Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Melting Point and Composition Distribution of Polyolefins by Fractionation

D. F. Slonaker[a]; R. L. Combs[a]; H. W. Coover JR.[a]
[a] RESEARCH LABORATORIES, TENNESSEE EASTMAN COMPANY, DIVISION OF EASTMAN KODAK COMPANY, KINGSPORT, TENNESSEE

To cite this Article Slonaker, D. F. , Combs, R. L. and Coover JR., H. W.(1967) 'Melting Point and Composition Distribution of Polyolefins by Fractionation', Journal of Macromolecular Science, Part A, 1: 3, 539 — 557
To link to this Article: DOI: 10.1080/10601326708053988
URL: http://dx.doi.org/10.1080/10601326708053988

J. MACROMOL. SCI. (CHEM.), A1(3), 539–557 (1967)

Melting Point and Composition Distribution of Polyolefins by Fractionation

D. F. SLONAKER, R. L. COMBS, and H. W. COOVER, JR.
RESEARCH LABORATORIES,
TENNESSEE EASTMAN COMPANY,
DIVISION OF EASTMAN KODAK COMPANY,
KINGSPORT, TENNESSEE

Summary

The fractionation technique described in this paper was used to characterize the melting-point, monomer, and blocking distributions for polymers and copolymers. It is different from the molecular-weight fractionation technique in that the fractions are obtained by using a single solvent to extract the solid polymer below its melting point at stepwise-increasing temperatures. The reproducibility of this technique is excellent, and the technique is sufficient to distinguish pellet-to-pellet variation in a commercially available polypropylene. It was used to show the influence of preparation variables on the melting-point distributions of polyethylene and polypropylene and on the monomer and blocking distribution of copolymers, and to distinguish copolymers from blends.

The molecular parameters which are most commonly considered to characterize a polymer are molecular weight, crystallinity, and, in a copolymer, concentration of the monomers. It is recognized that a polymer has a molecular-weight distribution as well as an average molecular weight; in the same manner, a crystalline polymer has a molecular stereoregularity or melting-point distribution in addition to its average crystallinity. In a copolymer, the monomer distribution can have a considerable influence on properties and does vary among the molecules.

The first work regarding the use of column methods to achieve elution of a polymer at stepwise-increasing temperature was reported by Desreux and Spiegels in 1950 (*1*). However, their work was aimed primarily at accomplishing separation on the basis of molecular weight. Several workers (*2–6*) used extractions to achieve separations on bases other than molecular weight. Hawkins and Smith (*2*) found a separation in polyethylene which occurred on the basis of short-chain branching frequency; Wija et al. (*3*) found the column technique to be sensitive to crystallinity as well as molecular weight in the fractionation of polypropylene when the elution temperature was kept below the melting point of the polymer. Natta and several other workers (*7–10*) reported the use of a series of two extraction steps to obtain three fractions for the characterization of polypropylene. The most refined experiments using different solvents of increasing boiling points to achieve fractionation of polypropylene on the basis of stereoregularity were recently reported by Nakajima and Fujiwara (*11*) and by Yamaguchi et al. (*12*).

Many workers (*13–15*) have been interested in theoretical calculations of the monomer distributions in copolymer molecules, but only a few (*16–17*) have attempted to measure these distributions. In one of these cases (*17*), no fractionation was done; rather, an interpretation of the infrared spectrum was used.

The technique used in our investigation is a modification of that used by Desreux and Spiegels (*1*). Extraction of the solid polymer below its melting point at stepwise-increasing temperature by using a single solvent is used to give as many as 15 fractions. These fractions differ in melting point, monomer content, or amount of blocking of the monomers. Some results from characterization by this technique have already been published (*18–22*). This paper describes the method in detail and gives further characterizations of polyolefins. Fractionation results from the characterization of five polypropylenes, one polyethylene, five propylene copolymers, and two blends of polyolefins are discussed.

EXPERIMENTAL

Melting-Point Fractionation

The melting-point fractionation column is 1 ft shorter than the column used for molecular-weight fractionation (*23,24*). Otherwise, the dimensions of the two columns are the same; but, in the fractionation, the entire column was kept at the same temperature at any given time rather than having a temperature gradient.

The solution to be loaded onto the column was prepared by dissolving 2.0 g of polymer in 160 ml of nitrogen-saturated Tetralin, which was stabilized with 0.1% Santonox R. The flask containing the solution was heated to 170°C ± 10°C until the polymer completely dissolved. When the inherent viscosity $\{\eta\}$, of the polymer was $\geqslant 3.0$, the loading was reduced to 0.5 g of polymer. With polyolefins of ultrahigh viscosity ($\{\eta\} \geqslant 6.0$), it was often necessary to use a high-boiling petroleum cut such as Bayol 35 in order to avoid column plugging due to gel formation.

The column was loaded with fine glass beads (Superbrite, No. 130, Minnesota Mining and Manufacturing Co.) to within 6½ in. of the top, and was kept filled with stabilized Tetralin to prevent the development of air locks or channels. The column was brought to a temperature of 150°C. The electronic system for the temperature and time control unit was specially prepared in our laboratories and is not commercially available. The hot polymer solution was added to the 6½-in.-deep free space at the top of the column, and a slow flow of nitrogen was directed into the top of the open column while the solution displaced pure Tetralin from the bottom of the column. The dissolving flask was rinsed with 40 ml of hot Tetralin, and the rinse was added to the top of the column when the polymer solution had just digested onto the glass beads. The flow was then stopped at the bottom of the column, the column heat turned off, and chilled water run through the cooling coils which surround the column. The column was normally cooled to about 10°C below the temperature which was to be used for the elution of the first fraction. These steps complete the loading procedure.

The remainder of the technique concerns the selective elution of the polymer from the column with Tetralin (other solvents or solvent mixtures may be required for some polymers) by increasing the elution temperature in a stepwise manner, and also concerns the recovery of the fractions from solution. Fifteen 10-turn potentiometers were provided on the control panel for the selection of the elution temperatures for each of the 15 fractions. Two typical temperature programs are shown in Table 1. In order to elute a volume which is twice the column free volume, it was necessary to use the time program given with each temperature program, because the flow rate increased with the column temperature. This

TABLE 1

Fractionation Programs[a]

Program 1—highly crystalline polyolefins			Program 2—moderately crystalline polyolefins		
Fraction no.	Temp., °C	Time, min	Fraction no.	Temp., °C	Time, min
1	40	138	1	25	145
2	65	121	2	44	132
3	85	104	3	64	119
4	95	99	4	77	112
5	102	99	5	87	106
6	105	94	6	94	99
7	108	94	7	100	99
8	111	88	8	104	99
9	114	88	9	107	92
10	116	88	10	109	92
11	117	88	11	111	92
12	118	88	12	113	92
13	119	88	13	116	86
14	122	82	14	120	86
15	150	66	15	150	66

[a] All programs were prepared for use with a 16-mil-I.D. capillary which is 2.53 in. long and is operated at 175 ± 7°C.

increase was due to the effective reduction in the Tetralin viscosity. Program 1 was used for highly crystalline polyolefins such as polypropylene and copolymers containing more than 95% propylene. Program 2 was used for moderately crystalline polyolefins such as copolymers of propylene containing less than 95% propylene.

If the first fraction was to be collected below 25°C, the cold water was left circulating through the column; otherwise the cooling water was turned off. The solvent reservoir was filled with nitrogen-saturated solvent containing a stabilizer, the necessary connections were made at the top of the column, the flow of solvent was started through the column, and the eluate was collected in 1-liter beakers. The rate of flow was partially controlled by a heated capillary attached to the bottom of the column. With our automatic collecting and temperature-programming control unit, the fractionation requires no further attention until the completion of the fifteenth fraction. The final fraction for all temperature programs was taken at 150°C. This procedure allows another polymer to be loaded onto the column immediately. Normally, 20 to 25 hr is required for each fractionation to be completed, and four polymers can be fractionated routinely per week. To confirm completeness of elution prior to terminating the fractionation, about 50 ml of eluate was added to 100 ml of acetone or a suitable precipitating agent. If no polymer precipitated within 10 min, the fractionation was terminated; otherwise additional quantities of Tetralin were added to the column and the elution was continued at 150°C.

A volume of acetone 1.5 times the amount of solvent collected was added with stirring to each fraction and allowed to stand 8 to 20 hr. Tared 150-ml fine-fritted-glass funnels were then used to vacuum filter each fraction. It was sometimes necessary to combine fractions to obtain enough sample for certain analyses. Each fraction was stabilized by just saturating it with a 0.1% solution of Santonox R in a 3% acetone and 97% pentane solution. The solvent was allowed to evaporate and the polymer was left with a coating of stabilizer.

The filtrates from the first few fractions were retained until the percentage of recovery of polymer had been established. If the recovery was greater than 97%, these filtrates were then discarded, but if the recovery was less than 97% the filtrates were combined and evaporated to dryness. Methanol was used to extract the residual stabilizer from the filtrate residue. The filtration funnels containing the polymer were dried for at least 6 hr and preferably overnight in a vacuum oven at 50°C and less than 3 mm Hg pressure. The tared funnels were reweighed, and the polymer was removed from each by using a sharp razor blade with such care that no glass was removed from the frit.

Polarized-Light Melting-Point Determination

For this analysis a Kofler Micro Hot Stage (Arthur H. Thomas Co., Cat. No. 6886A) was used. A small amount of the sample, less than 1 mg, was placed on a slide and covered with a thin cover glass. The cover glass was pressed down firmly to reduce the distance between the slide and cover glass so that light could be more easily transmitted through the polymer sample. The slide and cover assembly were placed on the hot stage, the microscope was focused, and a suitable field was selected. The heating rate was maintained at 1 to 2°C/min. The final disappearance of crystallinity was observed between crossed Nicol prisms and was recorded as the polymer melting point.

Infrared Analysis for Percentage of Ethylene and Percentage of 1-Butene in Copolymers of Propylene

Each fraction was pressed into a 6-mil-thick sample ($\frac{9}{16} \times 1\frac{5}{16}$ in.) in a heated laboratory press. This film was placed in a special, heated infrared cell between plates of NaCl. Sufficient voltage was applied to the cell heaters to melt the polymer and thus remove any crystallinity bands from the spectrum. The spectrum of the molten film was run between 8 and 14 μ.

In copolymers containing 1-butene, the ratio of the percentage of transmission of the polypropylene peak at 12.4 μ to the percentage of transmission of the poly-1-butene peak at 13.1 μ was used for samples containing less than 30% 1-butene. For samples containing more than 30% 1-butene, the polypropylene peak at 8.7 μ and the poly-1-butene peak at 13.1 μ were used.

The percentage of ethylene was calculated from the ratio of integrated absorbance of the polyethylene peak at 13.9 μ to the integrated absorbance of the polypropylene peak at 12.4 μ.

Standard blends of unfractionated homopolymers were used for calibration. The standard deviation of the analysis was found to vary with composition, but in all cases the standard deviation was less than ±10% of the percentage of ethylene or 1-butene found for samples containing more than 50% polypropylene.

Differential Scanning Calorimetry (DSC) Evaluation of Copolymer and Blend Fractions

A 6-mil-thick film was pressed from each polymer fraction at a temperature 10 to 60°C above its melting point. A 0.25-in.-diam disc was then diced from the film, weighed, and placed in an aluminum DSC sample pan. An aluminum lid was crimped over the sample to hold it against the bottom of the pan for good thermal contact. The temperature of the sample holder assembly was calibrated with metals of known, sharp melting points, e.g., indium. The temperature was generally held at 30 to 70°C (depending upon the polarized-light melting point) when the sample was added to the unit. The temperature was increased to 180°C at 20°C/min and then decreased immediately, also at 20°C/min. After the exothermic crystallization peak was registered, the temperature was again increased to 180°C at 20°C/min. The sample was kept under an atmosphere of nitrogen while in the unit. The melting peak or peaks observed during the second heating cycle were generally used to judge the different crystalline species and their degree of crystallite perfection relative to that of highly crystalline homopolymer of each type.

Reproducibility of the Melting-Point-Fractionation Technique

The reproducibility of the melting-point-fractionation technique is indicated in Fig. 1. Melting-point data are plotted versus *S*, the sum of the weight per cents of all preceding fractions plus the weight per cent of the fraction upon which the melting point was determined. To determine the reproducibility, two 4-g samples were removed on different occasions from a container of commercial polypropylene. The pellets from each of these samples were split in half so that the two original materials gave four samplings. All four 2-g samples were then fractionated by using program 1 of Table 1. The operator did not know the identification of the starting samples.

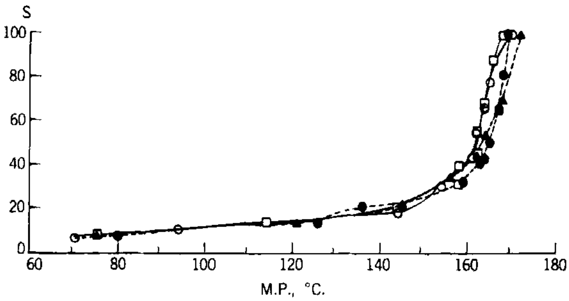

FIG. 1. Reproducibility of the melting-point fractionation technique on polypropylene A.

Molecular Weight and Melting-Point Distribution of Polypropylene

A commercial, molding-grade polypropylene was fractionated by the melting-point-fractionation technique of increasing elution temperature. The inherent viscosities of the fractions indicate that

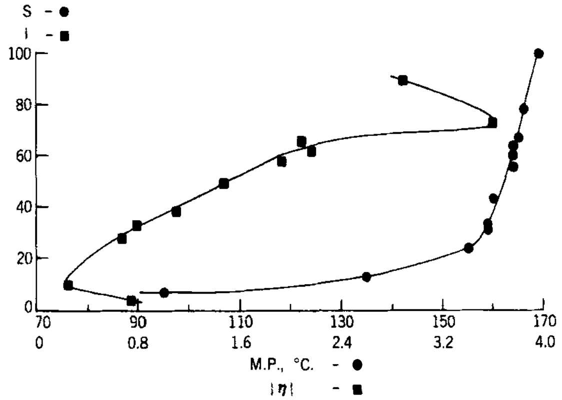

FIG. 2. Melting-point fractionation of polypropylene B.

separation on the basis of molecular weight also occurred (Fig. 2). The inherent viscosity, {η}, data are plotted versus *I*, the sum of the weight per cents of all preceding fractions plus one-half of the weight per cent of the fraction upon which the inherent viscosity was determined. The inherent viscosities were determined on a 0.1% (w/v) solution in Tetralin at 145°C. A sample of this same commercial polypropylene was also fractionated by a solvent-gradient elution technique, similar to that described by Guillet et al. (*24*), to separate the polymer according to molecular weight. As shown in Fig. 3, the inherent viscosity distribution in this case ranges from 0.16 to 5.09, compared to 0.24 to 3.6 for the melting-point fractionation shown in Fig. 2. The melting-point distribution of these fractions varies only from 148 to 169°C, compared to 95 to 169°C for the melting-point fractionation.

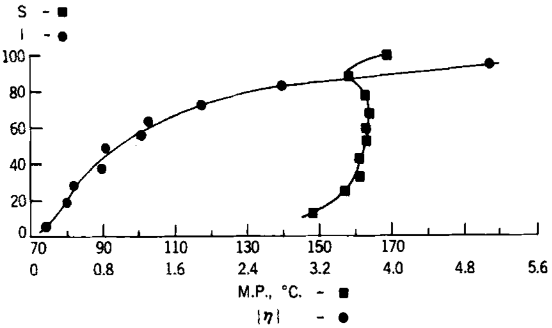

FIG. 3. Molecular-weight fractionation of polypropylene B on the basis of solvent gradient elution.

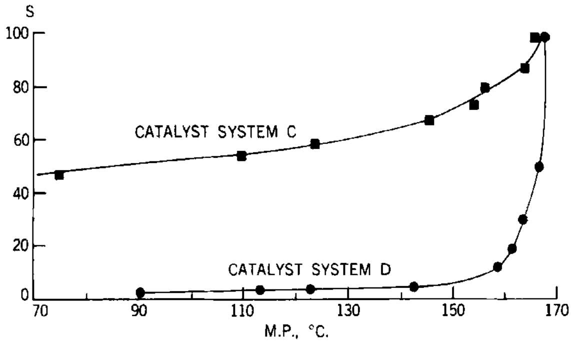

FIG. 4. Effect of polymerization catalyst on the melting-point distribution of polypropylenes C and D.

Effect of Catalyst on Melting-Point Distribution

Polypropylene made with catalyst system C has a very low degree of average crystallinity. The melting-point-distribution curve of this polymer is compared in Fig. 4 with that of a polypropylene prepared with another catalyst system, D.

Polyethylene Short-Chain Branching Distribution

A sample of commercial high-density polyethylene was fractionated by using an increasing-temperature program designed specifically for polyethylene. Because of the unusual shape of the curve obtained and the relatively large amount of low-melting polymer, the experiment was repeated. Both sets of data are plotted in Fig. 5 on the basis of melting point. The melting points of these

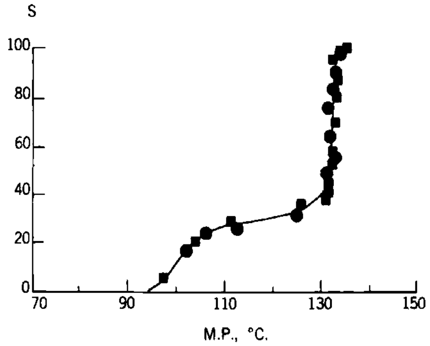

FIG. 5. Melting-point distribution of a commercial high-density polyethylene formulation.

fractions are indicative of the frequency of short-chain branching. The temperature program used for these fractionations was very similar to program 2 of Table 1.

Composition Fractionation of Homopolymer Blends

Composition fractionations of blends of homopolymers were used to indicate the limitations of the technique and to establish at what temperature such homopolymers would be expected to be eluted if they should be present in experimental copolymers. In Fig. 6, the monomer distribution as well as the melting-point dis-

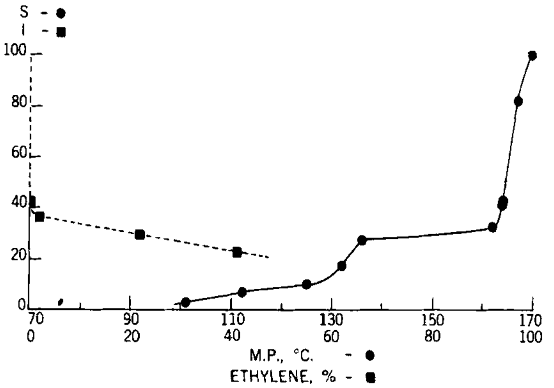

FIG. 6. Monomer and melting-point distributions of an 80/20 polypropylene/ polyethylene blend.

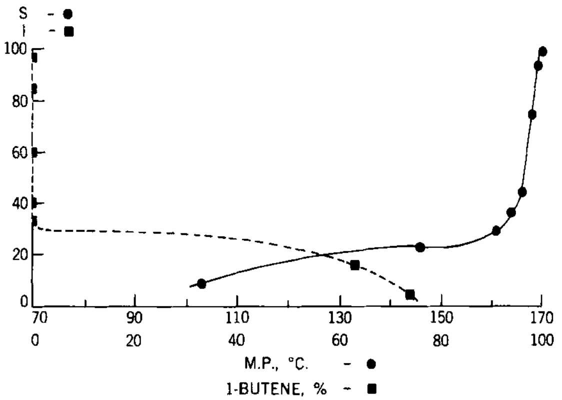

FIG. 7. Monomer and melting-point distributions of an 85/15 polypropylene/ poly-1-butene blend.

tribution of an 80/20 polypropylene/polyethylene homopolymer blend fractionation is shown. Comparable distributions are shown in Fig. 7 for an 85/15 polypropylene/poly-1-butene blend.

Composition Fractionation of Copolymers

The monomer distribution of 12% 1-butene and 88% propylene copolymer is compared with that of a physical blend of 85% polypropylene and 15% poly-1-butene in Fig. 8. The fractionation data of a propylene copolymer containing 40% 1-butene are given in Table 2.

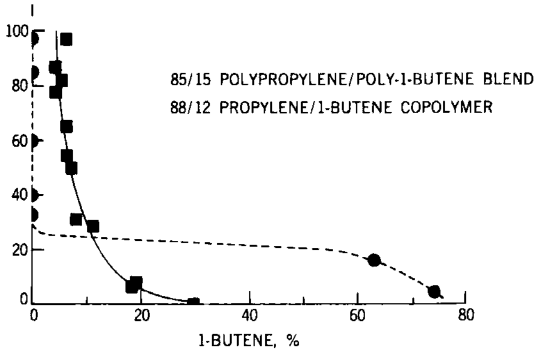

FIG. 8. Monomer distributions of a propylene/1-butene copolymer and a homopolymer blend.

TABLE 2

60/40 Propylene/1-Butene Cocrystalline Copolymer Fractionation Data

Fraction no.	Melting point, °C	$\{\eta\}$	1-Butene, %	X-ray-diffraction type	Extraction temp., °C
1	87	0.92	68	Polypropylene + mostly poly-1-butene	< 18
2	93	0.49	53	Polypropylene + poly-1-butene	33
3	108	0.64	48	Polypropylene + poly-1-butene	47
4	113	0.80	33	Polypropylene	53
5	122	0.81	26	Polypropylene	64
6	130	1.07	21	Polypropylene	72
7	143	0.96	15	Polypropylene	98
8	155	1.48	12	Polypropylene	130

TABLE 3

Characterization of Propylene/Ethylene Copolymer Fractions

				Differential scanning calorimeter data				
Copolymer	Fraction no.	S	Melting point, °C[a]	Recycle melting temp., °C[b]	Polyethylene crystallinity, %[c]	Polypropylene crystallinity, %[d]	Ethylene content by infrared analysis, %	Column extraction temp., °C
E	93-5	11.3	121	120, 140, 146	7.3	12.3	50	87
F	94-3-5	9.3	122	117	5.7	0	42	87
E	93-8	26.5	133	127, 153, 159	12.6	15.6	34	104
F	94-9	21.2	161	155, 162	0	23.9	10	107
E	93-12	57.1	167	159	0	26.1	0	113
F	94-13	55.6	167	166	0	22.1	0	116
E	93-16	100.0	169	163	0	25.5	0	150
F	94-15	100.0	169	164	0	24.9	0	150

[a] Disappearance of crystallinity under polarized light.

[b] Peak point of melting curve.

[c] Calculated by assuming 69.7 cal/g for the ΔH_f for 100% polyethylene.

[d] Calculated by assuming 61.9 cal/g for the ΔH_f for 100% polypropylene.

Stepwise increasing-temperature fractionation has been applied to the characterization of block copolymers, and the resulting fractions were subjected to several different analyses, among which were melting point, infrared spectroscopy, and DSC. The differential scanning calorimeter was used for establishing multicrystallinity species and the percentage of each crystalline species present in the individual fractions. Table 3 contains data concerning the fractions from two experimental copolymers, E and F, which have different physical properties. Another copolymer was prepared by using a two-stage reactor in which only propylene monomer was

TABLE 4

Molecular Characterization of 15% Ethylene Block Copolymer of Propylene

Species	Approximate amount, %
Propylene homopolymer	82
Crystalline propylene block—random propylene/ethylene block copolymer[a]	9
Cocrystalline fraction	9

[a] Highly soluble, yet contains high-melting-polypropylene crystallinity.

used in the first stage, and both propylene and ethylene were present in the second stage. A quantitative summary of the types of species present as indicated by our fractionation technique is given in Table 4.

DISCUSSION OF RESULTS

As shown in Fig. 1, the melting-point-distribution reproducibility of this fractionation technique is very good. The two solid lines represent the fractionations of the split-pellet sampling from one of the two original samples of polypropylene, and the dashed lines represent the fractionations of the split pellets from the second original sample. The greatest differences are seen in the area where *S* is 40 to 90; the curves pair up according to the original sample from which the pellets were taken. Statistical evaluation of the data established that the average reproducibility of the technique is ±2°C at the 95% confidence interval for any given point on the curves. However, the reproducibility of the two different samplings from the same container of polypropylene is only ±5°C at the 95% confidence interval. Thus the method is quite reliable, and is capable of detecting pellet-to-pellet variations within a given lot of polymer.

For polypropylene, separation on the basis of the stereoregularity or the melting point of the fractions is complicated by separation on the basis of inherent viscosity (Fig. 2). There are actually some molecules present which melt as low as 95°C; however, 80% of the polymer melts in the 150 to 170°C range. The melting points increase with each successive fraction as the extraction temperature is increased, but the inherent viscosity of the molecular-weight distribution starts at about 0.8 and drops to about 0.2 before beginning a more or less gradual ascension. The initial drop in the inherent viscosity curve is probably due to the fact that only highly amorphous polymer is soluble at very low extraction temperatures. This amorphous polymer can have a reasonably high molecular weight. Although the measurements of *S* and *I* were made on the same fractions, the locations of the points along the vertical axis are different because *S* and *I* are calculated differently.

Fractionation of a sample of the polymer used previously (Fig. 2) by a solvent-gradient constant temperature method (*24*) produced a broad molecular-weight distribution ($\{\eta\}$ 0.16 to 5.09) as opposed to the narrower inherent viscosity range (0.24 to 3.6) obtained when the sample was fractionated by the increasing-elution-temperature or melting-point technique. The data are shown in Fig. 3, and it can be seen that the melting-point distribution from these molecular-weight-separated fractions is quite narrow. Thus, both fractionation procedures are required to completely characterize a polyolefin distribution.

The effect of the polymerization catalyst on the crystallinity distribution of polypropylene can be quite striking (Fig. 4). About 50% of the polymer made with catalyst system C melts below 90°C, whereas only about 1% of the polymer made with catalyst system D melts below this temperature. Around 85% of the latter polypropylene melts above 160°C.

The ability of this fractionation technique to detect subtle differences in melting-point distributions is shown by a comparison of the distribution in Fig. 1 with the lower distribution in Fig. 4. These two polypropylenes were prepared with different catalysts.

The melting-point distribution of a high-density polyethylene shown in Fig. 5 is an indication of the short-chain branching frequency distribution of the polymer. About 60% of the polymer was found to melt between 130 and 135°C, which is typical for high-density polyethylene; however, an appreciable amount of polymer melted below 110°C. This indicates that the total polymer is a blend of low-density polyethylene in high-density polyethylene. Here, the melting-point fractionation technique was superior to other methods in confirming a blend formulation, since it also gave an indication of the amount of each component.

The fractionation of blends of high-molecular-weight homopolymers, such as those represented by the monomer and melting-point distributions shown in Fig. 6, was used to indicate the limitations of the fractionation method and to determine at what temperature such homopolymers would be expected to appear if they should be present in a sample which is presumed to be a copolymer. The complete separation of propylene and ethylene homopolymers has not yet been accomplished with this method, since high-density, high-molecular-weight polyethylene is not completely eluted from the column with Tetralin until a temperature of about 100 to 102°C is reached. At this temperature, a small but appreciable amount of polypropylene of relatively low crystallinity is also soluble (Fig. 1). However, about 60% of the blend which contained 80% polypropylene was separated into fractions containing only homopolymer of propylene. A somewhat better separation was achieved with the 85/15 polypropylene/poly-1-butene blend because 1-butene homopolymer is more soluble than high-density polyethylene of comparable molecular weight and is, therefore, eluted completely from the column at a lower temperature. About 70% of such a blend was separated into fractions which contained only polypropylene (Fig. 7).

The copolymer, the monomer distribution of which is given in Fig. 8, had a broad 1-butene monomer distribution; the distribution varied from 30% 1-butene in the most soluble fraction down to 4% in the highest melting fractions. This indicates that no homopolymer of either monomer is formed under the synthesis conditions, which consisted of using a highly stereospecific catalyst to continuously polymerize the premixed monomers in a single-stage reactor. The monomer distribution for the 85/15 polypropylene/poly-1-butene blend is shown in Fig. 8 to emphasize the ability of the method to separate the homopolymers had they been present. A 60/40 propylene/1-butene copolymer which was fractionated by this technique of increasing elution temperature was shown to contain cocrystalline fractions which were confirmed by X-ray diffraction (Table 2). The monomer distribution of this copolymer is broad (68 to 12% 1-butene); however, only fractions which contain more than 33% 1-butene show both poly-1-butene as well as polypropylene crystallinity by X-ray diffraction. Again, no homopolymers were found in this copolymer.

Data concerning fractions from two propylene/ethylene copolymers are given in Table 3. Copolymer E was made at a relatively high reaction temperature and the physical properties are not as good as those of copolymer F made at a lower temperature. Selected fractions were chosen from each polymer for further characterization by infrared spectroscopy and DSC. In Table 3, fractions from each polymer were matched according to the *S* value in order to compare them by pairs. For copolymer E, the fraction with an *S* value of about 10 gave DSC melting peaks at 120, 140, and 146°C. The peak at 146°C is thought to be due to polypropylene segments which are slightly irregular or less stereospecific; otherwise the segments would be expected to melt at around 162°C, as does highly crystalline polypropylene. The peak at 140°C is probably a premelting peak associated with the 146°C polypropylene peak; premelting was previously observed in our laboratory for unfractionated polymers of propylene. The melting peak at 120°C is most likely due to polyethylene. This fraction could possibly be a two-period block polymer, but it is most likely a physical blend of the two homopolymers which have the same solubility. Infrared analysis of the first fraction from copolymer F, extracted at 87°C, indicated that the fraction contained about 50% propylene; however, no DSC peak was observed which might be attributed to polypropylene. This is quite unique, because propylene homopolymer extracted at this temperature has a crystalline DSC melting peak. The molecules of this fraction appeared to contain ethylene blocks, sufficiently long to crystallize, which were chemically attached to propylene blocks which did not crystallize, probably because of insufficient length or insufficient stereoregularity.

Comparison of the two fractions eluted at an *S* value of approximately 25 showed the presence of both monomers in both fractions; however, now the fraction from copolymer F contained only polypropylene crystallinity. Since this fraction contained only 10% ethylene according to analysis by infrared spectroscopy, the ethelene units were probably not long enough to crystallize; however, since this fraction was 90% propylene, the polypropylene units were long enough to crystallize. This could well be the molecular species which imparted the unique properties to copolymer F. When the value of *S* was approximately 25, the fractions from copolymer E again showed both polyethylene and polypropylene crystallinity according to the evaluation by DSC. The last two pairs of fractions which are listed in Table 3 were essentially the same, in that they contained only propylene homopolymer. It is notable that both of these polymers contained as much as 60 to 70% propylene homopolymer. These data, which indicate more blocking at low temperatures than at high temperatures, agree with the results of Bier et al. (25).

Block polymers were also made with propylene in the first-stage reactor and with both propylene and ethylene in the second-stage reactor. Their fractionation data are summarized in Table 4. In addition to the propylene homopolymer, such a reaction sequence would be expected to produce a significant number of molecules with a long, highly stereospecific propylene block which is connected to a reasonably long block of more or less random propylene/ethylene copolymer. As expected, 9% of the gross polymer contained molecules which would well fit this description. This fraction was highly soluble (soluble in Tetralin at 25 to 45°C) and contained about 50% of each monomer according to the infrared analysis. It possessed highly stereospecific propylene segments indicated by a large DSC melting peak at 162°C; but it contained no ethylene crystallinity according to the evaluation by DSC. About 82% of the gross polymer was propylene homopolymer, whereas the remaining 9% was composed of fractions having polyethylene crystallinity and low-melting polypropylene crystallinity.

CONCLUSIONS

The increasing elution–temperature fractionation technique has been used routinely to obtain molecular distributions in high polymers on bases other than molecular weight. This is accomplished by selectively eluting the solid polymer from a column support of small glass beads. Successful separations on the basis of melting point (stereoregularity), homopolymer type (blends), comonomer concentration, and frequency of short-chain branching (density in polyethylene) were accomplished. This technique has been used in conjunction with infrared and differential scanning calorimetry data to characterize block copolymers.

The reproducibility of the technique is excellent, and the technique is sufficient to detect pellet-to-pellet variation in a commercially available polypropylene formulation on the basis of the polymer's melting-point distribution.

Acknowledgments

The authors thank Mrs. Jackie Kirn for the numerous polarized-light melting-point studies; Mr. Kenneth Fraley, Miss Zorah Curry, and Mrs. Emily Crawford for the infrared analyses; Mr. C. L. Sells for carrying out many fractionations; and Dr. F. B. Joyner and Dr. R. L. McConnell for many of the polymer samples.

REFERENCES

1. V. Desreux and M. C. Spiegels, *Bull. Soc. Chim. Belges*, **59**, 476 (1950).
2. S. W. Hawkins and H. Smith, *J. Polymer Sci.*, **28**, 341 (1958).
3. P. W. O. Wija, J. van Schooten, and J. Boerma, *Makromol. Chem.*, **36**, 115 (1960).
4. G. Natta, M. Pegoraro, and M. Peraldo, *Ric. Sci. Suppl.*, **28**, 1473 (1958).
5. M. Pegoraro, *Rend. Ist. Lombardo Sci. Lettere, A, P. 1*, **93**, 624 (1959).

6. K. Shirayama, T. Okada, and S. Kita, *J. Polymer Sci.*, **3A**, 907 (1965).
7. G. Natta, G. Mazzanti, G. Crespi, and G. Morgalio, *Chim. Ind. (Milan)*, **39**, 275 (1957).
8. C. A. Russell, *J. Appl. Polymer Sci.*, **4**, 219 (1960).
9. Z. Mencik, *Chem. Prumysl.*, **12**, 518 (1962).
10. W. R. Moore and G. F. Boden, *J. Appl. Polymer Sci.*, **9**, 2019 (1965).
11. A. Nakajima and H. Fujiwara, *Bull. Chem. Soc. Japan*, **37**, 909 (1964).
12. K. Yamaguchi, H. Kojima, and A. Takahashi, *Intern. Chem. Eng.*, **5**, 169 (1965).
13. G. Natta and G. Mazzanti, *Chim. Ind. (Milan)*, **42**, 125 (1960).
14. D. Prevorsek, *J. Polymer Sci.*, **B1**, 229 (1963).
15. H. J. Harwood, *J. Polymer Sci.*, **B2**, 601 (1964).
16. V. O. Fuchn, *Makromol. Chem.*, **58**, 65 (1962).
17. G. Bucci and T. Simonazzi, *J. Polymer Sci.*, **C7**, 203 (1964).
18. H. W. Coover, Jr., *J. Polymer Sci.*, **C4**, 1511 (1964).
19. H. W. Coover, Jr., and F. B. Joyner, *J. Polymer Sci.*, **A3**, 2407 (1965).
20. R. L. Combs, D. F. Slonaker, F. B. Joyner, and H. W. Coover, Jr., *J. Polymer Sci.*, **A1**, in press.
21. H. W. Coover, Jr., R. L. McConnell, F. B. Joyner, D. F. Slonaker, and R. L. Combs, *J. Polymer Sci.*, **A1, 4**, 2563 (1966).
22. H. W. Coover, Jr., R. L. McConnell, and F. B. Joyner, *Macromolecular Reviews*, Vol. 1, Wiley (Interscience), New York, 1966, Ch. 3.
23. J. E. Guillet, R. L. Combs, D. F. Slonaker, and H. W. Coover, Jr., *J. Polymer Sci.*, **47**, 307 (1960).
24. J. E. Guillet, R. L. Combs, D. F. Slonaker, J. T. Summers, and H. W. Coover, Jr., *SPE Trans.*, **2**, 164 (1962).
25. G. Bier, A. Gumboldt, and G. Lehmann, *Plastics Inst. (London) Trans. J.*, **28**, 98 (1960).

Zusammenfassung

Die in dieser Arbeit beschriebene Fraktioniertechnik wurde dazu benutzt um die Schmelzpunkt-, Monomer- und Blockverteilung in Polymeren und Kopolymeren zu charakterisieren. Diese Methode unterscheidet sich von der Molekulargewicht-Fraktionierungstechnik dadurch, dass die Fraktionen durch Extraktion mit einem einzigen Lösungsmittel erhalten werden, wobei das feste Polymer unterhalb des Schmelzpunktes bei stufenweise ansteigender Temperatur extrahiert wird. Die Reproduzierbarkeit dieser Methode ist ausgezeichnet und die Methode ist ausreichend um in handelsüblichen Proben von Polypropylen Variationen festzustellen. Diese Methode wurde benutzt um den Einfluss von Variablen während der Darstellung auf die Schmelzpunktsverteilung von Polyäthylen und Polypropylen zu untersuchen und auch die Monomer- und Blockverteilung. Diese Methode gestattet auch zwischen Kopolymeren und Mischungen zu unterscheiden.

Résumé

Description d'une technique de fractionnement utilisée pour caractériser les distributions de points de fusion, de monomères, et de blocks des polymères et des copolymères. Elle diffère de la méthode de fractionnement des poids moléculaires par l'usage d'un seul solvant pour l'extraction du polymère solide au-dessous de son point de fusion à des températures s'élevant graduellement. La reproductibilité de cette technique est excellente et suffit pour la distinction des variations granules à granules d'un polypropylène commerciale. On l'a utilisée pour montrer l'influence des différences de la preparation sur la distribution de points de fusion du polyethylène et du polypropylène, sur les distributions de monomères et de blocks des copolymères, et aussi pour distinguer entre les copolymères et les mélanges.

Received by editor August 22, 1966
Submitted for publication November 14, 1966