

Fractionation of Ethylene-Propylene Copolymers

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Synopsis

Ethylene-propylene (EP) copolymers were fractionated according to chemical composition, molecular weight, or monomer sequence length, which are fundamental distribution factors. Cloud points of polyethylene (PE), polypropylene (PP), and EP copolymer were determined prior to the fractionation. From the results, it was estimated that xylene-butyl cellosolve and tetralin-ethyl carbitol systems were suitable for the fractionations according to chemical composition and molecular weight, respectively. EP random-type copolymers were fractionated using a xylene-butyl cellosolve system. Separations according to chemical composition were obtained as expected. Then, the above polymer fractions were further fractionated in a tetralin-ethyl carbitol system and the dependence on molecular weight was observed fairly well. Furthermore, fractionation according to monomer sequence length was satisfactorily achieved by solvent extraction using ethyl ether, *n*-hexane, cyclohexane, and *n*-heptane. Therefore, it is concluded that the more detailed characterizations of EP copolymers are made possible by a combination of these techniques.

INTRODUCTION

Since the copolymer is generally composed of various polymer species, it is important to separate it into individual polymer groups having the same structure. Some reports concerning the fractionation of EP copolymer have been published.¹⁻⁴ However, these are not concerned with the fractionation method, but mainly with the analysis of copolymerization results, and many problems of characterization of each fraction are still left unsolved. Thus, the purpose of this paper is to establish the fractionation method of EP copolymer.

Three distribution factors, i.e., chemical composition, molecular weight, and monomer sequence length, have to be considered for the fractionation of this copolymer. Fractionation according to molecular weight (molecular fractionation) is generally carried out in liquid-liquid phase equilibrium, while the solubility of copolymer may be approximately estimated as the arithmetic mean of the solubility of homopolymers composed of each monomer component from the standpoint of the properties of such copolymers in a good solvent.^{1,5} Therefore, it is estimated that the fractionation according to chemical composition (compositional fractionation) or molecular fractionation is achieved in the state of liquid-liquid phase equilibrium.

On the other hand, the variation in monomer sequence length is generally considered to have little influence on the state of liquid-liquid phase equilibrium or on the solvent properties as compared with the solid properties as shown in Flory's theory⁶ concerning the depression of melting point of copolymers. Therefore, the fractionation according to monomer sequence length takes place in the state of solid-liquid phase equilibrium. On the basis of these considerations, the fractionations of EP copolymers according to these three fundamental distribution factors were investigated here.

EXPERIMENTAL

Samples. The copolymers were prepared by solution polymerization with a complex catalyst system. Monomer concentration and monomer ratio were kept constant by supplying the monomer continuously during the polymerization period. Samples A and B were polymerized with an $\text{AlEt}_2\text{-Cl-VOCl}_3$ system; and samples C, D, and E were polymerized with $\text{AlEt}_2\text{-Cl-TiCl}_3$ (activated).

Cloud Point Determination. Cloud points were determined to select the solvent-nonsolvent system suitable for compositional and molecular fractionation by the column method. Polymer, solvent, and nonsolvent were weighed in a test tube of 10 mm diameter. The test tube was purged with nitrogen and sealed as an ampoule. 2,6-Di-*tert*-butyl-*p*-cresol, 0.2 wt-%, was added as antioxidant to all solvents and nonsolvents used. The polymer samples which had been previously fractionated were used; average molecular weights were 2.0×10^5 and 1.7×10^5 for polypropylene (PP) and high-density polyethylene (PE), respectively. The cloud point was determined with the naked eye in an oil bath and was reproducible within $\pm 1.0^\circ\text{C}$.

On the other hand, a Sofica 42000M light-scattering instrument was used to study the dependence of cloud points on molecular weight. A solution of 0.5 mg sample/ml xylene was prepared, and the measuring cell containing the solution was mounted in the instrument. Measurement was performed in a xylene-butyl cellosolve system at 127°C . The intensity of scattered light (turbidity) in one direction (90°) was recorded in 10 min after every 1.0-ml addition of butyl cellosolve to the solution. The previously fractionated polymer samples were used for this determination; the D values (\bar{M}_w/\bar{M}_n) of these samples were less than 1.3, except those of copolymer. An example of turbidity versus xylene content is shown in Figure 1, and the cloud point of this sample is expressed as *A*.

Column Fractionation. A large-scale fractionation column (80 mm diam. \times 1000 mm) was used which was designed to regulate flow rate and eluent temperature exactly. The fractionation temperature was fixed in the vicinity of the melting point of polyethylene block in copolymer (Table I). The solvent-nonsolvent system was selected on the basis of the cloud point, and the composition of eluent was varied by the exponential gradient method. The stationary method in a solvent-nonsolvent (7:3 V/V)

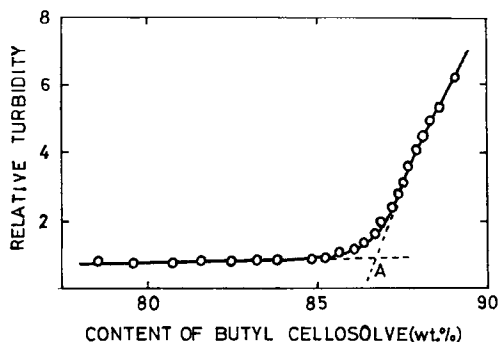


Fig. 1. Curve of turbidimetric titration: A, cloud point.

system was adopted for polymer deposition onto the support (Celite 545).⁷ Other procedures are the same as described previously.^{7,8}

Solvent Extraction. Solvent extraction was carried out in a Soxhlet extractor by using ethyl ether, *n*-hexane, cyclohexane, and *n*-heptane successively.

Infrared Analysis. A Hitachi Model EPI-G₃ infrared spectrophotometer was used to determine the ethylene content and monomer sequence length of the copolymer. Ethylene content was determined by Corish's method,⁹ which is based on the ratio of the intensity at 1380 cm⁻¹ to that at 1460 cm⁻¹ arising from the methyl group, and the methyl and methylene groups, respectively. Blends of commercial PP and PE (Hizex) were used for the preparation of the calibration curve.

In the determination of monomer sequence length, a film of 0.1-mm thickness was prepared with a heated press, and the intensity at 722 cm⁻¹ was measured at 150°C with a heating cell to remove the effect of crystalline band. The values of ethylene content were in good agreement with those obtained by NMR.

Gel Permeation Chromatography. A Shimadzu GPC Model-1A was employed with a combination of four columns, i.e., Poramina 1300 (the same as described previously¹⁰), crosslinked polystyrene gel of 1 × 10⁵, 1 × 10⁴, and 1 × 10³ Å permeability. *o*-Dichlorobenzene was used as

TABLE I
Fractionation Temperature of Samples

Samples	Melting point, °C	Fractionation temp., °C
A	116	123
B	none detected	119
C	120	120
D	117	117
E	120	120

* Obtained from DSC.

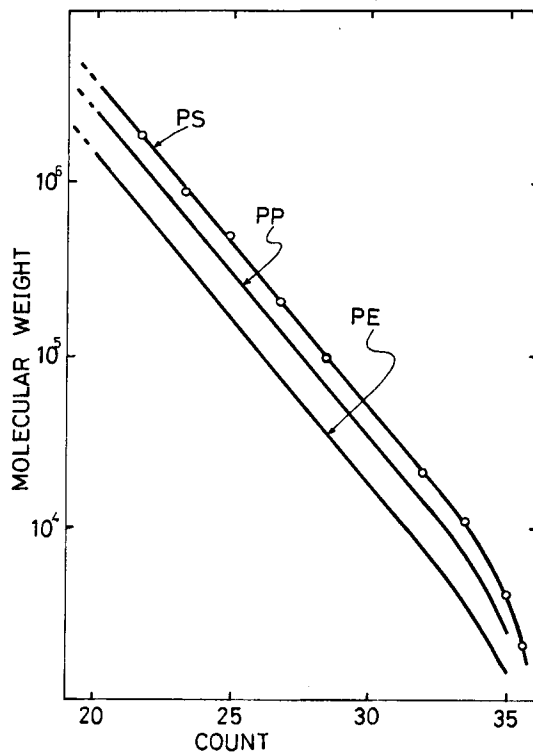


Fig. 2. Calibration curves of PE and PP deduced from that of PS. The curve of the EP copolymer was determined from ethylene content.

solvent at 135°C. Other experimental conditions were the same as reported previously.⁸

It was assumed that the calibration curve of EP copolymer was located between the curves of the two homopolymers composed of each monomer component and that the location was defined as the arithmetic mean of the ethylene content of each fraction. This assumption is considered to be reasonable from the standpoint of the properties of such copolymers in a good solvent, as discussed by Flory.⁵

The calibration curves of PE and PP were obtained as shown in Figure 2 by applying the universal rule of calibration from the polystyrene (PS) calibration curve,¹¹⁻¹⁴ which was determined by using standard samples (Pressure Chemical Co.). Applying this rule, the following viscosity-molecular weight relationships were adopted, which were determined by using fractionated samples and PS standard samples under the same conditions as employed in GPC:

$$[\eta] = 7.4 \times 10^{-5} \times \bar{M}^{0.75} \text{ (PS)} \quad (1)$$

$$[\eta] = 4.9 \times 10^{-4} \times \bar{M}^{0.74} \text{ (PE)} \quad (2)$$

$$[\eta] = 1.0 \times 10^{-4} \times \bar{M}^{0.78} \text{ (PP)} \quad (3)$$

However, strictly speaking, the calibration curves obtained above are available only when composition of each fraction is uniform.

Osmometry and Light Scattering. Average molecular weights of the fractions were determined mainly by GPC, and for some fractions by osmometry and light scattering.

A Hewlett Packard Model 502 high-speed membrane osmometer was employed to determine the number-average molecular weight. Determination was made in tetralin solution containing 0.2% Ionol (2,6-di-*tert*-butyl-*p*-cresol) with a conditioned ultracellafilter (allerfeinst) at 130°C.⁷

A Sofica 42000 M light-scattering instrument was employed to determine the weight-average molecular weight. Determination was made at 140°C for α -chloronaphthalene solution. A millipore filter holder with two pieces of fluororesin filter paper UF-6 was used in the filtration of the solution. The weight-average molecular weight was calculated by the Zimm plot method. Specific refractive index increment (dn/dc) of the EP copolymer was treated as the arithmetic mean of those of PP (-0.188) and PE (-0.191).^{15,16}

DSC Analysis. A Perkin Elmer Model DSC-1B differential scanning calorimeter was used as a heating rate of 20°C/min with each 5-mg sample. The thermogram was corrected by the peak position of high-purity indium.

RESULTS AND DISCUSSION

Solubility of Polymers

Solubility of PE, PP, and EP copolymer was first investigated for the selection of suitable solvent-nonsolvent systems. Cloud points of PE and PP determined in several solvent-nonsolvent systems as indication of solubility are shown in Figure 3. To fractionate EP copolymer satis-

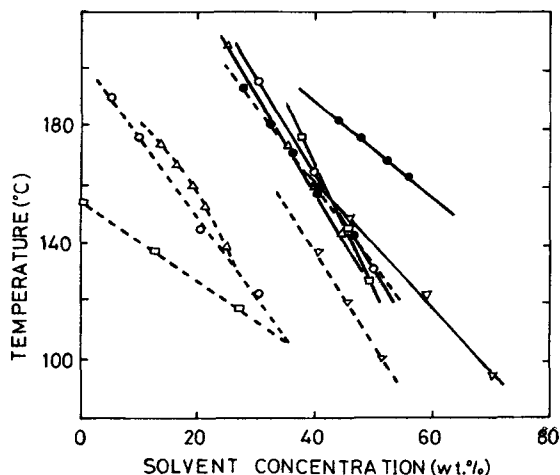


Fig. 3. Cloud points of PE and PP in various kinds of solvent-nonsolvent systems.

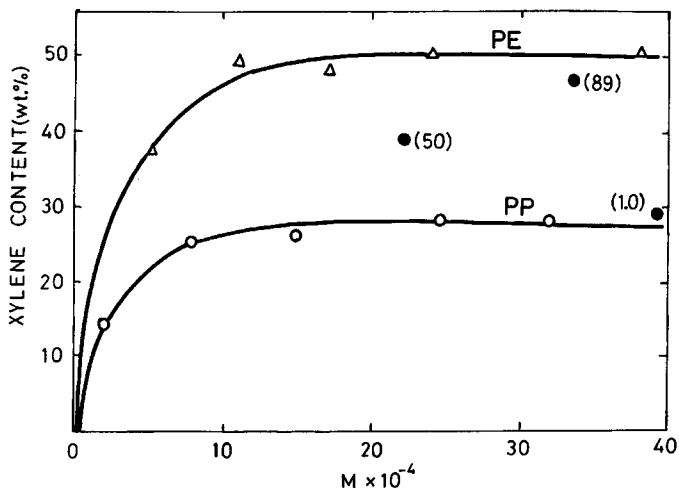


Fig. 4. Dependence of cloud points on molecular weight in xylene-butyl cellosolve system at 127°C; (Δ) PE; (\circ) PP; (\bullet) EP copolymer.

factorily according to chemical composition, a large difference is required between the solubility of PE and PP. In Figure 3, the xylene-butyl cellosolve system seems to be the most desirable system for this purpose. The solubilities of both homopolymers have to be consistent with each other for ideal molecular fractionation. However, this requirement was not exactly satisfied by any system shown in Figure 3. The most advisable system is tetralin-ethyl carbitol as far as we could determine, and this system is expected to be capable of molecular fractionation.

The dependence of cloud points on molecular weight was investigated in the xylene-butyl cellosolve system at 127°C, and the results are shown in Figure 4. Considerable dependence on molecular weight was recognized in both PE and PP in the molecular weight range below about 1.0×10^5 , and so it is anticipated that EP copolymer can be fractionated according to both chemical composition and molecular weight.

On the other hand, the dependence of cloud points on molecular weight was hardly noticeable in the molecular weight range above 1.0×10^5 . It was also confirmed that the cloud points of EP copolymer were located between those of PE and PP, and therefore they can be determined as arithmetic mean of those of the homopolymers. Therefore, in the molecular weight range above about 1.0×10^5 , the fractionation of EP copolymer is expected to proceed only according to chemical composition.

Compositional Fractionation

The fractionations of the original copolymers were carried out in a xylene-butyl cellosolve system on the basis of the cloud points obtained. Integral weight distribution curves are shown in Figure 5. It was found that compositional fractionation definitely took place in these samples.

Partial inversion in the distribution curve was observed in the early fractions of sample C. This is probably due to the dependence of the cloud points on molecular weight in this region, and that, therefore, the copolymers were fractionated according to both chemical composition and molecular weight. A similar tendency was observed in the case of isobutylene-styrene copolymer.¹⁷

Since this fractionation depends on only chemical composition in the molecular weight range above 1.0×10^5 , the fractions obtained are anticipated to have still a broad distribution in molecular weight. Molecular weight distributions of each fraction are shown in Table II in the form of

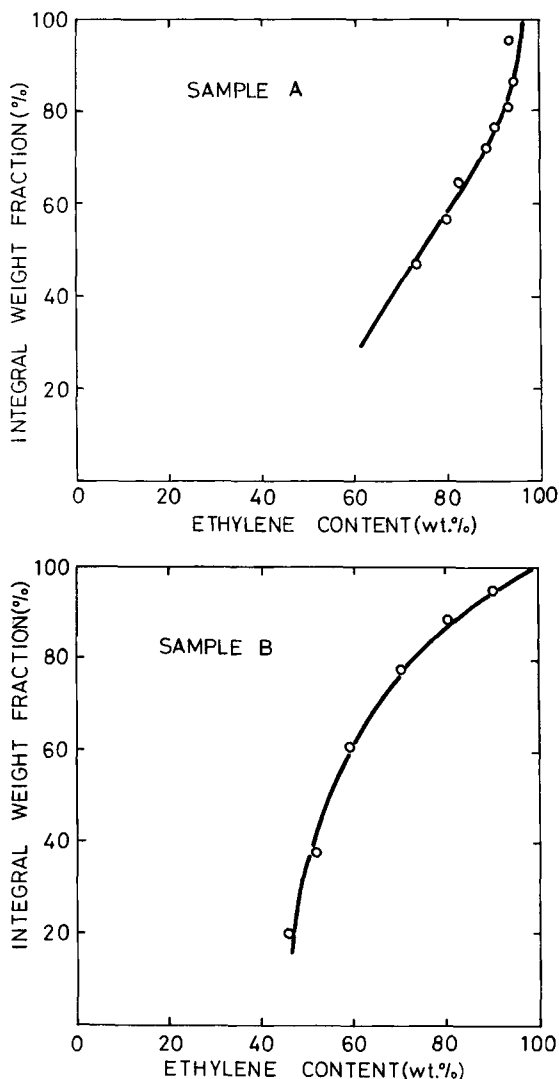


Fig. 5 (continued)

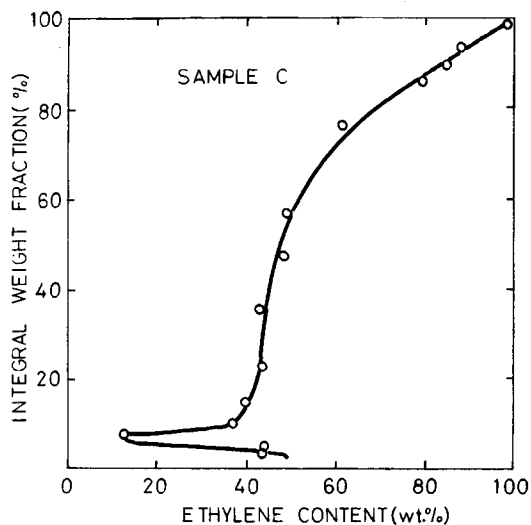


Fig. 5. Distribution curves of chemical composition for EP copolymers.

$D (= \bar{M}_w/\bar{M}_n)$. These values were obtained by GPC or osmometry and light scattering, no difference in D value was found between these two methods.

Although the D values of the fractionated polymer are usually less than 1.3 in the case of PE or PP, except at both ends of fractions, the copolymer fractions give considerably larger values (2.5 on the average), as shown in Table II. This is also an indication of a compositional fractionation. It seems that this average value is the probable D value when fractions of uniform chemical composition were obtained from original copolymer.

TABLE II
Molecular Weight and Molecular Weight Distribution of Fractions

Fraction	Method ^a	Ethylene			
		content, wt-%	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n (D)
A-4 } blend (7:3	LS, OS	63.8	7.5	3.0	2.5
A-5 } wt)					
A-6	GPC	73.8	7.4	4.4	1.7
A-7	GPC	79.5	10.5	6.1	1.8
A-8	GPC	82.0	17.0	6.2	2.8
A-9 } blend	LS, OS	89.0	33.3	11.1	3.0
A-10 } (7:3 wt)					
A-12 } blend	LS, OS	94.0	30.0	11.9	2.5
A-16 } (7:3 wt)					
C-4	GPC	12	12.6	4.8	2.6
C-5	GPC	37	27.6	11.2	2.5
C-13	GPC	61	41.6	14.3	2.9
C-17	GPC	87	60.8	29.9	2.0

^a LS = Light scattering; OS = osmometry; GPC = gel permeation chromatography.

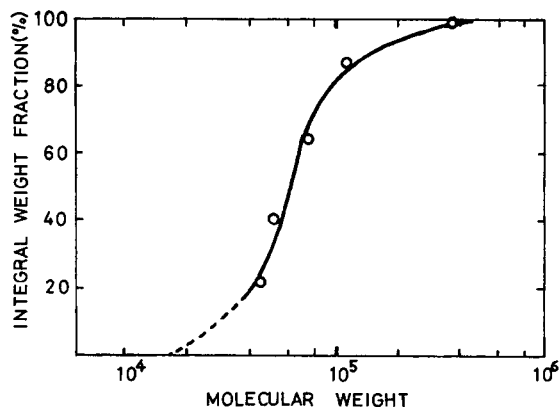


Fig. 6. Molecular weight distribution curve: fractions 6 and 7 (1:1 blend) upon compositional fractionation of sample C.

Molecular Fractionation

Some of the fractions obtained above were further fractionated depending on molecular weight in the system of tetralin-ethyl carbitol, which seems to be the most advantageous system for this purpose (cf. Fig. 3). The results are shown in Figure 6, where integral weight fraction was plotted against the peak position of the GPC curve for each fraction, although dependence on molecular weight was usually observed, D values of each fraction were estimated to be 1.3-1.8. This is considered to be caused by the fact that the fractionations were carried out in a system in which the solubilities of PE and PP were not completely consistent.

Fractionation According to Monomer Sequence Length

A solid-liquid phase equilibrium system was estimated to be suitable for the fractionation according to monomer sequence length, as described above. The fractionated polymers obtained by the compositional fractionation were successively extracted by various kinds of solvents, and the results are summarized in Table III. Considering the ethylene contents and the D values in this table, it can be said that fractionation was carried out almost independent of chemical composition or molecular weight, and that fractionation in this extraction depended only on monomer sequence length.

Detection of melting peak by DSC and measurement of infrared absorption bands in the region $700-850\text{ cm}^{-1}$ arising from the rocking mode of methylene groups were carried out to confirm the dependence of this fractionation on monomer sequence length. No peak was observed in thermograms of ether or n -hexane extracts, as shown in Figure 7, which shows that these extracts have high randomness with respect to the monomer sequence distribution in a polymer chain. A melting peak of PE block was detected in the n -heptane extract at 119°C . A further melting peak of PP became detectable in the n -heptane residue at 159°C together

TABLE III
Solvent Extraction of Fractions Obtained by
Column Fractionation in Xylene-Butyl Cellosolve

Fraction		Ether extract	<i>n</i> -Hex- ane extract	Cyclo- hexane extract	<i>n</i> -Hep- tane extract	<i>n</i> -Hep- tane extract
Sample C, no. 10, 11, 12 (1:1:1 wt blend)	Weight, %	9.3	15.6	No ex- traction	74.0	1.1
	Ethylene content wt-%	60.0	47.0	—	53.3	—
	<i>D</i> value	2.7	2.2	—	3.4	—
Sample D, no. 3	Weight, %	15.2	13.6	16.1	11.2	44.0
	Ethylene content wt-%	—	37.3	40.0	49.0	31.3
	<i>D</i> value	—	2.3	3.3	3.2	4.2
Sample E, no. 6, 7 (1:1 wt blend)	Weight, %	17.8	25.7	13.7	20.8	22.0
	Ethylene con- tent, wt-%	57.8	46.7	35.0	33.7	33.3
	<i>D</i> value	5.1	4.2	4.0	3.8	3.2

with that of PE at 120°C. The same tendency was also confirmed for other samples.

The infrared absorption bands arising from $-(\text{CH}_2)_{n>4}-$ (ca. 720 cm^{-1}) was investigated here, and block length of PE was evaluated according to Bucci's method.⁸ The results are shown in Table IV, with the theoretical values of EP random copolymer calculated by Bucci. As shown in this table, the deviation from theoretical value increases with the progress of solvent extraction.

Thus, it is evident that a fractionated polymer having a considerably uniform composition can be further fractionated according to monomer sequence length by this solvent extraction method.

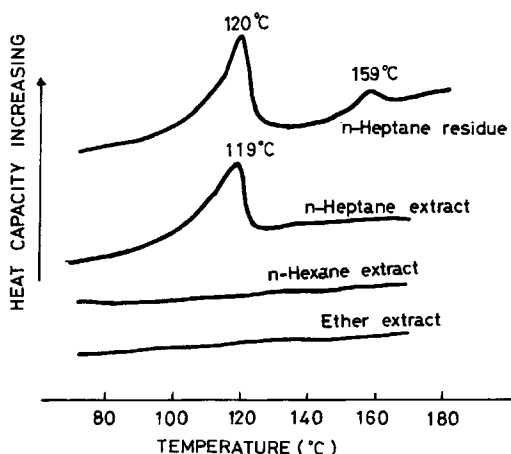


Fig. 7. Thermogram of solvent extracts: fractions, 10, 11, and 12 (1:1:1 blend) upon compositional fractionation of sample C.

TABLE IV
Solvent Extraction of a Fraction Obtained in Xylene-Butyl Cellosolve

Fraction	—(CH ₂) _{n>4} — Content		
	Theoretical, ^a wt-%	Observed, wt-%	Deviation, wt-%
Ether extract	8.5	12.4	3.9
<i>n</i> -Hexane extract	11.0	17.6	6.6
Cyclohexane extract	10.5	18.3	7.8
<i>n</i> -Heptane extract	12.0	20.5	8.5
<i>n</i> -Heptane residue	15.5	24.0	8.5

^a Estimated from ethylene content by Bucci's method.¹⁸

Distributions of Copolymer

It has become evident that compositional fractionation can be carried out in a xylene-butyl cellosolve system over a wide range of molecular weight. Therefore, since the fraction is regarded to have a uniform composition for all polymer species included, it is possible to draw a distribution range on chemical composition and molecular weight from ethylene contents and GPC curves, respectively, of each fraction without further fractionation. The results for sample C are shown in Figure 8, which shows that this polymer has a very broad distribution for both factors of chemical composition and molecular weight. The shape of this distribution range is expected to be considerably varied depending on the polymerization process as compared with the molecular weight distribution of the homopolymers. Details concerning the shape of the distribution range will be discussed in another paper in relation to the solubilities of the homopolymer and copolymer.

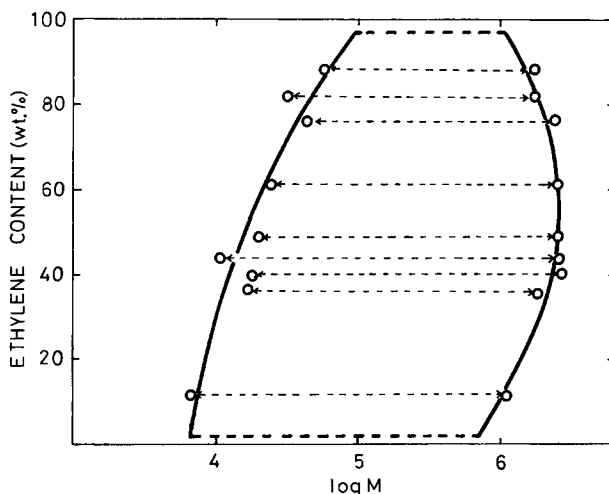


Fig. 8. Distribution range of chemical composition and molecular weight for sample C. The molecular weight range for each fraction was determined by both ends of the GPC curve.

The detailed distribution of monomer sequence length should be discussed in terms of solvent extraction of each fraction obtained by compositional and molecular fractionation. However, the characterization of extracts is usually difficult because of the extremely small amount of the extracts, with the exception of the case of large-scale fractionation, which is now under investigation in our laboratory. The distribution of the monomer sequence length was then roughly estimated for reference by solvent extraction of the original polymer. The results for sample C are shown in Table V.

CONCLUSIONS

Cloud points of polyethylene, polypropylene, and ethylene-propylene copolymers were determined prior to the fractionation for the purpose of selecting the appropriate systems for the fractionations according to chemical composition and molecular weight. It was then found that xylene-butyl cellosolve and tetralin-ethyl carbitol systems, respectively, were suitable for these purposes.

Ethylene-propylene random-type copolymers were fractionated by the column method in a xylene-butyl cellosolve system, and satisfactory results according to chemical composition were obtained.

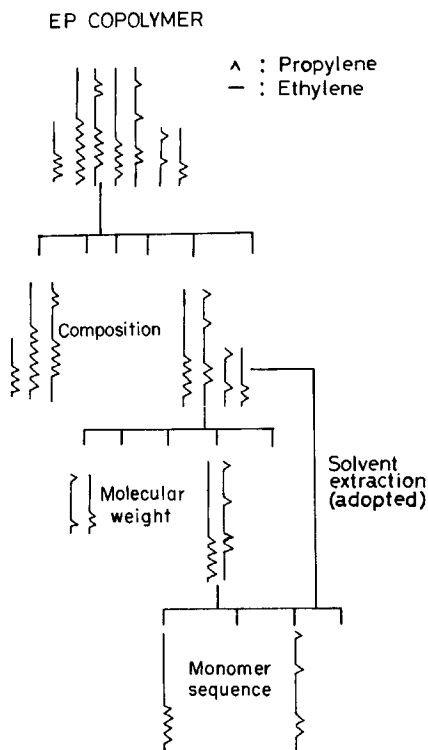


Fig. 9. Fractionation processes adopted in this study.

TABLE V
Solvent Extraction of Original Polymer (Sample C)

	Ether extract	<i>n</i> -Hexane extract	Cyclohexane extract	<i>n</i> -Heptane extract	<i>n</i> -Heptane residue
Weight, %	34.7	28.9	9.3	9.8	17.3
Ethylene content, wt-%	40.0	57.3	52.7	88.0	—

The above polymer fractions were further fractionated in tetralin-ethyl carbitol, and fractionation according to molecular weight was fairly consistent.

Furthermore, fractionation according to monomer sequence length was satisfactorily achieved by solvent extractions using ethyl ether, *n*-hexane, cyclohexane, and *n*-heptane.

As a result of these investigations, it was concluded that ethylene-propylene random-type copolymers have very broad distributions for these three factors.

It is believed that the more detailed characterizations of ethylene-propylene copolymers are possible by a combination of these techniques (Fig. 9).

The authors are indebted to Dr. S. Hoshino for suggestions with regard to this paper, and also thank Mr. T. Terada for his assistance.

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Received April 11, 1972