Properties of Syndiotacticity-Rich Poly(vinyl Alcohol) Thin Film in Water. IV. Elastic Behavior of Untreated Thin Film by Repeated Elongation and Contraction in Water

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Synopsis

The activation energy ΔE_a for diffusion of water molecules into untreated thin film of poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate was estimated as 30.3 kcal/mol from the temperature dependence of the initiation time of swelling. The degree of equilibrium swelling increases with the increase in temperature in the range of 10–70°C, passing through the constant range between 30 and 50°C. Under the forced, repeated elongation and contraction for swollen PVA_{VTFA} thin film in water, the perfect elastic behavior is kept up to higher elongation with the increase in temperature and especially up to about three times equilibrium swelling length at 70°C. Young's modulus of swollen PVA_{VTFA} thin film in water was 6.47×10^6 to 1.60×10^6 dyn/cm² at 25–70°C. The molecular weight between junctions M_c increased with the increase in temperature; M_c was nearly equal to about one-sixth of the molecular weight of raw polymer M at 25°C and about one-third of M at 70°C. The interaction parameter between PVA_{VTFA} and water X_1, was 0.493–0.497 at 25–70°C.

INTRODUCTION

In previous papers,[1-3] the authors studied the deformation behavior in water of very thin and untreated, annealed undrawn or drawn annealed films of poly(vinyl alcohol) (PVA_{VTFA}) derived from vinyl trifluoroacetate (VTFA) and showed that the untreated thin PVA_{VTFA} film was insoluble in water and obeyed Hooke's law in water below a certain load at 25°C,[1] and that the drawn thin films annealed at the temperatures below 190°C contracted to the saturation lengths in water at 25°C and with the elevation of temperature contracted up to about 80°C even under a certain load.[3] That is, thin PVA_{VTFA} films are considered to behave as an elastomer in water.

In this paper, the elastic behaviors of untreated thin PVA_{VTFA} film in water are examined by forced, repeated elongation and contraction at constant temperatures in the range 10–70°C.

EXPERIMENTAL

Sample and Films

PVA_{VTFA} sample used in this paper is the same sample used in the previous papers.[1-3] PVA_{VTFA} thin films were made by the same method de-

scribed in the previous papers.[1-3] Thickness of films was about 0.017 mm. The films were cut to a width of 2 mm.

FORCED ELONGATION AND CONTRACTION

The untreated tapelike films were fixed at a constant length of $l_0 = 4$ cm on a hand drawing machine. After an unannealed film set to the drawing machine was immersed in water of fixed temperature for 5 min, the film length after swelling l_s was measured. The swollen film was elongated to an integral number length in centimeters nearest l_s, named l_1 (see Table I), and then immediately the stress was removed until the film relaxed. Next, the relaxed film was again elongated to a length of $l_1 + 1$ cm and then the stress was immediately removed. Such procedures were repeated up to breaking of film. Film length at elongation was increased in turn to $l_1 + 1$ cm, $l_1 + 2$ cm, $l_1 + 3$ cm, and so on.

RESULTS AND DISCUSSION

Equilibrium Swelling

Figure 1 shows the effect of the temperature of water on the initiation time of swelling in water for unannealed thin PVA_{VTFA} films. The initiation time of swelling depends on the temperature of water at temperatures below 30°C and was independent (zero) at temperatures above 40°C.

The kinetic data were analyzed according to the Arrhenius relationship proposed by McCarthy et al.[4] for shrinkage in Nomex-solvent systems. Figure 2 shows the Arrhenius plots, that is, the temperature dependence of the initiation time of swelling for unannealed thin PVA_{VTFA} film in water in the range 0–30°C. The activation energy ΔE_a obtained from Fig. 2 was 30.3 kcal/mol, and it is considered to relate with the diffusion of water molecules into film. ΔE_a for the PVA_{VTFA}-water system was lower than that (40.1 kcal/mol) for the Nomex-dimethylacetamide system, higher than that (26.9 kcal/mol) for the Nomex-dimethyl formamide system, and similar to that (29.7 kcal/mol) for the Nomex-dimethylsulfoxide system.

The equilibrium swelling of unannealed thin PVA_{VTFA} films was accomplished a few minutes after the initiation of swelling. Figure 3 shows the relation between the ratio of film length after equilibirum swelling to film length in air, l_s/l_0, and temperature. The ratio l_s/l_0 increases with increase in temperature up to 30°C, is at a minimum at about 50°C, and then increases again with the increase in temperature. Such a result is consistent with that for changes in the bending or shear moduli of aqueous PVA_{VTFA} gels prepared at low temperature with the elevation in temperature and for the change in the elongation of untreated thin PVA_{VTFA} film in water under load with the elevation in temperature.[1,5,6] The result obtained in this experiment may be considered also to support the production and propagation of microcrystals in film with water in the neighborhood of 50°C. The crystallization of syndiotactic sequences may be promoted by the melting of the intermolecular hydrogen bonds of short range produced at lower temperature and by the coiling of isotactic sequences in amorphous parts with increasing temperature.[7]
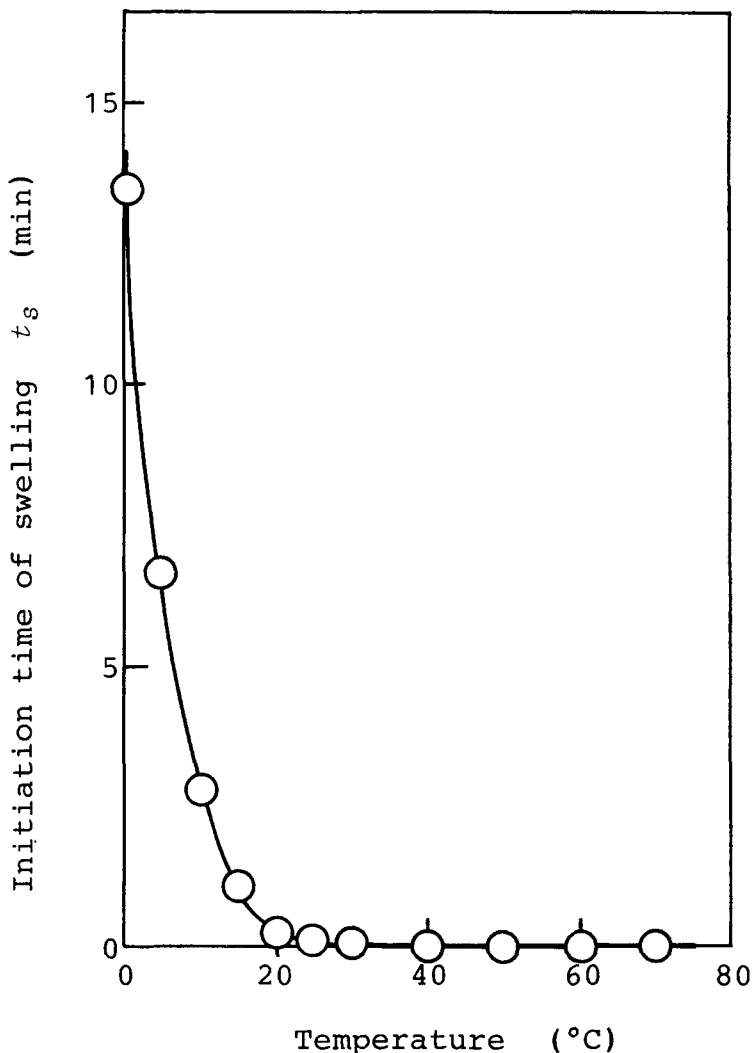
Fig. 1.   Effect of temperature on initiation time of swelling for untreated PVA_{VTFA} thin film in water.

Although untreated PVA_{VTFA} thin film is broken simultaneously with immersion in water at 80°C, it does not dissolve.

REPEATED ELONGATION AND CONTRACTION

Figure 4 shows the change in film length for untreated thin PVA_{VTFA} films in water by forced, repeated elongation and contraction. In order to permit a closer investigation, Fig. 5 is shown as an enlargement of Fig. 4. At 10°C, the length of untreated PVA_{VTFA} film changes from $l_0 = 4$ cm to $l_s = 4.4$ cm by equilibrium swelling in water. The swollen film is elongated up to an integral number length $l_1 = 5$ cm, closest to $l_s = 4.4$ cm, and then at once the stress is removed until the film relaxes (film length $= 4.5$ cm). If in the film plastic deformation occurs perfectly, the film length is 5 cm even after removing the stress. That is, the plots in Figs. 4 and 5 should
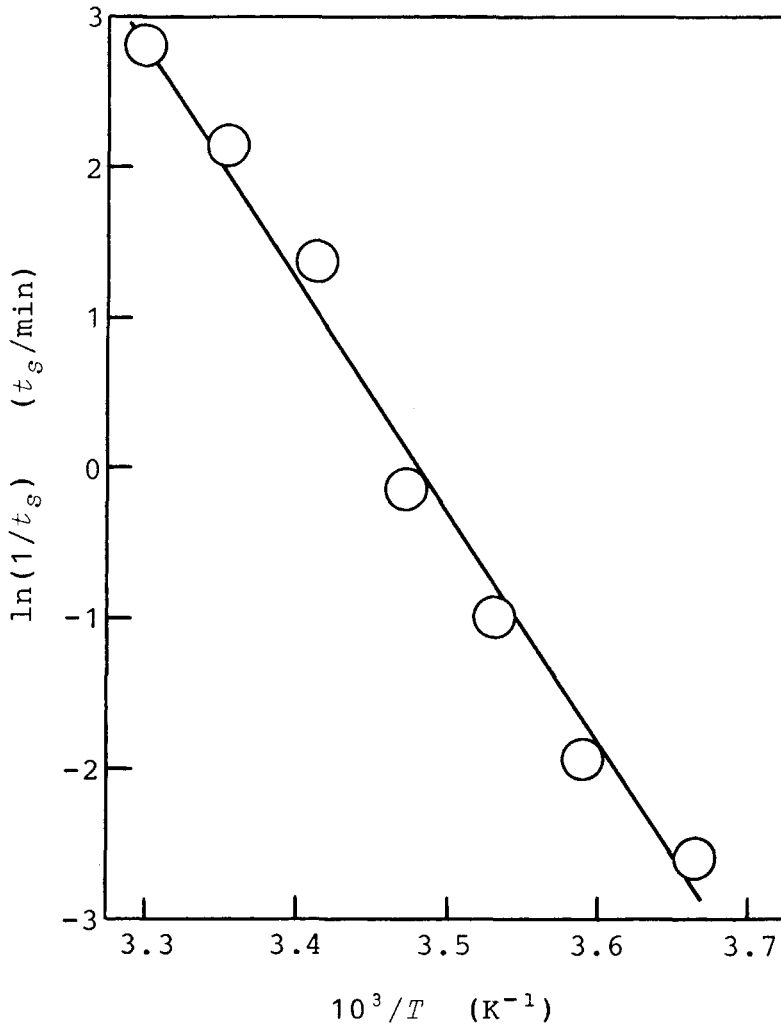
Fig. 2. Arrhenius-type temperature dependence of the swelling initiation time for untreated PVA$_{VTFA}$ thin film in water.

exist on the straight line shown in the figures. Therefore, the straight line is called a perfect plastic deformation line. After relaxation, the film is elongated to 6 cm = l_1 + 1 cm and then the stress is removed (film length = 4.7 cm). With the repeated treatment, the step-wise line approaches the perfect plastic deformation line. Δl_1 and Δl_2 shown in Fig. 4 are the lengths of relaxation and plastic deformation, respectively. Δl_2 increases with the repeated treatment.

In the case of 70°C, the length of untreated PVA$_{VTFA}$ film changes from l_0 = 4 cm to l_s = 6.05 cm by equilibrium swelling. The swollen film is elongated up to an integral number length l_1 = 7 cm, closest to l_s = 6.05 cm, and then the stress is immediately removed until the film relaxes (film length = 6.05 cm). At first relaxation, the film length returned to l_s. The change of Δl_2 with the repeated treatment is very small; that is, the thin
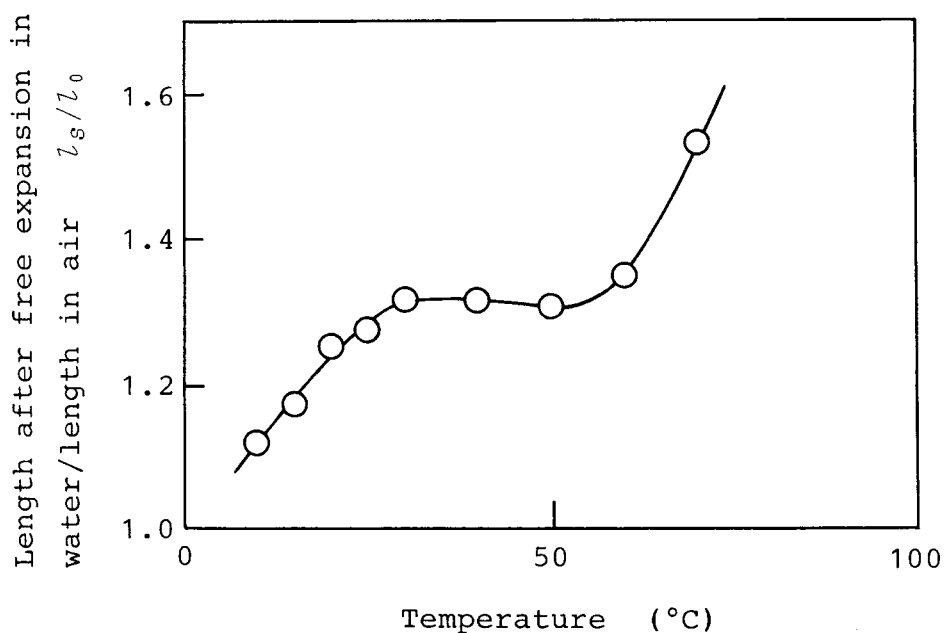
Fig. 3. Temperature dependence of the ratio of film length after free expansion in water to film length in air for untreated PVA_{VTFA} thin film.
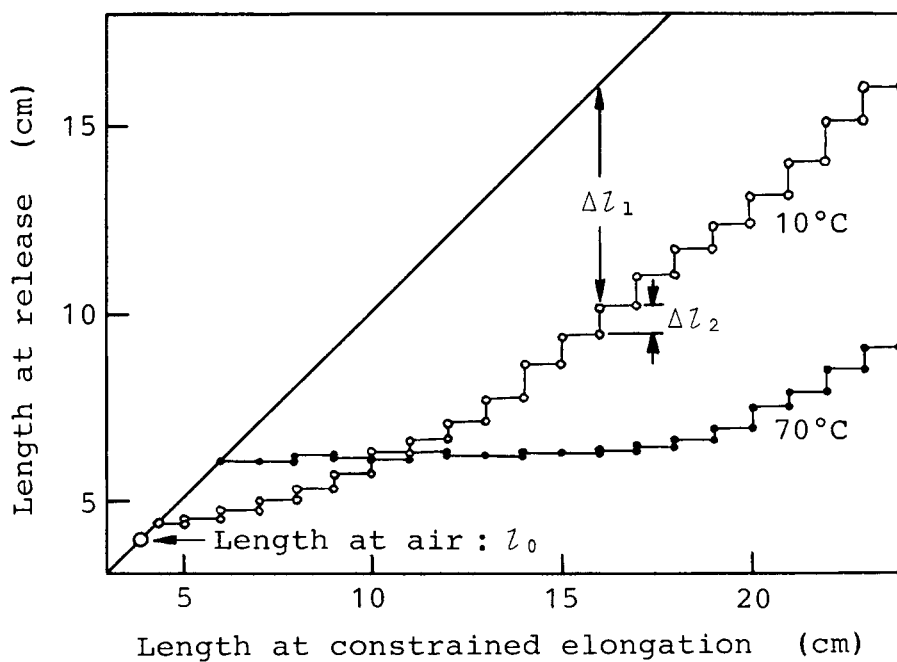
Fig. 4. Relations between the film length at release and the film length at constrained elongation at 10 and 70°C in water for untreated PVA_{VTFA} thin film.
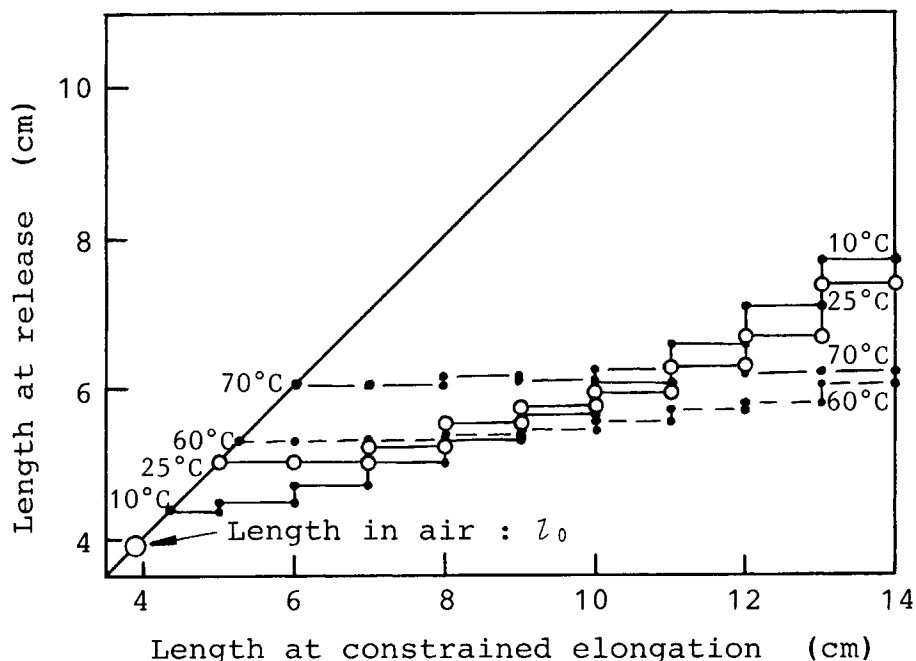
Fig. 5.　Enlargement of Fig. 4.

PVA_{VTFA} film behaves as an elastomer in water at higher temperature even if the film was elongated forcefully up to considerable length.

In the case of treatment at lower temperature, in the swollen films very little plastic deformation occurs even at the initial treatment. We postulate a perfect elastomer for swollen films with lengths of l_s–$1.1l_s$. Table I shows l_s, $1.1l_s$, l_1, and the upper limit length (l_e) of film under load that the plastic deformation does not occur. Figure 6 shows the relation between l_e/l_s and temperature: l_e/l_s increases with the increase in temperature. At temperatures above 40°C, l_e/l_s was above 2 and it was about 3 at 70°C. The increase of l_s, l_e, and l_e/l_s with the increase in temperature is due to the increase of

TABLE I
Changes in l_s, $1.1l_s$, l_1, the Upper Limit Length as a Elastomer Under Load l_e, and l_e/l_s at Various Temperatures

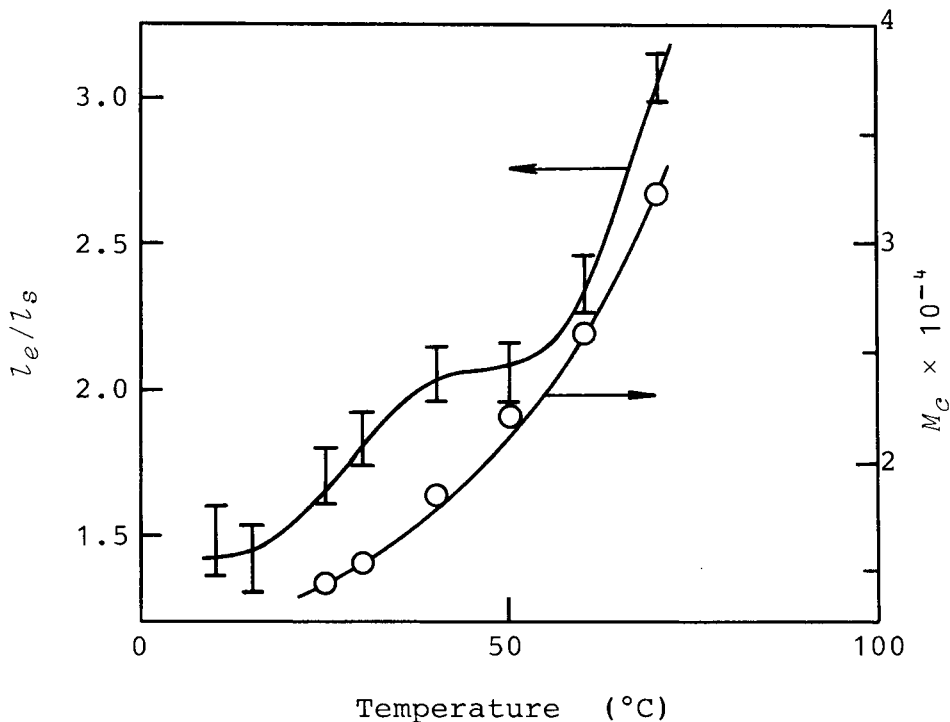| Temperature (°C)	l_s (cm)	l_1 (cm)	$1.1l_s$ (cm)	l_e (cm)	l_e/l_s
10	4.40	5	4.84	6–7	1.36–1.59
15	4.57	5	5.03	6–7	1.31–1.53
20	4.90	5	5.37	—	—
25	5.00	6	5.50	8–9	1.60–1.80
30	5.20	6	5.72	9–10	1.73–1.92
40	5.13	6	5.64	10–11	1.95–2.14
50	5.10	6	5.61	10–11	1.96–2.16
60	5.30	6	5.83	12–13	2.26–2.45
70	6.05	7	6.66	18–19	2.98–3.14

Fig. 6. Temperature dependence of l_e/l_s and M_c.

amorphous parts according to the dissolution of smaller microcrystals, that is, due to the decrease of microcrystals that constitute the networks of the swollen film with water. It is difficult to determine the length of micro-crystals in swollen films. We determined the heat of fusion of a network ΔH for the aqueous PVA_{VTFA} gel.[8] The ΔH was 20–40 kcal/mol, which corresponds to four to eight hydrogen bonds. The heat of fusion of a network in swollen PVA_{VTFA} films is considered larger than that in aqueous PVA_{VTFA} gels or nearly equal.

The swollen PVA_{VTFA} thin films were not broken up to the upper limit length (31.7 cm) obtainable by the drawing machine used in this experiment at temperatures above 30°C in water. At temperatures below 25°C, the length at break was 29.7 cm at 10°C, 27.0 cm at 15°C, 28.8 cm at 20°C, and 24.0 cm at 25°C, and the temperature-dependency of the length at break was not recognized.

YOUNG'S MODULUS

As the swollen PVA_{VTFA} films in water are considered an elastomer at lower draw ratio, the molecular weight between junctions M_c is determined from[9]

$$P_3 = \frac{RT}{v M_c\, v_2^{2/3}} \left(1 - \frac{2M_c}{M} \right) \left(\lambda - \frac{1}{\lambda^2} \right) \tag{1}$$

where P_3 (dyn/cm^2) is the initial stress per cross section, λ the draw ratio, M the molecular weight of raw polymer, v the specific volume of polymer (approximately 0.788 cm^3/g), v_2 the volume fraction of polymer in swollen film (see Table III, $v_2 = 1/q_m$), R the gass constant, and T the absolute temperature. As the strain e equals $\lambda - 1$, eq. (1) is translated to

$$P_3 = \frac{RT}{vM_c\, v_2^{2/3}}\left(1 - \frac{2M_c}{M}\right)\left[1 + e - \frac{1}{(1+e)^2}\right]. \qquad (2)$$

Therefore, when Hooke's law is established, Young's modulus ϵ is shown by

$$\epsilon = \frac{P_3}{e} = \frac{3RT}{vM_c\, v_2^{2/3}}\left(1 - \frac{2M_c}{M}\right) \qquad (3)$$

Therefore,

$$M_c = \frac{1}{\epsilon v v_2^{2/3}/3RT + 2/M} \qquad (4)$$

In the previous paper, we recognized that the film fits Hooke's law in the region of low load.[1] In this paper, we have determined Young's modulus from the relations of load-draw ratio at various temperatures by using the results of the previous paper.[1] Although the relations of load-draw ratio were obtained at elevated temperatures, we neglected the change of structure in films at these temperatures. We are considering relationship of stress to strain at various constant temperatures to determine the exact Young's modulus of swollen PVA$_{\text{VTFA}}$ thin films. The cross section of swollen films was determined using values of l_s/l_0 obtained in this experiment by postulating an isotropic swelling. l_{p_1} is the film length in water under load of P_1 and $\lambda = l_{p_1}/l_s$ is the draw ratio for the swollen PVA$_{\text{VTFA}}$ thin film. The swollen PVA$_{\text{VTFA}}$ film in water was the elastomer with a very low Young's modulus, which was about one-fifth of normal elastomer at 70°C. Table II shows the stress, the strain and M_c at various temperatures. M_c increases with the increase in temperature. Moreover, it was one-third of the molecular weight of raw polymer (81,400) at 70°C. At 70°C, if the plastic deformation was forced in addition to the elastic, the elongation must reach about five times l_s. l_s/l_0 has a minimum at 50°C, but M_c does not. These results give conclusions that microcrystals are not produced and propagated and that the isotactic sequence parts are coiled at 50°C in the state of free swelling.

SOLVENT-POLYMER INTERACTION PARAMETER

The solvent-polymer interaction parameter X_1 for swollen sample is obtained from the equation[9]

$$P_3 = \frac{RT}{v_1 q_m^{5/3}}\left(\lambda - \frac{1}{\lambda^2}\right)\left(\frac{1}{2} - X_1\right) \qquad (5)$$

TABLE II
Strain, Stress, and M_c in the Perfect Elastic Region at Various Temperatures for Swollen PVA$_{VTFA}$ Film in Water

Temperature (°C)	Strain			Stress			Young's modulus $\epsilon = P_3/e$ (dyn/cm², $\times 10^6$)	M_c
	l_s/l_0	Draw ratio $\lambda = l_{pl}/l_s$	$e = \lambda - 1$	P_1 (g)	P_2 (kg/cm²)	P_3 (dyn/cm², $\times 10^6$)		
25	1.25_0	1.30	0.30	1.05	1.98	1.94	6.47	14,590
30	1.30_0	1.30	0.30	1.15	2.00	1.96	6.53	15,400
40	1.28_3	1.30	0.30	0.81	1.45	1.42	4.73	18,640
50	1.27_5	1.30	0.30	0.57	1.03	1.01	3.37	22,280
60	1.32_5	1.30	0.30	0.47	0.790	0.774	2.58	25,940
70	1.51_3	1.30	0.30	0.38	0.480	0.480	1.60	32,240

TABLE III
Stress, Strain, and X_1 at Various Temperatures for Swollen PVA_{VTFA} in Water

Temperature (°C)	P_3 (dyn/cm², × 10^6)	$\lambda - \dfrac{1}{\lambda^2}$	$q_m = V/V_0$	X_1
25	1.94	0.708	1.953	0.493_9
30	1.96	0.708	2.197	0.492_6
40	1.42	0.708	2.109	0.495_2
50	1.01	0.708	2.073	0.496_8
60	0.774	0.708	2.326	0.497_0
70	0.480	0.708	3.460	0.496_1

where v_1 is the molar volume of solvent ($v_1 \fallingdotseq 18$ cm³/mol) and q_m is the volume ratio of swollen sample to solid sample V/V_0. V was also determined by postulating an isotropic swelling. Table III shows the stress P_3, the strain $\lambda - 1/\lambda^2$; and X_1. X_1 was 0.493–0.497 in the temperature range 25–70°C, and it has a minimum value at 30°C.

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