Studies on the Cold-drawing of Polymers (Part III).[1] *The Quasi-static Drawing of Polycapramide. III.** *The Effects of Heat-treatments and the Temperature Dependencies of the Heterogeneous Structure in Polymers*

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Introduction

In the development of the investigation on the cold-drawing of polymers (for example, polycapramide), the influences of temperature and humidity (the moisture adsorption) on the quasi-static drawing have been reported in Part I[2] and Part II[1]. In succession the effects of heat-treatment were investigated.

In addition to drawing behaviors, densities were chosen for the measure of the structure change through heat-treatment. Each of various singular temperatures obtained is considered as the transition temperature of each micro-region in the heterogeneous structure. Then the temperature dependencies of polycapramide are brought to light and some experimental foundations for conjecturing the drawing mechanism are established. Such experimental results and the discussion on them are the subject of this paper.

Experiments

(1) The Specimens.—60 denier (ϕ 0.086 mm.) polycapramide semidull unstretched monofilament was used which was spun from the melt through chilling by air and contained about 2% of caprolactam monomer and oilgomers.

(2) The Methods of Heat-Treatments.—For the heat-treatment in the dry state, the above specimen had been inserted in a glass tube, which was sealed after substituting air with carbon dioxide, and was heated at a constant temperature ($\pm 1^\circ$C) from 50° to 200°C in a bath of an appropriate boiling organic liquid or in an electric thermostat. For the heat-treatment in water or in the saturated water vapor, water was let into a tube together with the specimen before sealing; in case of the former the specimen was entirely steeped in water and in case of the latter the specimen was placed apart above the water in the tube. The heating procedure of the sealed tube was the same as in the case of the treatment in the dry state. The specimens in the tube were always tensionless.

After the heating, the tubes were always cooled in room temperature without particular means for rapid or slow cooling.

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[1] H. Yumoto, This Bulletin, 29, 141 (1956).

* H. Yumoto, presented at the 8th annual meeting of the Chemical Society of Japan in Tokyo, April 2, 1955.

[2] H. Yumoto, This Bulletin, 29, 45 (1956).

(3) The measurements of Isothermal Quasi-static Elongation-Stress Curves.—The methods were the same as those described in Part I. Measuring was performed on the drawing at 80°C in completely dried state or at 20°C in water.

(4) The Measurements of Densities.—The densities in dried state were measured at 25± 0.005°C by the floatation method using ethylene chloride: xylene mixtures[a] as media. Specimens were previously cut into about 0.5 mm. of length and dried completely with phosphorous pentoxide in a desiccator. The mixture was poured on to pieces so finely cut and dried under the vacuum as to avoid bubbles remaining on the pieces and the equilibrium between floatation and precipitation was brought about by controlling the mixture ratio of medium at 25°C. The densities of media at the equilibrium were measured with an Ostwald picnometer. The error of measurement was about ±0.0005 g./cc.

Results of Measurement

(1) Density

The densities (25°) of specimens subjected to various heat-treatments are shown in Table I. The specimens treated in air give slightly larger densities than those treated in carbon dioxide; this fact may be attributed to the increase of molecular weight owing to the combination of oxygen, because polycapramide kept in air at high temperature suffers oxidation. When the temperature and the medium for treatment are the same, the density seems to converge to a certain level; i.e. even if the time of treatment is prolonged, the density does not increase apparently beyond a certain value. Such limiting values are shown in Fig. 1.

TABLE I

DENSITIES OF POLYCAPRAMIDE SUBJECTED TO VARIOUS HEAT-TREATMENTS AT 25°C

Heat-Treatment			Density at 25°C (g./cc.)
Temp. (°C)	Time (hr.)	Medium	
	Untreated		
50	168	air	1.1355
60	50	〃	1.1350
〃	〃	CO_2	1.1355
80	20	air	1.1355
〃	20	CO_2	1.1345
〃	50	〃	1.1350
〃	100	〃	1.1350
100	50	air	1.1375
〃	0.5	CO_2	1.1345
〃	1.0	〃	1.1345
〃	5.0	〃	1.1355
〃	10	〃	1.1350
〃	20	〃	1.1345
〃	30	〃	1.1350
〃	40	〃	1.1355
	Untreated		1.1340
115	10	air	1.1375
〃	5.0	CO_2	1.1355
138	2.0	air	1.1410
139	1.0	CO_2	1.1410
〃	3.0	〃	1.1420
150	2.0	air	1.1450
158	2.0	air	1.1465
〃	3.0	CO_2	1.1425
〃	5.0	〃	1.1420
168	1.0	CO_2	1.1430
171	3.0	〃	1.1465
183	1.0	〃	1.1505
〃	3.0	〃	1.1505
190	1.0	〃	1.1590
〃	3.0	〃	1.1580
203	1.0	〃	1.1705
205	3.0	〃	1.1720
ca. 20	240	benzene	1.134
〃	240	H_2O liquid	1.135
40	30	〃	1.137
60	2.0	〃	1.140
80	20	〃	1.143
100	2.0	〃	1.148
120	2.0	〃	1.157
140	2.0	〃	1.168
60	2.0	H_2O vapor	1.137
80	2.0	〃	1.141
100	2.0	〃	1.142
120	2.0	〃	1.156
140	2.0	〃	1.170

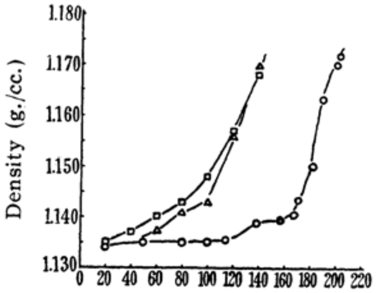

Fig. 1. Densities at 25°C limitted with various treatment-temperatures.
○ Treatment in dried state
□ Treatment in liquid water
△ Treatment in saturated vapor of water

The heat-treatment is the process where some of the distortions in substances diminish through the thermal Brownian motion of structural elements; therefore the time of treatment is an important factor. In polymers some microscopic movements cannot come into effect before exceedingly long elapse of time. Nevertheless the

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[a] Using carbon tetrachloride: xylene mixture, the same values were obtained. Using benzene: nitrobenzene mixture slightly lower values were obtained.

transfiguration due to the movements, which will be caused after times of treatment have elapsed, can be considered to be negligibly small because of the limit of density increment as above described.

Fig. 1 indicates the following facts. In case of the treatment in dried state, the increase of density is not apparent at the temperature below ca. 100°C, but becomes apparent beyond ca. 120°C, and is remarkable at 180–200°C. In case of the treatment in water (liquid), the specimen treated even at room temperature gives somewhat greater density than the untreated one. The increase of density with rise of the treatment temperature, is just noticed from 40°C and is remarkable beyond ca. 100°C. In case of the treatment in water vapor the increase of density is similar to that in case of the treatment in liquid water; the densities in both cases at the same treatment-temperature are the same above 120°C, but the former is somewhat less than the latter below 100°C.

Under the apprehension that the increase of density through steeping in water for 240 hrs. might be attributed to the removal of caprolactam monomer through extraction, the density of specimen which had been freed from monomer by steeping in benzene for 240 hrs. was measured on trial; but the increase of density was not noticeable. Therefore, the increase of density through steeping in water is caused in conclusion not by the removal of monomer but by the transfiguration of fine structure.

(2) Drawing Behaviors

Only the specimens, which had attained to the limit of density increment by heat-treatment at each of the temperatures, were subjected to the drawing experiment. The elongation-stress curves at 80°C in dried state and at 20°C in water are given in Figs. 2, 3 and Figs. 4, 5. Polycapramide, even if heat-treated, can be easily stretched in these conditions; but below 80°C in dried state it is quite difficult to stretch it and breaking happens mostly before 20–30% elongation. The obtained curve takes the similar shape with that of the untreated specimen, which gives the steep rise of stress from the environs of 100% elongation at any case. When the temperature of treatment is higher, the stress at the same elongation and the Young's modulus are higher. It is noteworthy that, in spite of exhibiting maximum and minimum of stress in case of drawing at 80°C in

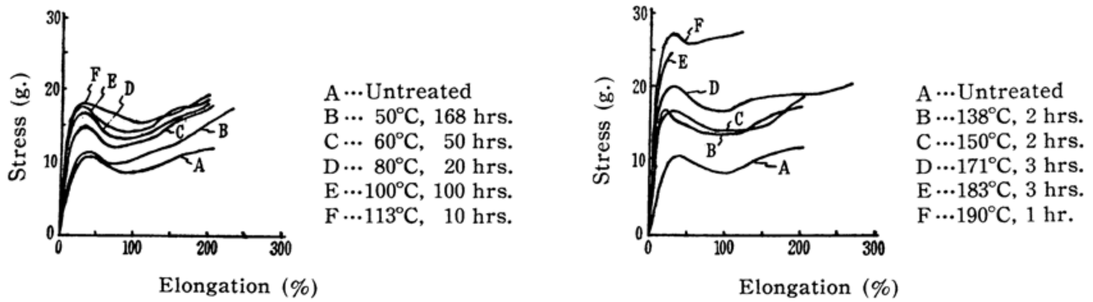
(1)

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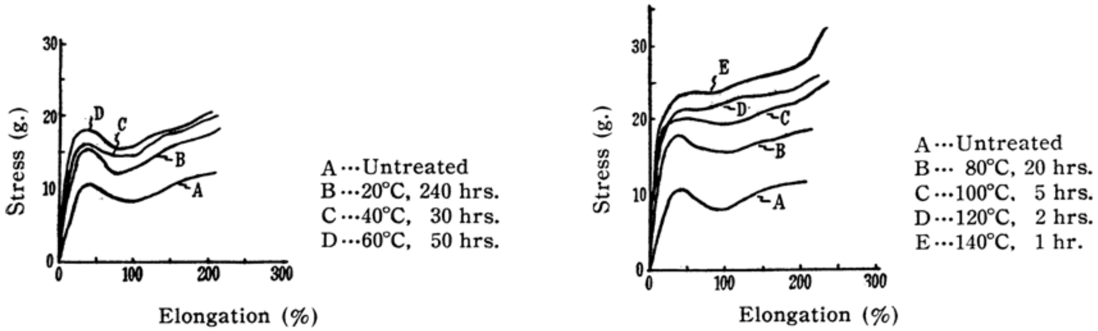
Fig. 2. The quasi-static elongation-stress curves of polycapramide subjected to heat-treatments in dried state at various temperatures on drawing at 80°C in completely dried state.


(1)

(2)

Fig. 3. The quasi-static elongation-stress curves of polycapramide subjected to heat-treatments in liquid water at various temperatures on drawing at 80°C in completely dried state.

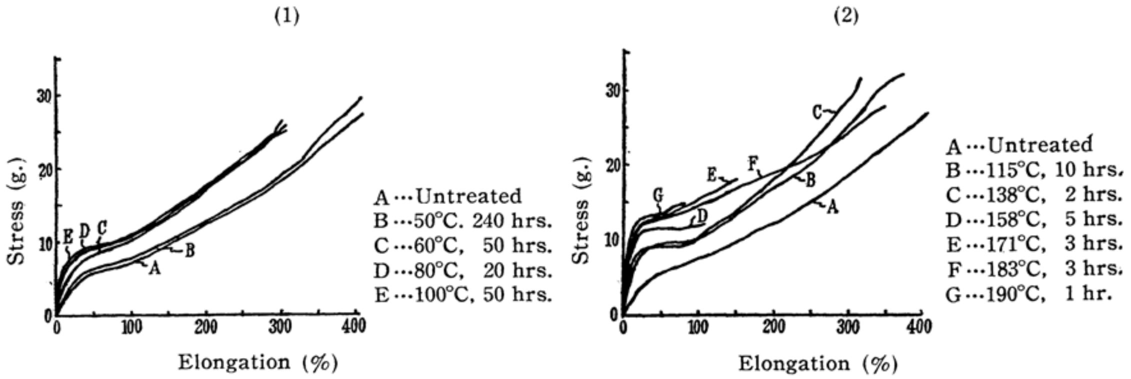


Fig. 4. The quasi-static elongation-stress curves of polycapramide subjected to heat-treatments in dried state at various temperatures on drawing at 20°C in water.

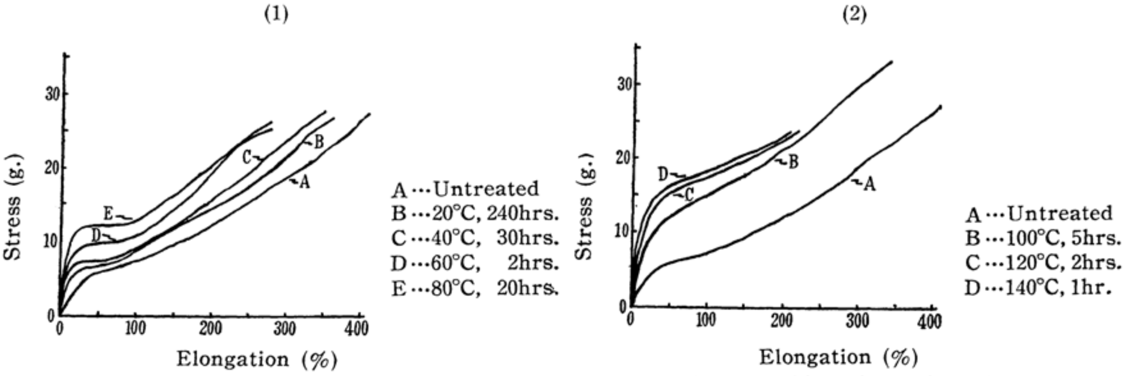


Fig. 5. The quasi-static elongation-stress curves of polycapramide subjected to heat-treatments in liquid water at various temperatures on drawing at 20°C in water.

dried state, most[b] of the heat-treated specimens are stretched homogeneously, without necking, towards rupture. In case of the drawing at 20°C in water, all are stretched homogeneously, and neither maximum nor minimum of stress are found in the curves. But an inflection part is found as shown in Fig. 4; the part following after the inflection lies on the identical line in every case of dry treatment below 140°.

(i) Drawing at 80°C in Dried State.—The tentative yield stresses (*Wc*), which are the minimum stresses in curves as explained in Part I or II, are plotted against the temperatures of heat-treatment in Fig. 6.

Fig. 6 indicates the following facts. In case of the treatment in dried state, *Wc* increases with temperature below ca. 120°C, especially at ca. 60°C, and is almost invariable from ca. 120°C to ca. 170°C; but the great increase of *Wc* is noticed between 170–180°C. In case of the treatment in liquid water, even if merely being steeped for a long time in water at room temperature, *Wc* is somewhat higher. *Wc* increases peculiarly at ca. 40°C and 80–100°C, but scarcely alters in the other temperature ranges.

Consequently it is found that the increase of yield stress is not parallel with the increase of density (cf. Fig. 8).

(ii) Drawing at 20°C in Water.—The stress at the inflection part, which is well assumed as the tentative yield stress (*Wc*), increases with rise of the treatment-temperature as shown in Fig. 7.

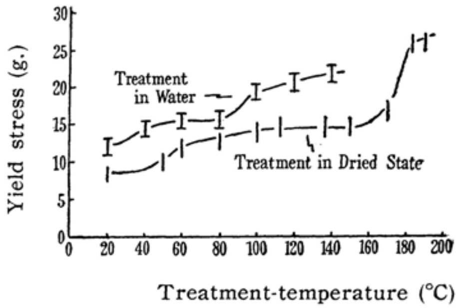


Fig. 6. The relations between yield stresses at 80°C in completely dried state and treatment-temperatures.

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[b] No specimens treated in water above 40°C or in dried state at higher temperature gave necking in this drawing condition. If treatment was executed in dried state at lower temperatures (the limit of temperature could not be determined), the necking appeared. On the other hand the untreated specimen showed the necking distinctly, even if drawing was carried out at 160°C. Although appearance of necking depends on the rate of drawing, it is evident that the appearance of max. and min. in the curves is not always attended with the appearance of the necking.

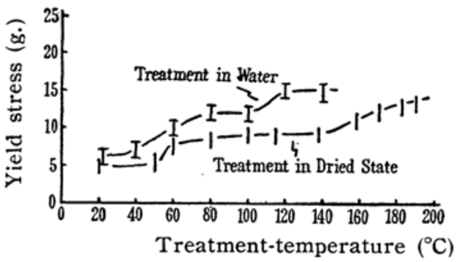

Fig. 7. The relations between yield stresses at 20°C in water and treatment-temperatures.

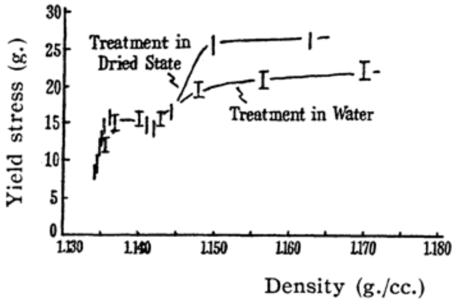

Fig. 8. The relations between yield stresses at 80°C in completely dried state and densities at 25°C.

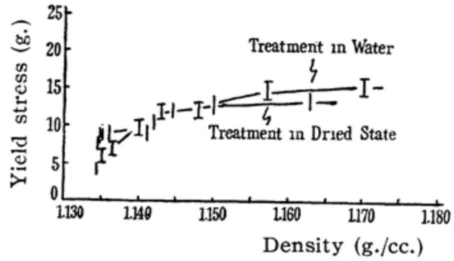

Fig. 9. The relations between yield stresses at 20°C in water and densities at 25°C.

Discussion

(1) The Dry Heat-Treatment

The singular temperatures in respect to the treatment in dried state exist at near 60°, 120°, and 180°C; those at 120° and 180°C are noticed on both of density and yield stress but at 60°C on the yield stress alone. (Fig. 10, where maxima of stress in Fig. 2 are plotted against treatment-temperature, gives singularities more clearly than Fig. 6.) Any of them is thought to be a sort of transition temperature. The temperature near 180°C is assumed as the softening temperature explained in Part I[2], at which the macro-Brownian motion in any micro-region begins to be effectual. Hence there will be tow transition temperatures, 60°C and 120°C, in which the micro-Brownian motion participates. This indicates the coexistence of two micro-regions; the one where the micro-Brownian motion comes into effect easily, and the other where it is relatively difficult for it to do so. Presumably the former can be assumed as the amorphous region [Am.], but the latter cannot be simply assumed as the crystalline region. The sharp increase of density by heat-treatment above 120°C suggests the latter to be assumed as the intermediate state between amorphous and crystalline, i. e. the mesomorphous state [Qcr.]. Therefore the complete crystalline region [Cry.] (containing a little disorder) must exist as the another region. The thermal behaviors of these three hypothetical regions may be taken into account under the experimental facts, setting aside the question how such regions are distributed.

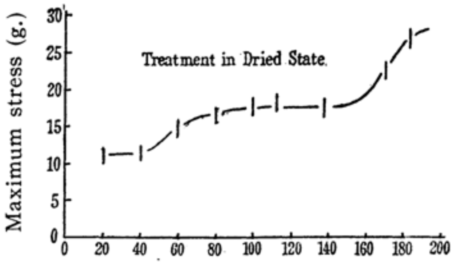

Fig. 10. The relation between maximum stresses at 80°C in completely dried state and treatment-temperatures.

The peculiar temperature at which the micro-Brownian motion becomes effectual[c] is denoted by Tf. The heat-treatment relaxes the frozen distortion and brings about the thermal equilibrium. The treatment at above Tf of [Am.] makes part of [Am.] transformed into [Qcr.] or [Cry.] (1st.-transformation), and still that at above Tf of [Qcr.] makes [Qcr.] transformed into [Cry.] (2nd.-transformation). Hence it can be said from Figs. 1, 4, 6, and 10, that through the 1st.-transformation the stress at deformation is increased but the density is scarcely altered, and on the other hand through the 2nd.-transformation the increase of stress is little but the increase of density is large. The relation is recognized more explicitly in Fig. 8 where *Wc* are plotted against densities. Therefore it is proved that, by drawing, the large flow between the chain molecules is caused only in the amorphous regions [Am.] and is not done in more or less orderly regions [Cry.], [Qcr.]. If this prove to be the case, the crystallization[3] brought about

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[c] The meaning of "effectual,' is that the effects of elementary transfiguration, owing to the movement within ordinary time of observation or heat-treatment, become observable.

[3] K. Fuchino and A. Okada, *Scientific Reports of Toyo Rayon Co.*, No. 13, 1 (1949) (in Japanese). J. Fankuchen and H. Mark, *J. Appl. Phys.*, 15, 364 (1944).

by drawing must be attributed to the transformation of [Qcr.] into [Cry.] resulting from the slip of small extent in [Qcr.] caused by the stress; the elongation due to this slip is negligibly small in comparision to the entire elongation. Tf is lowered under the large stress[4] (about the motion only parallel to the stress) and the transformation becomes possible at the temperature where it is impossible in the ordinary state.

The reason, why the increase of density is not apparent through the 1st.-transformation, is probably due to the little difference between densities of [Am.] and [Qcr.][d].

By treatment at the temperature above the softening temperature (ca. 180°C), both the yield stress and the density are markedly increased. In polymer there are distortions which cannot be removed by the micro-Brownian motion of each individual element (segment) but can removed by the simultaneous co-operative movement of some individual elements. The simultaneous co-operative movement of many elements means the macro-Brownian motion, and the temperature at which such a movement becomes effectual is denoted by Tm. The experimental facts show that the distortions are markedly removed through heating at the temperature above the softening temperature, which is considered to be Tm of the amorphous region. (Tm of the orderly region can be assumed as the melting point 220°C).

(2) The Heat-Treatment in Water

The singular temperatures in respect of the treatment in water exist at about 100°C and 40–50°C. The latter is obscure; but taking into account the fact that, when lactam monomer and oligomers are removed from the chip of polycapramide by scouring with water, the rate of extraction is very much smaller below 40°C than from 60°C to 100°C, it is also supposed to be a certain singular temperature. It is found in Figs. 1, 6, and 8 that singularities at 100°C and 40°C in water resemble those at 180°C and 120°C in dried state, respectively; this indicates Tf of [Qcr.] in water to be ca. 40°C and Tm of [Am.] in water to be ca. 100°C. Tm and Tf are much largely lowered in water than in dried state.

The specimens of the same density give generally the same yield stress, but the density being beyond 1.15 g./cc. the dry treatment gives larger yield stress than the wet treatment as shown in Fig. 8. Such distinction of properties among specimens of the same density also appears on the elongation to rupture; namely the dry treatment gives apparently small value as shown in Figs. 2 and 3. Besides it has been observed qualitatively that the wet treatment gives the lower water adsorption and higher dyeability than the dry treatment. Even if the mean value of density is the same, the variation of density distribution in the structure of polymers will probably cause such distinction of properties.

(3) The Effects of Water

The effects of water on the heat-treatment is very remarkable. If water molecules coexist with polyamide molecules, it is expected that the resistance against flow between chain molecules decreases, Tf is lowered, and the internal pressure is generated by swelling. Some of these effects are revealed on experiment as described already. That Tf of [Qcr.] is lowered by steeping the samples in water, indicates the penetratability of water molecules into [Qcr.] regions.

It is noteworthy that the effects of heat-treatment are much smaller in the case of the drawing in water at 20°C than in the case of the drawing in dried state at 80°C; especially such tendency is large in the case of the dry treatment. For example, the specimens subjected to the dry treatment between 60–138° give the same elongation-stress curve beyond 100% elongation (Fig. 4). This fact suggests that the drawing in water can bring about the similar effect with some of the effects caused by heat-treatment.

(4) Further Considerations of Each Micro-Region

The above description has been deduced on assuming the coexistence of [Am.], [Qcr.], and [Cry.] micro-regions and the transformation among them, but the aspect, how these regions are mixed, has not yet been mentioned. Such aspect cannot be ascertained only by this experiment, nevertheless it can be discussed under consideration of the facts formerly known.

The spherulites are observed in various polymers under the microscope[7,10]. The spherulite is an aggregate of crystallites which is thought to be the inevitable form

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[4] R.F. Boyer and R.S. Spencer, *J. Appl. Phys.*, **16**, 594 (1945).

[d] The density of [Am.] at 25°C is presumed to be about 1.1 by extrapolating densities of the melt at the various temperatures[5]. The density of [Qcr.], which is well assumed as the defective crystallite of frozen α-form as described later, is presumed to be about 1.13 from X-ray data[3,6]. The density of [Cry.] is presumed to be 1.21 from X-ray data[8,6]. Then the difference of density between [Am.] and [Qcr.] is very smaller than that between [Qcr.] and [Cry.].

[5] H. Yumoto, *Scientific Reports of Toyo Rayon Co.*, No. **25**, 6 (1953) (in Japanese). Y. Kinoshita, ibid. No. **27**, 1 (1954) (in Japanese).

[6] R.Z. Brill, *Z. Phys. Chem.*, B **53**, 61 (1943); *C.A.*, **37**, 4576 (1943); *J. Prakt. Chem.*, **161**, 49 (1942); *C.A.*, **37**, 4608 (1943).

[7] C.W. Bryant, *J. Polymer Sci.*, **2**, 547 (1947).

in the crystallization of linear polymers. Concerning polycapramide, although spherulites have been observed practically in the case of the specimens crystallized by slow cooling of the melt or by evaporation of the solution, spherulites which are too small to be observable are generally be expected to be formed. It has been known that spherulites are deformed in proportion with the deformation of specimen[8] and the rupture occurs only along the boundaries between spherulites or along the radii of them[10]. Then [Am.] regions, where flow can occur, must exist in both the boundary and the interior of spherulites. Consequently a spherulite is constituted from [Am.], [Qcr.], and [Cry.] micro-regions, and [Qcr.] or [Cry.] is assumed as a sort of crystallite.

It was already reported in 1925[11] that the crystal structure of paraffine (C_{20}—C_{30}) transforms at much lower temperature than the melting point, and also on polyethylene[12], polyamide[12,3,6] such phenomena were observed. The structure stable at lower or higher temperature has been called by β- or α-form. The transition temperature of polycapramide, although uncertainly, a has been found to be about 150°C[3,6] by means of X-ray. α-Form does not take the stable configuration as the ordinary crystal and is rather assumed as the state where chain molecules arrange in parallel lines into a bundle, having lower entropy-than the amorphous state; i. e. all of the elements of chain molecule do not take the *trans*-configuration of rotational isomers. (All of the structural elements take the *trans*-configurations in β-form.) The micro-Brownian motion in α-form always alters the configuration but it does so only partially so as not to lose the whole arrangement. It is most reasonable to suppose that [Cry.] is the crystallite of β-form and [Qcr.] is that of α-form frozen at lower temperature by rapid cooling. If the transition temperature as regard the α, β-transformation is said to be about 150°C[e], it should be Tf of [Cry.]. In the course of the treatment at a higher temperature than Tf of [Cry.], [Cry.] (β-form) can transform into α-form while it is heated, but it can retransform, if not rapid, into β-form on cooling. Then, as far as the effect of heat-treatment is concerned, the singularity can not be observable at about 150°C.

Now let us consider the relations to the micro-regions, U, Vab, and Vc described in Part II[1]. U region, i. e. the micell, where chain molecules are fairly arranged, corresponds to [Cry.] or [Qcr.], and Vab region, i. e. the boundary region between micells, where molecules are partially arranged, and Vc region, i. e. the intermiceller region, where each of the molecules is completely entangled, both correspond to [Am.]. Therefore [Am.] is divided into two sorts which are different in the order. Taking all things together, Tf of [Am.] in this paper will correspond to Tf (70–80°C) of Vab in the previous paper. Then another Tf of [Am.] corresponding to Tf of Vc must be found; the singularity found at about −40°C on polycapramide[13] will be probably due to Tf of Vc.

Summary

The obtained results are summarized in Tables II and III.

The values in these tables are not precise because of the methods of evaluation, and the shift of ca. ±10°C will be admitted.

All of these temperatures is not always observed in any experiment. The revelation of this singularity is dependent on the character measured and the state of the specimen.

TABLE III

THE EFFECTS OF HEAT-TREATMENT

	Temp. °C	Increase of Density	Increase of Yield Stress	Change in Structure
Treatment in Dry State	below ca. 60	none	none	none
	ca. (60–120)	small	large	Am.→Cry. or Qcr.
	ca. (120–180)	large	small	Qcr.→Cry.
	above ca. 180	very large	very large	Am.→Cry.
Treatment in Water	below ca. 50	small	large	Am.→Cry. or Qcr.
	ca. (50–100)	large	small	Qcr.→Cry.
	above ca. 100	very large	very large	Am.→Cry.

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[8] C.M. Langkammer and W.E. Catlin, *J. Polymer Sci.*, **3**, 305 (1948).

[9] C.W. Bunn, "Fibres from Synthetic Polymers", R. Hill, Elsevier Publ. Co. (1953), pp. 251-6.

[10] F.P. Reding and A. Brown, *Ind. Eng. Chem.*, **46**, 1962 (1954).

[11] Müller and Saville, *J, Chem. Soc.*, **127**, 599 (1925).

[12] W.O. Baker, "Advancing Fronts in Chemistry", S.B. Twiss. Reinhold Publ. Corp. (1945), p. 145.

[13] T. Kawaguchi, Unpublished.

TABLE II

THE MICRO-REGIONS IN POLYCAPRAMIDE AND THEIR TRANSITION TEMPERATURES

(1) At Lower Temperature

	Micro-Region	Temp. at which the micro-Brownian motion becomes effectual in relaxed state (Tf), °C	
		Dry State	In Water
Am.	Completely amorphous region (Vc)	ca. −40[13]	*
	Partially arranged region (Vab)	ca. 60, 70∼80	below 20
Qcr.	Defective crystallite (U) of frozen α-form	ca. 120	ca. 40–50
Cry.	Crystallite (U) of β-form	ca. (150)[e]	*

(2) At Higher Temperature

	Micro-Region	Temp. at which the macro-Brownian motion becomes effectual (Tm), °C	
		Dry State	In Water
Am.	Vc	—	—
	Vab	ca. 180 (softening pt.)	ca. 100
Qcr. (Cry.)	Mesomorphous state of α-form (U)	215–220 (melting pt.)	*

Conclusions

The densities and drawing behaviors of polycapramide subjected to various heat-treatments give the useful facts in fiber manufacturing applications. And the reasonable considerations on them suggest the coexistence of some micro-regions, i. e. the heterogeneity of polymer structure. In connection with the results described in Part II, where influences of humidity are considered, the following are concluded. Polymers are constituted from micells (U), boundaries between micells (Vab), and intermiceller regions (Vc). The crystallites of β-form [Cry.] and the defective crystallites of frozen α-form [Qcr.] are U regions. Both of Vab and Vc are amorphous regions [Am.]; Vab indicates a partial arrangement and Vc is completely amorphous. Various singular temperatures can be assigned as the following. At dried state Tf (the temperature at which the micro-Brownian motion becomes effectual) of Vc, Vab, [Qcr.] and [Cry.] are about −40°C[13], 70°C, 120°C and (150°C)[e] respectively. In case when the sample is steeped in water Tf of Vab is lower than 20°C and that of [Qcr.] is about 40°C. (Water molecules can penetrate into [Qcr.]). At dried state Tm (the temperature at which the macro-Brownian motion becomes effectual) of Vab and [Qcr.] are about 180°C (softening point) and 220°C (melting point). (Above Tf of [Cry.] discrimination of [Cry.] and [Qcr.] is lost.) At the state of the sample steeped in water Tm of Vab is about 100°C. The effects of various heat-treatments are compatible with the characters above described.

The other important conclusion is that, by drawing, flow between chain molecules can occur in [Am.] alone; but only a slip of some extent, negligibly small in comparision with the entire elongation, can be caused in [Qcr.].

The density is largely increased by the transformation of [Qcr.] into [Cry.], and the yield stress is largely increased by that of [Am.] into [Cry.] or [Qcr.].

Such precise definitions of micro-regions may be unaccountable, but considerable definite divisions among them can be suggested from the experimental facts. Later, it is hoped that the theoretical interpretation on it can be given.

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[e] The value of 150°C is quoted from the X-ray diffraction data of Dr. Fuchino[3], but the thermal analysis[14] gives no singularity at this temperature and gives development of a slight latent heat at 168-173°C. Whether this latent heat is due to the beginning of macro-Brownian motion in [Am.] or to transformation of β to α owing to the beginning of micro-Brownian motion in [Cry.], and then 150°C is still uncertain.

[14] Y. Kinoshita, Unpublished.