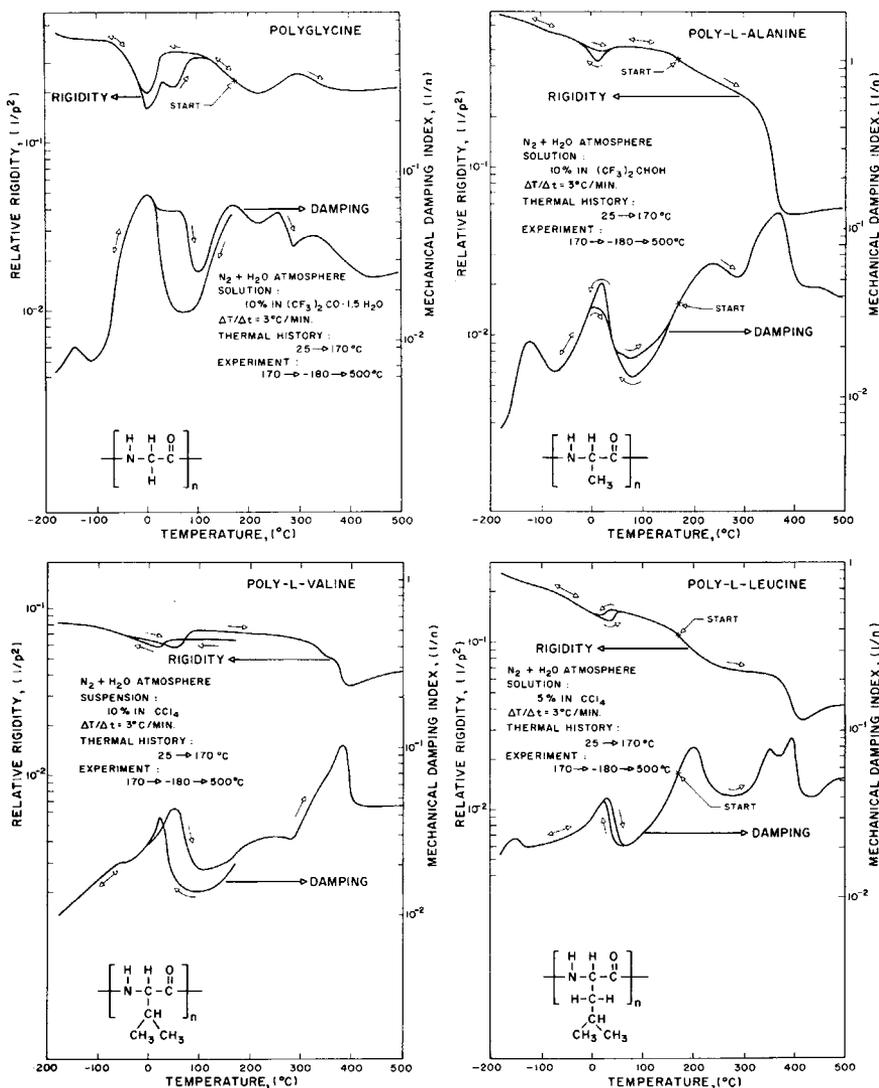
Fig. 3. Effect of water on the thermomechanical behavior of the polypeptides.

cine, removal of solvent from the composite specimens was essentially complete at 110°C at a heating rate of 3°C per minute (the heating rate for all experiments) and that 170°C was a temperature to which the polymers could be heated without degradation.

RESULTS AND DISCUSSION

The thermomechanical spectra of the polymers reveal three damping peaks below the temperature at which acute loss of weight begins, at T_1, T_2, and T_3 ($T_1 > T_2 > T_3$, see Table II), and one or two damping peaks at higher temperatures.

TABLE II
Temperatures (°C) of Damping Peaks (<1 cps)

Polymer	Nitrogen atmosphere			Nitrogen/H₂O atmosphere			
	T_1	T_2	T_3	T_1	T_2[a]		T_3
					cooling	heating	
Polyglycine	100–200	....	....	170	0	5, 55	−140
Poly-L-alanine	240	....	−150	240	10	20	−120
Poly-L-valine	220	....	−150	220	20	50	....
Poly-L-leucine	220	....	−150	200	20	35	−150

[a] Temperature of rigidity minima corresponding to T_2 damping peaks.

The T_3 Damping Peak

In a dried nitrogen atmosphere, the alkyl-substituted polypeptides have low-temperature damping peaks, whereas polyglycine does not (Fig. 1). The temperatures of the T_3 peaks were about the same, whereas their intensities relative to the backgrounds increased with increasing size of the alkyl groups. The peaks were reversible and reproducible upon thermal cycling (Fig. 1) below about 170°C, but upon thermal cycling (Fig. 2) about a high-temperature damping peak T_1 (see later), they diminished in intensity for poly-L-alanine and poly-L-valine and remained unchanged for poly-L-leucine.

The presence of water (Fig. 3) created a T_3 damping peak in polyglycine, intensified and shifted that of poly-L-alanine to a higher temperature, appeared to eliminate that of poly-L-valine, and decreased the intensity of that of poly-L-leucine relative to its background damping level. The effect of the addition of water on the T_3 damping peak of the alkyl-substituted polymers may be masked by overlapping of water-produced T_2 damping peaks (see later). For instance, the T_3 damping peak of poly-L-valine may be the shoulder on the T_2 damping peak (Fig. 3). The appearance of a T_3 damping peak in polyglycine indicates that the mechanism of this relaxation involves water.

The T_2 Damping Peak

The T_2 damping peaks (Fig. 3) of the polypeptides exist only in the presence of water. They are generally coincident with rigidity minima, and since the latter appear to be more distinguishable than the damping maxima, the temperatures in Table II for T_2 are for rigidity minima. The thermomechanical behavior of poly-L-alanine and poly-L-leucine displayed reversible thermohysteresis (closed loops) upon thermal cycling below 170°C, whereas the damping curve of polyglycine and both the rigidity and damping curves of poly-L-valine displayed irreversible thermohysteresis (open loops) (Fig. 3).

The hysteresis effects in thermomechanical behavior upon thermal cycling in a moist nitrogen atmosphere are attributed only in part to different rates of acquisition and loss of water. In addition to water acting as a simple plasticizer by disrupting physical bonds and thereby lowering the transition temperatures, water may be bonded or associated with the "dry" polymer forming an entirely new material with its own properties. Morphological changes are also to be anticipated. Since these events occur to different extents with the different polymers, there must be some positive interaction between these polymers and water (see reference 4 for similar behavior in the vicinity of 0°C with only a trace of water). The nature of the effects of water on the polymers requires further study which should include investigation of the transient minima in rigidity under isothermal conditions in environments of controlled relative humidity.

Plasticization by water is highly evident for polyglycine in the rigidity curve at temperatures as low as −70°C, and also in the damping curve to even lower temperatures, further showing that the mechanism of the T_2 damping peak is not merely the melting of ice or freezing of water on the polymer surface. As might be expected from their greater hydrophobicity, the polypeptides with the alkyl side chains were affected somewhat less by water.

The T_1 Damping Peak

The T_1 damping peaks occurred (Fig. 1 and Table II) at slightly higher temperatures with decreasing size of the alkyl side groups. The magnitude of the decrease in rigidity which accompanied the T_1 damping peak (Fig. 1) with increasing temperature was in the following order: polyglycine > poly-L-leucine > poly-L-alanine > poly-L-valine. The T_1 damping peak was eliminated by the thermal cycling about the T_1 temperature (Fig. 2) for poly-L-alanine and poly-L-valine. In contrast, the intensity of the T_1 damping peak was only diminished for polyglycine and poly-L-leucine by the thermal cycling. The addition of water to the polymers appeared to have little or no effect (Fig. 3) on either the temperature or intensity of the T_1 damping peak. However, the T_1 peak for polyglycine (for a thermal prehistory to 170°C) appeared to be better resolved from a subsequent pyrolysis peak (cf. Figs. 1 and 3) in the presence of water vapor.

The T_1 damping peak could not be located with certainty for the "dry" polyglycine, perhaps because of overlapping with solvent-removal at low temperatures or because of overlapping with degradation at high temperatures. Thus, the range of temperatures (100–200°C) was assigned to the polyglycine T_1 temperature.

The Pyrolysis Damping Peaks

The alkyl-substituted polypeptides undergo one-step weight loss below 500°C, whereas above 170°C polyglycine undergoes a two-step weight loss. One damping peak corresponds to each step of weight loss, except for poly-L-leucine which has one damping peak corresponding to the onset and one damping peak corresponding to the termination of weight loss.

CONCLUSIONS

Torsional braid analysis has been shown to be a convenient method for discovering phenomena in biomaterial-related polymers. A main reason for this is the ability to prepare specimens with ease, since the most difficult step in a mechanical analysis is generally the preparation of mounted specimens. Although composite specimens are used, the results are internally consistent as can be ascertained by superposition of the thermomechanical spectra from the different experiments on the same polymer. The latter procedure shows that, in general, thermal cycling and the presence of water vapor simply result in addition or subtraction of regions of the rigidity and damping curves.

As far as the results on the polymers *per se* are concerned, the dramatic influence of water is noteworthy in explaining a role of water in biomaterials such as proteins. The complexities introduced in the presence of water are pertinent to the material behavior of proteins in permitting inherently rigid materials to be soft and flexible *in vivo*.

The presence of a low temperature damping peak in poly-L-alanine, which presumably is due to the presence of the methyl group, is of interest (5) to mechanical spectroscopy since it is not at all certain that the onset of motion of methyl groups attached to a carbon chain (e.g. as in polypropylene) is dynamic mechanically active, even though it may be dielectrically and NMR active.

The temperatures and intensities of the transitions revealed in this study are highly dependent on the thermal history used to prepare the specimens, the heating rates used in the thermomechanical experiments, and on the level of water in the atmosphere.

References

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