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WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

RELATIONSHIP BETWEEN MOLECULAR CHARACTERISTICS AND PHYSICAL PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENES

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Relationship between molecular characteristics and physical properties of linear low density polyethylenes

Abstract - The relationship between molecular characteristics and physical properties of linear low density polyethylenes (LLDPE) was investigated in comparison with low density polyethylenes produced by high pressure processes (HP-LDPE). Differences in molecular characteristics, such as branching structure, spherulite structure and solution properties between LLDPE and HP-LDPE were made clear. A comparison of both polymer films in an impact strength and heat resistance was made. The higher Vicat softening point of LLDPE compared with HP-LDPE could be attributed to the thicker lamella of LLDPE than that of HP-LDPE because of the difference of the branching structures. Some comparisons of LLDPE with HP-LDPE on rheological properties and processability parameters were tried. There are apparent differences between both polymers in the dynamic viscoelastic properties and the extensional viscosity development. The melt flow rate value, which is widely used as a processability parameter, of LLDPE is more than one decade lower than that of HP-LDPE at a given molecular weight because of the difference of the molecular dimension. The melt tension, which is another processability parameter widely used, of LLDPE is lower than that of HP-LDPE at a given melt flow rate. The melt tension data also suggest that the melt tensional properties and processability are mostly governed by a nonlinear extentional properties of the melts in a long time scale.

INTRODUCTION

The manufacturing method of low density polyethylenes by radical polymerization under conditions of high temperature and pressure (200 ∿ 280°C, 1000 ∿ 3000 Kg/cm^2) was found by Imperial Chemical Industries in 1933. Later on, a new method for manufacturing low density polyethylenes by copolymerization of ethylene and α-olefins with Ziegler catalysts (Ti-catalyst systems) or Phillips catalysts (Cr-catalyst systems) under moderate conditions of temperature and pressure (60 ∿ 200°C, 5 ∿ 200Kg/cm^2) was developed. This method for manufacturing linear low density polyethylenes (LLDPE) by copolymerization of ethylene and α-olefins has suddenly appeared before the footlights since several grades of LLDPE by gas-phase polymerization were commercialized by Union Carbide Corporation in 1977. However, Du Pont Canada and Mitsui Petrochemical Industries had already succeeded in the commercialization of the same type of polymers by solution polymerization processes which were developed by themselves in 1960 and 1972, respectively. Especially, Mitsui Petrochemical Industries has been manufacturing LLDPE by the solution polymerization process having no section for removing catalyst residue by applying its own developed Ti-catalyst system of high activity.

Although LLDPE thus developed has been replacing high pressure low density polyethylenes (HP-LDPE) in various fields of the market, quite a few academic reports on structures and/or properties of LLDPE commercially manufactured have been published (ref. 1,2). The Sub-Group meeting in Japan of IUPAC Working Party IV-2-1 has worked to investigate the relationship between molecular characteristics and physical properties of commercially manufactured LLDPE in comparison with HP-LDPE and high density polyethylenes (HDPE). This report describes the result of the experiments and discussions which have been made by the Sub-Group for these two years. Molecular characteristics of LLDPE are given in the third section. In the forth and fifth sections, mechanical and thermal properties and rheological properties of LLDPE are discussed in relation to molecular characteristics, respectively. We believe that these studies incorporated herein would be very useful for the accurate understanding of the qualities of LLDPE which will be more prevalent in the future.

MATERIALS

Linear low density polyethylenes (LLDPE) employed in this report are commercially available

ones which were manufactured by solution polymerization processes of Mitsui Petrochemical
(Neo-zex, Ultzex) and Dow Chemical (Dowlex). Other types of polyethylenes (HDPE, HP-LDPE),
polybutene-1 and polyoctene-1 were also used for comparisons. These polymers were
commercially manufactured except polyoctene-1 which was prepared in the laboratory scale.
The weight-average molecular weights M_w, the molecular weight distributions M_w/M_n, the
densities and the manufactureres (trade names) are given in Table 1.

TABLE 1. Molecular characteristics of polymers employed

Resin	M_w x 10^4	M_w/M_n	d g/cm^3	Resin manufacturer (Trade name)
HDPE	5 ∿ 15	5 ∿ 7	0.955 ∿ 0.968	Mitsui Petrochemical (Hi-zex)
LLDPE	5 ∿ 20	3 ∿ 7	0.920 ∿ 0.945	Mitsui Petrochemical (Neo-zex, Ultzex) Dow Chemical (Dowlex)
HP-LDPE	18 ∿ 31	6 ∿ 10	0.920 ∿ 0.929	Mitsui Polychemical (Mirason)
Polybutene-1	100	7	0.915	Shell Chemical (Shell Polybuthylene)
Polyoctene-1	10	6	——	(experimental resin)

The Sub-Group IV-2-1-2 (Eastern Europe, Chairman: Dr.Stejskal) kindly cooperated in deter-
mining M_w of our LLDPE samples (3 samples) by a light scattering method. Unfortunately,
there was difference between their data measured in diphenylmethane solutions and ours in
1-chloronaphthalene. Accordingly, we could not adopt their data in this report to our
regret.

CHARACTERISTIC STRUCTURES AND PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENES

LLDPE is different from HP-LDPE in the molecular structure, such as branching structure,
molecular weight distribution and chemical composition distribution, and also in higher
order structure, such as crystalline/amorphous structure and spherulite structure. In this
section, the characteristic structures and the solution properties of LLDPE are described in
comparision with HP-LDPE and a few other polyolefins.

Branching structure and density
HP-LDPE manufactured by conventional radical polymerization has long-chain branchings main-
ly. On the other hand, LLDPE is a linear polymer with short-chain branchings originated
from α-olefin used as a comonomer. Figure 1 shows that the density of LLDPE decreases as
the comonomer content in a chain increases. The density of ethylene/4-methylpentene-1
copolymer decreases more rapidly with the comonomer content than ethylene/butene-1 copolymer
does. The reason would be that 4-methylpentene-1 is not incorporated into the cystal
lattice, while butene-1 is easily incorporated into the crystal lattice (ref. 3).
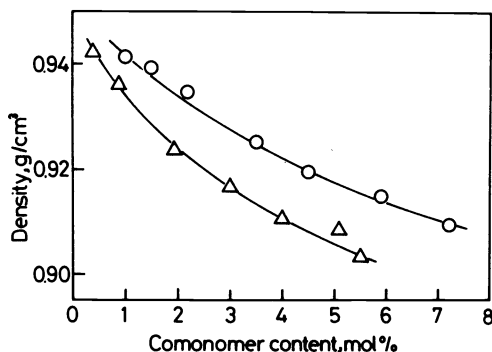

Fig. 1. Density vs. comonomer content correlation for LLDPE: Open
circles and triangles denote for the values for ethylene/butene-1
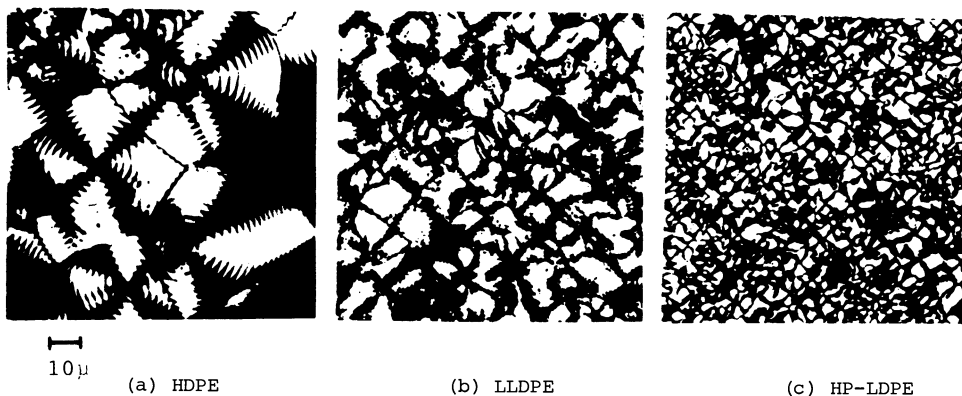copolymers and ethylene/4-methylpentene-1 copolymers, respectively.

10μ   (a) HDPE   (b) LLDPE   (c) HP-LDPE

Fig. 2. Spherulite structures of polyethylenes: (a);d=0.968, (b);d=0.920 (c);d=0.929

Spherulite structure

Figure 2 shows spherulite structures of HDPE, LLDPE and HP-LDPE. The differences among them are fairly clear. HDPE has the well-grown spherulite structure. On the other hand, LLDPE has the small and indistinct spherulite structure because the short-chain branchings hinder the crystallization and the formation of spherulite. This is more remarkable in the case of HP-LDPE having long-chain branchings. These facts shows that the shape and size of spherulites of the polyethylenes are strongly dependent on the length and frequency of branching in the molecules.

Solution property

The whole polymers of HDPE, LLDPE and HP-LDPE were fractionated by a column fractionation method. Then, the weight-average molecular weights M_W of the fractions were measured by a light scattering method in 1-chloronaphthalene at 135°C. The intrinsic viscosities [η] were measured in decalin at 135°C. Relations between M_W and [η] for different series of polyethylenes are shown in Fig. 3. [η] of LLDPE is almost equal to that of HDPE at a same M_W, but higher than that of HP-LDPE. This result well corresponds to that obtained through the comparison between HDPE and HP-LDPE by Trementozzi (ref. 4). The result shown in Fig. 3 suggests that the molecular dimension in decalin solution for HP-LDPE having long-chain branchings is smaller than that for linear polyethylenes of the same M_W. In the case of HP-LDPE, the higher the molecular weight becomes, the more easily the long-chain branchings are formed because of the increasing opportunity of chain transfer from polymer radicals to polymer chains during polymerization. This is the reason why the slope of [η] vs. M_W curve for HP-LDPE decreases in the high M_W region as is seen in Fig. 3 : Molecular dimension of polymer chain having many long brnchings is much smaller than that of linear counterpart with the same molecular weight. The schematic representations of LLDPE and HP-LDPE chains in good solvent are illustrated in Fig. 4.
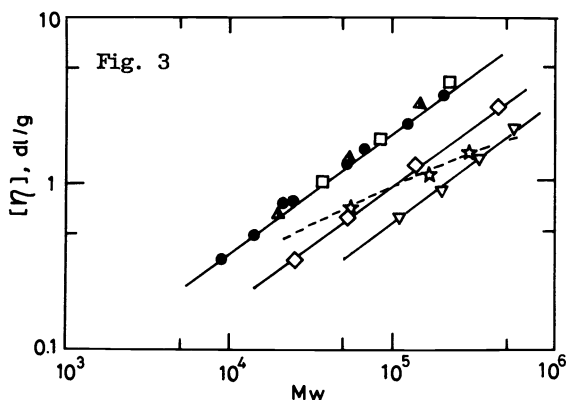

LLDPE   HP-LDPE

Fig. 4

Fig. 3. Intrinsic viscosity [η] vs. weight-average molecular weight M_W correlation for fractionated polymers: □;HDPE(d=0.960), ●;ethylene/ butene-1 copolymer(d=0.935), ▲;ethylene/octene-1 copolymer(d=0.929),☆; HP-LDPE(d=0.929), ◇;polybutene-1, ▽;polyoctene-1. M_W of fractions were measured in 1-chloronaphthalene at 135°C and [η] of fractions were measured in decalin at 135°C.
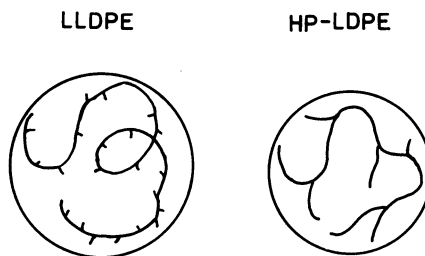
Fig. 4. Schematic representations of LLDPE and HP-LDPE chains in good solvent.

Figure 3 also shows the relations between M_w and $[\eta]$ for fractions of polybutene-1 and polyoctene-1, in which ethyl and hexyl branchings are alternately connected to carbons of main chains, respectively. Two straight lines drawn on the $[\eta]$ date for both polymers are parallel to those for HDPE and LLDPE. $[\eta]$ values for the series of linear polyolefins seem to depend on the length of main chain. In Fig. 5, $[\eta]$ values of the four series of poly-olefins (HDPE, LLDPE, polybutene-1 and polyoctene-1) are plotted against the weight-average molecular weights of main chains M_w'. For polybutene-1 and polyoctene-1, $M_w'=(1/2)M_w$ and $=(1/4)M_w$, respectively. It is apparent from this figure that linear polyolefins with the same main chain length have approximately the same molecular dimension in good solvent, regardless of length of short-chain branchings. Taking a good look at the figure, the data points for polybutene-1 and polyoctene-1 are located a little lower than those for the linear polyethylenes. The reasonable explanation for this difference has not come out yet.
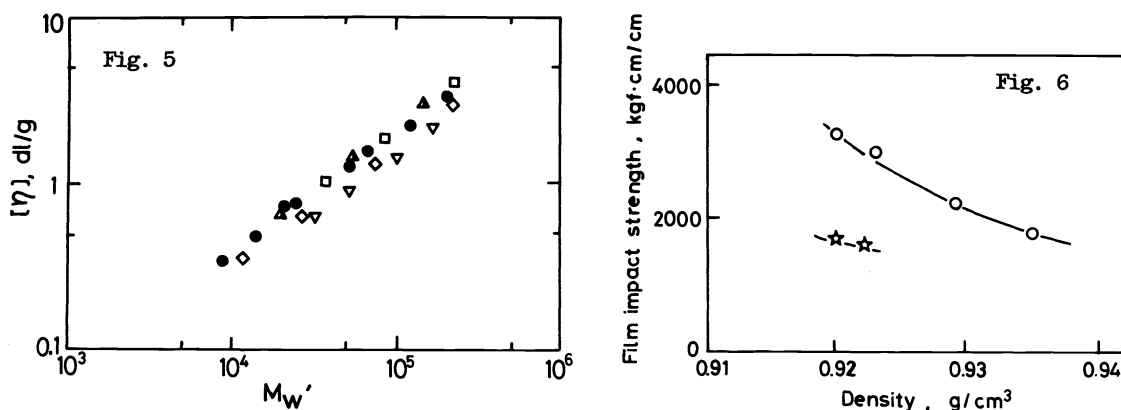

Fig. 5. Intrinsic viscosity $[\eta]$ vs. weight-average molecular weight of main chain M_w' correlation for fractionated polymers. Symbols are the same as in Fig. 3.

Fig. 6. Impact strength vs. density correlation for LLDPE and HP-LDPE films: Open circles and stars denote the values for LLDPE(MFR=2~3) and HP-LDPE(MFR=2~3), respectively. Tubular films were tested at room temperature.

MECHANICAL AND THERMAL PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENE FILMS

As was seen in the preceeding section, molecular characteristics of LLDPE are different from those of HP-LDPE in spite of similar density of both polyethylenes. Accordingly, it is very important that the physical properties of both polymers of the same density are compared with each other and differences are made clear. In this section, such a comparision of both polymer films in an impact strength and heat resistance have been made.

Impact strength
One of the physical properties of LLDPE film superior to that of HP-LDPE film is the extremely high impact strength. The film impact strengths of LLDPE and HP-LDPE measured by the film impact tester (Toyoseiki Co.) at room temperature are plotted against the density in Fig. 6. Tested samples are 30μm thick and of similar melt flow rate (MFR). As is shown in this figure, LLDPE film gives about two times higher impact strength than HP-LDPE film at the same density.

As a major factor to improve the impact strength, the existence of impact relieving portion is conceivable. The storage modulus E' and loss modulus E" of two LLDPEs and HP-LDPE were measured by Rheovibron-II at 110Hz. No difference in the viscoelastic properties was recognized among them as shown in Fig. 7. Then, elctron microscopic investigation of the fracture portions of polyethylene films at room temperature revealed that ductile fractures developed mainly. In fact, Fig. 8 which exhibits the result of high speed tensile test (tensile speed is 1000mm/min), clearly shows the much higher tensile strength and elongation for LLDPE film than for HP-LDPE film.

Considering this experimental results from the view point of higher order structure, there presumably exist more tie molecules connecting the lamella of LLDPE having long main chain than HP-LDPE having short main chain due to long-chain branchings. Consequently, LLDPE shows the higher toughness (the total energy absorbed to the break point) and the higher impact strength than HP-LDPE.
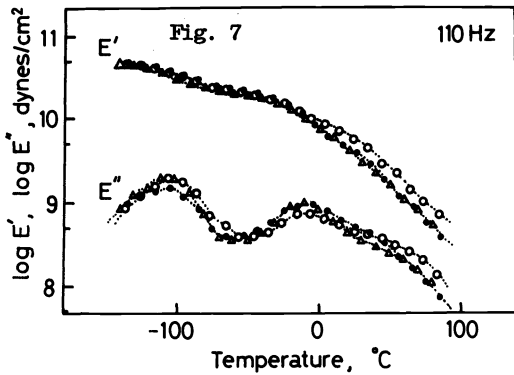
Fig. 7.   Storage modulus (E') and loss modulus (E") of polyethylenes as a function of temperature at 110Hz. Open circles, triangles and closed circles denote the values for ethylene/butene-1 copolymer(d=0.935, MFR= 1.6), ethylene/4-methylpentene-1 copolymer(d=0.920, MFR=2.1) and HP-LDPE(d=0.921, MFR=2.9), respectively. E' and E" were measured by Rheovibron-II.
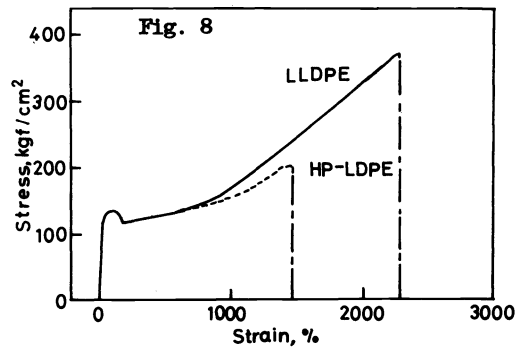
Fig. 8.   Stress-strain curves for LLDPE(d=0.920, MFR=2.1) and HP-LDPE(d=0.921, MFR=2.9). Tensile speed is 1000mm/min.

Heat resistance
As a yard-stick for judging the use-limitation at high temperatures, the Vicat softening point is generally used. As is understood from Fig. 9, LLDPE has the Vicat softing point about 10°C higher than HP-LDPE of the same density, suggesting that LLDPE is superior to HP-LDPE in terms of the heat resistance. The data for HDPE are located on the extension of those for LLDPE.

Figure 10 shows DSC melting behavior of LLDPE and HP-LDPE of almost the same density (d=0.920 and 0.921, respectively). HP-LDPE gives a broad pattern of melting with the peak at 107°C. On the other hand, LLDPE shows three peaks in the DSC melting endotherm at 106, 119, 123°C. Considering the fact that each fraction of LLDPE by chemical composition shows a respective single peak, the overlaping pattern of DSC for LLDPE would be due to the chemical composition distribution.
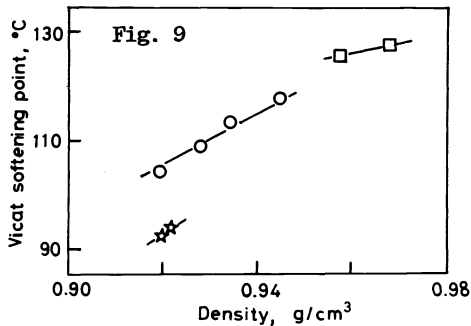

Fig. 9.   Vicat softening point vs. density correlation for polyethylenes. Squares, open circles and stars denote the values for HDPE(MFR= 5~10), LLDPE(MFR=0.2~4) and HP-LDPE(MFR=2~3), respectively.
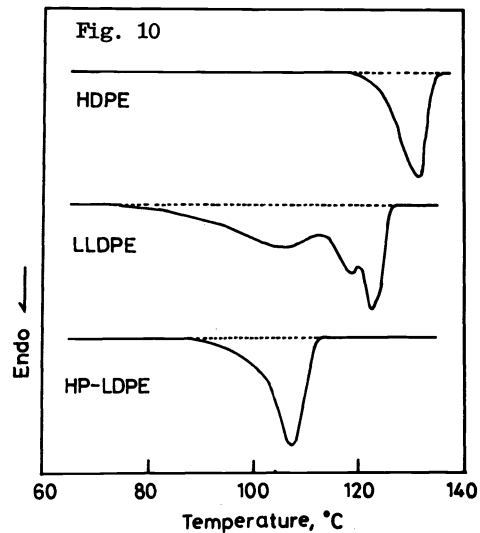
Fig. 10.   DSC curves for polyethylenes: HDPE(MFR=5, d=0.968), LLDPE (MFR=2, d=0.920), HP-LDPE(MFR=3, d=0.921). Data were taken with DSC-II (Perkin-Elmer).

A good correlation between the melting point determined by DSC and the lamella thickness measured by a Raman spectroscopic method for HP-LDPE and fractionated LLDPE is shown in Fig. 11. In this figure, a (LLDPE) and b (HP-LDPE) are of approximately the same density, i.e. d=0.920 ∿ 0.921. It is conceived that the lamella of HP-LDPE can not grow thick due to the existence of the long-chain branchings. On the other hand, the thick lamella of LLDPE is resulted from that the linear structure affects positively the formation of perfect lamella. Accordingly, the higher melting point of LLDPE than HP-LDPE of the same density would be attributed to the thicker lamella of LLDPE than HP-LDPE because of the difference of the branching structures.
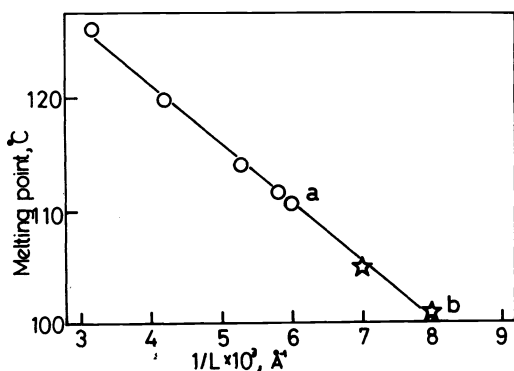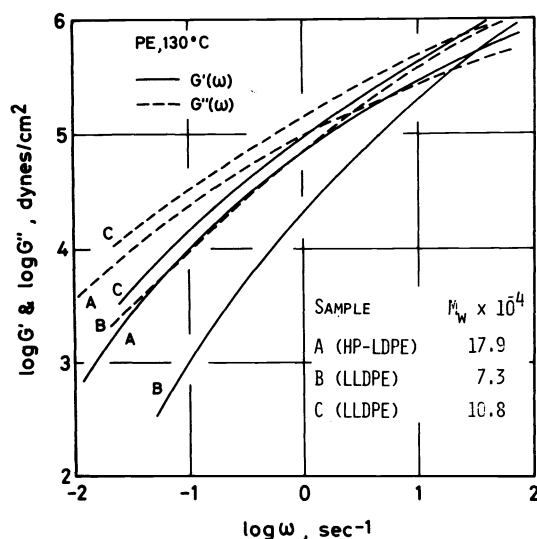

Fig. 11

Fig. 12 →

Fig. 11. Melting point vs. lamella thickness (L) correlation for HP-LDPE and fractionated LLDPE. Open circles and stars denotes LLDPE(d=0.940 ∿ 0.921) and HP-LDPE(d=0.928 ∿ 0.920), respectively.

Fig. 12. Frequency dependences of dynamic storage modulus G'(ω) and loss modulus G"(ω) for a HP-LDPE sample (A) and two LLDPE samples (B and C) at 130°C. The weight-average molecular weights of the samples are indicated in the figure.

RHEOLOGICAL PROPERTIES AND PROCESSABILITY OF LINEAR LOW DENSITY POLYETHYLENES

The processability of polymeric materials is closely related to the rheological properties in the molten state. As is well known,for example, the bubble stability in the film blowing process of LLDPE is much inferior to that of HP-LDPE with a similar melt flow index. This unstableness often makes problems in processing of the commercial polymers. But the reason has not fully understood yet. Accordingly, it is significant to investigate the rheological properties of LLDPE in the molten state and the processability of the same material.

In the present section, some comparisons of LLDPE with HP-LDPE on various rheological properties and processability parameters are tried and the origin of the difference in processability between the two types of commercial polyethylenes is discussed in terms of the rheological properties. For better comparisons, the three particular samples, one of HP-LDPE (A) and two of LLDPE (B and C) were picked up from various samples shown in Table 1. The weight-average molecular weights M_w measured in 1-chloronaphthalene at 135°C, the intrinsic viscosities [η] measured in decalin solutions at 135°C and the molecular weight distribution M_w/M_n for the sample A, B and C are as follows.

A (HP-LDPE) : $M_w = 1.79 \times 10^5$, [η] = 1.07 dl/g, $M_w/M_n = 6.4$

B (LLDPE) : $M_w = 7.3 \times 10^4$, [η] = 1.50 dl/g, $M_w/M_n = 4.5$

C (LLDPE) : $M_w = 1.08 \times 10^5$, [η] = 1.86 dl/g, $M_w/M_n = 7.0$

Dynamic viscoelastic properties
The frequency dependences of the dynamic linear viscoelastic functions, the storage shear modulus G'(ω) and loss modulus G"(ω), of HP-LDPE (A) and LLDPE (B and C) measured with a Rheometrics Mechanical Spectrometer are shown in Fig. 12. The weight-average molecular weights for the samples are shown in the figure.

The frequency dependence curves of LLDPE melts are clearly different from those of HP-LDPE in the shapes: Both G' and G" curves for LLDPE are much steeper than those for HP-LDPE. This suggests that the distribution of relaxation times is broader in HP-LDPE as compared with that in LLDPE. It is well known that the broader molecular weight distribution (ref. 5) and branching of the polymer chain (ref. 6,7) make the distribution of relaxation times associated with the entanglement slippage in the polymeric liquids be broad. On account of the similarity in M_w/M_n values for the samples, Fig. 12 presumably shows the effect of branchings rather than that of molecular weight distribution, although one can not be separated exactly from the other in this figure. The same observation is possible in the flow curves, the relations between shearing stress σ and rate of shear $\dot\gamma$, for LLDPE and HP-LDPE samples with similar melt flow rates as shown in Fig. 13. σ vs. $\dot\gamma$ relations are often regarded as giving a similar information to G" vs. ω relations. Shearing stress values of LLDPE and HP-LDPE sample used here are not far off at low rates of shear, suggesting near zero-shear viscosities. However, the difference in σ of the two samples becomes greater with increasing rate of shear owing to the difference in slopes of the curves, which was also observed G" vs. ω curves for the samples A and C in Fig. 12.

Extensional viscosity development
In connection with the polymer processing, especially with film blowing and blow moulding processes, the extensional properities of materials in the molten state are undoubtedly important. The extensional viscosity development curves for the three samples are shown in Fig. 14. The extensional stress development $\sigma_E^+(t)$ as a function of time after applying a constant rate of strain $\dot\varepsilon$ was measured with Meissner-type (ref. 8) of apparatus. Then the extensional viscosity $\eta_E^+(t) = \sigma_E^+/\dot\varepsilon$ was calculated. η_E^+ includes not only viscous effects but also elastic ones caused by the deformation of macromolecular chains in the molten materials. The experimental results measured at three rates of strain (I, II and III) for each sample (A, B or C) are drawn as illustrated in the figure.
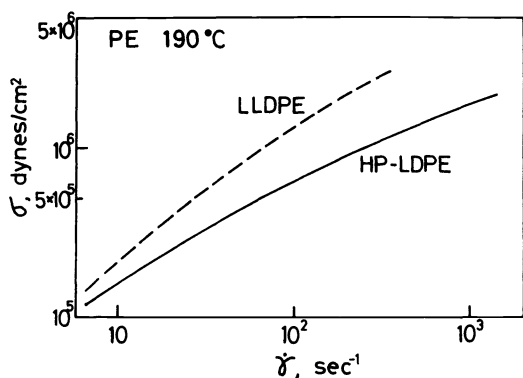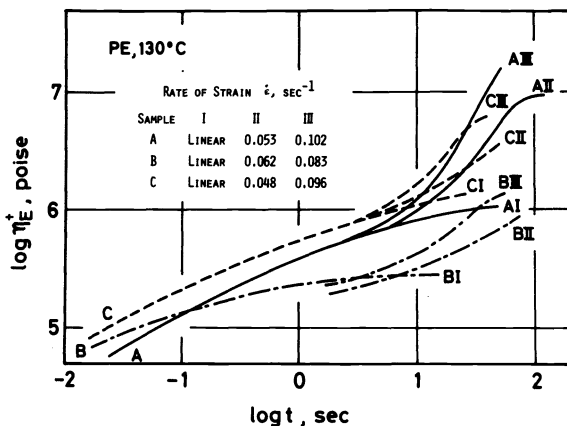

Fig. 13

Fig. 14

Fig. 13. Shearing stress σ and rate of shear $\dot\gamma$ relations for typical samples of LLDPE and HP-LDPE at 190°C.

Fig. 14. Extensional viscosity (η_E^+) development curves for a HP-LDPE (A) and two LLDPE (B and C) at 130°C.

The "Linear" curves in the figure (I) were calculated from the linear vicoelastic functions G' and G" shown in Fig. 12 and correspond to $\eta_E^+(t)$ when $\dot\varepsilon \to 0$.

The η_E^+ at finite $\dot\varepsilon$ exhibits an up-turn deviation from the "Linear" line in long time region and it becomes more remarkable with increasing $\dot\varepsilon$. The curves for LLDPE samples (B and C) are similar in the shapes but different in the values; the sample C having higher molecular weight gives higher extensional viscosity. η_E^+ curves for HP-LDPE (A) are quite different in shape from those for LLDPE. The viscosity development is much faster in short time region and the up-turn deviation from "Linear" curve is much more marked at long times. The extensional viscosity of HP-LDPE becomes the highest among the samples at the long-time end of the curves, although it was the lowest at short-time end. This behavior would also be due to the long-chain branchings of HP-LDPE.

Melt flow rate
The melt flow rate or melt flow index has been widely used as a common measure for judging
the processability of commercial thermoplastic materials. In Fig. 15, the molecular weight
dependence of melt flow rate, MFR, for LLDPE are compared with that for HP-LDPE. The MFR
was measured under the weight of 2kg at 190°C according to ASTM D1238E. Among the data
points for various samples given in Table 1, those of the particular samples A, B and C used
for the measurement of rheological properties shown in Fig. 12 and 14 are marked by the
sample codes.

The slope of the straight lines is -2.9, suggesting that MFR is proportional to $M_w^{-2.9}$ for
both materials. This power index 2.9 is a little lower than 3.5, the well known number for
the molecular weight dependence of viscosity. The lower dependence is, of course, due to
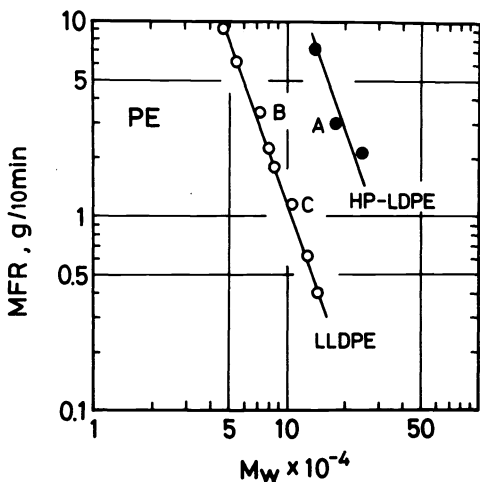that MFR is a flow rate at fixed shearing stress in the non-Newtonian flow regime. As is

Fig. 15

Fig. 16

Fig. 15. Melt flow rate, MFR, plotted against weight-average molecular
weight M_w for HP-LDPE and LLDPE. A, B and C correspond to the samples
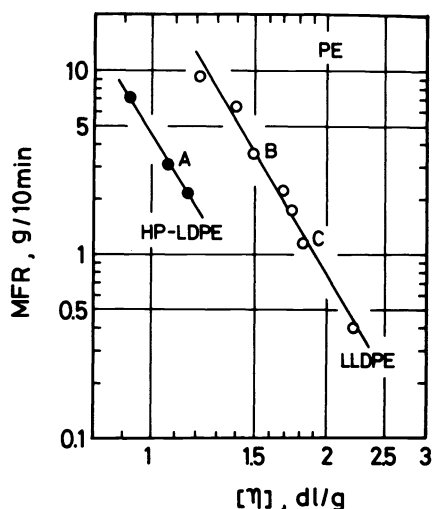used in Figs. 12 and 14.

Fig. 16. Melt flow rate, MFR, plotted against intrinsic viscosity [η]
for HP-LDPE and LLDPE. A, B and C correspond to the samples used in
Figs. 12 and 14.

seen from this figure, MFR value of LLDPE is more than one decade lower than that of HP-
LDPE at a same molecular weight; the viscosity of LLDPE is higher than that of corresponding
HP-LDPE. These difference is clearly due to the fact that the molecular dimension of LLDPE
is larger than that of HP-LDPE as discussed in the previous section (Solution property) and
also illustrated in Fig. 4.

MFR values of the same samples as those in Fig. 15 are plotted against the intrinsic
viscosity [η] in Fig. 16. The zero-shear viscosities η_0 of branched polymer melts and the
linear counterparts have been found to be successfully expressed (ref. 6,7,9-12) by a unique
line when those are plotted against the molecular dimension and/or intrinsic viscosity.

In the case of the polyethylenes studied in this report, however, the data for HP-LDPE did
not fall on the line for LLDPE as can be seen in Fig. 16. The reason would be that the
LLDPE is not exactly the counterpart of the branched low density polyethylene.

Melt tension
Besides the melt flow rate, the melt tension, MT, has also widely used for the evaluation of
processability of commercial polymers. The MT becomes more significant in the case that the
extensional deformation and elastic properties play a important role in polymer processing
such as film blowing and blow moulding. The MT data are plotted against the MFR for LLDPE
and HP-LDPE samples in Fig. 17. The MT was measured under the conditions; the extrusion
speed of 10mm/min, take-up speed of 12.6m/min and the die diameter of 2.1mm. Both series of
polyethylene samples make the respective linear relations between log MT and log MFR. At a
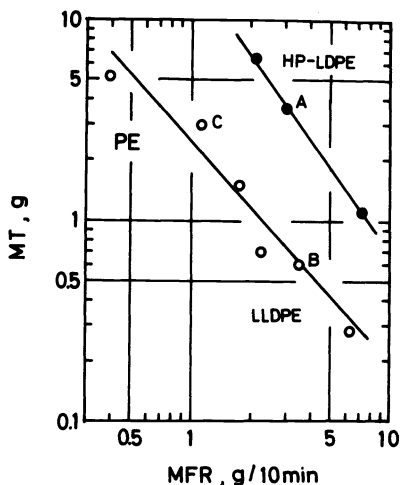
Fig. 17. Melt tension MT plotted against melt flow rate MFR for HP-LDPE and LLDPE. A, B and C correspond to the samples used in Figs. 12 and 14.
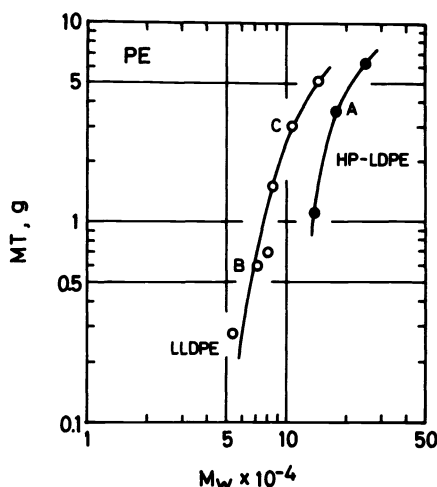
Fig. 18. Melt tension MT plotted against weight-average molecular weight M_w for HP-LDPE and LLDPE. A, B and C correspond to the samples used in Figs. 12 and 14.

same value of MFR, MT of HP-LDPE is higher than that of LLDPE, suggesting that the bubble stability of film blowing process is worse for LLDPE as compared with that for HP-LDPE. It is also interesting that the order of MT values of the samples A, B and C indicated in this figure is exactly the same as that of the extensional viscosities in long-time region at finite rates of strain (II and III) as shown in Fig. 14. This fact suggests that the melt tensional properties and processability in film blowing are mostly governed by a nonlinear (at high rates of strain) extensional properties of the melts in a long time scale.

Figure 18 shows the molecular weight dependences of MT for the two series of polyethylenes. The MT strongly depends on molecular weight and the values of LLDPE is higher than that of HP-LDPE at a same M_w, but not at same MFR as was shown in Fig. 17. It can finally be concluded that a high MFR (= a low viscosity at low rates of shear) and a high MT (= a high nonlinear extensional viscosity at long times) are necessarily required to attain a better processability of polyethylenes. These somewhat contradictory requirements would be satisfied by making the linear chains be lightly crosslinked to give a branched molecules or by blending a small amount of long branched polymer to the linear polymer.

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