

## **Turbidimetric Thermal Gradient Technique for the Estimation of Compositional Distribution of Ethylene Copolymers**

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### **Synopsis**

A new experimental technique has been developed for determining the compositional distribution of ethylene copolymers and blends of ethylene homopolymers and copolymers. The method is similar to the turbidimetric titration procedure, but with crystalline precipitation of the various structural species effected by lowering of the temperature. Experimentally, a Brice-Phoenix light-scattering photometer, equipped with a stirred heated cylindrical cell is used as a turbidimeter for measuring the light transmission through a liquid system. The decreasing light transmission of a 0.01% solution in a fixed ratio of solvent and nonsolvent of  $\alpha$ -chloronaphthalene and dimethyl phthalate, with a temperature drop of 2°C./min., is plotted against temperature on an X-Y recorder. The more highly branched molecules, that is, those containing higher comonomer content, are the less crystalline, hence are more soluble and precipitate at the lower temperatures. Compositional distribution is estimated from the cooling curves by two procedures: (1) the broader temperature range over which a nonuniform resin precipitates out of solution is compared to that of a more uniform resin, and (2) the higher initial cloud point of a mixture or nonuniform copolymer is compared to the cloud point-comonomer content relationship developed for uniform resins. The effects of molecular weight and molecular weight distribution are shown to be small relative to the effects of structural distribution. The compositional distribution of the ethylene-propylene copolymers studied varies from narrow to broad, depending on the specific coordination catalyst and polymerization method used. Ethylene-vinyl acetate copolymers, on the other hand, are uniform because of the 1:1 reactivity ratios of ethylene and vinyl acetate. Synthetic mixtures of ethylene-vinyl acetate resins of varying vinyl acetate content exhibit the expected nonuniformity. This technique has also been successfully applied to mixtures of high- and low-density polyethylenes, further demonstrating the utility of this new rapid tool for structural characterization. Experimental time is about 2 hr.

### **INTRODUCTION**

During the past few years, many techniques have been described for measuring the molecular weights and molecular weight distributions of homopolymers. Recently, copolymers have become important. Since their properties are also sensitive to their composition and uniformity of composition, methods for determining these structural features have become necessary. As a relatively rapid means of estimating compositional dis-

tribution or uniformity of ethylene copolymers, our laboratory has investigated a turbidimetric thermal gradient technique.

The initial studies of this technique were carried out by Bronsted<sup>1</sup> and Adams and Powers.<sup>2</sup> Morey and Tamblin<sup>3</sup> are usually credited with the basic theory and its first detailed application. Until recently, previous investigators had used a titration technique wherein a polymer in solution was titrated with a nonsolvent. The increase in turbidity due to the fine suspended particles of precipitating polymer was measured by recording either the decrease in intensity of directly transmitted light or the increase in scattered light at 90° to the incident beam.

By using the titration technique, either of two problems has been attacked. The first was the estimation of the molecular weight distribution of various homopolymers such as poly(methyl methacrylate),<sup>4</sup> cellulose acetate butyrate,<sup>3</sup> polystyrene,<sup>5-8</sup> poly(vinyl acetate),<sup>9</sup> poly(vinyl chloride),<sup>10,11</sup> and nylon 66.<sup>12,13</sup> Generally, as precipitant or nonsolvent is added, the highest molecular weight species are precipitated first, followed by the lower molecular weight molecules.

Hall<sup>14</sup> has summarized the disadvantages of the turbidimetric titration method as used in the past. Goberman<sup>6</sup> used two methods (Claesson<sup>15</sup> and Morey and Tamblin<sup>3</sup>) to derive the molecular weight distribution from a turbidity titration, using an empirical saturation law. Recently, Beattie<sup>16</sup> has used light-scattering theory to calculate the concentration of precipitated polymer from the maximum turbidity and hence has placed the turbidimetric titration method for determining solubility distributions on an absolute basis.

The titration technique has also been used to estimate compositional distribution of block copolymers, such as styrene-methyl methacrylate,<sup>17-19</sup> vinyl acetate-methyl methacrylate,<sup>20</sup> and epoxide/butadiene-styrene rubber,<sup>21</sup> and graft copolymers such as vinyl acetate or vinyl chloride grafted to poly(methyl methacrylate).<sup>22</sup> This method affords simple differentiation of such copolymers from mixtures of homopolymers. Generally, the chemical nature<sup>19</sup> of the polymer has a much greater influence on its solubility than its molecular weight. A copolymer will normally display solubility characteristics intermediate between those of the homopolymers.

Two recent publications described a turbidimetric thermal gradient technique to determine the molecular weight distribution of polyolefins. In this method, the polymer is dissolved in a solvent-nonsolvent mixture at an elevated temperature, then cooled and turbidity recorded as a function of temperature. Taylor and Tung<sup>23</sup> determined the molecular weight distribution of linear polyethylene by relating the S-shaped curve from the turbidity-temperature plot to the Wesslau distribution. Gamble and co-workers<sup>24</sup> determined the molecular weight distribution of ethylene-propylene rubbers by a similar method.

Our investigation is the first known use of a turbidimetric cooling curve technique to estimate the compositional distribution of copolymers. It

was chosen because the titration technique at some constant elevated temperature required for polyethylene and its copolymers would have involved more experimental problems and inclusion of a molecular weight effect.

Other techniques have recently been used to examine the compositional distribution of ethylene copolymers. Bombaugh et al.<sup>25</sup> have examined ethylene-ethyl acrylate copolymers using a combination of pyrolysis gas chromatography and differential thermal analysis, and White<sup>26</sup> has used an elution fractionation technique, followed by infrared analysis for the comonomer content of ethylene copolymer fractions.

Monodisperse fractions of copolymers, at a fixed composition, should precipitate at a specific temperature at a fixed solvent-nonsolvent ratio as the temperature is dropped at a specific rate. The cloud point is defined as the temperature at which turbidity first appears as the dilute polymer solution is cooled. This cloud point is only very slightly molecular weight-dependent, as will be shown later. Practically, these monodisperse molecules should precipitate over a relatively narrow temperature range in a finely divided crystalline form. For a polymer of varying composition, the molecules containing the larger concentrations of comonomer are the less crystalline, hence more soluble, and will have the lower cloud points. Samples containing a broader distribution of compositions, such as non-uniform resins, will have a broader distribution of cloud points. Such nonuniform resins can be obtained either by mixing compositionally monodisperse copolymers of varying composition or via polymerization techniques which yield compositionally polydisperse resins.

This paper describes the study of ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, mixtures of ethylene-vinyl acetate copolymers, and mixtures of ethylene homopolymers of varying densities. The effects of molecular weight and molecular weight distribution and the reproducibility of the cooling curves are also discussed. In the case of the ethylene-propylene copolymers, the breadth of the compositional distributions has been correlated with polymerization variables and with such physical effects of polymer nonuniformity as ether extractibles and "sweat-out."

Although the present investigation of this new tool for assaying compositional distribution of copolymers has been restricted to ethylene copolymers, it is believed that this technique should have wide utility in many polymer systems.

## EXPERIMENTAL

### Photometer and Recording System

A Brice-Phoenix light-scattering photometer, with its light source, cell table, and phototube detector, and auxiliary recorders are used.

A 43 mm. O.D. cylindrical light-scattering cell (110 ml. capacity) is encased in a specially constructed copper cell block into which are cut grooves for copper cooling coils. For heating, two Chromalox heaters

encircle the cell block and are jacketed with asbestos insulation. The cell block is placed on a specially constructed Teflon cell table to further insulate the block.

About 100 ml. of solution are placed in the cell, into which is placed a Teflon stirrer driven by a 200 rpm Synchron clock motor. A copper-constantan thermocouple in the solution is connected to a Weston strip-chart recorder which plots temperature versus time. The thermocouple voltage is also fed to the  $x$ -axis amplifier of a Moseley  $X$ - $Y$  Autograph recorder. The voltage output of the 1P-21 multiplier phototube, proportional to the intensity of transmitted light, is fed to the  $y$ -axis amplifier. These recorders have two independent voltage-current amplifiers. Transmission is plotted as a function of temperature.

### Materials

The ethylene-vinyl acetate copolymers were prepared by free-radical high-pressure polymerization techniques. The ethylene-propylene copolymers were prepared by various low-pressure anionic catalyst systems. The polyethylene resins were commercial high- and low-density products.

The  $\alpha$ -chloronaphthalene (Matheson, Coleman and Bell, b.p. 133–135°C./20 mm.) and dimethyl phthalate (Fisher Scientific Co., purified) were pressure filtered through a No. 03 Selas filter (Selas Corp.) before use.

### Experimental Procedure

The best solvent-nonsolvent system was found to be a previously reported<sup>23</sup> mixture of  $\alpha$ -chloronaphthalene and dimethyl phthalate, usually at an 80/20 ratio (by volume), although other ratios were investigated as indicated. Choice of concentration of the polymer solution was one of compromise. A too dilute solution introduces problems of precision in sampling and in obtaining a sufficiently large change in turbidity. A too concentrated solution results in problems of agglomeration of suspended polymer and yields a light intensity-temperature plot which is overly biased in favor of the copolymer structures precipitating out initially, that is, the ethylene-rich molecules. A 0.01% solution provides good sensitivity with approximate linearity between concentration of precipitant and light transmission.

The cooling rate of 2°C./min. was regulated by adjusting the rate of water flowing through the cooling coils.

A further choice was the measurement of either the decrease in transmission of the directly transmitted light, or the increase in turbidity, that is, the light scattered at 90° to the incident beam. The transmitted light was selected since it yields a better overall estimate of distribution.<sup>9</sup> The 90° scattered light yields a sharper initial cloud point and more precisely defines the molecules first precipitated. It does not, however, ac-

curately characterize the more soluble molecules, that is, those of high comonomer contents. For the purpose of our investigation, the distribution obtained from the directly transmitted light was considered to be more meaningful. However, if a more precise estimate of the molecules initially precipitated was desired, for example, in a blend containing a minor amount of a more crystalline or less soluble component, the 90° scattered light would be preferred.

In practice, the cylindrical cell is heated to about 100°C.; then 100 ml. of preheated (100°C.)  $\alpha$ -chloronaphthalene-dimethyl phthalate solution is added. Finally, a pipetted preheated 1 ml. solution of a 1.0% solution of the copolymer in  $\alpha$ -chloronaphthalene (containing antioxidant) is added, the cell block heater turned off, and the stirrer, cooling water, and recorders turned on.

In our work, white light from the mercury lamp was used for increased sensitivity. An earlier investigator<sup>13</sup> indicated that the turbidity curves from white, yellow (5780 Å.), blue (4360 Å.), and green (5460 Å.) light are equivalent.

Two parameters, derived from the transmission-temperature curves, are used to estimate the compositional distribution of copolymers. The first method is based on the determination of the temperature range ( $\Delta T$ ) over which a given sample precipitates. This range is determined graphically from the experimental light transmission-temperature curve. Three straight lines are drawn to idealize the experimental curve. The first line is drawn through the high-temperature portion of the curve obtained before precipitation begins; the second straight line is drawn through the portion of the curve formed during precipitation (the intersection of these two lines locates the previously described cloud point); the third line is drawn through the portion of the curve obtained after precipitation is complete. The temperature range or  $\Delta T$  over which a polymer precipitates is then measured in terms of the two intersections of these three lines. This  $\Delta T$  method, applied to a given copolymer type, does not require an accurate knowledge of the comonomer content to estimate uniformity.

A second method is also useful for estimating uniformity from the transmission-temperature plot. For a series of compositionally uniform copolymers, an almost linear relationship exists between decreasing cloud point and increasing comonomer content, over the range of comonomer contents discussed in these studies. In the case of ethylene-vinyl acetate copolymers, this range covers, at a minimum, acetate contents between 10 and 25% by weight, using an 80/20 ratio of  $\alpha$ -chloronaphthalene and dimethyl phthalate. This range is, however, dependent on the solvent-nonsolvent ratio, and can be broadened, as will be shown later. Resins which have cloud points displaced from the predetermined cloud point-comonomer content relationship for uniform copolymers are increasingly less uniform, the further from the base line. This technique, along with  $\Delta T$ , gives a rapid semiquantitative measure of compositional distribution.

### Testing Methods

**Comonomer Contents.** Determination in the case of the ethylene-vinyl acetate copolymers was by elemental analysis. For ethylene-propylene copolymers, propylene content was determined by using the  $8.7 \mu$  infrared band which had been calibrated from polymerization material balance determinations.

**Ether Extractibles.** Powdered polymer samples were extracted in vapor-jacketed Soxhlet extractors with boiling diethyl ether for 24 hr. The polymer was recovered from the solvent by concentration, precipitation into methanol, and drying at  $50^{\circ}\text{C}$ . under vacuum.

**Sweat-out.** Samples  $1\frac{1}{2} \times \frac{1}{2}$  in., were bent  $180^{\circ}$ , set in a holder to maintain the bend, and placed in an air oven at  $70^{\circ}\text{C}$ . A visual qualitative estimate of sweat-out was made after 1 and 4 days.

**Melt Index.** Melt index, in decigram/minute, was determined according to ASTM D1238-62T.

**Density.** Density, in grams per cubic centimeter, was determined according to ASTM D1505-57T.

## RESULTS AND DISCUSSION

### Ethylene-Vinyl Acetate Copolymers

The cloud point-vinyl acetate content relationship is shown in Figure 1. As noted, the ethylene-vinyl acetate copolymers deviate very little from the least-squares line (baseline), indicating that all the ethylene-vinyl acetate copolymers are of about equivalent uniformity. The  $\Delta T$  of these copolymers, polymerized under various high-pressure conditions, is usually between  $7$  and  $10^{\circ}\text{C}$ ., again indicating a narrow compositional distribution. The fact that ethylene-vinyl acetate copolymers are quite uniform is expected, since the reactivity ratios of ethylene and vinyl acetate are in the relation:  $r_1 = r_2 = 1$ .<sup>27</sup> It has also been experimentally verified by elution fractionation<sup>26</sup> followed by infrared analysis of the fractions.

Shown also on Figure 1 are data for several synthetic mixtures. As this tailor-made compositional distribution is broadened, the cloud point deviates increasingly from the base line.

Previously it was noted that usually an  $\alpha$ -chloronaphthalene-dimethyl phthalate ratio of 80/20 (by volume at  $100^{\circ}\text{C}$ .) was used. Other concentrations were used to suit the purpose. For example, if an ethylene polymer of unknown origin was to be characterized, the initial turbidimetric curve would be run with the use of 100%  $\alpha$ -chloronaphthalene, since high-density and low-density polyethylenes have cloud points of about  $85$  and  $60^{\circ}\text{C}$ ., respectively, in  $\alpha$ -chloronaphthalene, but over  $140^{\circ}\text{C}$ . in an 80/20 mixture.

On the other hand, high comonomer-containing copolymers have low cloud points in an 80/20 mixture, and would be more suitably run in 70/30 or 60/40 mixtures of  $\alpha$ -chloronaphthalene-dimethyl phthalate. As shown

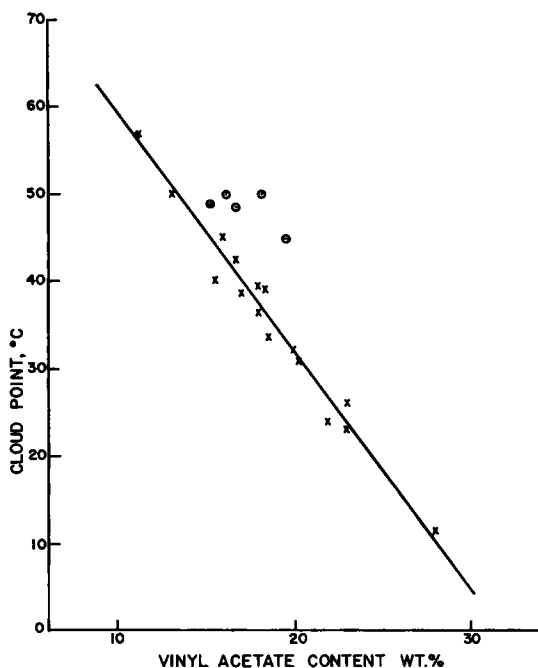


Fig. 1. Cloud point-comonomer content relationship for ethylene-vinyl acetate copolymers at an 80/20 ratio of  $\alpha$ -chloronaphthalene and dimethyl phthalate: (X) directly polymerized copolymers; (O) blends of copolymers of differing comonomer contents.

in Figure 2, the ability to vary the solvent-nonsolvent ratio gives added flexibility for better utilization of this technique. As expected, increasing the per cent of nonsolvent progressively increases the cloud point of a specific copolymer.  $\Delta T$  increases slightly with increasing nonsolvent concentration.

### Mixture of Ethylene-Vinyl Acetate Copolymers of Varying Vinyl Acetate Content

In Figures 3 and 4, actual cooling curves of per cent light transmission versus temperature as obtained on the  $X$ - $Y$  recorder, are shown. The cooling curves of 50/50 by weight mixtures of two ethylene-vinyl acetate copolymers of varying comonomer contents with 0.005% of each are compared to the curves of the uniform component resins. The concentrations of total polymer in solution in each of the curves was 0.01%. Cooling curves determined on 0.005% solutions of the individual resins closely resemble the curves of each component in the mixture, indicating that the turbidity effects are qualitatively additive.

In Figure 3, the two component resins differ by 5% vinyl acetate content.  $\Delta T$  of mixture M-2 is about 22°C., whereas the component resins have  $\Delta T$  of 8 and 11°C. The cloud points of mixture M-2 and the less soluble resin

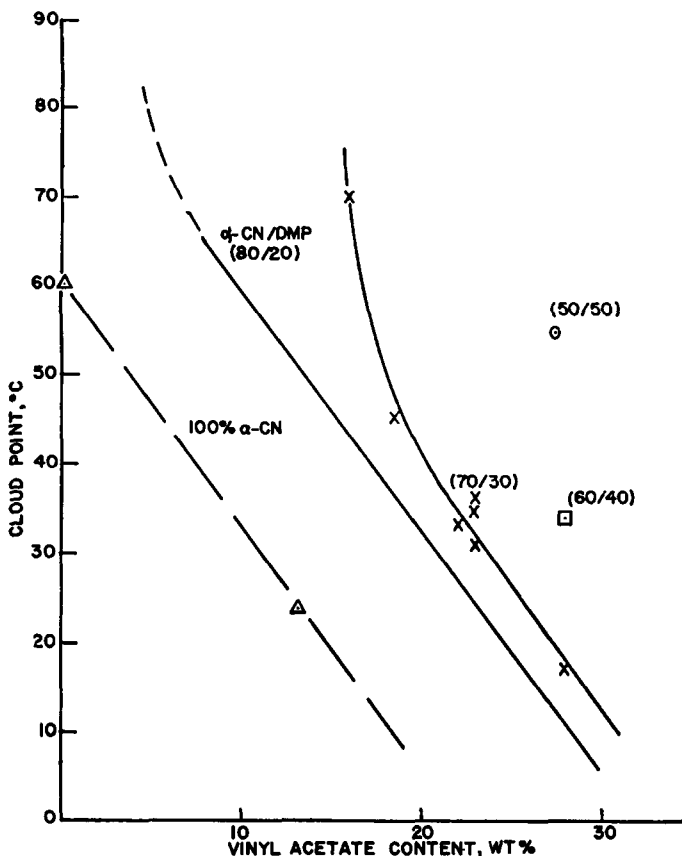


Fig. 2. Effect of solvent-nonsolvent ratio on the cloud point-comonomer content relationship for ethylene-vinyl acetate copolymers; expressed as volume per cent of  $\alpha$ -chloronaphthalene ( $\alpha$ -CN) and dimethyl phthalate (DMP). The 80/20  $\alpha$ -CN/DMP curve is reproduced from Fig. 1.

A-1 having the lower vinyl acetate content (13.2%) are about the same, as expected. The 49°C. cloud point of the mixture, coupled with its higher average vinyl acetate content (15.8%) compared to sample A-1, places it above the line for uniform resins, as shown in Figure 1.

In the second mixture (M-4, Fig. 4), the compositional distribution has been broadened by blending equal weights of copolymers containing 16 and 23% vinyl acetate and having cloud points of 45 and 23°C., respectively.  $\Delta T$  of this mixture is 32°C. The smaller transmission decrease of sample A-5 on precipitation is typical of copolymers of the higher vinyl acetate contents at a solvent-nonsolvent ratio of 80/20.

Table I shows data on a number of 50/50 mixtures and their component resins, giving the comonomer contents, cloud points and  $\Delta T$ . Note the good agreement between the cloud points of the various resins run individually and in mixtures and between the  $\Delta T$  values of the mixtures



obtained experimentally and those calculated from the measurements on the individual copolymers.

It should be pointed out that these "as recorded" integral curves were not differentiated, nor reduced to a simpler form. We believe that  $\Delta T$  and

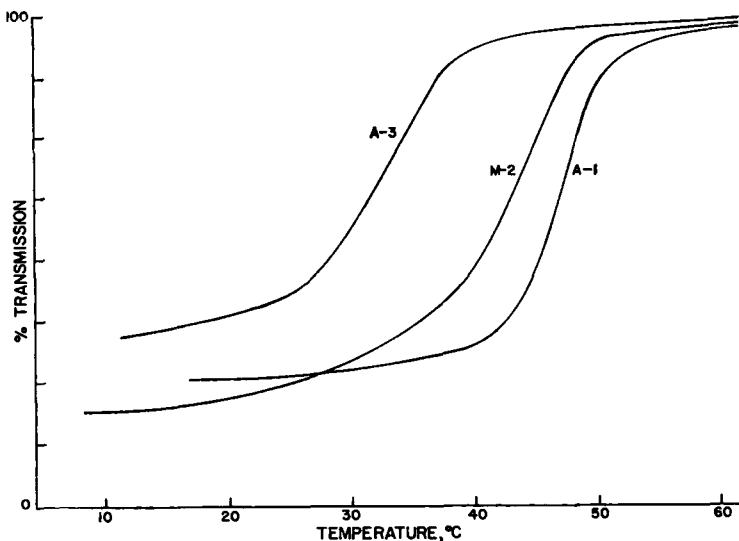


Fig. 3. Transmission-temperature curves for two ethylene-vinyl acetate resins and a 50/50 mixture: A-3, 18.4 wt.-% VA resin; M-2, 15.8 wt.-% VA mixture of A-1 and A-3; A-1, 13.2 wt.-% VA resin.

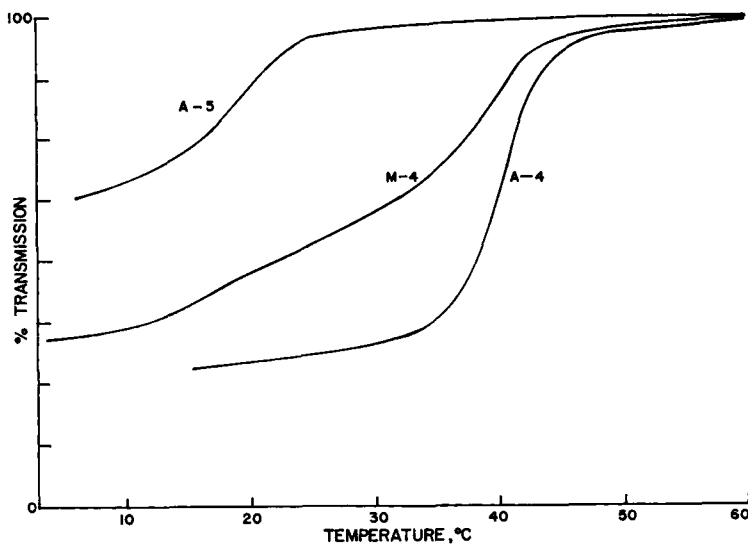


Fig. 4. Transmission-temperature curves for two ethylene-vinyl acetate resins and a 50/50 mixture: A-5, 23.0 wt.-% VA resin; M-4, 19.5 wt.-% VA mixture of A-4 and A-5; A-4, 16.0 wt.-% VA resin.

TABLE I  
Analysis of Transmission-Temperature Curves for Mixtures of Ethylene-Vinyl Acetate Copolymers<sup>a</sup>

Sample no.	Single copolymer runs <sup>b</sup>			Mixture runs <sup>c</sup>			
	[VA], wt.-%	Cloud point, °C.	$\Delta T$ , °C.	[VA], wt.-%	Cloud point, °C.	$\Delta T$ , °C.	
						Exptl.	Calcd.
M-1	13.2	50	8	18.1	50	34	35
	23.0	23	8				
M-2	13.2	50	8	15.8	49	22	21
	18.4	39	11				
M-3	13.2	50	8	16.7	49	26	28
	20.2	31	9				
M-4	16.0	45	7	19.5	45	32	30
	23.0	23	8				
M-5	13.2	50	8	16.1	50	29	24
	19.0	35	9				

<sup>a</sup>  $\alpha$ -Chloronaphthalene-dimethyl phthalate, 80/20.

<sup>b</sup> 0.01%.

<sup>c</sup> 0.005% of each component.

the cloud point plotted versus comonomer content are the most useful parameters.

### Ethylene-Propylene Copolymers

The compositional distributions of several ethylene-propylene copolymers, prepared by different low-pressure processes and catalyst systems, were estimated from the transmission-temperature curves, and correlated with polymerization conditions, extraction tests, and observations on sweat-out.

In Table II, the first two samples, C-1 and C-2, made by a batch tech-

TABLE II  
Polymerization, Analysis, and Turbidimetry Data on Ethylene-Propylene Copolymers

Sample no.	Polymerization			Melt index	Ether extractibles, %	Sweat-out	Cloud points, °C. <sup>a</sup>	$\Delta T$ , °C.
	Reactor type	Catalyst <sup>b</sup>	[C <sub>3</sub> ], wt.-%					
C-1	Batch	D	19.0	0.5	13	High	72	17
C-2	Batch	D	10.3	0.1	10	High	74	16
							75	15
C-3	Continuous	E	15.2	7.0	2	None	34	5
							35	7
C-4	Continuous	D	15.4	2.0	9	Some	60	32
C-5	Continuous	D	14.4	2.4	9	Some	67	>18
C-6	Continuous	D	19.2	5.8	27	Some	50	24
C-7	Continuous	F	19.5	5,000	40	High	49	>20
C-8	Continuous	D	22.6	5,000	37	High	57	>20

<sup>a</sup> 0.01% in 100%  $\alpha$ -chloronaphthalene.

<sup>b</sup> D, E, and F are various low-pressure coordination catalysts (transition metal halides and aluminum alkyls).

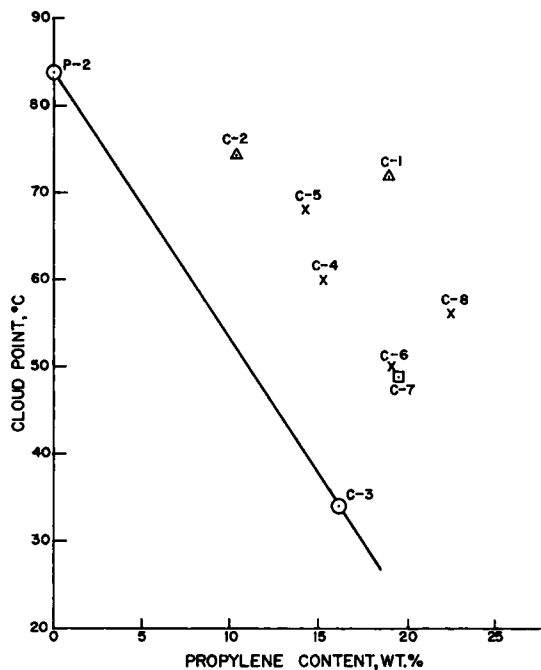


Fig. 5. Cloud point-comonomer content relationship for ethylene-propylene copolymers: baseline shown for uniform copolymers; points above line are for copolymers of varying nonuniformity (data in Tables II and III).

nique with catalyst D, are of very broad compositional distribution, as evidenced by their high ether extractibles and excessive sweat-out. Sample C-3, made with the use of catalyst E and shown to have both narrow molecular weight and compositional distribution,<sup>28</sup> has a very low  $\Delta T$  of 5–7°C. and has almost no sweat-out. Samples C-4, C-5, and C-6, prepared in a continuous reactor with catalyst D, showed high sweat-out and extractibles and, as expected, a high  $\Delta T$ . Finally, samples C-7 and C-8, also nonuniform and having low molecular weight (melt indexes of 5,000), demonstrate the minor effect of molecular weight and molecular weight distribution.

The cloud point-comonomer content relationship for ethylene-propylene copolymers is shown graphically in Figure 5. Uniform copolymer sample C-3, along with an ethylene homopolymer prepared in a similar polymerization system, has been used as the baseline for uniform copolymers. The nonuniformity of the other ethylene-propylene copolymers, having  $\Delta T$  of at least 15°C. is corroborated by their cloud points which fall significantly ( $\geq 20^\circ\text{C}.$ ) above the base line for uniform copolymers.

#### Mixtures of Ethylene Homopolymers

The problem of differentiation between homopolymers and mixtures of homopolymers of varying densities or linearities was investigated using several experimental and commercial homopolymers and blends. The data

TABLE III  
Turbidimetry Data on Ethylene Homopolymers and Mixtures

Sample no.	Type	Density, g./cm. <sup>3</sup>	Cloud point, °C. <sup>a</sup>	$\Delta T$ , °C. <sup>a</sup>
P-1	C <sub>2</sub>	0.960	89	4
P-2	C <sub>2</sub>	0.950	84	4
P-3	C <sub>2</sub>	0.918	62	5
P-2, 50%	Blend	0.933	76	24
P-3, 50%				
P-2, 30%	Blend	0.927	70	28
P-3, 70%				
P-4	Commercial blend	0.933	80 and 60	28
P-5	Commercial blend	0.932	82 and 66	25

<sup>a</sup> 0.01% total concentration in 100%  $\alpha$ -chloronaphthalene.

from the cooling curves determined with the use of 100%  $\alpha$ -chloronaphthalene solvent are presented in Table III.

From the data, some observations can be made: (1) the cloud point decreases with decreasing density (increasing short-chain branching and decreasing crystallinity) of the homopolymer; (2)  $\Delta T$  of homopolymers are quite low (about 5°C.); (3) our limited data on laboratory blends of P-2 and P-3 indicate that the presence of a more branched second component may slightly reduce the cloud point of the higher-density component; and (4) both commercial resins, P-4 and P-5, are blends, with the high-density component precipitating at 80°C. and 82°C., respectively. Figure 6 shows the transmission cooling curve for resin P-4, which shows a bimodal branching distribution.

It should be clear that this technique is capable of resolving blends of ethylene homopolymers. Previously, the turbidimetric curves of mixtures of copolymers of ethylene and vinyl acetate were discussed and the practicality of differentiation again shown. Blends of copolymers are easily distinguished from blends of homopolymers and copolymers.

#### Effect of Molecular Weight and Molecular Weight Distribution

The effects of molecular weight and molecular weight distribution on the cloud point and  $\Delta T$  are very minor relative to the effects of comonomer content and compositional distribution. This conclusion is based on the following observations: (1) at a 70/30 solvent-nonsolvent ratio, ethylene-vinyl acetate copolymers of 15 and 350 melt index, both containing 28% vinyl acetate, have cloud points of 16–17°C.; (2) at an 80/20 ratio, a series of ethylene-vinyl acetate copolymers prepared under like polymerization conditions and having melt indexes of 0.1, 0.2, 2.0, and 30, have cloud points of 38–39°C. and the same  $\Delta T$  (8°C.); (3) a series of copolymer fractions of narrow molecular weight distribution, obtained by an elution column technique,<sup>26</sup> follow the same cloud point-comonomer content relationship as whole resins, and have equivalent  $\Delta T$ ; and (4) ethylene-propylene copolymers of very low molecular weight (5000 melt index, samples C-7 and C-8 of Table II) maintain about the same cloud point-comonomer

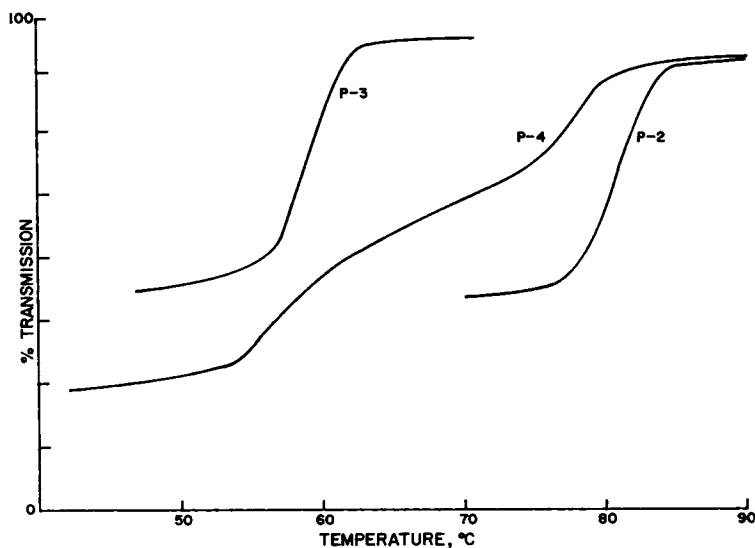


Fig. 6. Transmission-temperature curves for polyethylene resins, P-2 and P-3, and a commercial blend, P-4 (see data in Table III).

content relationship as the products of low melt index prepared with equivalent polymerization systems. The  $\Delta T$  values are also in the same range ( $\geq 15^\circ\text{C}$ ).

#### Reproducibility of the Cooling Curves

In general, the reproducibility of both cloud point and  $\Delta T$  is reasonably good. Table IV demonstrates that the cloud point can be reproduced within about  $\pm 1^\circ\text{C}$ .  $\Delta T$ , at the 5–15 $^\circ\text{C}$ . level, has about the same reproducibility.

TABLE IV  
Reproducibility of the Cooling Curves of Ethylene-Vinyl Acetate Copolymers

Sample no.	[VA], %	Run no.	Cloud point, $^\circ\text{C}$ .	$\Delta T$ , $^\circ\text{C}$ .
A-4	16.0	55	45	7
		67	45	7
		68	46	7
		69	43	7
		142	45	10
		146	46	9
A-5	23.0	63	28	6
		68	26	8
A-6	11.3	61	58	14
		111	56	12

#### CONCLUSION

We have shown that a turbidimetric cooling curve technique can be used successfully for the estimation of compositional distribution of ethylene

copolymers and mixtures, and can probably be applied to many other copolymer types. This method has also been applied to mixtures of ethylene homopolymers containing different amounts of short-chain branching. Since a turbidimetric measurement is possible with as small a sample as 10 mg., this technique can be used for the characterization of fractions obtained by the more usual methods. This turbidimetric technique takes less than 2 hr. per run.

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### Résumé

Une nouvelle méthode expérimentale a été développée pour déterminer la distribution de composition de copolymères d'éthylène, des mélanges d'homopolymères d'éthylène et de copolymères. La méthode est semblable au procédé de titration turbidimétrique, mais avec précipitation cristalline des différentes espèces structurales assurée par abaissement de la température. Expérimentalement, le photomètre de Brice-Phoenix équipé avec une cellule cylindrique agitée et chauffée a été utilisé comme turbidimètre pour mesurer la transmission de lumière à travers un système liquide. La transmission de lumière décroissante d'une solution à 0.01% dans un rapport fixe de solvants et non-

solvants d' $\alpha$ -chloronaphtalène et de phthalate de diméthyle avec une diminution de température de 2°C par minute, est mise en diagramme en fonction de la température sur un enregistreur X-Y. Les molécules fortement branchées, c'est-à-dire celles contenant une teneur importante de comonomère sont les moins cristallines, d'où les plus solubles et précipitent aux plus basses températures. La distribution de composition est estimée au départ des courbes de refroidissement par deux procédés. (1) Le domaine de température plus large sur lequel une résine non-uniforme précipite au départ de sa solution est comparé à celui d'une résine plus uniforme et (2) le point de trouble initial plus élevé du mélange ou d'un copolymère uniforme est comparée au point de trouble de teneur en comonomère développé pour des résines uniformes. Les effets du poids moléculaire et de distribution des poids moléculaire, sont montrés être relativement faibles comparés aux effets de distribution structurale. La distribution de composition de copolymères éthylène-propylène étudiés variait d'une distribution étroite à large suivant le catalyseur de coordination spécifique et la méthode de polymérisation utilisés. Les copolymères éthylène-acétate de vinyle par ailleurs sont uniformes par suite de leur rapport de réactivité 1/1 de l'éthylène avec l'acétate de vinyle. Les mélanges synthétiques de résines polyéthylène-acétate de polyvinyle avec une teneur en acétate de vinyle variable montraient une non-uniformité à laquelle il fallait s'attendre. Cette technique a été également appliquée avec succès à des mélanges de polyéthylène de haute et basse densité, démontrant en outre, l'utilité de cette nouvelle méthode rapide pour la caractérisation de la structure. La durée de l'expérience est d'environ deux heures.

### Zusammenfassung

Eine neue Versuchsmethodik zur Bestimmung der Zusammensetzungsverteilung von Äthylenkopolymeren sowie von Mischungen von Äthylenhomo- und kopolymeren wurde entwickelt. Die Methode ähnelt der Trübungstiteration, jedoch wird durch Temperaturerniedrigung eine kristalline Ausfällung der verschieden strukturierten Bestandteile bewirkt. Es wird ein mit einer gerührten, heizbaren zylindrischen Zelle ausgestattetes Brice-Phoenix-Lichtstreuungsphotometer als Trübungsmesser zur Bestimmung der Lichttransmission eines flüssigen Systems verwendet. Die Abnahme der Lichttransmission einer 0,01% Lösung in  $\alpha$ -Chlornaphthalin und Dimethylphthalat in bestimmtem Verhältnis als Lösungs- und Fällungsmittel wird bei einem Temperaturabfall von 2°C/Min auf einem X-Y-Recorder gegen die Temperatur aufgetragen. Die stärker verzweigten Moleküle, d.h. diejenigen mit höherem Komonomergehalt, sind weniger kristallin und daher besser löslich und fallen erst bei tieferen Temperaturen aus. Die Zusammensetzungsverteilung wird aus den Abkühlungskurven nach zwei verschiedenen Verfahren ermittelt: (1) der breitere Temperaturbereich, in welchem ein nichteinheitliches Polymeres aus der Lösung ausfällt, wird mit demjenigen eines einheitlicheren Polymeren verglichen und (2) der höhere erste Trübungspunkt einer Mischung oder eines nichteinheitlichen Polymeren wird mit der Trübungspunkt-Komonomergehalt-Beziehung für einheitliche Polymere verglichen. Der Einfluss von Molekulargewicht und Molekulargewichtsverteilung ist klein im Verhältnis zum Einfluss der Struktur. Die Zusammensetzungsverteilung der untersuchten Äthylen-Propylenkopolymeren variiert in Abhängigkeit vom spezifischen verwendeten Koordinationskatalysator und der Polymerisationsmethode von einer engen bis zu einer breiten Verteilung. Äthylen-Vinylacetat-kopolymere dagegen sind wegen der 1:1-Reaktivitätsverhältnisse von Äthylen und Vinylacetat einheitlich. Synthetische Mischungen von Äthylen-Vinylacetatkopolymeren mit variiertem Vinylacetatgehalt zeigen die erwartete Uneinheitlichkeit. Das Verfahren wurde auch erfolgreich auf Mischungen von Polyäthylen hoher und niedriger Dichte angewendet, was einen weiteren Beweis für die Brauchbarkeit dieses neuen und raschen Methode zur Strukturcharakterisierung liefert. Die Versuchsdauer beträgt etwa zwei Stunden.

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