Thermoelasticity of Elastin

THERE is some controversy about the presence in elastin of an ordered structure[1-3]. Mammi et al.[4] now report evidence for the occurrence of some degree of α-helix conformation in the native protein. The conformation was previously[5] observed in soluble elastin; the temperature coefficient of the α-helix had different values in solvents such as water or glycol. We have studied the thermoelastic behaviour of elastin in order to gain information on its conformation[6].

Earlier workers[7,8] have found a large negative value for the energy component of the tensile force measured at constant length, pressure and under equilibrium swelling in water. They attributed this value to stress-induced crystallization.
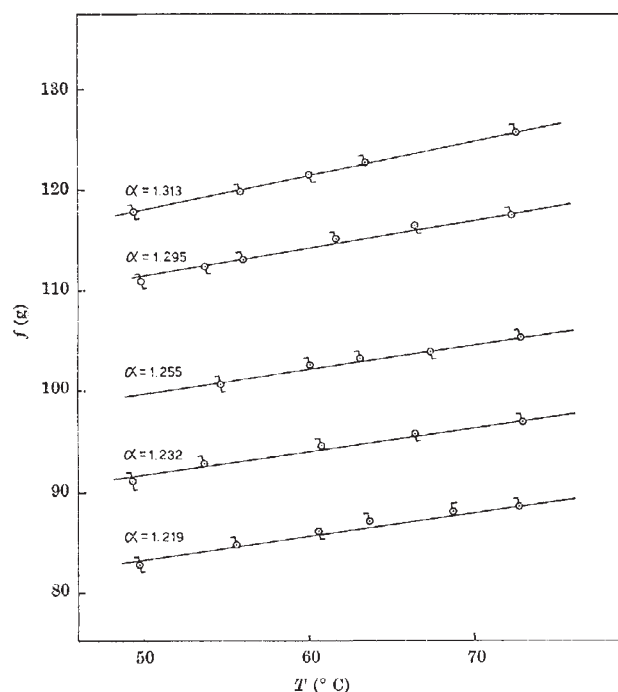

Fig. 1. Variation of the tensile force f with temperature T for a collagen-free elastin sample in equilibrium swelling with water (the cross-sectional area of the dry sample is 0·033 cm²). The elongation ratio (measured at 50° C) is shown by ⟳ decreasing temperature; ⟲ increasing temperature.

Hoeve and Flory[9,10], however, attributed the internal energy changes to a reduction of the degree of swelling of elastin in water with increasing temperature. They tried to get round the effect by performing a thermoelastic analysis in the presence of a water–glycol mixture where the total volume V of the swollen (unstressed) network was independent of temperature; that is, $(\partial V/\partial T)_{p\ eq}=0$ (eq denotes swelling equilibrium throughout the measurements). They concluded that elastin behaved as an ideal rubber: the fundamental elastic mechanism was purely entropic.

Hoeve and Flory were criticized[11] for neglecting possible complications from water–glycol disproportionation during the measurement. This might, in fact, be significant in view of the solvent role of the temperature-coefficient of the α-helix conformation mentioned here[5].

We have investigated the variation of length, width and thickness with temperature for a collagen-free elastin sample immersed in water. The volume of the sample (obtained from frozen ox ligamentum nuchae, cutting the sample in the direction parallel to the fibre axis of the ligamentum and removing the collagen component by

autoclaving for 12 h at 120° C) did not change over the range 50°–74° C. Measurements were fully reversible. The elastin–water system in this temperature range thus seems well suited for a thermoelastic analysis at constant volume. Such a method would avoid the difficulties experienced by early investigators[7,8], who worked in a different temperature interval, and by Hoeve and Flory[9], who used a two-component diluent.

The variation of the tensile force f with temperature for elastin samples immersed in water and stretched at constant length L is shown in Fig. 1. Measurements were made as described elsewhere[6,12], with excellent reproducibility and reversibility. The elongation ratio α reported was referred to the swollen unstretched length measured at 50° C. The stress temperature coefficient actually measured, $(\partial f/\partial T)_{p\ L\ eq}$, can be taken[10,13] as equal to the corresponding constant volume coefficient, $(\partial f/\partial T)_{VL}$, because of the constancy of volume with temperature. The ratio of the energy component $f_e=(\partial E/\partial L)_{VT}$ to the total retractive force f can therefore be written as

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{p\ L\ eq}$$

Table 1 shows our results.

Table 1. THERMOELASTIC DATA FOR AN ELASTIN SAMPLE IN EQUILIBRIUM SWELLING WITH WATER IN THE TEMPERATURE RANGE 50°–74° C

$\overline{T}=62°$ C		$(\partial V/\partial T)_{p\ eq}=0$	
$a_{bo}°$	f,g	$\left(\dfrac{\partial f}{\partial T}\right)_{p\ L\ eq}$	f_e/f
1·219	86·8	0·233	0·10
1·232	95	0·241	0·15
1·254	103	0·255	0·17
1·295	115·2	0·282	0·18
1·313	123	0·319	0·13
			Average = 0·14

There is clearly a non-vanishing energy component, amounting to about 15 per cent of the total retractive force. Because the measurements pertain to constant volume conditions the results characterize the deformation of the molecular chains. Although we are confident that the fundamental elastic mechanism in elastin is not purely entropic, it is not easy to interpret the observed energy component in molecular terms. We suggest that non-isoenergetic minima might occur in the potentials of internal rotation of the polypeptide chain. Moreover, f_e is positive, and so relatively compact conformations seem to be energetically favoured.

D. VOLPIN

Institute of Histology,
University of Padua,
Padua, Italy.

A. CIFERRI

Research Laboratory for
Polymer Technology and Rheology,
National Research Council,
Arco Felice (Naples),
Italy.

[1] Gotte, L., and Serafini-Fracassini, A., J. Atheroscler. Res., 3, 247 (1963).
[2] Gotte, L., Mammi, M., and Pezzin, G., in Symposium on Fibrous Proteins (edit. by Crowther, W. G.), 236 (Butterworths, Australia, 1968).
[3] Cox, R. C., and Little, K., Proc. Roy. Soc., B, 155, 232 (1961).
[4] Mammi, M., Gotte, L., and Pezzin, G., Nature, 225, 380 (1970) (see preceding article).
[5] Mammi, M., Gotte, L., and Pezzin, G., Nature, 220, 371 (1968); see also Chemistry and Molecular Biology of Intercellular Matrix (edit. by Balasz, E. A.) (in the press).
[6] Ciferri, A., Trans. Farad. Soc., 57, 846 (1961).
[7] Meyer, K. H., and Ferri, C., Pflüg. Arch. ges. Physiol., 238, 78 (1936).
[8] Wöhlisch, E., Weitnauer, H., Gruning, W., and Rohrbach, R., Kolloid-zeitschrift, 104, 14 (1943).
[9] Hoeve, C. A. J., and Flory, P. J., J. Amer. Chem. Soc., 80, 6523 (1958).
[10] Hoeve, C. A. J., and Flory, P. J., J. Polymer Sci., 60, 155 (1962).
[11] Oplatka, A., Michaeli, J., and Katchalsky, A., J. Polymer Sci., 46, 365 (1960).
[12] Puett, D., Ciferri, A., and Rajagh, L. V., Biopolymers, 3, 461 (1965).
[13] Bashaw, J., and Smith, K. J., J. Polymer Sci., 6, 1041 (1968).