Development of Automatic Cross Fractionation: Combination of Crystallizability Fractionation and Molecular Weight Fractionation

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Synopsis

An automatic cross-fractionation system is presented by combining a newly developed crystallizability fractionation device based on the principle of isothermal dissolution with a commercially available GPC. The detail design, procedure, and operation variables are described. The fractions eluted from the device are characterized by use of an infrared spectrometer and a differential scanning calorimeter for clearing the mechanism of it. As the result of the study, it is found that the system is very useful for characterizing semicrystalline polymers.

INTRODUCTION

Gel permeation chromatography (GPC) because of its rapidity and good reproducibility has been much utilized for clarification of qualities of a large number of commercial polymers through molecular weight distribution (MWD) and many useful informations have been obtained. However, in case of such semicrystalline polymers as polyethylenes and polypropylenes, most of qualities have not yet been clarified enough. This is because the qualities of such semicrystalline polymers are also dependent upon other structural variables than MWD. Short- and long-chain branching in polyethylenes, stereoregularity in polypropylenes, and monomer sequence length of copolymers are typical and important structural variables beside MWD.

Some investigators have thereupon tried to couple GPC and other measurements in order to get such structural variables simultaneously with MWD, for example, viscometer for detecting long-chain branching,[1] turbidity measurement for chemical composition,[2] and so on. However, as in each of these cases the structural variables were considered from the standpoint of variation of molecular weight, the overall qualities of semicrystalline polymers are not still revealed. It is therefore necessary to study the relation between molecular weight and crystallizability of semicrystalline polymers. The authors have pursued this aspect over the past several years.

Recently, Wild and Ryle[3] published a very interesting technique (the Analytical Temperature Rising Elution Technique) for crystallizability fractionation having a possibility of combination with GPC.

In this paper, we further developed the technique and completed a new automatic cross fractionation system. By this completion it becomes to be able to analyze the relation between molecular weight and crystallizability with bewildering rapidity.

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INSTRUMENTATION AND PROCEDURE

The outline of the system is described in Figure 1. A newly developed crystallizability fractionation device (CFD) based on the principle of isothermal dissolution is placed before a commercially available GPC (Water Assoc. Model 200). A polymer sample solution is first injected into CFD to be fractionated according to crystallizability. Next the fractions are automatically eluted from CFD and injected into GPC every a certain period to be fractionated according to molecular weight. However, it is generally not easy to place other measurements before GPC. Because, as well known, GPC chromatograms are much influenced by a little change of solvent flow and temperature. In this system, moreover, it is required to elute the fractions from CFD by a constant volume of solvent and to continuously inject them into GPC.

After some trials, to overcome the problems, we have manufactured an automatic cross fractionation system, shown in Figure 2. The success is the development of CFD having the following special components: a syringe for injecting a polymer sample solution, a sample loop for holding a constant volume of the solution, a small column packed with a inert support for crystallizability fractionation, and two valves (a six-port and a four-port one) for smooth solvent flow. The temperature is controlled by an aluminum block heater and an air cooler on the instruction of a programmed temperature controller. The working of the valves follows the instruction of a valve controller. Figure 3 shows the way of the valve working.

The following procedure is performed. A polymer solution is injected into the sample loop by the syringe under valve position 2 and the excess solution is

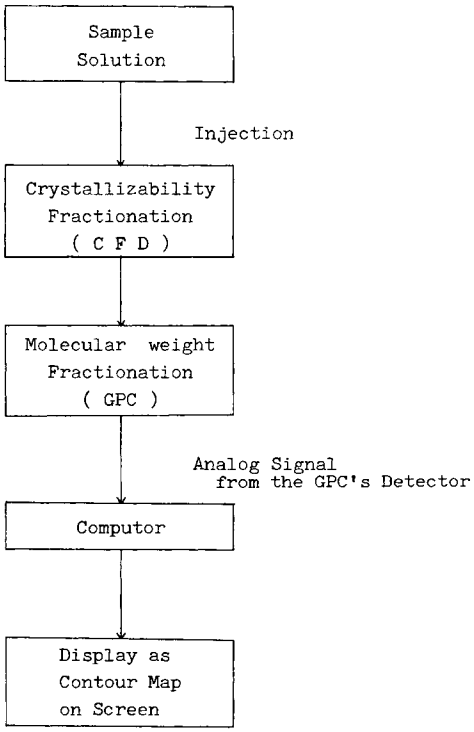


Fig. 1. Schematic diagram of the cross fractionation system.

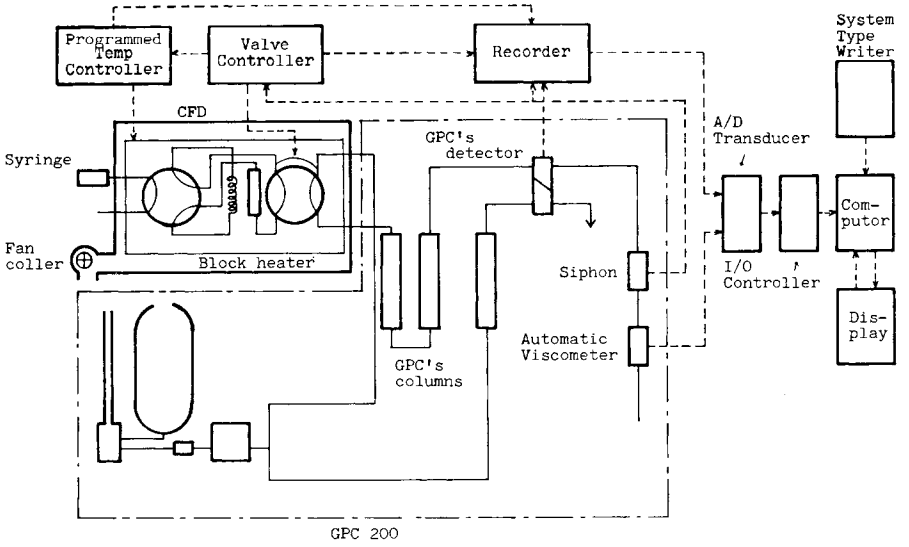


Fig. 2. Detail combination method of the crystallizability fractionation device (CFD) and GPC.

drained away from outlet 4. By change of valve position from 2 to 3 through 1, a constant volume of the solution in the sample loop is introduced into the column with flow of solvent through the route 15–12–11–6–5. When it gets at the just

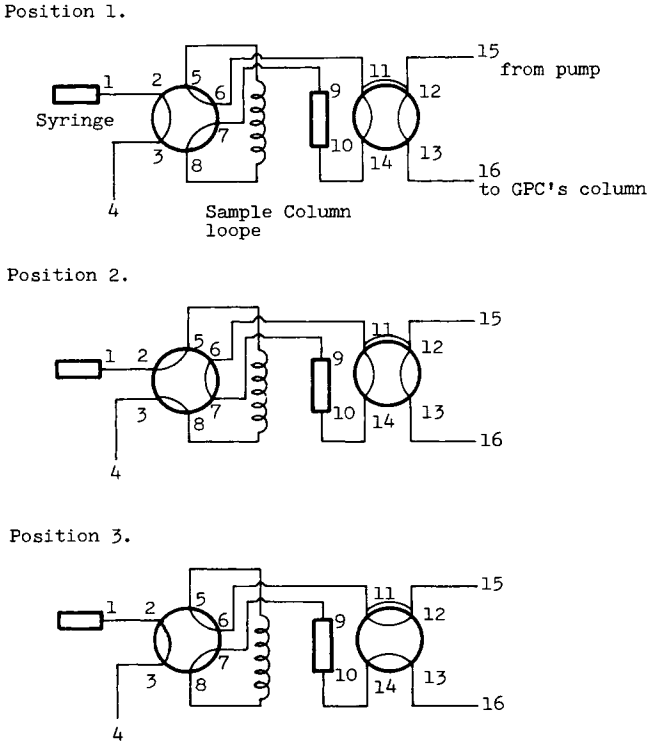


Fig. 3. Working of valves.

middle of the column, the valve position returns to 1 to confine it in the column. The timing of the valve working is previously programmed from the volume between 8 and 10 and the solvent flow rate. This procedure is carried out under a high temperature at which the polymer species do not precipitate. The temperature is then decreased until all of the polymer species are deposited upon the inert support. During the cooling some troubles, for example, air contamination and change of the position of polymer species in the column due to thermal contraction occur. This causes irregularity or ghost peaks in GPC chromatograms.

Therefore, the valve ports 11 and 12 are jointed each other and both sides of the column are compressed by solvent flow pressure. This is a very important design. CFD is again heated up to a certain temperature and kept for a certain period to dissolve the lower crystallizability polymer species. The dissolved polymer species are then eluted from CFD and injected into GPC under the valve position 3 with a constant volume solvent supplied through 15–12–11–6–5–8–7,

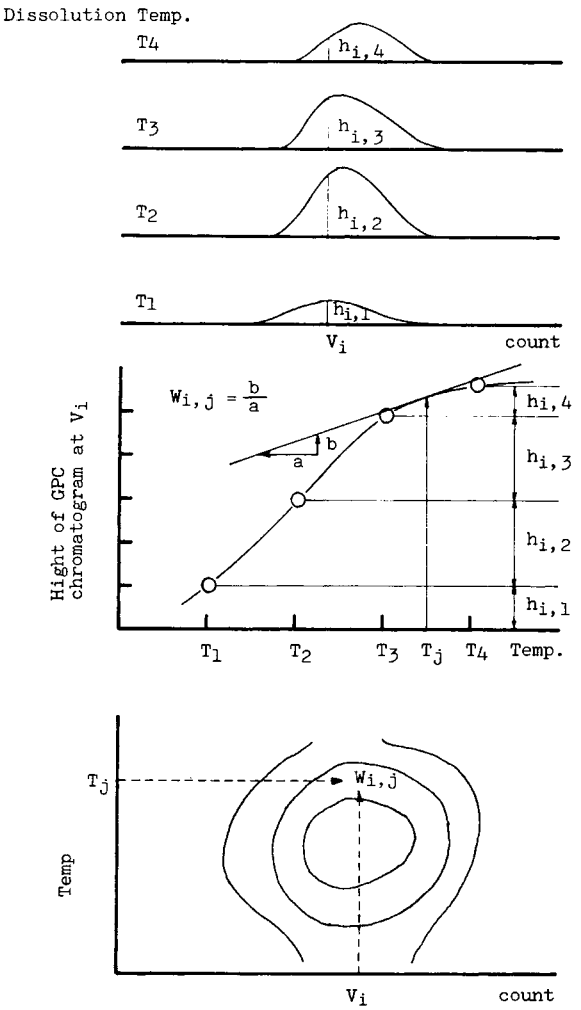


Fig. 4. Schematic diagram for obtaining a contour map.

TABLE I
Characteristics of Samples

Sample	D[a]	MFR[a]	—CH_3/1000C[a]
A	0.921	0.86	21.1
B	0.921	3.90	31.9
C	0.921	2.20	89.9
D	0.924	4.00	29.5
E	0.978	2.07	2.0

[a] D = density (ASTM D1505-67); MFR: melt flow ratio (ASTM D1238-65T); —CH_3/1000C: terminal methyl group (IR).

as the first fraction. The solvent volume must be enough to elute all the species, but at the same time it must be as little as possible for analyzing GPC chromatograms.

In order to elute the second fraction, CFD is further heated by a constant temperature to dissolve the higher crystallizability polymer species under valve position 2. After a period long enough to dissolve the species and not to interfere the GPC chromatogram of the first fraction, the second fraction is eluted from CFD and injected into GPC in the above mentioned manner. In this way an automatic cross fractionation on crystallizability and molecular weight is successively run.

DATA REDUCTION

The analog signal from a GPC detector is directly stored in a memory disk through an analog-digital transducer. At the end of each experimental run the stored data are transmitted to a computer and a contour map is calculated according to the process shown in Figure 4.

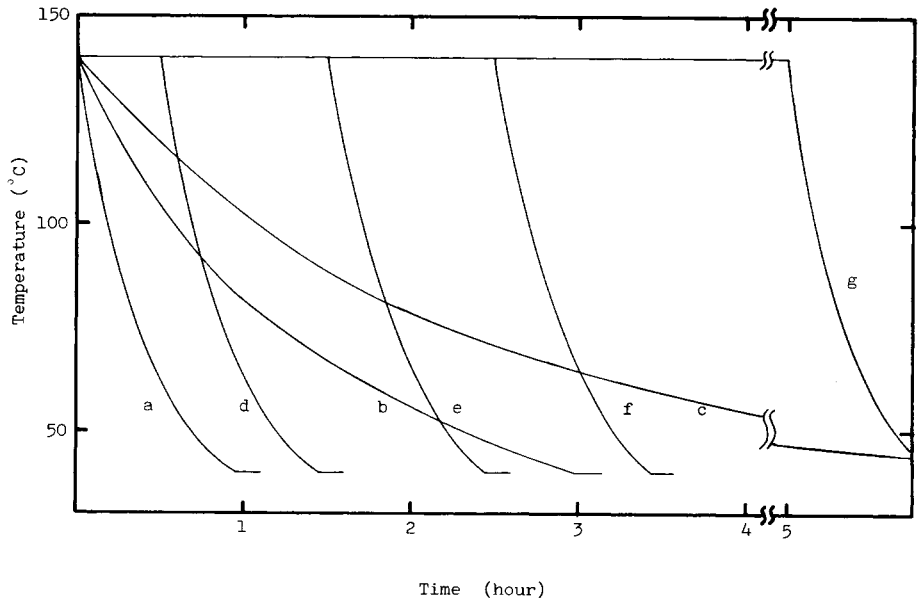


Fig. 5. Cooling curves.

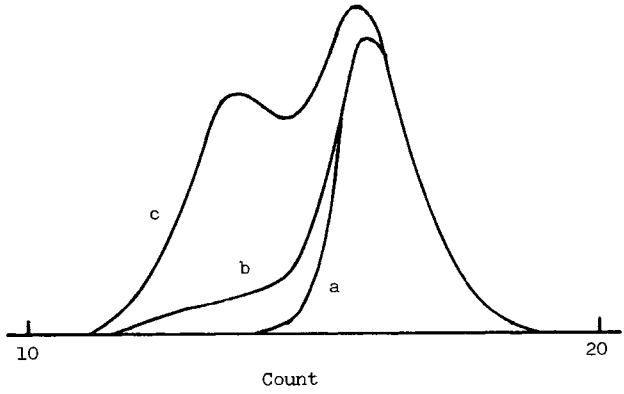


Fig. 6. Effect of cooling rate upon GPC chromatograms. The chromatograms are given for the first fractions (40°C) after cooling as curves a, b, and c.

That is, the height (h_{ij}) of GPC chromatograms of the species eluted at each temperature (T_j) is read off at the same count number (V_i) and the cumulative height is plotted against the temperature. The differential value (W_{ij}) of it with respect to the temperature (T_j) is calculated and plotted as the height (Z axis) of a contour map (X axis: V_i; Y axis: T_j). The contour map showing the quantity of the species with a molecular weight (count number) and a crystallizability (elution temperature) is projected on a Brown tube.

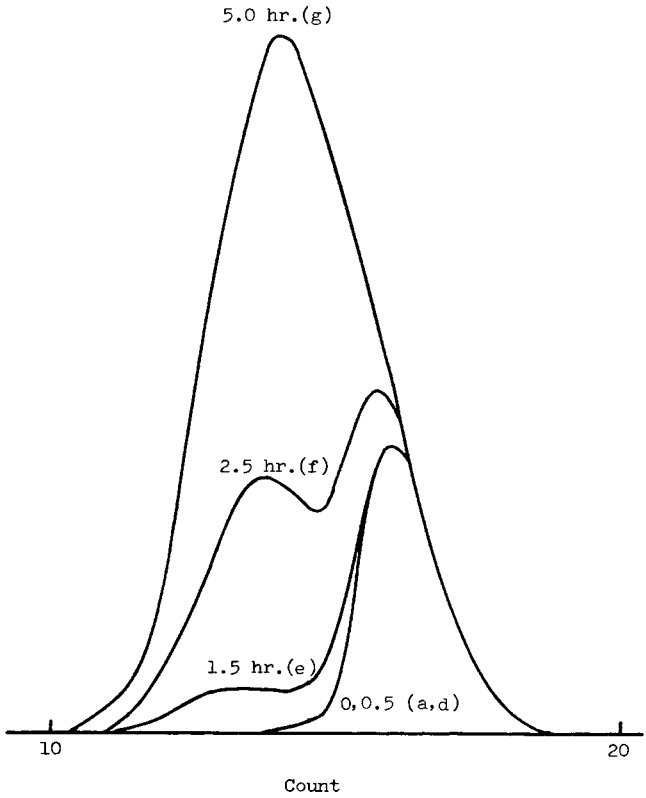


Fig. 7. Effect of residence period at 140°C upon GPC chromatograms. The chromatograms are given for the first fractions (40°C) after cooling as curves a, d, e, f, and g.

EXPERIMENTAL AND DISCUSSION

Materials

A standard high density polyethylene (NBS 1745) was used to determine the most appropriate operation variables for polyethylenes. Four low-density polyethylenes and one high-density polyethylene were used to discuss the mechanism and usefulness of the system. Table I shows their characteristics. *O*-dichlorobenzene (ODCB) and a mixed polystyrene gel column produced by Toyo-Soda Chemical Co., Ltd., were used as solvent and a GPC gel column, respectively.

Operation Variables

Polymer species injected into CFD are deposited on the inert support and then dissolved in a constant solvent under various temperatures according to their crystallizability.

Sample concentration, size, and amount of the inert support, cooling rate for deposition, dissolution temperature, and period are very important operation variables of CFD. These must be first examined in order to minimize experimental errors and obtain good reproducible results. Other variables such as solvent flow rate and solvent volume for elution, that is, injection volume into GPC, are profitably fixed as 1 mL/min and 2.5 mL, respectively, from our experience with conventional GPC measurements.

Sample Concentration

Polymer species fractionated by CFD are finally detected by a GPC detector. The chromatogram is generally recorded as the difference in the refractive indices between solvent and solution as a function of elution volume.

Here, let us suppose the number of the fractions in the crystallizability fractionation to be about 20. The concentration of the least one of the fractions should then become less than $1/20$ of the initial sample concentration. As well known, it is very difficult to calculate exact molecular weight and its distribution from the chromatogram when a very dilute solution is injected into GPC, because the chromatogram becomes indistinguishable from irregularity of the base line. As the minimum concentration for qualitative analysis in GPC measurements

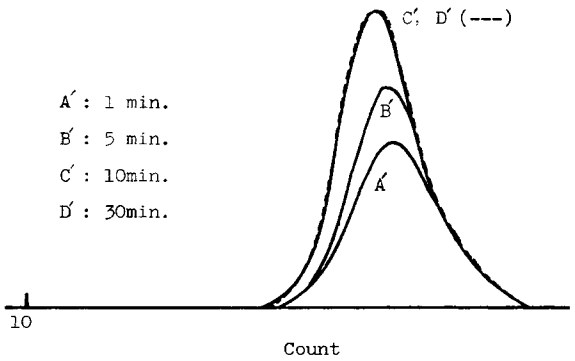


Fig. 8. Effect of dissolution period upon GPC chromatograms.

TABLE II
Most Appropriate Operation Condition for Crystallizability Fractionation of Polyethylenes —ODCB

Column size	150 × 8 mm
inert support kind	glass beads (GCC 110)
amount	3.5 g
Initial sample concentration	10 mg/mL
Cooling rate	a in Fig. 5
Solvent	ODCB
Dissolution temp	140°C–40°C
Temp of GPC	140°C
Solvent flow	1 mL/min

of polyethylene—ODCB is generally about 0.5 mg/mL from our experience, an initial sample concentration more than 10 mg/mL must be required. It is concentrated as a polymer solution. One is therefore anxious about stopping solvent flow when polyethylene species are deposited upon the inert support. As a matter of fact, this trouble occurred very often, especially in measurements of high-molecular-weight polyethylenes. The initial sample concentration must be then set up as concentrated as solvent flow can not be stopped.

In this study the concentration of 10 mg/mL was fixed as the initial sample concentration, and other operation variables were examined to avoid the trouble.

Column for CFD

The size and amount of the inert support are also important factors to avoid the trouble. The thickness of polymer species deposited upon it becomes thinner with decrease of its size and increase of its amount. This results in a smooth solvent flow. But, in case of its being too small, it passes through the filter of the column or the solvent flow is blocked. On the other hand, in the reverse case, some polymer species cannot be deposited upon it, but suspend in solvent in the column. The suspending polymer species are eluted as the first fraction. This makes measurements meaningless.

It is therefore very important to choose the inert support having the most appropriate size and amount.

A vacant space in the column, where it is usually occupied with solvent, is important from the viewpoint of the elution volume. If the space is too large, a large solvent will be obliged to elute the fractions from CFD to GPC. This leads to less precise chromatograms. On the other hand, if it is too small, some polymer species transferred to the column will not be able to get in. As the volume of the sample loop is 2 mL, the vacant space should be set up as 2 mL and a little more. As a matter of course, it is dependent upon the size and amount of the inert support and the volume of the column.

From the foregoing description standpoints, the following were found to be the most appropriate column size and inert support for polyethylenes—ODCB.

Column size: inner diameter, 0.8 cm; length, 15 cm.

Inert support: glass beads (GCC 110 produced by Applied Sci. Lab. Inc.), 3.5 g.

The glass beads were packed in the column according to the conventional procedure for GPC gel columns.

Cooling Rate

As crystallinity of polymer species is generally dependent upon crystallization rate, it is very important to discuss how fast polymer species are deposited upon the inert support. Wild and Ryle examined the effect of cooling rate upon experimental results and concluded that it is necessary to decrease temperature at such a low rate as 4°C/h in order to obtain a good relation between the dissolution temperature and the amount of methyl group per 1000 carbon. We also examined the effect of cooling rate. Polyethylene—ODCB solution transferred from the sample loop to the column was cooled from 140°C at three different rates, a, b, and c, as shown in Figure 5, and injected into GPC. At 40°C some polyethylene species being low crystalline or low molecular weight are not precipitated, but still dissolved. Figure 6 is the chromatograms of them. Their area become larger and a shoulder appears in region of low count number in order of c, b, and a. Since polyethylene generally becomes higher crystallinity with decrease of crystallization rate, this is a very curious result. In order to clarify the reason, the solution transferred from the sample loop to the column was kept under 140°C for several hours and then cooled according to d, e, f, and g in Figure 5. Figure 7 shows the chromatograms in this case. The shoulder in low count number and the area become larger with increase of holding period at 140°C. In case of 5 h the peak in region of high count numbers almost disappears and the chromatogram nearly becomes one peak in low count numbers. This is caused by diffusion of some polyethylene species outside the column during the procedure of dissolution. The solution transferred from the sample loop to the column should be cooled as fast as possible in order to avoid this trouble.

Wild and Ryle did not report such a phenomenon. This is because they independently made columns already having inert support coated by polymer species apart from the fractionation system. Diffusion of some polymer species out of the columns did not occur.

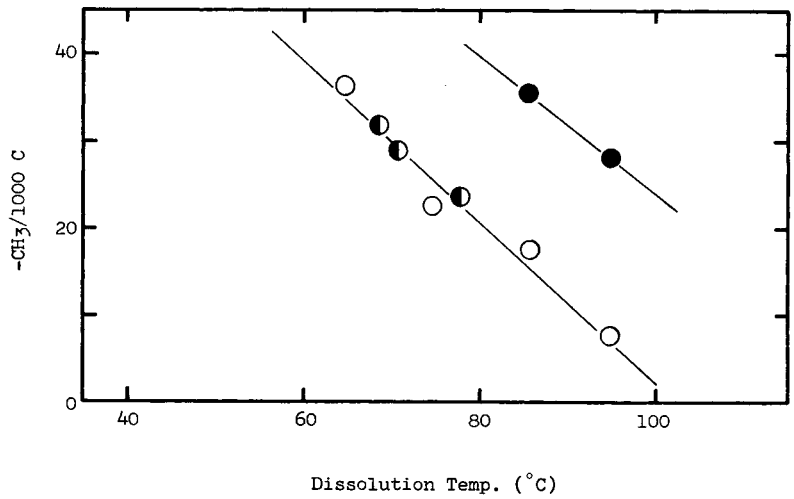


Fig. 9. Relation between —CH_3/1000C and dissolution temperature. (○) A, (◐) B, (●) C.

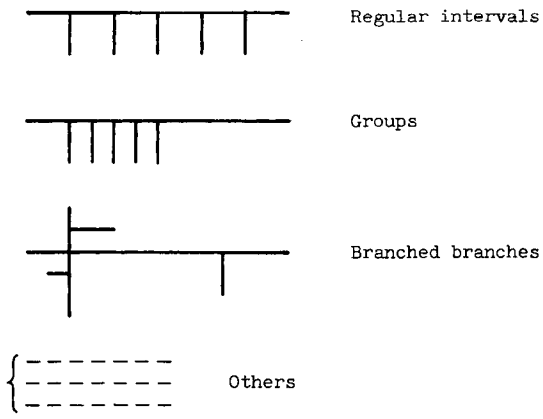


Fig. 10. Various types of branching of polyethylenes having the same degree of —CH_3/1000C.

Dissolution Period

Polyethylene species deposited upon the inert support are stepwise dissolved in a constant solvent by increasing temperature. In general, the dissolution of polymer species in solvent is dependent upon temperature, pressure, period, amount of the ratio of solvent to polymer species, and so on.

In this case, pressure, temperature, and amount of solvent to polyethylene species in the column are nearly constant within a process for obtaining one fraction. Therefore, the only variable making sure of solubility is the dissolution period. All polyethylene species having the same crystallizability should be dissolved and eluted as one fraction. If the dissolution period is too short, some of the species are not dissolved and involved in the next fraction. In order to see the effect of the dissolution period upon the results, some experiments were made under the same condition except the dissolution period. Figure 8 shows

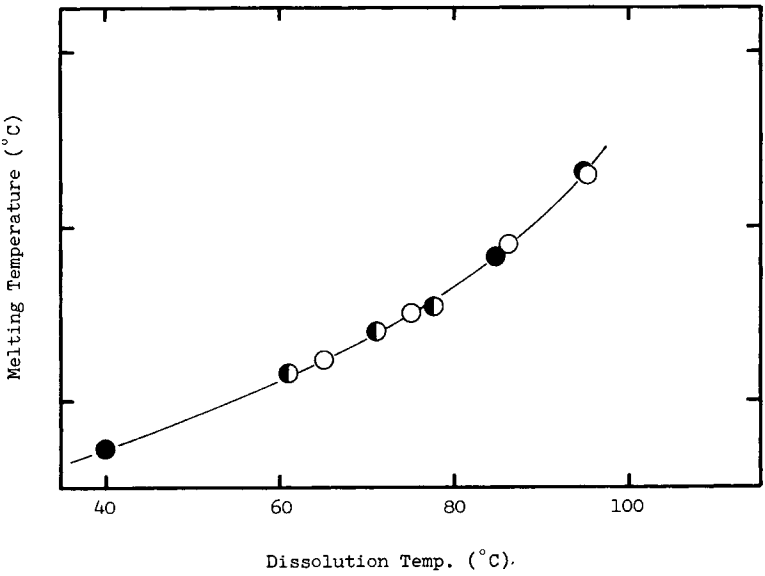


Fig. 11. Relation between melting temperature and dissolution temperature. (○) A, (◐) B, (●), C.

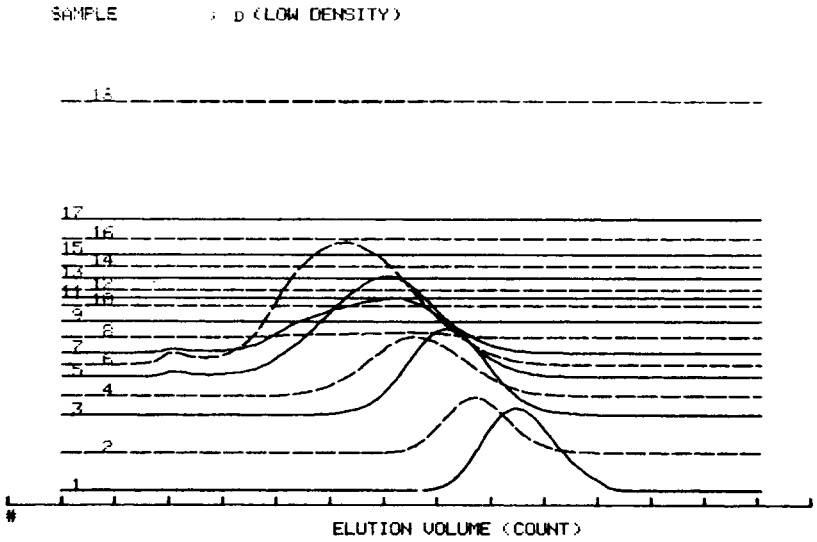


Fig. 12. GPC chromatograms of Sample D. The number shows the order of the dissolution temperatures.

the chromatograms of the fractions eluted by varing the dissolution period at a temperature, 101°C, from which it is seen that 10 min is enough to dissolve all polyethylene species.

Table II shows the most appropriate operation variables of the crystallizability fractionation for polyethylene—ODCB system determined from the foregoing considerations.

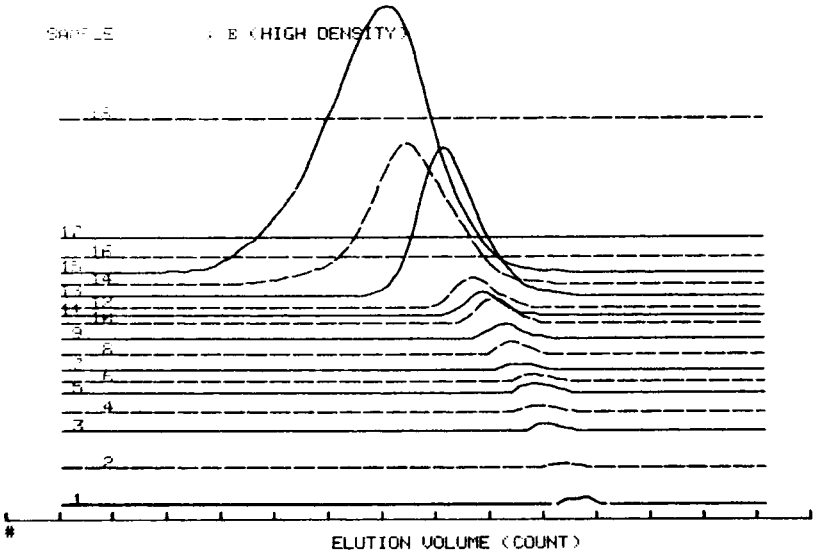


Fig. 13. GPC chromatograms of Sample E. The number shows the order of the dissolution temperatures.

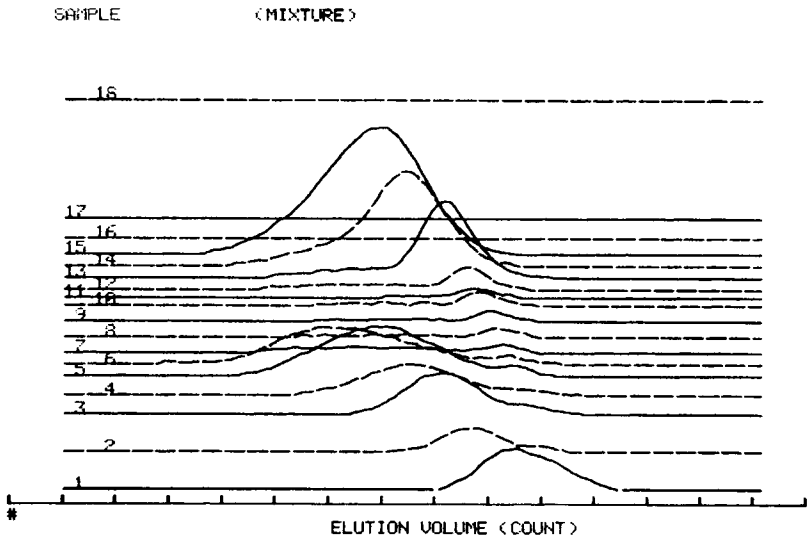


Fig. 14. GPC chromatograms of the mixture of Sample D and Sample E (1:1).

Characterization of the Fractions

In order to consider the mechanism of the crystallizability fractionation, three polyethylenes (A, B, and C) produced by different processes were fractionated. The fractions eluted from CFD were taken out of a bypass specially prepared after it, precipitated in acetone, filtered, and dried in vacuo at 80°C for 1 day.

The fractionation was repeated several times to obtain a large enough amount of the fractions for measurements of infrared spectrometer and differential scanning calorimeter. Figure 9 shows the relation between the amount of methyl group per 1000 carbons and the dissolution temperature. It is seen from Figure 9 that the methyl group of the fractions obtained from samples B and C is on a straight line against the dissolution temperature, but in case of sample A it is not on it. This is different from the results obtained by Wild and Ryle. As a matter of fact, it is strange to conclude that there is a straight-line relation between the amount of methyl group and the dissolution temperature in any polyethylenes, because it is well known that crystallizability of polyethylene depends upon the type of short chain branching, even if the degree of it is same, as shown in Figure 10. It is therefore more reasonable to conclude that there is no universal straight line between them.[4] Figure 11 shows the relation between the melting point and the dissolution temperature of the fractions. It is seen from Figure 11 that there is a complete straight line between them. Since crystallinity closely relates to the melting point, it can be concluded that the mechanism of the fractionation is certainly performed according to crystallinity.

Usefulness of the System

A low density (D) polyethylene, and a high density (E) polyethylene and their mixture (1:1) were examined to check up on the usefulness of the system. They were measured under the operation variables previously described. The temperature of CFD was stepwisely increased in order of the temperature of 40, 50,

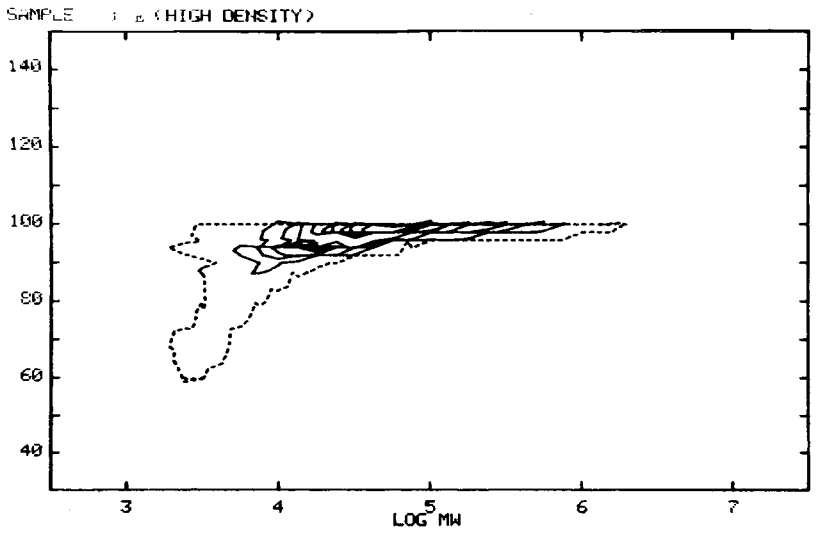


Fig. 15. A contour map of Sample D.

60, 65, 70, 73, 76, 80, 84, 88, 90, 92, 95, 98, 101, 105, 110, and 140°C. It took about 10 h to carry out a cross fractionation of one sample.

Figures 12, 13, and 14 are the GPC chromatograms of the species eluted from CFD at each temperature. Figures 15, 16 and 17 are the contour maps calculated from the GPC chromatograms according to the data reducing process. Figure 18 shows a bird's-eye view of the mixture. The mountains in Figure 17 caused of the low- and high-density polyethylenes are wholly isolated and consistent with ones in Figures 15 and 16. This shows that the system is effective for separation of polyethylenes according to crystallizability and it makes it possible to get the quantitative relation between molecular weight and crystallizability.

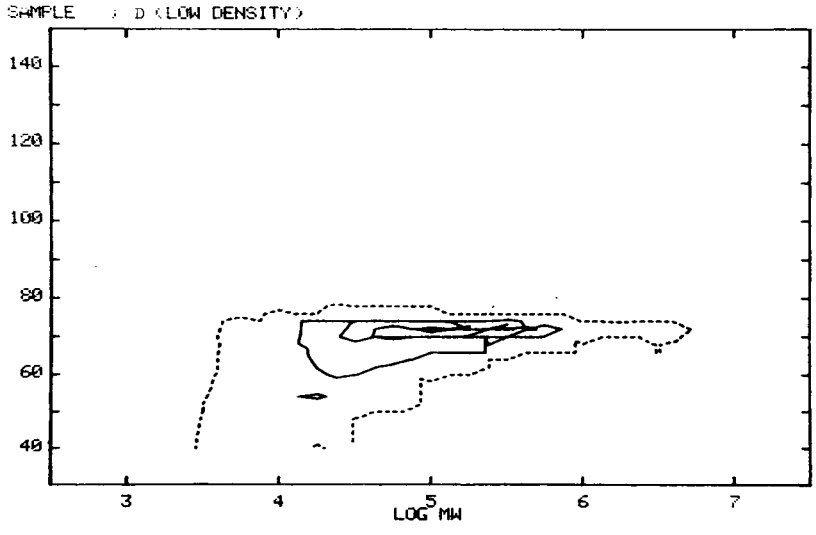
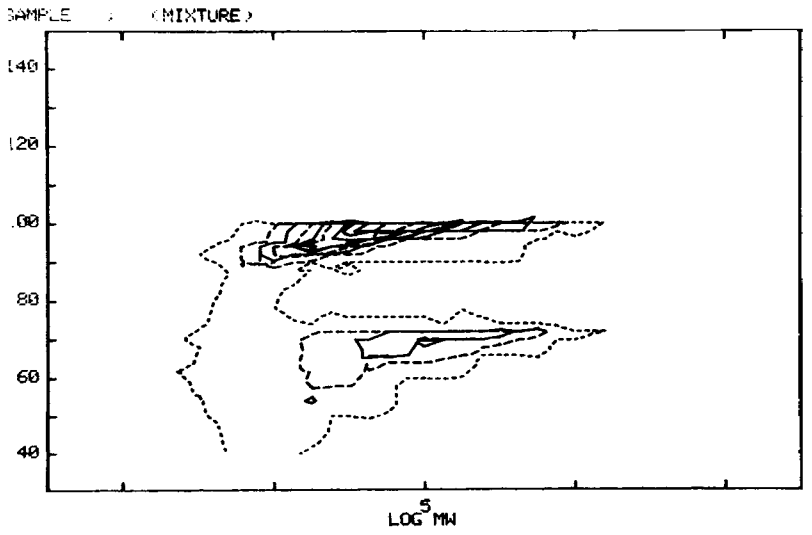
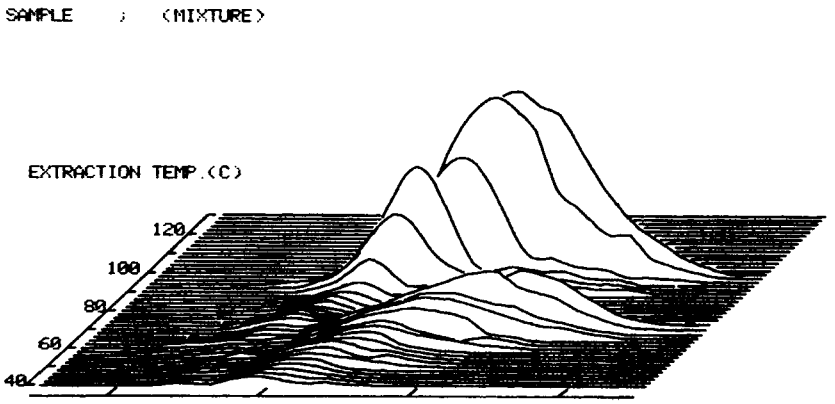


Fig. 16. A contour map of Sample E.



In general, most of qualities of semicrystalline polymers are dependent upon molecular weight distribution and crystallizability distribution. It is therefore very important to know them, but it does not suffice for full consideration of the qualities when they are independently considered. For example, Figure 19 shows an imaginary example having the possibility of an erroneous conclusion, if we independently examine them.

Let us suppose that samples 1 and 2 have the quite same molecular weight and crystallizability distributions, but most of their qualities are different. Such a phenomenon may result when the dependency between molecular weight and crystallizability is different for each sample, that is, sample 1 has a dependency of increase of crystallizability with molecular weight, but on the other hand sample 2 has a reverse dependency, as shown in Figure 19. This automatic cross fractionation system should show its ability in such a case.



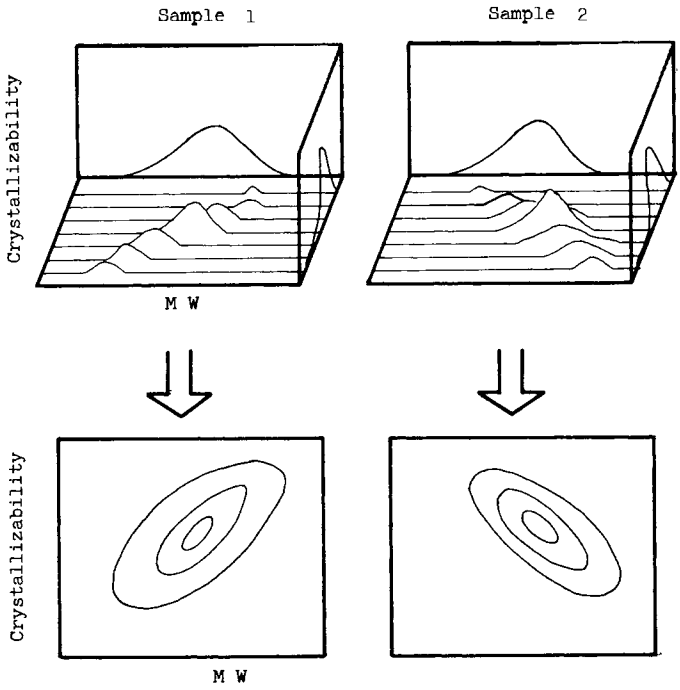


Fig. 19. An imaginary example having same MWD and crystallizability distribution, but a different dependency on each distribution.

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