Studies on the Cold-drawing of Polymers (Part II).[1] *The Quasi-Static Drawing of Polycapramide. II. The Effects of Humidity, the Heterogeneity of Polymer's Fine Structure investigated through the Moisture Adsorption and the Behavior of Deformation, and Lowering of the Second-order Transition Temperature by Adsorbed Water**

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Introduction

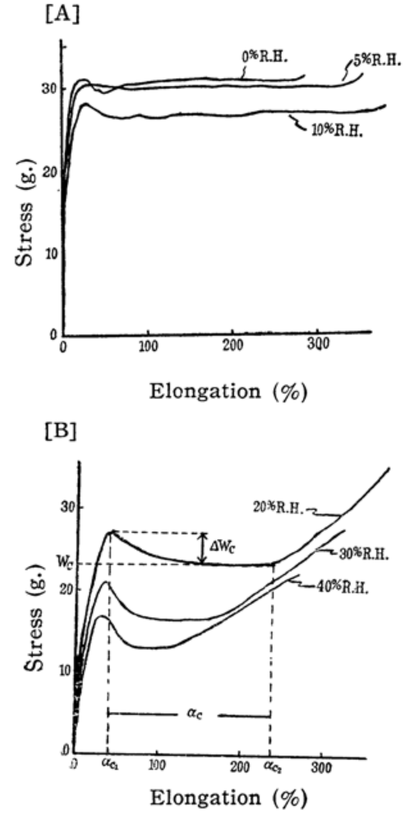
The effects of temperature of the quasi-static drawing of polycapramide in the completely dried state were described in the previous paper[1]. In succession, the effect of humidity on the occasion of drawing at constant temperature of 20°C and the effects of temperature on the occasions of drawing at constant humidities of 10% and 65% or of drawing in water were investigated. In this paper the experimental information and its discussions are treated.

The procedures, with which the quasi-static isothermal elongation-stress curves were estimated, are identical with those in Part I[1]. The apparatus shown in Fig. 1 (A) and (C) of Part I were used[a]. The test materials were common with Part I; i. e. the unstretched polycapramide monofilament of 60. 0 denier (ϕ 0. 086 mm.), spun from the melt through chilling with air, were used.

In course of drawing, one or two neckings occur under coexisting of stretched and unstretched phases excepting the case of drawing in water. During the procession of necking, the stress was kept almost constant (*Wc*); but the additional stress (ΔWc) was demanded besides *Wc* for the formation of the necking. *Wc* is temporarily assumed to be the yield stress. The elongations, where the necking appears and disappears, are denoted with α_{c1} and α_{c2} respectively and $(\alpha_{c2}-\alpha_{c1})$ is denoted with α_c. These notations (Wc, ΔWc, α_{c1}, α_{c2}, and α_c) are illustrated, for example, at 20% relative humidity in Fig. 1 [B].

The Results of Measurements

The elongation-stress curves obtained in various humidities at 20°C are given in Fig. 1 [A]-[D]. When the relative humidity was less than 10%, stretching was not smooth and sometimes rupture happened midway of stretching, and moreover the randomness among all measurements was large; but when the relative humidity was more than 20%, the behavior was reversed. In case the stretch was not smooth the curve obtained is zigzag partially, which is smoothed in Fig. 1. In case of drawing in water, no necking was observed and the specimen seemed to be elongated homogeneously in the whole course of drawing to rupture. The values of *Wc* and α_{c2} are larger in lower humidities. All of the curves at various humidities have each an inclination to converge



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* Presented at the symposium on polymer science of the Chemical Society of Japan in Nagoya, November 11, 1954.

[1] Contributed to This Bulletin.

[a] The test material had been stored for 24-48 hr. in the humidity at which measurement was intended. Measuring was started 2-3 hr. later, than the setting of the specimen to the cramp in the measuring vessel. Especially, in case of 0% humidity, the specimen was previously dried out with phosphorous pentoxide for seven days and furthermore dried for twelve hours in the measuring vessel after setting to the cramp.

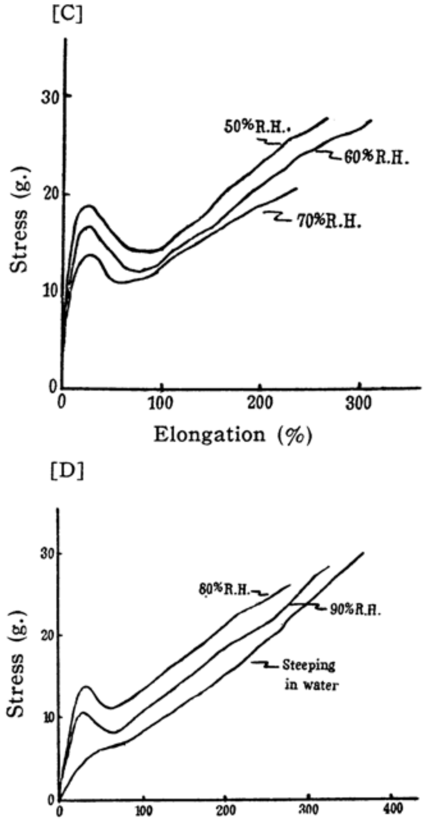

Fig. 1. The elongation-stress curves of polycapramide at various relative humidities and constant temperature of 20°C.

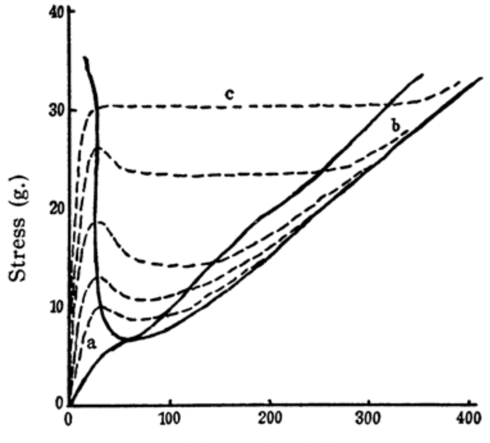

Fig. 2. Three domains schematically divided in the elongation-stress phase space at 20°C (a: Only unstretched phase existing, b: Only stretched phace existing, c: Unstretched and strectched phases coexisting).

to the curve of the sample drawn in water as schematically shown in Fig. 2. In Fig. 2 the phase space can be distinctly divided in three domains; in the first domain only the unstretched phase exists, in the second domain the unstretched and the stretched phases coexist, and in the third domain only the stretched phase exists. It is noteworthy in appearance but it is not considered to have profound physical meaning.

The additional stress (ΔWc) has a maximum at about 30% relative humidity.

The values of the stress and elongation in relation to rupture were random, so the humidity effects on them could not be studied. The values of them are always in the range of 20–25 g. stress and 200–400% elongation.

The elongation-stress curves of the samples drawn at various temperatures and a constant relative humidity of 10% or 65%, are given in Fig. 3 and Fig. 4. The curves of the samples drawn in water at various temperatures, are given in Fig. 5. In case of 10% relative humidity, smooth stretchings were possible above 40°C but not below 30°C. In other cases stretchings were always smooth.

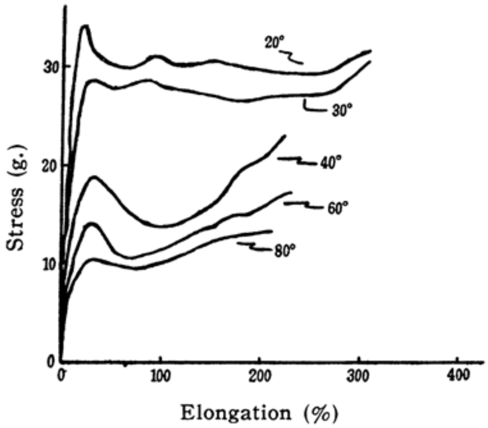

Fig. 3. The elongation-stress curves of polycapramide at various temperatures and constant relative humidity of 10%.

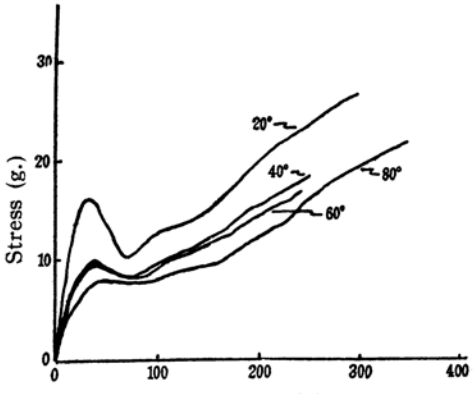

Fig. 4. The elongation-stress curves of polycapramide at various temperatures and constant relative humidity of 65%.

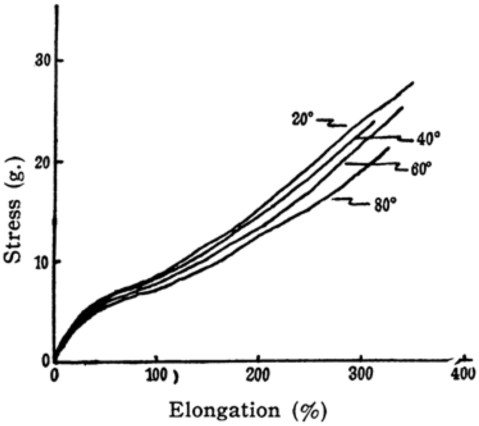

Fig. 5. The elongation-stress curves of polycapramide at steeping in water of various temperatures.

Discussion

The values of Wc and ΔWc at 20° are plotted against the relative humidities (R. H.) and against the values of weight percent of moisture adsorbed (w) in equilibrium with each of the relative humidities in Fig. 6 and Fig. 7. The values of α_{c1} and α_{c2} are similarly plotted in Fig. 8 and Fig. 9. In these figures the length of lines at the positions plotted indicates the measure of randomness. The values of w are quoted from the date[2] about the isothermal moisture adsorption of unstretched polycapramide filaments which are not heat-treated.

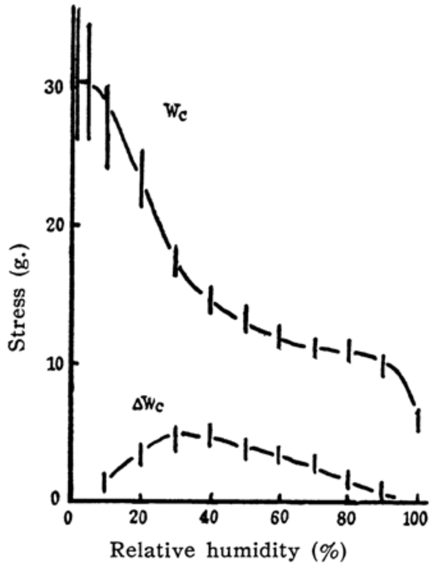

Fig. 6. The yield stresses (W_c) and the additional stresses (ΔW_c) at various relative humidities.

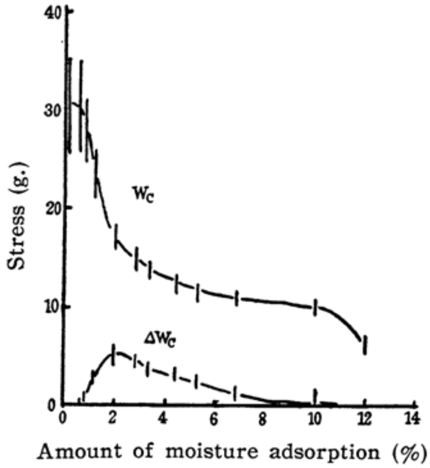

Fig. 7. The yield stresses (W_c) and the additional stresses (ΔW_c) at various amounts of moisture adsorption.

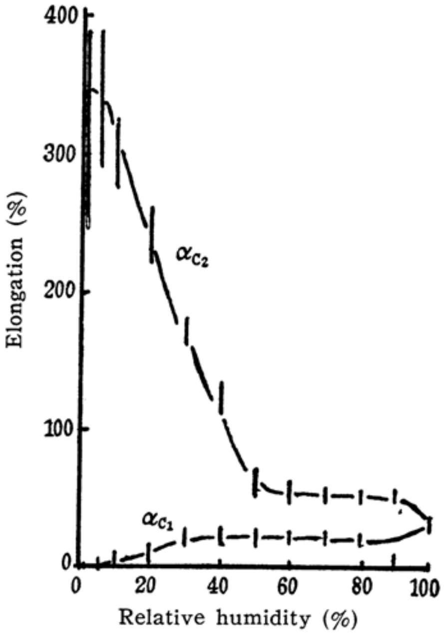

Fig. 8. The two phases coexisting regions of elongation ($\alpha_{c2}-\alpha_{c1}$) at various relative humidities.

In Fig. 6 or Fig. 7, a singular point is explicitly recognized at 10–30% R. H. or 1.0–2.0% moisture adsorption. The boundary between the smooth and the non-smooth stretching or the maximum of the additional stress lies roughly on the environs of the above limits. But in Fig. 8 or Fig. 9, the singularity is recognized at about 50% R. H. or 3.5% moisture adsorption.

Fig. 10 represents the empirical relation between the amount of water adsorbed and the isosteric differential heat of adsorption

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[2] K. Hoshino and H. Yumoto, *J. Chem. Soc. Japan*, **70**, 104 (1949) (in Japanese).

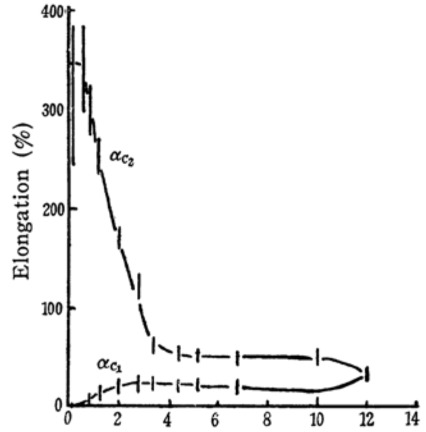
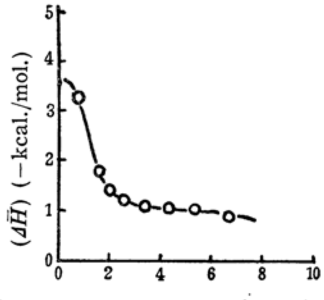


Fig. 9. The two phases coexisting regions of elongation (α_{c2}–α_{c1}) at various amounts of moisture adsorption.

from liquid water ($\Delta\bar{H}$)²⁾. The shape of the curve in Fig. 10 is similar to that in Fig. 6. If the values of *Wc* are plotted against $\Delta\bar{H}$ on trial, the nearly linear relation is obtained as shown in Fig. 11. Making use of this empirical relation, $\Delta\bar{H}$ of the initial adsorption, which is difficult to be determined from the data of isothermal adsorption, is easily evaluated by extrapolation and found to be −(3.5–4.0)kcal./mol. Besides, it is verified from this linear relation that each of the singular points found in both of the curves of Fig. 6 and Fig. 10 lies on the same value of *w*. Therefore the remarkable change of the mechanical property of polycapramide at 1–2% moisture adsorption is suggested to be concerned with some change in the situations of water molecules adsorbed.

On the other hand another singularity found at 50% R. H. or 3.5% moisture adsorption as seen in Fig. 8 or Fig. 9 does not appear at all in Fig. 10. But beyond this humidity the amount of adsorption increases sharply and moreover begins to deviate from the values estimated semiempirically with the general equation of Brunauer, Emmett, and Teller²⁾.



Amount of moisture adsorption (%)

Fig. 10. The isosteric differential heats of moisture adsorption to polycapramide ($\Delta\bar{H}$) at various amounts of moisture adsorption (Hoshino and Yumoto).

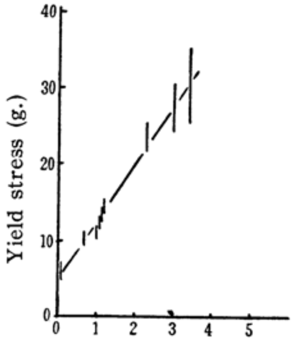


Fig. 11. The relation between the isosteric differential heats of moisture adsorption (ΔH) and the yield stresses (W_c).

In addition to the experiment in which fine filaments (φ 0.086 mm.) are used as the sample, the elongation-stress curves of unstretched polycapramide monofilament (φ 1.67 mm.) which was manufactured by quenching the extruded melt with water, were recorded by means of the Schopper-style tensile tester; the rate of elongation was about 5.6% per second. The test materials had been stored in the vessels, where the relative humidity was kept constant in the range from 0% to 95%, for more than three weeks in order that they can be brought sufficiently into equilibrium of moisture adsorption. Measurements were performed in atmosphere of 65% R. H. as soon as the specimens were taken out from the vessel. The result of these measurements also shows that the singularity in regard to α_{c2} appears at 50–60% R. H. And also the necking is not observed in the whole course of drawing when the specimen has been steeped in water for twenty-two hours. It was observed that, throughout the coexistent state of unstretched and stretched phases, elongation in either of the two phases scarcely ever occurred and the stretch of the entire specimen was almost entirely attributed to the elongation through transformation from unstretched into stretched phase.

Then approximate sectional areas of each phase during the coexistent state can be tentatively calculated from the values of α_{c1} an α_{c2}[b]. The ratio (r) of the sectional

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[b] If the initial sectional area of specimen is A, the sectional area of unstretched phase is $A/(1+\alpha_{c_1}/100)$, and that of stretched phase is $A/(1+\alpha_{c_2}/100)$. The ratio (r) is $(1+\alpha_{c_2}/100)/(1+\alpha_{c_1}/100)$.

area of the stretched phase to that of the unstretched phase is larger, the lower the humidity. These ratios are plotted against the amounts of moisture adsorbed in Fig. 12, where the singularity can be found only at ca. 3.5% adsorption.

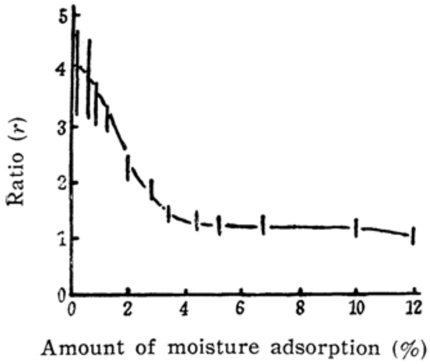

Fig. 12. The ratios of sectional area of stretched phase to that of unstretched phase at various amounts of moisture adsorption.

M. Tsuboi investigated the molecular state of water adsorbed in polycapramide by means of the infrared absorption bands[3]. The infrared spectrum was measured, the specimen being exposed to air of 76% R. H. at 11°C; therefore its moisture adsorption must be ca. 6%. His result shows that O-H band of adsorbed water is observed at 2.86 μ only. According to his consideration none of the adsorbed water molecules has any free OH groups and both of two OH groups are perturbed through O-H……O bonding by the two peptide oxygen atoms (located near to each other). This fact may indicate that all of the adsorbed water molecules are directly linked to polycapramide molecules and then they are situated *in the adsorption of the first layer.* If this proves to be the case, the singular change of $\Delta\bar{H}$ at 1–2% moisture adsorption is conceivably due to altering of the sort of sites for adsorption. $\Delta\bar{H}$, below and above this singular point, may be assumed to be ca $-(3.5–4)$ kcal./mol. and ca -1 kcal./mol.

Consequently, the next conclusions are deducible: below 1.2% adsorption the water molecules are linked to some sites in the region, where flow cannot occur, because they can not easily affect the yield stress. Such a region may be considered to be that where the chain molecules are arranged into a lattice. The water molecules are adsorbed to the sites which are the disordered places contained in this lattice, and take comparatively stable configurations. Because the adsorbed water begins to have a large influence on the yield stress beyond 1.2% adsorption, it follows that, almost of the sites in the lattice having been already occupied by the water molecules, the sites in the region where flow can occur begin to be occupied by water molecules[c]. From 1.2% to 3.5% adsorption the effect of adsorbed water on the drawing behavior is exceedingly large, but beyond 3.5% it is a good deal smaller (Fig. 12). In the following consideration of the polymer's structure it may be possible that the former is an adsorption on the sites in the partially arranged regions which make the boundary of the arranged regions (micelles) and the latter is that on the sites in the completely amorphous regions. The author believes that the deformation of polymer can be regarded as that of the complex structure made of strong and weak networks. The former, which is tentatively called the *primary network,* is constituted from bundles of chain molecules and contains the arranged regions (micelles) together with their boundaries. The latter, which is tentatively called the *secondary network,* is constituted from the single chain molecules which are entangled with each other and fill the space among the primary networks. On deforming such a complex network, the micell behaves like a rigid body and the flow in the primary network must occur only at the boundaries of the micells. The measured yield stress is the sum of individual resistances caused against flow in the primary and the secondary networks and the stress caused in the primary network should be expected to hold the leading proportion. The behavior of the secondary network, however, has an important function in determining the deforming features of the entire complex network. The detailed discussion[4] on the mechanism of deformation shall be described in a subsequent paper. At any rate, the results obtained can give some experimental foundations to establish the fine structure of polymer and the mechanism of its deformation.

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[3] M. Tsuboi, This Bulletin, 25, 160 (1952).

[c] If the number of sites for adsorption with $\Delta\bar{H}$ of -3.8 kcal./mol. is N_1, that with $\Delta\bar{H}$ of -1.0 kcal./mol. is N_2, and the number of sites already occupied by water molecules is N_1' or N_2' respectively, the ratio (P_2/P_1) of probabilities with which one of sites not yet occupied in either of both groups will be occupied by next water molecule is as following; $P_2/P_1=(N_2-N_2')\exp\left(\frac{1000}{RT}\right)/(N_1-N_1')\exp\left(\frac{3800}{RT}\right)\simeq(N_2-N_2')/(N_1-N_1')\ 1/100$ ($R=2$ cal., $T=300$°K). Then division can be made fairly definitely.

[4] H. Yumoto, presented at the symposium on rheology of the Chemical Society of Japan in Tokyo, June 3, 1955.

The temperature dependency on the behavior of drawing at 10% or 65% R. H. is discussed as follows. The values of *Wc* and *ΔWc* obtained from Fig. 3 and Fig. 4 are plotted against the temperature in Fig. 13 and Fig. 14.

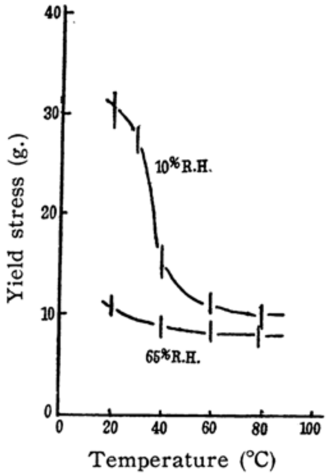

Fig. 13. The yield stresses at various temperatures and constant relative humidities of 10% and 65%.

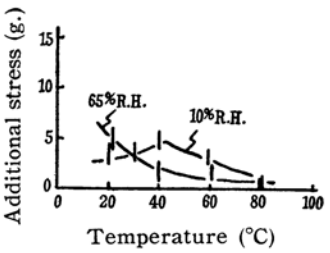

Fig. 14. The additional stresses at various temperatures and constant relative humidities of 10% and 65%.

In case of 10% R. H. a singular point is found at 30–40°C in both figures. This singularity has presumably the same physical meaning as that revealed at 70–80°C on the occasion of drawing at 0% R. H., i. e. in completely dried state. (cf. Fig. 3 in Part I[1]) In case of 65% R. H. there is no singular temperature within the observed range, but it seems likely to exist below 20°C.

The amount of adsorption is less at a higher temperature even if the relative humidity is the same; for instance, the amount of water adsorbed on the unstretched, polycapramide filaments which are not heat-treated is 0.77% at 25°C or 0.58% at 40°C in case of 10% R. H. and 4.8% at 25°C or 4.4% at 40°C in case of 65% R. H.[2] Although *Wc* should decrease with increase of water adsorbed, as a matter of fact, *Wc* becomes smaller at a higher temperature. This indicates the direct influence of temperature to be strong. Therefore this singularity must be ascribed to the fact that the micro-Brownian motion is either frozen or not in the region where flow between chain molecules can occur practically. Moreover, according to the complex network presented above, the microscopic state of the boundary region between micells gives the exceedingly great influence on the value of *Wc* and, therefore, the micro-Brownian motion under discussion will not be that in the completely amorphous region, i. e. in the secondary network, but that in the boundary region between micells.

It is proved consequently that the so-called polymer's second-order transition temperature, which is considered to be related to the microscopic state in any amorphous region, is lowered with increase of the amount of water adsorbed; e. g. it is 70–80°C at completely dried state (cf. Part I[1]), 30–40°C at less than 1% adsorption, or lower than 20°C at 4–5% adsorption. These values of the adsorption are the weight per-centage of entire amount of water adsorbed to the entire adsorbent; at present the weight percentage of water adsorbed in regard to only the adsorption on any limited region, i. e. the boundary region between micells, cannot be estimated.

The results of drawing in water at various temperatures given in Fig. 5 exhibit no singular temperature in the observed range.

Conclusion

The effects of humidity, namely water adsorption, in case of isothermal quasi-static drawing of unstretched polycapramide filaments at constant temperature of 20°C were investigated. Interesting results, suggestive of the fine structure of polymers and the mechanism of its deformation, were obtained. Generally the necking appears under coexistence of unstretched and stretched phases in course of drawing, but the necking is not observed in case of drawing in water. During the state, in which both phases exist, the stretch of the entire specimen is almost entirely attributed to elongation through transformation of the unstretched into the stretched phase. The yield stress (*Wc*) for proceeding of necking shows sharp increase at the moisture adsorption of less than 1–2% and the additional stress (*ΔWc*) required for formation of the necking exhibits a maximum as shown in Fig. 7. The amount of water adsorbed where this singular point lies is identical with the position at which the isosteric differential heat of adsorption ($\varDelta\bar{H}$) changes markedly. $\varDelta\bar{H}$ of the initial adsorption can be evaluated to be −(3.5–4) kcal./mol. from the empirical relation between $\varDelta\bar{H}$ and *Wc*. Such a result suggests that a deformation of the heterogeneous fine structure of polymer bears a close relation to moisture adsorption. The ratio (*r*) of sectional areas of both phases during the state of their coexistence increases sharply at the water adsorption less than 3.5% (50% R. H.) as shown in Fig. 12.

The molecular state of the water adsorbed, which has been revealed with the infrared absorption bands by M. Tsuboi, indicates that all of the adsorbed water molecules are directly bound to the polycapramide molecules; therefore the variety in the heat of adsorption should be due to the variety of adsorption sites. If water is adsorbed to the sites located in the region where flow can occur, it may facilitate the deformation of polymer. Now it may be possible to conclude as follows. Water molecules of less than 1.2% adsorption are situated at the sites in the fairly arranged regions, that is micells (U), and have no influence upon the magnitudes of *Wc* and *r*. Water molecules corresponding to the range of adsorption from 1.2% to 3.5% are situated at the sites in the partially arranged boundary regions between micells (Vab) and have a great influence upon the magnitudes of *Wc* and *r*. Water molecules corresponding to more than 3.5% adsorption lie at the sites in the completely amorphous intermiceller regions (Vc) and have little influence upon the magnitudes of *Wc* and *r*. As the magnitude of yield stress (*Wc*) is mainly determined by the steric resistance against flow in Vab regions, the so-called polymer's second-order transition temperature (*Tf*) of polycapramide seems to be the temperature, at which the micro-Brownian motion in Vab regions becomes effectual within the time of observation.

The effects of temperature on the occasions of drawing at constant humidities of 10% and 65% or of drawing in water were investigated. It is proved from this result that *Tf* is at 70–80°C in the completely dried state (cf. Part I), at 30–40°C if the moisture adsorption is less than 1%, and at the temperature lower than 20°C if the moisture adsorption is 4–5%.

The detailed arguments on the subject of the deformation mechanism, which can be deduced from this series of studies, shall be described in a subsequent paper.

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