Studies on the Cold-Drawing of High Polymers (Part I). The Quasi-Static Drawing of Polycapramide. I. The Temperature Dependencies, the Softening Temperature and the Second-order Transition Point*

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Introduction

The phenomenon of cold-drawing observed on polymeric substances is important for manufacturing synthetic fibres, e. g. polyamaide, polyester, polyethylene, afterchlorinated polyvinylchloride etc., because their mechanical properties are improved markedly by drawing. Even in the solidified state below the softening temperature, they can be elongated extremely beyond the yield point toward rupture. Such a phenomenon is also a very interesting problem on the chemical physics of high molecular substance. About the mechanism[1-7] of this phenomenon several opinions have been known, but their fundamental proposals are different from each other. None of them are sufficient to interpret the experimental facts, and the principal key of mechanism is considered not to have yet been grapsed. The main and ultimate objects of this study are to discover the general mechanism of cold-drawing which can interpret the experimental facts extensively and to give instructions for the manufacturing application.

The comprehensive experiments of drawing at the various conditions have been attempted about polycapramide and the elongation-stress curves of melt spun unstretched polycapramide fibre have been investigated as the first step. The following factors are concerned in the behavior of drawing, 1) the temperature, 2) the adsorbed water (also plastisizer in wider sense), 3) the rate of drawing, and 4) the microstructure (e. g. the heat-treatment or various operations at the time of spinning). It is necessary to investigate each factor separately. As the development of heat is accompanied by drawing, if the rate of drawing is large, the unevenness of temperature is caused in regard to time and space so that temperature and humidity cannot be kept constant. Then firstly the isothermal behaviors have been studied at the quasi-static deformation, where the rate of drawing is very small and further temperature and humidity are kept constant. In order to experiment at any chosen temperature and humidity below 100°C, the test materials must be completely isolated from the open atmosphere. The dependencies on temperature at completly dried state (R. H.

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

1) V. W. Broser, K. Goldstein and H. E. Krüger, *Kolloid-Z.*, **106**, 187 (1944).

2) C.W. Bunn and T.C. Alcock, *Trans. Faraday Soc.*, **41**, 317 (1945).

3) W.M.D. Bryant, *J. Polymer Sci.*, **2**, 547 (1947).

4) F.H. Müller, *Kolloid-Z.*, **115**, 118 (1949), ibid., **126**, 65 (1952).

5) F.H. Müller and K. Jäckel, *Kolloid-Z.*, **129**, 145 (1952); *Makromol. Chem.*, **9**, 97 (1953).

6) I. Marshall and A.B. Thompson, *Nature*, **171**, No. 4340, 38 (1953); *Proc. Roy. Soc.*, **221A**, 541 (1954).

7) K. Jäckel, *Kolloid-Z.*, **137**, 130 (1954).

0%), the observed singular temperatures, and the discussions about them are described in this paper.

Measurement of the Elongation-Stress Curves

The measuring apparatus for the elongation-stress curves are shown in Fig. 1. In all cases the stress was measured with a cantilever equipped with the electrical strain-gauge[8,a]; the strain of cantilever was indicated as the change of the electrical resistance of the strain-gauges. The stress subjected to lever was found through the calibration indicating the relation between the stress of cantilever and the electrical resistance of the gauges. The observational error was about ± 0.5 g. (2–5%). The elongation of the test material was measured with the cathetometer.

Fig. 1 (A) is the apparatus used for the measurement below 100°C where the test material must be isolated from the open atmosphere in order to keep the water adsorption constant; the humidity in the container was controlled with phosphorus pentoxide or aqueous solution of sulphuric acid. As the uniformity of temperature between strain gauges which are fixed on both faces of the cantilever is severely demanded in order to measure the stress correctly, the container is heated through a jacket of water[b]. The outside lever, held with the cathetometer, is linked to the inside cramp of the test material with the glass rod; at the path of this rod the container is sealed with mercury or liquid paraffine in the manner shown in Fig. 1 (A).

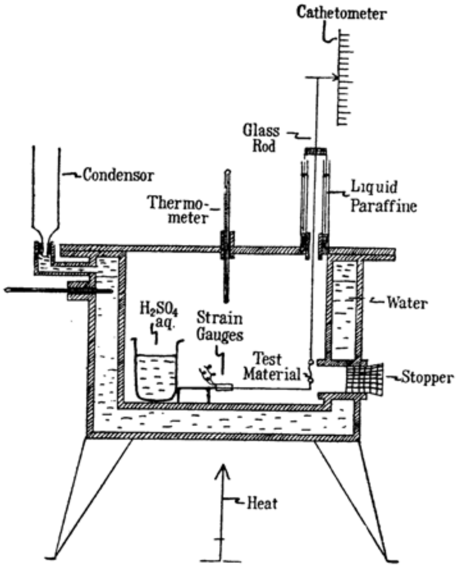

Fig. 1 (A). The apparatus for measuring the elongation-stress curves.

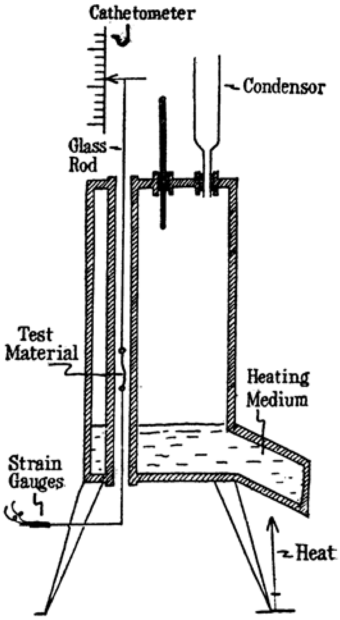

Fig. 1 (B)

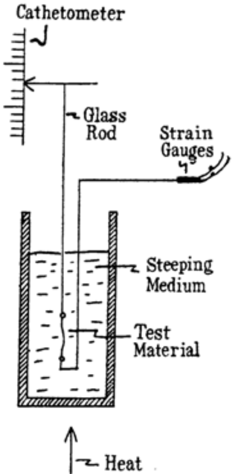

Fig. 1 (C)

Fig. 1 (B) is the apparatus used for the measurement above 100°C where sealing is not necessary because of the slight effect of the atmospheric humidity. As the effect of temperature is larger at higher temperature, the specimen is heated at a constant temperature through the medium of vapor of some appropriate boiling organic liquid.

Fig. 1 (C) is the apparatus used for the measurement in which the test material is steeped in the liquid (e.g. water)[c].

The test materials were 60.0 denier (ϕ 0.086 mm.) polycapramide (nylon 6) unstretched semi-dull mo-

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8) H. Hindman and C. M. Krook, *Text. Res. J.*, **15**, 233 (1945).

a) The zero-method measuring was used.

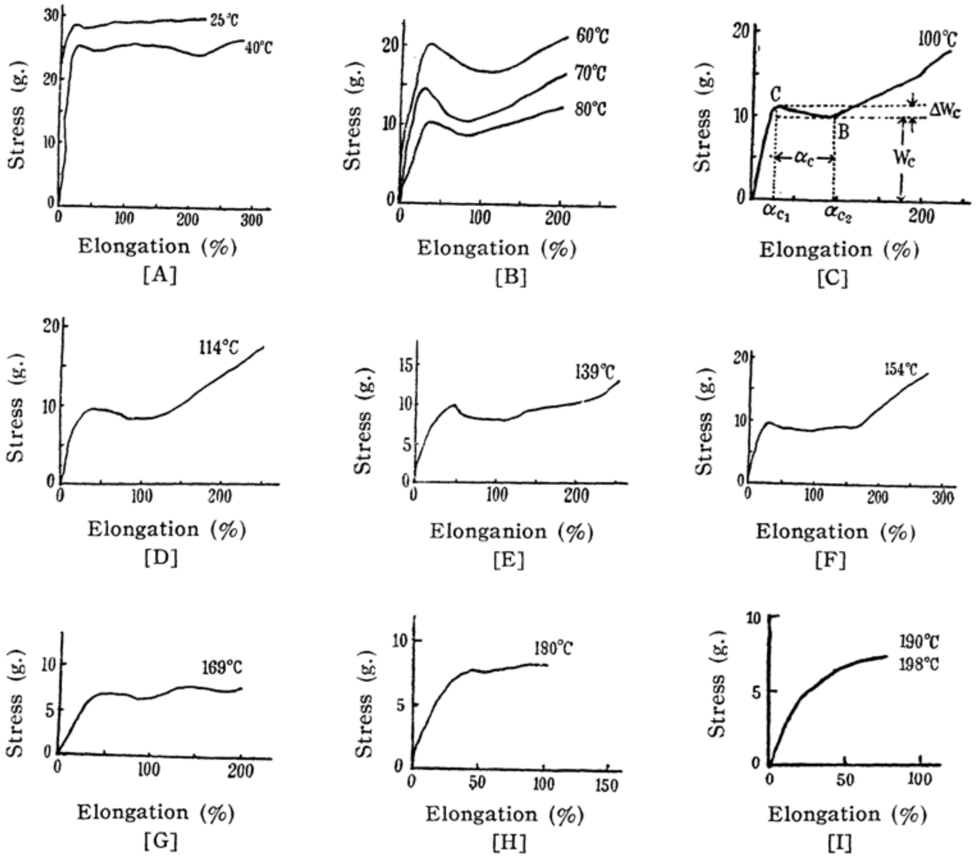
b) For the stability of adhesion of the strain gauge, Bakelite A was used as the adhesives and baked at 120-130°C for thirty minutes.

c) This apparatus was not used for measuring in this paper (Part I), but used for measuring in following papers.

nofilament containing 1–2% caprolactam monomer and oligomers. They were spun by only chilling (without water) from the chips whose degree of polymerization was about 100. On rapid cooling from the melt, the mesomorphous state called α-form[8], which is stable at a higher temperature, is frozen at room temperature without transformation into the crystalline state called β-form which is stable at a lower temperature.

The original sample was 1.50 cm. in length and was manually stretched step by step until breaking[d]. Three minutes after each step, the stress was measured. On account of the structural elements of the much ratarded relaxation in polymer, the correctly static experiment is practically impossible. Persuing the stress relaxation curve after stretching of any extent, it was observed that after three minutes the rate of stress relaxation became much smaller: then the elapsed time of three minutes was chosen for convenience; therefore it can be conventionally considered that such measuring procedure reveals the quasi-static behavior. As the stretching rate is sufficiently small to disperse the heat generated by stretching, such a deformation is assumed to be isothermal.

When the experimental temperature is high, the effect of heat-treatment may be expected to occur. Therefore it must be considered how many minutes are spent till the start of the stretch since the temperature of the specimen has attained to the experimental temperature, where the stretch is to be excuted. The next test was made to examine such effect. Stretching was started either fifteen or sixty minutes later since the specimen is brought to the experimental temperature of 114°C, but the distinctness of behavior between both cases was not observed. In case of these experiments, stretchings were always started thirty minutes later after the setting of the specimens in the container, the temperature of which had been previously kept at the measuring temperature.



[A] [B] [C]

[D] [E] [F]

[G] [H] [I]

Fig. 2. [A]–[I] The elongation-stress curves of polycapramide at various temperatures in completely dried state.

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[9] R. Brill, *Z. Phys. Chem.*, B53, 61 (1943); *J. Prakt. Chem.*, **161**, 49 (1942); K. Fuchino and A. Okada, *Scientific Reports of Toyo Rayon Co.*, No. 13, 163 (1949) (in Japanese).

[d] When the specimen was elongated from initial (1.50 cm.) to 2.30 cm., from 2.30 cm. to 5.00 cm. or from 5.00 cm. to rupture, the extent of stretching per each step was 0.10 cm., 0.30 cm., or 0.50 cm. respectively. Shortening the stretched extent per one step, the similar curves were obtained. This procedure was adopted but only in order to save the time and investigate closely the important portion of the curve. The examples where the stress was measured at the constant rate of elongation shall be described in a subsequent paper.

The Results of Measurement

The quasi-static elongation-stress curves obtained at the R.H. of 0% and from the room temperature to 200°C are shown in Fig. (A)-(I).2 Below 40°C, the randomness in each of the measurings is large and breaking sometimes happens on the way of stretching and the curves are always zig-zag. (The zig-zag points are smoothed in Fig. 2.) Above 60°C, all curves are smooth and the reproducibilities are excellent[e].

How to define the cold-drawing is thought to have not yet been established. From the standpoint of the fiber manufacturing application the author will temporarily regard it as the process where the permanent several hundreds per cent elongation and the work hardening phenomenon with the increment of molecular orientation occur by stretching. But if one accepts such a definition the phenomenological peculiar feature of the cold-drawing should be only quantitatives, that is to say, the permanent elongation is particularly large. When stretching is carried out, the state of coexisting of two phases, stretched and unstretched, occurs in most cases; and the necking appears at the boundary of two phases. In such a case the unstretched phase transforms into the stretched one with elongation and during this state the stress stays almost constant as if the liquid solidifies at a constant temperature. But the cold-drawing is an irreversible process and is profoundly distinct from the reversible process of the solidification which can be treated with the conventional thermodynamics. F. H. Müller and K. Jäckel[5,7] have defined the cold-drawing by the coexistence of two phases discriminating it from the ordinary drawing. Stretching polycapramide in water, such a coexistent state does not appear until breaking; the whole system is uniformly elongated. (The details shall be mentioned in the next paper.) However, in spite of the permanent several hundreds per cent elongation and the orientation of molecules, such drawing is not said to be the cold-drawing from the standpoint of the Müller-Jäckel's definition. The definition can be established by determining the general mechanism[10] of drawing which shall be described in a subsequent paper. Nevertheless this coexistent state is quite a characteristic feature so that it is requisite to take close consideration upon it.

The coexistence of the two phases (necking) corresponds to the curious shape of elongation-stress curve. The relation between the necking and the shape of curve is illustrated by Fig. 2 (C) for example; it is apparently observed that from the origin to the point C only unstretched phase, from the point B to breaking only stretched phase, and between points C and B both phases are found. Once the stretched phase appears from the unstretched phase, the stress decreases a little (gradually[f] in case of polyamide). And then as far as both phases coexist, the stress si almost kept constant. Once the unstretched phase disappears, the stress begins to increase sharply again. For the present, assuming the difference of stress (ΔWc) between the points C and B as the additional stress for the formation of the necking, the stress at B (Wc) is taken as the stationary stress for the proceeding of the necking. The number of neckings is generally one or two.

Smoothing the obtained curves below 40°C, ΔWc are possibly considered to be almost zero. With the rising of the temperature, ΔWc increases to maximum 4–5 g. at 70°C, and decreases to almost constant value 1–2 g. from 80°C to about 170°C, and then decreases to zero again.

The stationary stress for the proceeding of the necking (Wc), the elongation region in which the necking exists (α_c), and the additional stress required for forming the necking (ΔWc) are respectively plotted against the temperature in Figs. 3, 4 and 5. The stress and elongation at breaking,

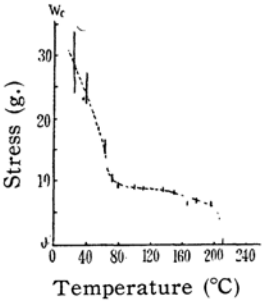

Fig. 3. The yield stresses at various temperatures.

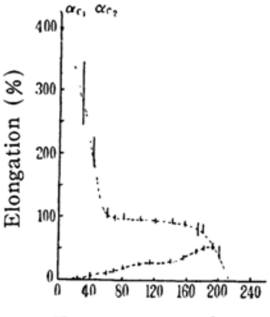

Fig. 4. The two phases coexisting regions of elongation at various temperatures.

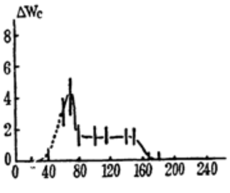

Fig. 5. The additional stresses for formation of the necking at various temperatures.

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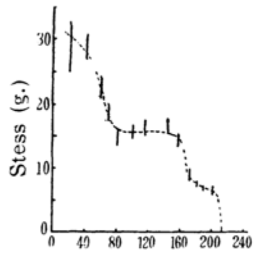
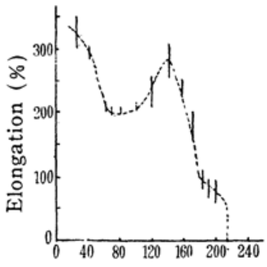
e) The times of measurement are three in the case of better reproducibility and from five to ten in the case of worse reproducibility.

10) H. Yumoto, presented at the symposium on rheology in Tokyo, June 3, 1955.

f) The stress once decreases gradually in the case of polyamide or afterchlorinated polyvinylchloride, but sharply in the case of polyethyleneterephthalate.



Temperature (°C)
Fig. 6. The stresses to rupture at various temperatures.



Temperature (°C)
Fig. 7. The elongations to rupture at various temperatures.

which have generally large values of randomness, are plotted aginst the temperature in Figs. 6 and 7. In these figures the length of lines at the positions of the plots indicates the magnitude of randomness.

In all these figures the singular point is explicitly found at 70–80°. Considering that the zigzag unevenness in the obtained elongation-stress curve is much smaller above this temperature than it is below this temperature as previously stated, it is probably the so-called polymer's second-order transition temperature. Because the melting point (68–70°C) of caprolactam monomer, about 1% or less of which is contained in the test materials, is near this temperature, the effect of this monomer should not be neglected. The lactam monomer free test material which was prepared by extracting it with water or benzene for seven days at room temperature, showed the same value of *Wc* with that of untreated materials. It is concluded from this result and the humidity effect which shall be described in the next paper that this singular point has no relation to the melting point of caprolactam monomer which is contained.

Another singular point, not so clear as at 70–80°C, appears in each figure at 170–180°C. Practically above this temperature no maximum or minimum is found in the elongation-stress curves. This will probably be thes oftening point, which will be discussed in the following section.

Furthermore one may find the maximum near 140°C in Figs. 6 and 7. But the singularity at this temperature does not appear in other figures; therefore this singularity is assumed to be related only to the behavior toward rupture.

Below 40°C the necking sometimes remains in the broken test material and the milky regions are always observed in the stretched phase. The milky regions are readily produced after the unstretched phase is transformed into the stretched one. Above 40°C no necking remains in the broken test material and the milky regions are not observed until just before breaking. When the milky region is observed under a microscope, for instance, the cloudy bands of 24 μ in length and the transparent bands of 20 μ in length are found alternately in stripes along the specimen of 56 μ in diameter.

Discussion

(1) The Singularity at 170–180°.—The singular point at 170–180°C is found in Figs. 3–7, which is conclusively regarded as the statical softening point from the results of the following experiments.

The polycapramide filaments of 0.5 mm. or 00.4 mm diameter, which had been cold-drawn to four times their original length, were steeped in a diphenyl-diphenyl ether bath which was heated with an oil bath (±1°C) and the shrinkages of them were measured with the cathetometer: the results are shown in Table I. Attaining 190°C the breaking through melting or the partial melting occurs (m. p. 220°). These phenomena are not considered to be affected with the steeping media. The experiments in air, where the uniformity of heating is rather incomplete, also showed the similar phenomena at near 190°C.

TABLE I
THE SHRINKAGES OF THE STRETCHED POLYCAPRAMIDE

$\phi=0.5$ mm.

Temp. °C	Minute	Shrinkage %
150	15	7
170	15	12
190	30	20 (partly melted)
200	15	melted and broken

$\phi=0.04$ mm.

Temp. °C	Minute	Shrinkage %
120	5	5
150	10	6.5
170	10	11
190	10	melted and broken

Besides, the stability of the pleats, which had been given by ironing for thirty seconds at various temperatures, were examined on polycapramide clothes: the result showed that the pleats bearable to washing with boiling water were obtained by ironing above 180°C. When clothes had been wetted on ironing, the durable pleats were obtained above 80–100°C. (These values were the temperatures of iron.)

These results show the presence of softening temperature near 180°C, which are considered to be attributed to the macro-Brownian motion of any regions (amorphous) in the polymer[11]. This temperature may be related to the optimum temperature for crystallization, 180°C or 185–200°C, found by K. Kanamaru et al. with the dilatometry[12] or by T. Arai et al. with the electrical conductivity method[18], and the temperature where the premelting anomaly occurs, 170–180°C, found by E. Nagai et al.[13] or by S. Ueno and K. Fuchino[14] as regards the Young's modulus.

(2) The Singularity at 70–80°C.—It has been revealed by the measurements about various properties of polymer that a singular temperature much lower than melting point, the so-called polymer's second-order transition point, exists. The examples of the known second-order transition temperatures of polycapramide are exhibited in Table II.

TABLE II

THE SECOND-ORDER TRANSITION TEMPERATURES OF POLYCAPRAMIDE (*Tf*)

	Tf °C	The method of measuring	Reference
I	near 60	dilatometer	12)
II	near 40	ibid.	13)
III	near 30	static Young's modulus of the unstretched yarn	15)
IV	near 60	damping oscillation (dynamic viscosity and Young's modulus	19)
V	40–50	change of tension	17)
VI	50–60	electrical conductivity	18)
VII	70–80	this study	

Considerable differences are apparent in the presented values. This temperature of polycapramide descends with the adsorption of water and such effect is unexpectedly large even in R. H. 10%[11] (cf. Part II). The values from static measurements of the mechanical properties in atmosphere are lower than the value of this study obtained from measuring in completely dried state; this lowering is considered to be due to the above humidity effect. The effect of less than 1% caprolactam monomer contained in polymer is not perceptible in the result of experiments about specimens in which monomer is removed by steeping in benzene for two hundreds forty hours.

The physical interpretation about the polymer's second-order transition seems not to have been completely established. Polyethylene exhibits such transitions at −68°C and 81°C. (m. p. 115°C) The temperature −68°C is considered to be apparently the brittle point, but 81°C interpreted as the premelting anomaly[19]. According to the structural hetero geneity of polymer a few of the transition temperatures can be observed, but anyhow these may be regarded to be based on the micro-Brownian motion in the regions of less orderliness. The singular temperature on the static yield stress of polycapramide at 70–80°C seems to correspond to the higher transition temperature 81°C of polyethylene. Another transition phenomenon on the dielectric constant of polyamide has been found at −40°C[20] corresponding to the lower transition point −68°C of polyethylene. The detailed discussion of the transition phenomenon shall be described in another report.

(3) From the results of these experiments the singlar temperatures are found to be at 70–80°C and 170°–180°C.

The transformation of the crystal structure of polycapramide has been observed to take place between 100–150°C by the X-ray diffraction method[9] or near 120°C by the specific volume method[12]. It is worth noting that the static yield stress exhibits no singularity at this temperature region: it shall be the underlying experimental foundation for considering the mechanism of cold-drawing[10,11]. (cf. Part III). The Young's modulus also exhibits no singularity at this temperature region[14]. For the present, one cannot simply assume the above described maximum of the elongation to rupture near 140°C as the crystal transformation temperature. Besides the singular point at 160°C on the static viscosity measurement[21], and the development of latent heat at 168–173°C on the thermal analysis[22] have been observed. The singularity relating to the transformation of the crystal structure shall be discussed on the subject of the effect of heat-treatment in Part III.

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

12) K. Kanamaru, I. Uematsu and K. Fukuta, *J. Soc. Polymer Sci. Japan*, 7, 4 (1950) (in Japanese).

13) E. Nagai, N. Aine and Y. Konishi, ibid., 8, 407 (1951) (in Japanese).

14) S. Ueno and K. Fuchino, *J. Soc. Text. Cell. Ind. Japan*, 7, 324 (1951) (in Japanese).

15) K. Ishikawa, ibid., 9, 614 (1953) (in Japanese).

16) K. Fijino, H. Kawai and I. Nakano, presented at the symposium on rheology in Tokyo, Dec. 6, 1951.

17) E. Nagai and N. Aine, *J. Soc. Text. Cell. Ind. Japan*, 8, 429 (1952) (in Japanese).

18) T. Arai and Y. Ito, presented at the 6th annual meeting of the Chemical Society of Japan in Kyoto, April 2, 1952.

19) R.F. Boyer and R.S. Spencer, *J. Appl. Phys.*, 15, 398 (1944).

20) T. Kawaguchi, unpublished.

21) K. Fuchino, A. Okada and N. Aine, *J. Soc. Polymer Sci. Japan*, 7, 19 (1950) (in Japanese).

22) Y. Kinoshita, unpublished.

The various mechanisms about the cause of the necking formation by elongation have been supposed[1-7]. Some of them[5,6,7], in which the necking is mainly attributed to the heat generated by stretching, seem to be questionable from the fact that the necking can occur even in the isothermal stretching. The two phase coexisting state of after-chlorinated polyvinylchloride has been treated by Müller with the thermodynamic equilibrium, the van der Waals' equation being applied[4], but on polycapramide such discussion seems to be unreasonable because of the irreversible nature of the process; the stretched specimen cannot shrink to the initial length even if it is heated over the softening temperature. The cause of the necking formation shall be described in the subsequent paper[10].

Conclusion

According to the program in which the comprehensive studies on the cold-drawing of the polymer were intended, the author obtained firstly some informations concerning the effects of temperature upon the drawing of polycapramide. The test material was quasi-statically elongated under the constant temperature in completely dried state, and then the corresponding stress was measured by means of the electrical resistance strain-meter. Polycapramide can not be smoothly elongated below 40°C, but can be smoothly done above 60°C: moreover the reproducibility becomes better above 60°C. The necking appears in course of stretching under the coexistence of unstretched and stretched phases, and during such state the stress (Wc) stays almost constant which is assumed temporarily as the yield stress. For the formation of the necking an additional stress (ΔWc) besides Wc is observed. Plotting the values of Wc, the region of elongation during the state of the two phases coexisting and the stress or the elongation to rupture against temperatures, two singular points are found at 70–80°C and 170–180°C. The former is considered to be seemingly the so-called polymer's second-order transition temperature and the latter to be the softening temperature. At the temperature region where the transformation of crystal is possible, no singularity is observed.

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