Surface Tension and Spinnability of Molten Poly-ε-capramide

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Surface tension of a liquid means the tension in the boundary between a liquid and a gas or the free energy of the surface. As surface tension tends to make the area of surface as small as possible, it is expected that the spinnability of a liquid would have relation with its surface tension and hence physical properties concerning its surface can be estimated. Surface tension of molten ε-caprolactam and poly-ε-capramide has been measured and their surface properties have been studied.

Experimental

Polymerization of ε-Caprolactam. — ε-Caprolactam was polymerized at 257°C for 15 hr. in the presence of 5% of ε-aminocaproic acid and 2, 1 or 0.5 mol. % of benzoic acid. The degree of polymerization of polymers was estimated from the solution viscosity in *m*-cresol at 25°C by the following equation[1].

$$\overline{P}=127[\eta]^{1.435} \qquad (1)$$

Measurement of Surface Tension. — Surface tension of molten ε-caprolactam or poly-ε-capramide was measured by the method of maximum bubble pressure[2]. When a capillary is immersed in a liquid and gas pressure is raised slowly, a bubble is formed at the tip of the capillary. If gas pressure is further raised, the bubble breaks away from the tip and the pressure decreases. Hence, the pressure passes through a maximum. When the main radius of curvature at the largest bubble is R and the depth of the tip of the capillary is h, the maximum pressure is given by the following equation.

$$P=2\gamma/R+Dgh \qquad (2)$$

where γ, g and D mean surface tension, gravity constant and density, respectively. If the radius of a capillary is narrow enough, R can be approximated to the capillary radius r.

The tip of the capillary of 0.02~0.05 cm. radius was immersed in the melted substance at 1 cm. in depth and nitrogen gas was introduced slowly at the pressure rate of 0.1 cm. H_2O/min. and the maximum bubble pressure was measured.

Measurement of Spinnability.—The apparatus is shown in Fig. 1. A glass stick of radius of 0.2 cm. was immersed in molten poly-ε-capramide at 0.5 cm. in depth and was pulled up at the constant rate. The clutch was cut off immediately at the break of the thread and the length was measured.

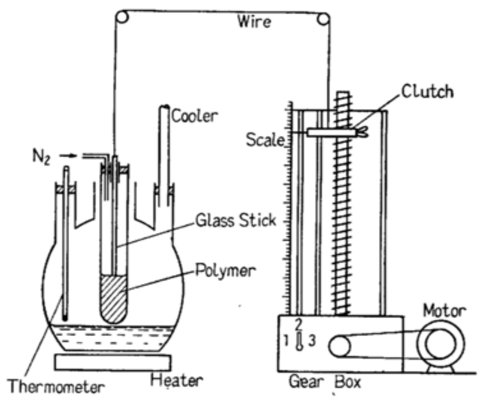

Fig. 1. Apparatus for the measurement of spinnability of poly-ε-capramide.

Results

Surface Tension of Molten ε-Caprolactam and Poly-ε-capramide. — Surface tension values of molten ε-caprolactam and *N*-acetyl-ε-aminocaproic acid to nitrogen gas at various temperatues are shown in Fig. 2.

Surface tension values of poly-ε-capramide of various polymerization degrees and at various temperatures are shown in Figs. 3 and 4. The poly-ε-capramide

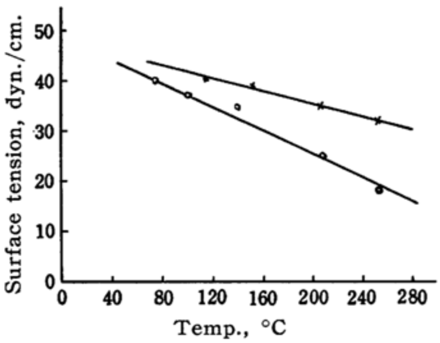

Fig. 2. Surface tension of ε-caprolactam and *N*-acetyl-ε-aminocaproic acid at various temperatures.
× *N*-Acetyl-ε-caprolactam
○ ε-Caprolactam

1) O. Fukumoto, *J. Polymer Sci.*, **22**, 263 (1956).
2) J. J. Bikerman, "Surface Tension", 2nd Ed., Academic Press, Inc., New York (1948), p. 17.

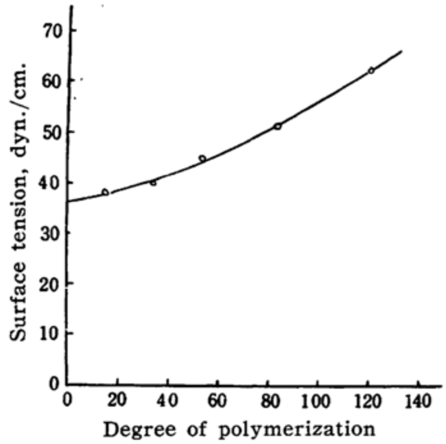

Fig. 3. Surface tension of poly-ε-capramide.

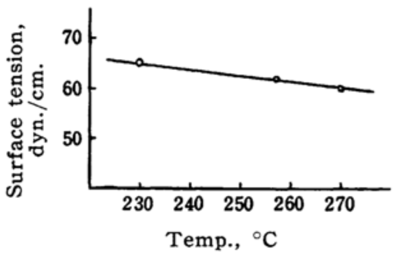

Fig. 4. Surface tension of poly-ε-capramide ($\overline{P}_n=120$) at various temperatures.

used was an equilibrium polymer containing about 10% of ε-caprolactam and its oligomers.

Thread Length of Poly-ε-capramide.—The thread lengths of poly-ε-capramide of various polymerization degrees at 230 or 257°C and at various pulling rates are shown in Fig. 5. The thread length of poly-ε-capramide ($\overline{P}=120$) at 257°C and at the pulling rate of 0.74 cm./sec. is proportional to the radius of a glass stick as shown in Fig. 6. Each polymer contained about 10% of ε-caprolactam and its oligomers.

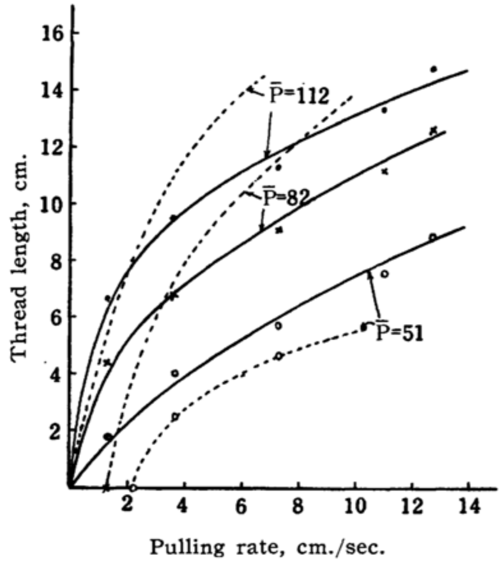

Fig. 5. Thread length at various pulling rates.
—— 230°C, ------ 257°C.

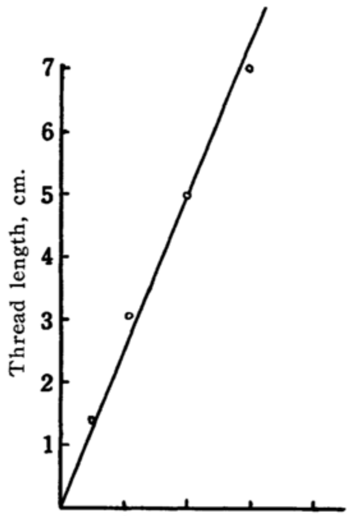

Fig. 6. The relation between thread length and radius of glass stick.
($\overline{P}=120$, $V=0.74$ cm./sec., $t=257$°C)

Discussion

Ramsay and Shields[3] found a linear relation between surface tension of a liquid and temperature as the following equation:

$$\gamma(M/D)^{2/3}=k(T_c-T-6) \qquad (3)$$

where γ is surface tension, M is molecular weight, D is density, T_c is critical temperature and k is a constant characteristic for a liquid.

The value of k for a normal liquid is usually about 2.12. The value of k and the critical temperature of ε-caprolactam is estimated to be 2.77 and 463°C, respectively.

Surface tension of poly-ε-capramide increases as the degree of polymerization increases. When the logarithms of surface-tension γ are plotted against the polymerization degree $\overline{P}$, a linear relation is

3) W. Ramsay and J. Shields, *Z. physik. Chem.*, **12**, 433 (1893).

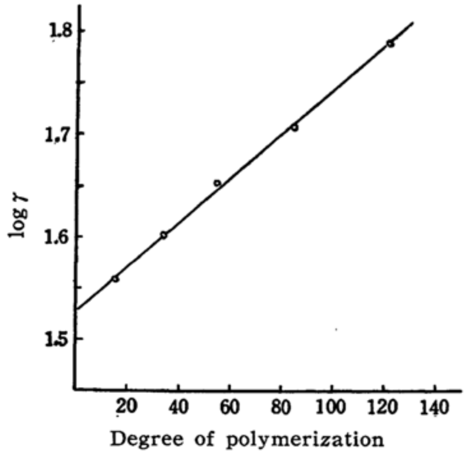

Fig. 7. Relation between log γ and $\bar{P}$.

obtained as shown in Fig. 7 and the following equation is obtained at 257°C.

$$\log \gamma = 0.0022\bar{P} + 1.53 \quad (5)$$

As the surface tension of poly-ε-capramide ($\bar{P}$=120) is nearly proportional to temperature from Fig. 4, the value of $d\gamma/dT$ is about −0.06 dyn./cm. deg. and that of *N*-acetyl-ε-aminocaproic acid is also −0.06 dyn./cm. deg. Therefore, the value of $d\gamma/dT$ of linear poly-ε-capramide is expected to be −0.06 dyn./cm. deg. independent of the polymerization degree, and the following equation is obtained, where t is temperature in degrees centigrade.

$$\gamma = 10^{(0.0022\bar{P}+1.53)} + 0.06(257-t) \quad (6)$$

Surface tension of ε-aminocaproic acid at 252°C is estimated from Eq. 6 to be about 34 dyn./cm. This value is not consistent with the surface tension value of ε-caprolactam (18 dyn./cm.), but is nearly approximated to that of *N*-acetyl-ε-aminocaproic acid (32 dyn./cm.). Therefore, it is expected that the surface tension of ε-aminocaproic acid is about 16 dyn./cm. greater than that of ε-caprolactam.

Since surface tension means intermolecular forces among molecules, this result suggests that the intermolecular force of ε-aminocaproic acid is greater than that of ε-caprolactam.

The total surface energy U is given[2] by

$$U = \gamma - T\partial\gamma/\partial T \quad (7)$$

The total surface energies of ε-caprolactam, *N*-acetyl-ε-aminocaproic acid and poly-ε-capramide are shown in Tables I and II.

The total surface energy of ε-aminocaproic acid is estimated to be about 66 erg/cm² from Table I and is 16 erg/cm² smaller than that of ε-caprolactam. This result is very interesting in relation to the exothermic reaction of the ε-caprolactam polymerization[4,5].

It is presumed that the increase in surface tension of poly-ε-capramide with the increase of its polymerization degree may be caused by the difference in thermal movement of macromolecules.

It is assumed that the thread of molten poly-ε-capramide may be broken at the point at which the surface energy reaches equilibrium with the friction energy of viscous liquid. Hirai[6] introduced the following equation in relation to surface tension γ and thread length L, and ascertained this equation for the thread length of glycerine.

$$L = R_0 V\mu/\gamma \quad (8)$$

TABLE I. TOTAL SURFACE ENERGY OF ε-CAPROLACTAM, *N*-ACETYL-ε-AMINOCAPROIC ACID AND POLY-ε-CAPRAMIDE

Sample	Temp. °C	γ(dyn./cm.)	$\partial\gamma/\partial T$	U(erg/cm²)
ε-Caprolactam	76	40	−0.12	82
	100	37	−0.12	82
	140	35	−0.12	85
	208	25	−0.12	83
	252	18	−0.12	81
Mean value	—	—	−0.12	82
N-Acetyl-ε-aminocaproic acid	116	40	−0.06	63
	152	39	−0.06	65
	205	35	−0.06	64
	252	32	−0.06	64
Mean value	—	—	−0.06	64
Poly-ε-capramide ($\bar{P}$=120)	230	65	−0.06	95
	257	62	−0.06	94
	270	60	−0.06	93
Mean value	—	—	−0.06	94

TABLE II. TOTAL SURFACE ENERGY OF POLY-ε-CAPRAMIDE

$\bar{P}$	γ(dyn./cm.)	U(erg/cm²)
15	38	70
34	40	72
54	45	77
84	51	83
121	62	94

4) S. M. Skuratov et al., *Kolloid Zhur.*, **14**, 185 (1952); *Faserforsch. u. Textiltech.*, **4**, 390 (1953).
5) H. Yumoto, This Bulletin, **28**, 94 (1955).
6) N. Hirai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1019 (1954); *Chem. Abstr.*, **46**, 9357*h* (1955).

In this equation R_0 is the radius of a glass stick, μ is the viscosity and V is the pulling rate. In case of poly-ε-capramide, L is not proportional to V as shown in Fig. 5. However, a linear relation is obtained by plotting $\log L$ against $\log V$, as shown in Fig. 8.

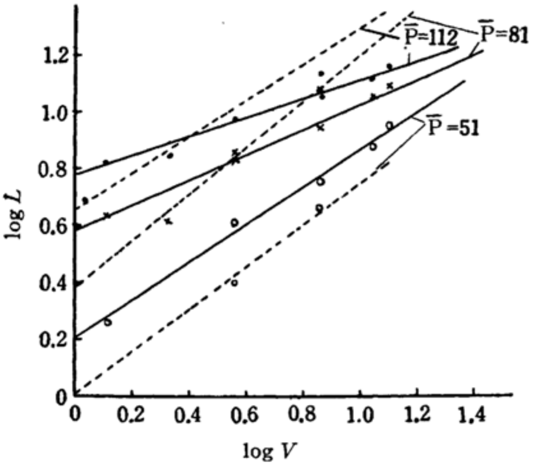

Fig. 8. Relation between $\log L$ and $\log V$.
—— 230°C, ------ 257°C.

Since L was proportional to the radius R_0 of a glass stick, the following equation is given:

$$L = kR_0V^a \quad (9)$$

The values of k and a at various polymerization degrees and temperatures are shown in Table III, where R_0 and V are given in cm. and cm./sec. units, respectively.

TABLE III. THE VALUES OF k AND a IN $L=kR_0V^a$

Temp., °C	$\bar{P}$	k	a
230	51	8	0.6
	82	16	0.4
	112	30	0.4
257	51	5	0.7
	82	12	0.7
	112	23	0.6

The value of a is almost invariable and its mean value is 0.5. Therefore, the thread length is proportional to the square root of the pulling rate.

The values of μ/γ, which are shown in Table IV, were estimated from the following equation derived by K. Hoshino[7].

$$\log \mu = -7 + 2300/T + 6.2([\eta]^{25°C}_{cresol})^{1/2} \quad (10)$$

7) K. Hoshino and S. Fujii, *Chem. High Polymers* (*Kobunshi Kagaku*), 1, 14 (1944); *Chem. Abstr.*, **44**, 5147*b* (1950).

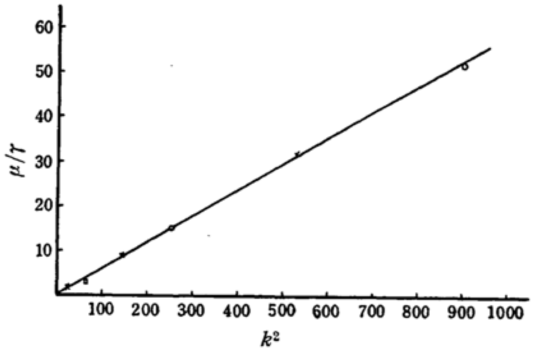

Fig. 9. The relation between k^2 and μ/γ.

TABLE IV. THE VALUE OF μ/γ

Temp. °C	$\bar{P}$	$[\eta]^{25°C}_{cresol}$	μ (poise)	μ/γ	k^2
230	51	0.53	123	3	64
	82	0.74	810	15	256
	112	0.92	3240	52	900
257	51	0.53	73	2	25
	82	0.74	480	9	144
	112	0.92	1900	32	529

When the value of k^2 is plotted against μ/γ, a linear relation is obtained as shown in Fig. 9 and the following equation is given.

$$\mu/\gamma = 0.059k^2 \quad (11)$$

From Eqs. 9 and 11, the thread length of poly-ε-capramide can be represented as follows:

$$L = 4.13R_0(\mu V/\gamma)^{1/2} \quad (12)$$

It can be estimated from the above-mentioned results that the thread length of molten poly-ε-capramide of $\bar{P}=100\sim120$ at 257°C may be approximately 12 cm., when the polymer is spun at the rate of 400 m./min. from a nozzle of 0.02 cm. radius, and the fiber must be cooled within this length to obtain a continuous filament.

Summary

Surface tension of molten ε-caprolactam and poly-ε-capramide has been measured by the method of maximum bubble pressure. Surface tension of ε-caprolactam at 252°C is 18 dyn./cm. and it is 16 dyn./cm. smaller than that of ε-aminocaproic acid (34 dyn./cm.). It is estimated from the Ramsay-Shields' equation that the critical temperature of ε-caprolactam is 463°C. Surface tension of poly-ε-capramide of the polymerization degree $\bar{P}$ is given by the following equation.

$$\gamma = 10^{(0.0022\bar{P}+1.53)} + 0.06(257-t)$$

The thread length of molten poly-ε-capramide has been measured by pulling up a glass stick and is represented by the following equation, where L (cm.) is thread length, R_0 (cm.) radius of a glass stick, μ (poise) melt viscosity, γ (dyn./cm.) surface tension and V (cm./sec.) pulling rate:

$$L=4.13R_0(\mu V/\gamma)^{1/2}$$

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