

2. Physical Constants

2 • 1 Average Molecular Weight

As a general rule, the molecular weight of a polymer is distributed in a certain range and in view of this, it is possible to obtain only the average value. Consequently, the average molecular weight gives the different result depending on the average method. For example, there are the weight average molecular weight (M_w), number average molecular weight (M_n) and the viscosity average molecular weight (M_v) and generally, the following relation exists among these,

$$M_n < M_v < M_w$$

The properties of polymers such as mechanical strength and melt viscosity can be inferred, as a general rule, from the average molecular weight and in view of this, it is first necessary to know the average molecular weight.

Determination of the molecular weight of Iupilon / NOVAREX is carried out by the viscosity method, as indicated below.

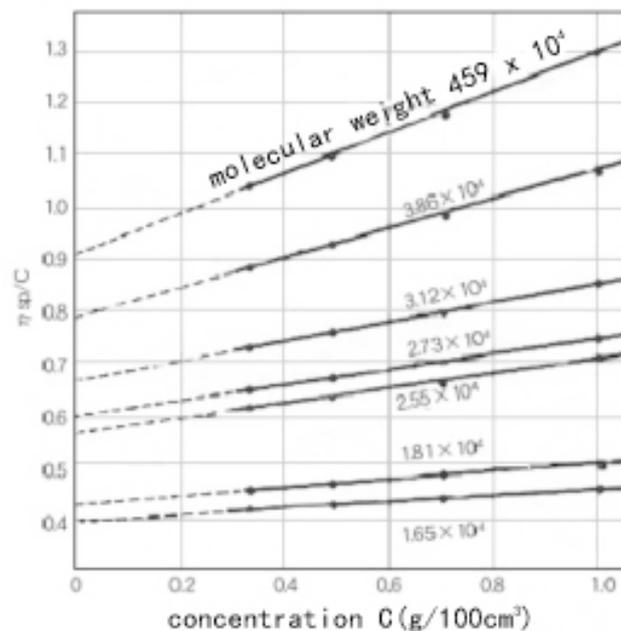


Fig. 2 • 1 – 1 Relation between concentration of Iupilon / NOVAREX and reduced viscosity
(Solvent is methylene chloride, temperature 20°C)

1g of the resin is weighed accurately and dissolved uniformly in 100 cm³ of methylene chloride and the specific viscosity η_{sp} is determined with an Oswald viscosimeter. Then the concentration is changed variously and specific viscosity determined similarly, and the concentration c versus η_{sp}/c is plotted on a graph and

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (2.1-1)$$

is obtained. $[\eta]$ is called the intrinsic viscosity and the relation between $[\eta]$ and average molecular weight was expressed by Schnell as follows:

$$[\eta] = 1.23 * 10^{-4} M^{0.83} \quad (2.1-2)$$

The η_{sp}/c and c relation of Iupilon / NOVAREX is shown in Fig. 2 · 1 – 1. These straight lines satisfy the relation of

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad (2.1-3)$$

k' does not depend on the molecular weight but is a constant of

$$k' = 0.45$$

Consequently, if η_{sp} at a certain concentration c is determined, it will be possible to obtain $[\eta]$ by calculation as k' is known. This method is called the one point determination method.

Fig. 2.1-2 shows Equation 2.1-2 when indicated graphically.

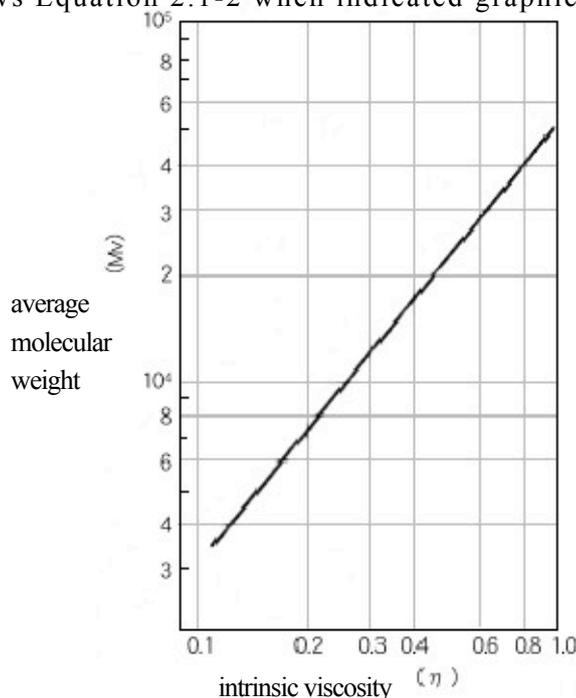


Fig. 2 · 1 – 2 Graph showing the intrinsic viscosity – average molecular weight relation

A lot of reports concerning the solution physical properties of polycarbonate have been presented.

The summary of the relation between $[\eta]$ and various molecular weights in these reports is indicated in Table 2-1-1.

Table 2 · 1—1 Related equation of $[\eta]$ and average molecular weight

Name	Temperature	Measuring method	Solvent	Related equation
H. Schnell	20°C	Osmometry	MC	$[\eta] = 1.23 \times 10^{-4} M_n^{0.83}$
C. V. Schulz	20°C	Ultracentrifugation	THF	$[\eta] = 3.99 \times 10^{-2} M_w^{0.70}$
	“	“	MC	$[\eta] = 1.11 \times 10^{-2} M_w^{0.82}$
	“	Light scattering method	MC	
General Electric	25°C	Light scattering method	Dioxane	$[\eta] = 5.54 \times 10^{-4} M_w^{0.67}$
S. H. Merrill		Ebulliometry	Chlorobenzene	$[\eta] = 5.7 \times 10^{-45} M_n^{1.01}$
A. Chirico	20°C	Light scattering method	Chloroform	$[\eta] = 0.277 \times M_w^{0.5}$
Kouda		Freezing point depression method	Dioxane	$[\eta] = 1.33 \times 10^{-4} M_n^{0.96}$
Teramachi	20°C	Light scattering method	Dioxane	$[\eta] = 9.15 \times 10^{-4} M_w^{0.60}$
	“	“	THF	$[\eta] = 1.0 \times 10^{-1} M_w^{0.57}$
	“	Osmometry	“	$[\eta] = 2.3 \times 10^{-2} M_w^{0.76}$
G. Sitaramaiah	25°C	Light scattering method	EC	$[\eta] = 2.04 \times 10^{-4} M_w^{0.76}$
	“	“	TCE	$[\eta] = 1.34 \times 10^{-4} M_w^{0.82}$
	“	“	THF	$[\eta] = 3.89 \times 10^{-4} M_w^{0.70}$
	“	“	Chloroform	$[\eta] = 1.20 \times 10^{-4} M_w^{0.82}$

Notes MC : Methylene chloride,
EC : Ethylene chloride,

THF : Tetrahydrofuran
TCE : Tetrachloroethane

2 · 2 Molecular Weight Distribution

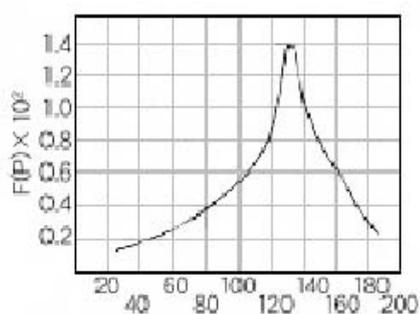
After the average molecular weight has been obtained, it is next important to know the average value of its distribution. The characteristics of the resin differ considerably even if the average molecular weight is the same, depending on its distribution.

There are many methods for determining molecular weight distribution but all of these are based on the principle of fractionating according to each molecular weight (although actually there is a range) by utilizing the difference in solubility, sedimentation velocity, absorbability etc. and obtaining the weight % of each.

The result when Iupilon film (molecular weight 3.2×10^4 , film thickness 0.08mm) is dissolved gradually in a mixed solvent of acetone-methylene chloride and fractionated is shown in Fig. 2.2-1.

The degree of polymerization in the figure was obtained by dividing the molecular weight by the molecular weight of the repeating unit of polymerization (= 254).

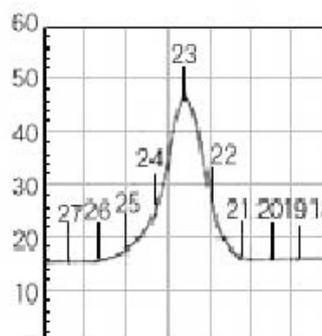
Also, the result of measuring the molecular weight distribution of Iupilon by the GPC method was shown in Fig. 2.2-2.



Degree of polymerization P

Fig. 2 · 2—1

Molecular weight distribution of



Equipment Waters. ALC/GPC301 Type

Sample Iupilon 2.5mg Injecting time 120sec
 Concentration 1/8w/v% Column temperature 20
 Solvent THF Column 10⁵, 10⁴, 10³, 10², nm
 Flow rate 10cm³/min STYRAGEN

Fig. 2 · 2—2

Molecular weight distribution of Iupilon by GPC

It can be seen from this figure that the molecular weight distribution of Iupilon is very symmetrical, and moreover the width is narrow, $U(M_w / M_n - 1)$ value is in the range of 1~2.

2 · 3 Specific Gravity and Crystallinity

The specific gravity is as shown in Table 2.3-1.

Table 2 · 3—1

300°C	1. 06	Injection molded product	1. 19
250°C	1. 10	Pellet	1. 19
Complete crystal	1. 30	Compression molded product	1. 19
Casting film	1. 22		

If polycarbonate is heat-treated at temperature below T_g (glass transition point), hardening phenomenon is observed, but as shown in Fig. 2.3-3, almost no change is observed in the X-ray diffraction, it is thought that crystallization does not take place. However, various measurements such as electronic microscope, differential thermal analysis, specific gravity measurement etc. are done recently, and the area where the packing is highly concentrated at least locally (it is thought that there is a considerably high arrangement though the growth to crystal is not observed) is indicated.

The change in density by heat treatment is shown in Fig. 2.3-1.

In addition, the change in specific gravity when plasticizer is added to Iupilon is shown in Fig. 2.3-2.

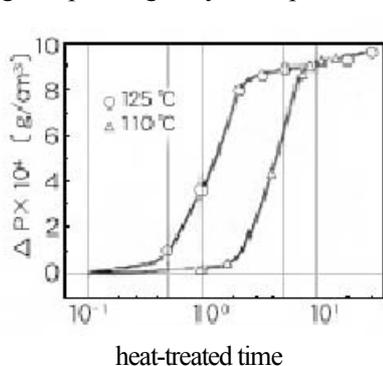


Fig. 2 · 3—1 Change in density by heat treatment

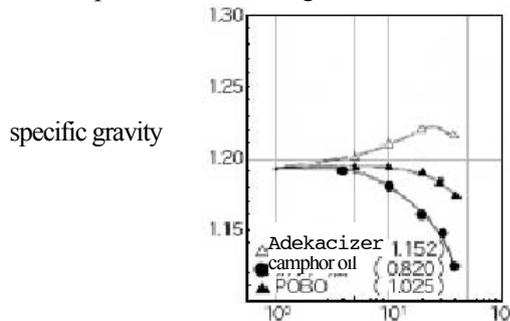


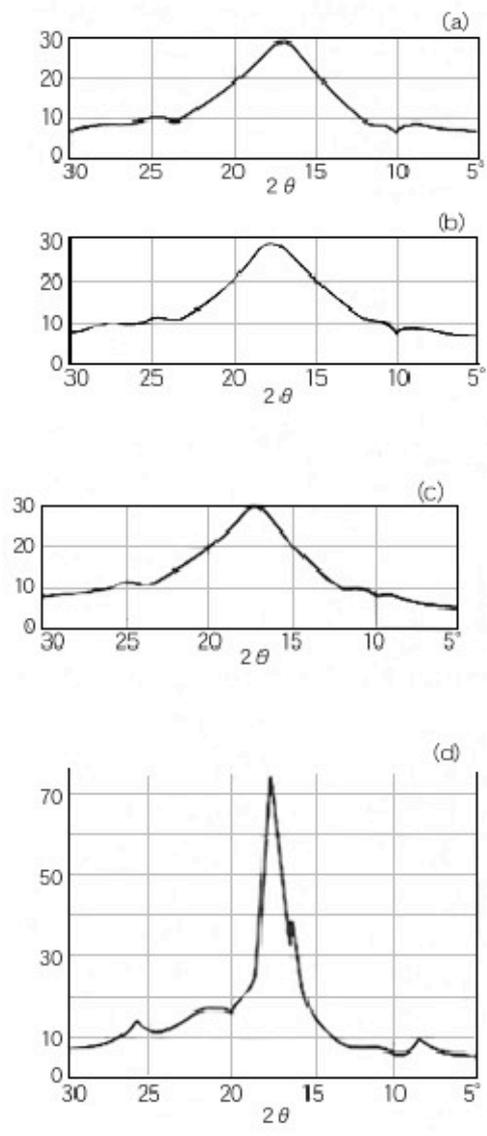
Fig. 2 · 3—2 Change in specific gravity by adding plasticizer

A comparison with other commercial resins is shown in Table 2 · 3—2.

Table 2 · 3—2 Specific gravity of various polymers

Polymer	Average specific gravity	Polymer	Average specific gravity
Teflon	2. 2	High impact strength polystyrene (HIPS)	1. 06
Chlorofluoroethylene	2. 1	Polystyrene	1. 06
Polyacetal	1. 4	Polyphenylene ether (PPE)	1. 06
Rubber degenerated vinyl chloride	1. 35	High impact strength ABS	1. 05
Cellulose acetate	1. 3	ABS	1. 05
Polysulphone	1. 24	High density polyethylene	0. 95
Cellulose butyrate	1. 2	Medium density polyethylene	0. 93
Cellulose propionate	1. 2	Low density polyethylene	0. 92
Polycarbonate	1. 2	Polypropylene	0. 90
Nylon	1. 14	Glass fiber reinforced nylon	1. 33
Ethyl cellulose	1. 13	Glass fiber reinforced polystyrene	1. 3
Acryl (PMMA)	1. 12		

In general, the crystallization of Iupilon / NOVAREX does not take place easily. As shown in Fig.2 · 3—3, the temperature for crystallization is around 190°C but the induced time of 130-170 hours for crystallization is necessary even at this temperature, and the achievement of crystallinity is about 30%. This relation is indicated in Fig. 2 · 3—4 and it is clear that there is an influence of the molecular weight. In addition, the relation between the treatment temperature and the crystallinity is shown in Fig. 2 · 3—5.



- a) Molten state at 280°C c) Heat treated 20 days at 130°C
 b) Glass state at 20°C d) Heat treated 8 days at 190°C

Fig. 2 · 3—3 Strength X-ray diffraction of Lupilon

When a suitable organic substance is added to Iupilon, the induced time for crystallization is shortened.

As shown in Fig. 2.3-6, the induced time for crystallization of a sample containing 10% of diphenyl ether is about 5 hours. However, when the molecular weight is 5.0×10^4 or more, the crystal is not observed at 190°C , 20hrs. In addition, when a small amount of nucleic agent is added to this, the crystallization takes place rapidly as shown in Fig. 2.3-7. The tendency to such a crystallization decreases rapidly when the molecular weight is $M_v=4.0 \times 10^4$ or more due to the influence of the molecular weight as shown in Fig. 2.3-8.

A similar crystallization phenomenon is also observed by the sedimentation from the dilute solution and the immersion to the swelling agent etc. for example, when making casting film excluding heat treatment. The degree of crystallization when Iupilon of various molecular weights is immersed in toluene is shown in Fig. 2.3-9. The degree of crystallization which can be reached does not change greatly when the molecular weight is $M_v=4.0 \times 10^4$ or more. The ketone, aldehyde, ether, and ester play the role as swelling agents.

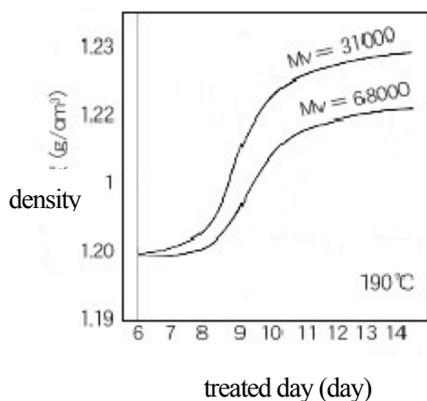


Fig. 2 · 3—4 Change in density by heat treatment

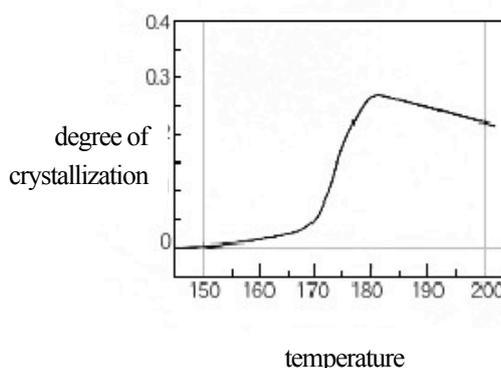


Fig. 2 · 3—5 Relation between temperature and degree of crystallization

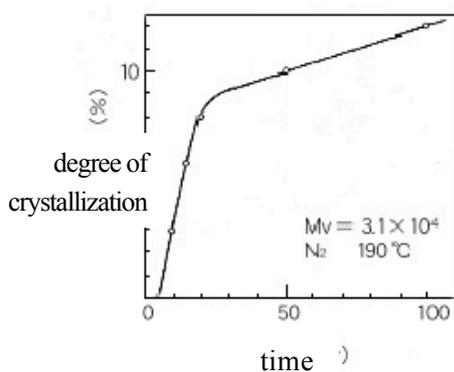


Fig. 2 · 3—6 Degree of crystallization of sample containing diphenyl ether

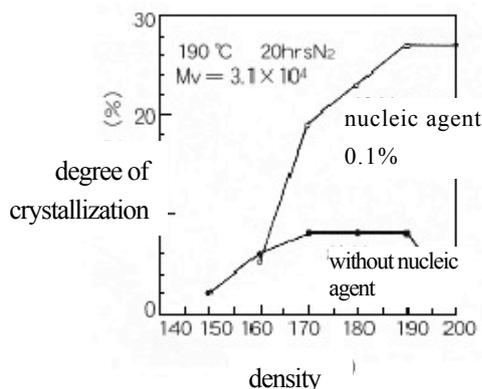


Fig. 2 · 3—7 Relation between temperature and degree of crystallization of sample containing diphenyl ether

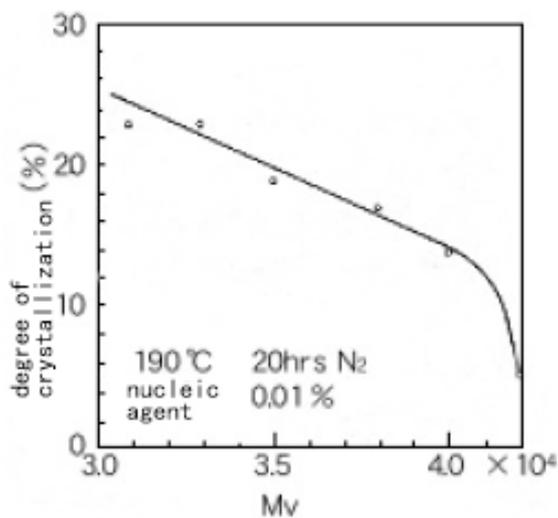


Fig. 2 · 3—8 Influence of molecular weight on degree of crystallization of sample containing diphenyl ether

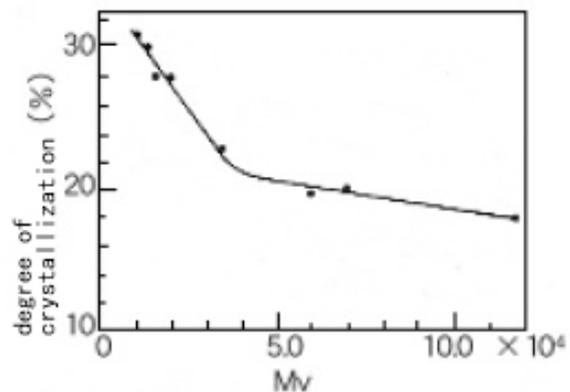


Fig. 2 · 3—9 Saturated degree of crystallization of sample immersed in toluene

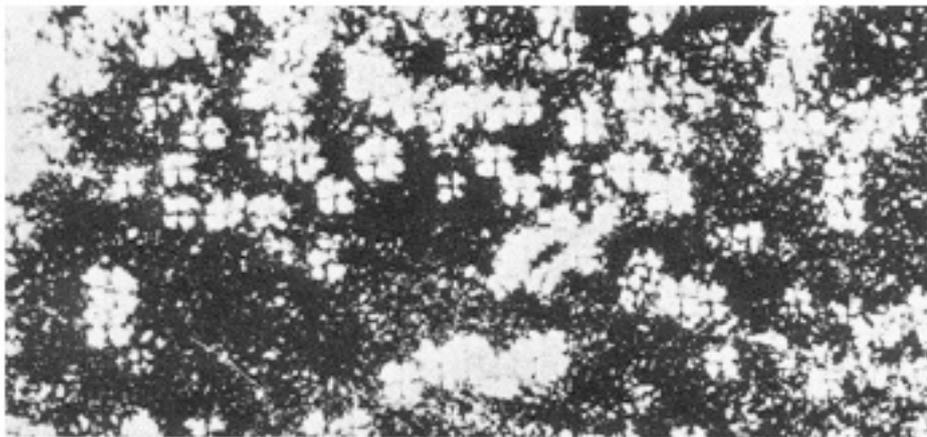


Fig. 2 · 3—10 Spherical crystals of Iupilon / NOVAREX (Polarizing microscope photograph)

In almost all cases, the crystals of Iupilon / NOVAREX are spherical as shown in Fig. 2.3-10. Iupilon / NOVAREX molding material may be actually considered as being amorphous and it can be considered that there is almost no change in performance by crystallization in the molding process and in the environment in which it is used.

2 • 4 Melt Viscosity

Iupilon / NOVAREX has a higher melt viscosity than other resins.

Also, the melt viscosity is influenced by pressure and temperature but in case of Iupilon/NOVAREX the effect of temperature is larger than that of pressure.

The results obtained when determined by the Koka type flow tester are shown in Fig. 2 • 4–1, 2 • 4–2, 2 • 4–3 and 2 • 4–4.

The slope of the straight line obtained from Fig. 2 • 4–2 is -0.2 for Iupilon / NOVAREX and this is very small when compared with acetyloid, polystyrene and polyethylene. That is, the melt viscosity of Iupilon / NOVAREX does not receive almost any effect of pressure. Consequently, it is possible to treat Iupilon / NOVAREX practically as a Newton liquid at a high temperature.

When fluid activation energy is obtained from the slope of the straight lines of Fig. 2 • 4–4, this is 26-29 kcal/mol in case of Iupilon / NOVAREX, which is the next largest after the 47 kcal/mol of acetyloid. It can therefore be seen that the decrease in melt viscosity with rise in temperature is very large.

When the relation between the molecular weight of Iupilon / NOVAREX and melt viscosity is consolidated with Flory's relative equation, it becomes as shown in Fig. 2 • 4–5, and when the constant of Flory's relative equation is obtained from the slope of the straight line and the ordinate intercept, the following relative equation is obtained.

$$\log Q = 2.39 - 0.023M^{1/2}$$

Also, when the relation between the molecular weight of Iupilon / NOVAREX and melt viscosity is consolidated with Fox's relative equation, $\log \eta = a \log Mw - B$, it becomes as shown in Table. 2 • 4–1.

Table 2 • 4–1 Relation between melt viscosity and molecular weight

Name	Sample	Determination conditions		α	B
		τ	Temperature		
J. Bojarski	Separated sample U=1.2~1.3	0	280°C	5.52	20.6
		10^4	“	5.15	19.0
		10^5	“	4.46	16.0
		2×10^5	“	4.27	15.2
J. Bojarski	Unseparated	0	280°C	3.02	9.6
G. F. Baumann	Unseparated	2.6×10^5	302°C	3.23	10.73
Mitsubishi Gas Chemical Company, Inc.	Unseparated	40×10^5	280°C	4.5	15.9

τ unit: dPa (dyne/cm²)

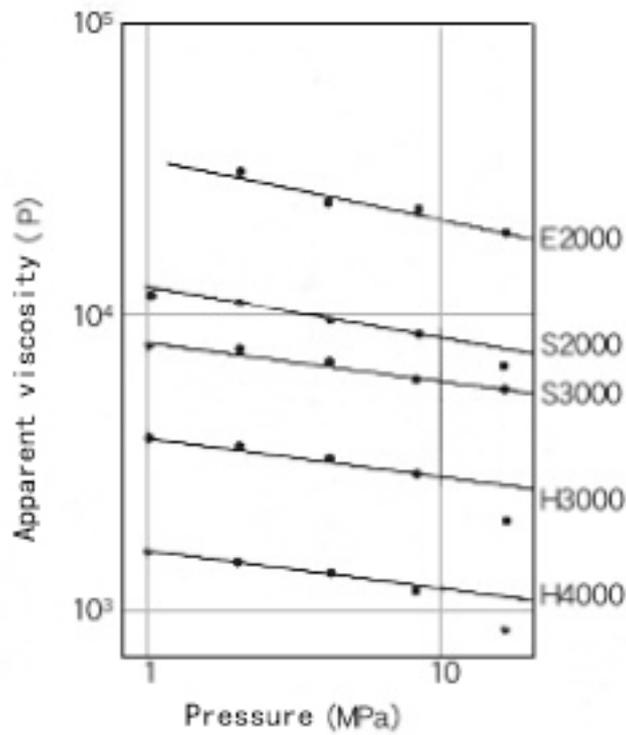


Fig. 2 · 4—1 Relation between melt viscosity and pressure of Lupil (Koka type flow tester, temperature 280°C, nozzle ϕ 1×10mmL)

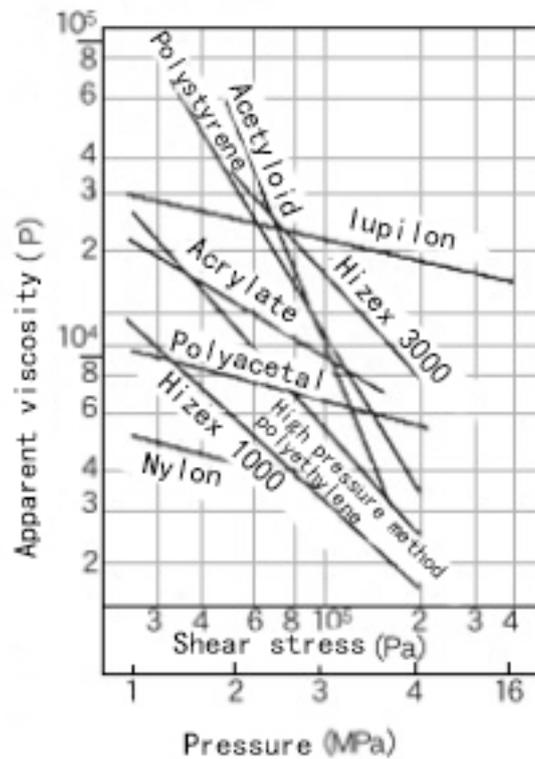


Fig. 2 · 4—2 Relation between melt viscosity and pressure of various resins (Koka type flow tester, nozzle ϕ 1×10mmL, temperature 280°C for Lupilon, 180°C for acetyloid, 230°C for nylon and acrylate, and 200°C for all others)

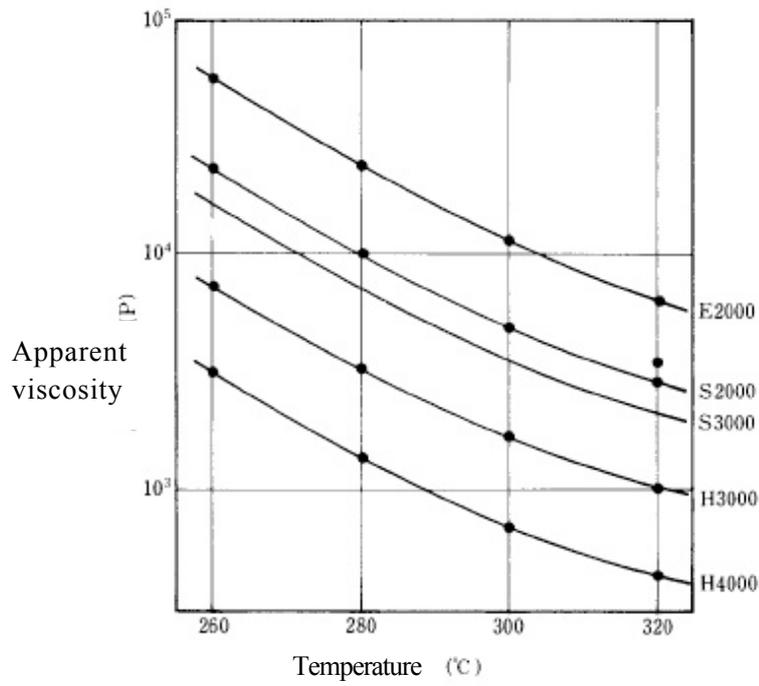


Fig. 2 · 4-3 Relation between melt viscosity and temperature of Iupilon (Koka type flow tester, pressure 3.9 MPa , nozzle $\phi 1 \times 10 \text{mmL}$)

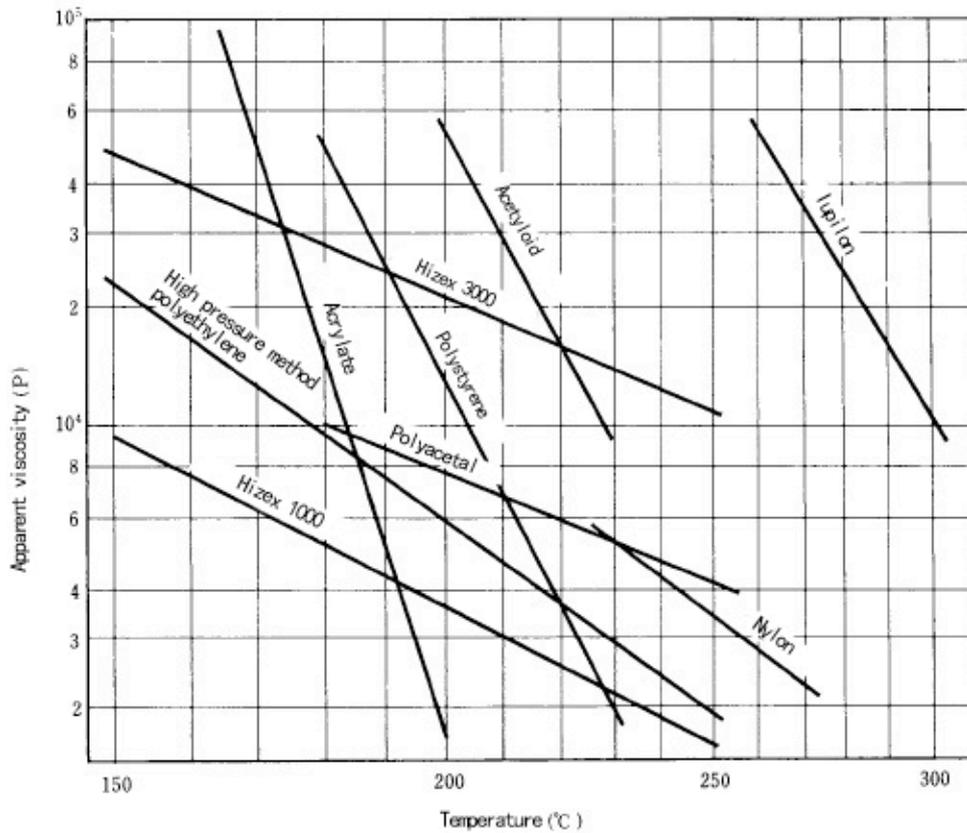


Fig. 2 · 4-4 Relation between melt viscosity and temperature of various resins (Koka type flow tester, nozzle $\phi 1 \times 10 \text{mmL}$, pressure 0.98MPa for nylon, 3.9Mpa for others)

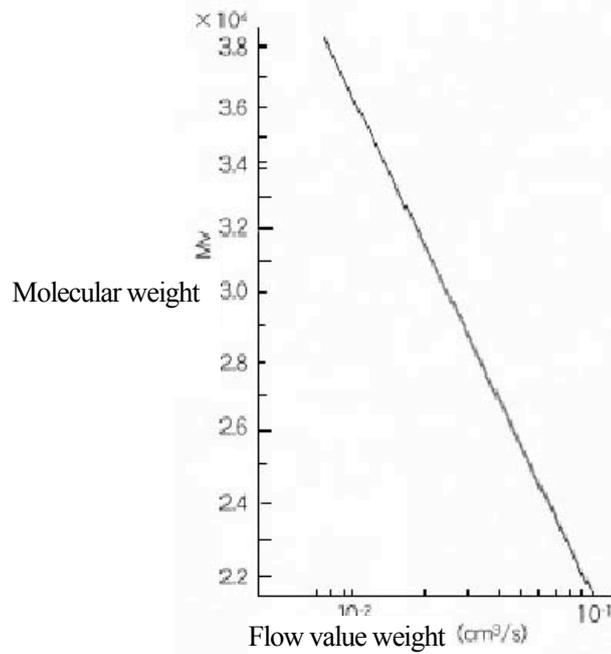


Fig. 2 · 4—5 Relation between molecular weight and flow value of Iupilon / NOVAREX (Koka type flow tester, nozzle ϕ 1×10mmL, pressure 15.7 MPa [160kgf/cm², temp. 280°C])

“Flow value” is used as a measure for expressing the moldability of Iupilon / NOVAREX and this “flow value” is measured with Koka type flow tester. The determination conditions are 280°C, 15.7 Mpa (160kgf/cm²) and nozzle ϕ 1×10mmL. The determination value is shown in cm³/s. The melt viscosity is calculated from this value by the conventional method and this “flow value” is sufficient as a practical comparison value. As the method for indicating “flow value”, this is indicated as 3.0 when the determination value is 3.0 x 10⁻²cm³/s.

	Unit	Conditions	E—2000 7027A	S2000 7025A	S3000 7022A
Melt volume index	cm ³ /10min	ISO—1133 300°C 1.2kg	4~6	9~12	12~19
Flow value (Q value)	10 ⁻² · cm ³ /s	280°C 15.7MPa (160 kgf/cm ²)	0.5~3	3~7	5~12

Note : Representative values of measuring values based on test method.