

NOTES

Properties of Poly(L-leucine) Fiber and Film Prepared by an Improved Method

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Membrane of poly(L-leucine), a model peptide for the hydrophobic part of protein, showed prove with respect to properties such as the excellent tensile strength, transparency, and permeability of oxygen or small particles.¹ Among other polyamino acids, this polypeptide is very close to plastics in its properties owing to hydrophobic side chains consisting of alkyl groups. However, it has been reported that the preparation of poly(L-leucine) fiber and film is very difficult because gelation occurs in benzene even at higher temperatures.² The gel formation could be suppressed either by lowering polymer concentration below 1% or by adding a high concentration of dichloroacetic acid (DCA) at a temperature higher than 70°C.

In the present study, trichloroethylene was found to be a much better solvent for poly(L-leucine), and to be able to simplify the procedures for preparing poly(L-leucine) fiber and film. The tensile properties of poly(L-leucine) fiber and film so prepared were compared with those from the benzene-DCA solvent system. Optical rotatory dispersion and viscosity measurements were also carried out.

EXPERIMENTAL

Poly(L-leucine)

L-Leucine *N*-carboxylic anhydride (L-Leu NCA) was prepared following the method of Noguchi *et al.*^{2,3} and allowed to polymerize with 1/200 mol. equivalent of triethylamine in benzene at a concentration of 15% (w/v) and at 40°C for one week.

The number-average molecular weight of the polymer was estimated by *N*-terminal titration² after repeated precipitation by trichloroethylene (TCE) and ethanol.

Spinning Solution

Two grams of poly(L-leucine) were dissolved in 60 ml of TCE at 50—60°C and spun into ethanol at room temperature through a platinum nozzle (0.2 mm ϕ , 30 holes) after the addition of DCA immediately before spinning (final concentration of DCA, 7.7% v/v). The spinning conditions are summarized in Table I.

Preparation of Film

Poly(L-leucine) film was prepared by coagulating

Table I. Spinning conditions of poly(L-leucine) fiber

Spinning solution	Polymer concn	3.1% (w/v)
	DCA concn	7.7% (v/v)
	Solvent	Trichloroethylene
Nozzle	Pt (0.2 mm ϕ , 30 holes)	
Coagulation bath	1st	Ethyl alcohol (50 cm of length)
	2nd	Methyl alcohol (75 cm of length)
Stretching bath	Hot water (50°C)	
Spinning rate	1st roller;	6.3 m min ⁻¹
	2nd roller;	8.6 m min ⁻¹
Spinning temperature	Spinning solution; 50—60°C	
	Coagulation bath; room temp.	

the spinning solution with ethanol after the solution was cast on a glass plate and debubbled at a slightly reduced pressure. The film was dried by pressing it between a pair of filter papers at room temperature after being washed thoroughly with ethanol.

Tensile Strength

The strain-stress curve was obtained by the method reported previously.⁴

Optical Rotatory Dispersion and Viscosity Measurements

A 0.1% solution of polymer in TCE was prepared at 40°C for measurement of optical rotatory dispersion (ORD) and viscosity. The helix content was estimated using Moffitt–Yang's equation,⁵ and the b_0 of 630 was considered to indicate a 100% helix. The reduced viscosity of the polymer solution was determined at 45°C and at various polymer concentrations using a Ubbelohde-type viscometer (flow time of TCE: 61.4 sec).

X-Ray Diffraction Pattern

The fiber pattern of poly(L-leucine) fiber was obtained with Cu- $K\alpha$ radiation through a Ni filter from a Toshiba X-ray generator ADX-401. The spacings were calculated from the fiber pattern using silicon powder as the standard. The fiber pattern suggested that poly(L-leucine) molecules are well oriented in the direction of the fiber axis.

RESULTS AND DISCUSSION

The number-average molecular weight of the poly(L-leucine) sample prepared was estimated to be 9.8×10^4 from the *N*-terminal titration. The polymer was dissolved at 50°C. Since the helix content estimated in TCE was about 25% ($b_0 = 160$, $c = 0.1$) at 40°C, the α -structure of poly(L-leucine) could

hardly be maintained in TCE. However, no destruction of the secondary structure seemed to take place by the addition of DCA, because the value of b_0 changed little with increasing DCA concentration up to 11% (v/v). However, the slope of the reduced viscosity vs. polymer concentration curve decreased with the amount of added DCA, although no significant change occurred in intrinsic viscosity, as shown in Figure 1. For this reason, DCA was added in order to reduce the viscosity of the spinning solution. Since, the poly(L-leucine) fiber was prepared at a stretching ratio of 1.37 in hot water despite the relatively lower polymer concentration, the polymer molecules must have orient-

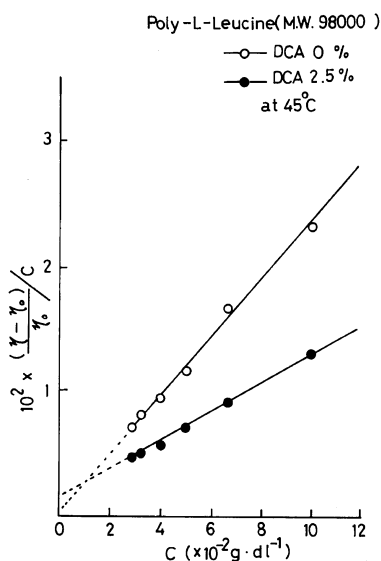


Figure 1. Dependence of reduced viscosity on polymer concentration. A Ubbelohde-type viscometer (flow time for trichloroethylene, 61.4 s) was used. Poly(L-leucine) (M.W. 98000): —○—, DCA 0%; —●— DCA 2.5% at 45°C.

Table II. Tensile properties of poly(L-leucine) fiber

	Denier	Young's modulus	Strength	Elongation
		g d^{-1}	g d^{-1}	%
Dry (20°C, 65%RH)	3.32	42.2	1.37	37.2
Wet (20°C, 100%RH)	4.82	42.4	1.32	18.4
Wet (90°C, 100%RH)	3.68	25.4	1.00	48.0
Knot strength (20°C, 65%RH)	2.49	—	1.32	31.5

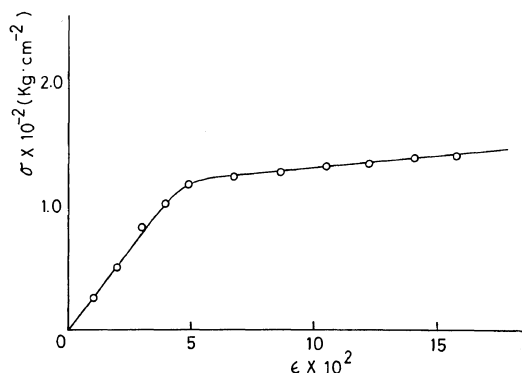


Figure 2. Strain-stress curve of poly(L-leucine) film: sample length, 25 mm; rate, 5 mm min⁻¹; full scale, 5 kg; thickness, 0.2 mm; room temperature. Tensile modulus, 2.7×10^9 dyn cm⁻²; tensile strength, 1.4×10^8 dyn cm⁻²; elongation at break, 0.16.

ed well in the direction of the fiber axis. The X-ray diffraction pattern of the fiber confirmed this expectation. The spacings of the poly(L-leucine) fiber were calculated as follows: 8.9, 4.4, 4.0, and 3.4 Å on the equator (fiber axis) and 4.7, 4.4, 3.2, and 2.7 Å on the meridian. The spacing of 3.4 Å on the equator and that of 4.7 Å on the meridian suggest that the poly(L-leucine) fiber contains much β -structure as found by Noguchi *et al.* for copoly-(γ -methyl-L-glutamate/L-methionine)-*S*-methyl sulfate fiber.⁶

The tensile properties of poly(L-leucine) fiber are listed in Table II. The better tensile strength and elongation in the wet state indicate the advantage of the present procedure, although the dry strength did not change significantly. On the other hand, poly(L-

leucine) film prepared under the present simplified conditions promises physical properties better than those prepared from the benzene-DCA system. The plastic flow as in the case of poly(L-leucine) fiber was first observed for the poly(L-leucine) film at higher strains as shown in Figure 2. The film prepared from the benzene-DCA mixed solvent is reported to be brittle and rigid unless converted to a hydrophilic membrane. The transparent film became turbid on absorption of water, but its tensile strength and flexibility changed little.

Further studies on the preparation of fiber from a solution of higher polymer concentration and the permeability of oxygen or small molecules through poly(L-leucine) membranes are now under investigation.

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