

Rapid Method for the Determination of Molecular Weight Distribution in High Polymers: A Thermal Gradient-Turbidity Technique

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Synopsis

A rapid method for determining the molecular weight distribution of polymers has been the aim of polymer chemists for a long time. The method presented here requires less than two hours, including dissolution of the polymer. It is an extension of a photoelectric turbidimetric technique presented by Taylor and Tung in 1961. The equipment has been completely redesigned and presently consists of a copper block containing a turbidity cell, optical system and attendant electronic circuitry for measuring relative changes in turbidity of polymer solutions as a function of temperature. An X-Y recorder is used to plot turbidity versus temperature. A parameter determined from the plot is correlated with a measure of molecular weight distribution determined on known samples for each type polymer by another means. Based on this correlation unknown samples may be analyzed. The instrument is easy to operate and has shown excellent stability over a two year period. Polymers studied by this technique include ethylene-propylene copolymer (EPR), polypropylene, polyethylene, and butyl, however, the only results to be reported here are those on ethylene-propylene copolymer.

INTRODUCTION

The search for a rapid method of determining the polydispersity or molecular weight distribution of polymers has been the aim of polymer chemists for a number of years. Experimental methods for characterizing polydispersity involve the separation of the whole polymer into fractions, each of which is more homogeneous in molecular weight than the original polymer. This process of fractionation may be performed in many ways but can be classified¹ into two general types: (a) preparative, in which actual fractions are isolated and their properties examined, and (b) analytical, in which distribution curves are obtained without isolating individual fractions.

Of the fifteen to twenty different schemes that have been used for fractionation, nearly all, no matter how they differ in detail, are based on differences in solubility of different molecular weight species in a solvent-

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nonsolvent system: The lowest molecular weight species are the most soluble. In the analytical type of fractionation falls the turbidimetric technique. Several workers²⁻⁶ have investigated the turbidimetric titration approach to fractionation. Although the method is rapid, it is open to question as a quantitative procedure because of poor reproducibility caused by differences in refractive indices of the solvent and nonsolvent, swelling of precipitate, titration rate, changes in particle size of the precipitate, and others.

Taylor and Tung⁷ have used a turbidimetric technique which in a way is similar to the thermal gradient preparative method in that it employs polymer solubility as a function of temperature. A solution of solvent and nonsolvent which contains a very low concentration of polymer is slowly cooled. The high molecular weight species become insoluble and separate out causing a small amount of turbidity. As the temperature continues to decrease, increasing amounts of polymer are precipitated out according to their molecular weight. Finally, a point is reached at which even the lowest molecular weight species become insoluble in the solution. At this point the turbidity is greatest, and ideally all of the polymer is precipitated but remains in suspension as very fine particles. If the increase in turbidity is plotted against the decreasing temperature, a cumulative plot is obtained which is similar to a cumulative weight per cent versus molecular weight. The increase in turbidity is related to the cumulative weight per cent and the molecular weight is related to the decrease in temperature.

The research reported in this paper is an extension of the work reported by Taylor and Tung and was performed with a photoelectric turbidimeter of improved design. A technique has been developed for measuring molecular weight distribution of poly- α -olefins and ethylene-propylene copolymers. This instrument consists of a cell, optical system, and attendant electronic circuitry for measuring changes in turbidity as a function of temperature. An X - Y recorder plots the turbidity versus temperature. A parameter from the plot is correlated with a measure of polydispersity determined by the thermal gradient-elution technique. Based on this correlation, unknown samples can be analyzed.

The new turbidimetric method reduces the elapsed time of analysis to less than 2 hr. This makes it possible to run polydispersity measurements as a plant control test. Reproducibility of the test is excellent.

DESCRIPTION OF THE INSTRUMENT

The instrument (Fig. 1) consists of (a) a cell contained in a copper block equipped with quartz glass windows, (b) an optical system to detect and measure changes in the turbidity of a solution placed within the cell, (c) an electronic controller to program the temperature, and (d) a recording system to continuously record temperature and turbidity of the solution in the cell. A schematic view of the cell is given in Figure 2. The copper block gives rapid distribution of the heat supplied by eight electric heaters

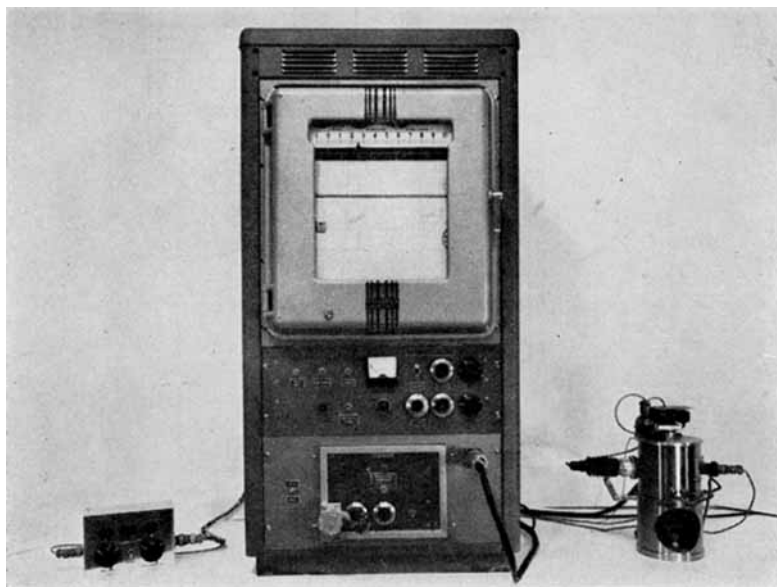


Fig. 1. Photoelectric turbidimeter.

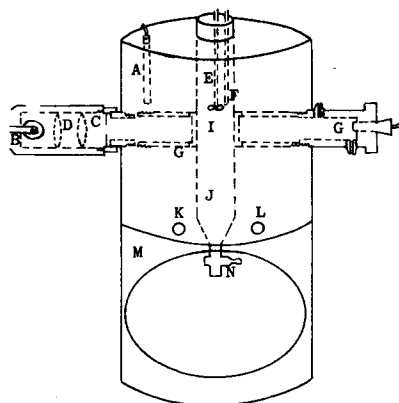


Fig. 2. Cell for turbidity measurements: (A) temperature-sensing element; (B) light; (C) iris diaphragm; (D) lenses; (E) stirrer; (F) cell thermocouple; (G) photo-sensing element; (H) Teflon gaskets to seal windows; (I) quartz windows; (J) cell; (K,L) water inlet and outlet; (M) block support; (N) drain valve. Note: heaters and stirrer motor not shown.

surrounding the cell cavity. The block is evenly cooled by water circulating through the network of drilled holes. A stainless steel insert in the copper block forms the wall of the 27-ml. capacity cell except for the two quartz windows, thus providing even, rapid heat transfer and eliminating the need for stirring during the cooling cycle. The windows are held in place by bushings and sealed with Teflon gaskets. The copper block is surrounded by insulation and an aluminum shield. A small motor-driven

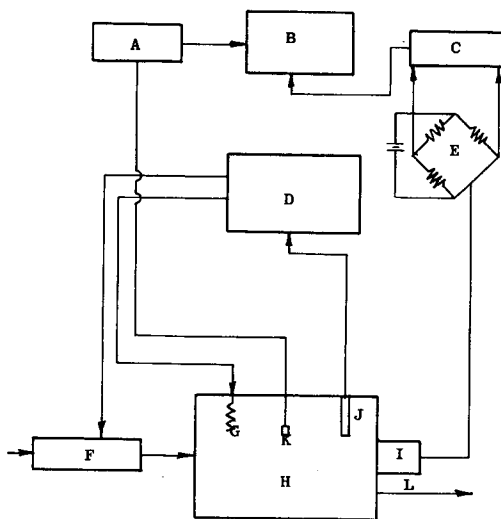


Fig. 3. Instrument schematic: (A) Y amplifier; (B) X-Y recorder; (C) X amplifier; (D) temperature programmer; (E) photo bridge; (F) solenoid switch for water; (G) heaters; (H) turbidity cell; (I) photoelectric sensing element; (J) temperature-sensing element; (K) thermocouple; (L) water outlet.

two-bladed stirrer and motor is fitted into a standard taper (24/40) opening at the top of the cell. A thermocouple suspended from the stirrer assembly measures the temperature of the solution.

The cell is also equipped with a sensitive optical system consisting of a microscope light assembly as a light source, an iris, and a Clairex resistance type photocell. The photosensitive element is mounted in Micarta, a good insulating material. The light source is rigidly braced to the block support to prevent movement due to vibration or expansion in the Micarta connector between the cell and the iris.

The temperature of the cell block is maintained by an electronic controller which actuates either the heaters or the water supply solenoid to maintain the temperature set on the control potentiometer. This potentiometer is driven by a small constant speed motor, thus providing linear cooling of the block. Two variable potentiometers are placed in series with the motor-driven potentiometer so that the cooling rate may be changed from $0.5^{\circ}\text{C./min.}$ to $2.89^{\circ}\text{C./min.}$ The temperature and turbidity of the solution are recorded by an X-Y recorder, the temperature signal coming from the thermocouple and the turbidity signal coming from the photoelectric bridge circuit as shown in Figure 3. Electronic span adjustments make it possible to select any level of sensitivity desired.

RELATIONSHIP OF TURBIDITY AND TEMPERATURE

The shape of the turbidity plot is that of an S. It will be seen from Figure 4 that a typical plot actually does resemble the integral molecular

weight distribution expected from a cumulative distribution. It will be noted that in the middle of the S-shaped plot the slope is quite constant and can be represented by a straight line. Various samples having different molecular weight distributions show a different slope at this middle portion of the turbidity curve as well as a different shape on the two ends.

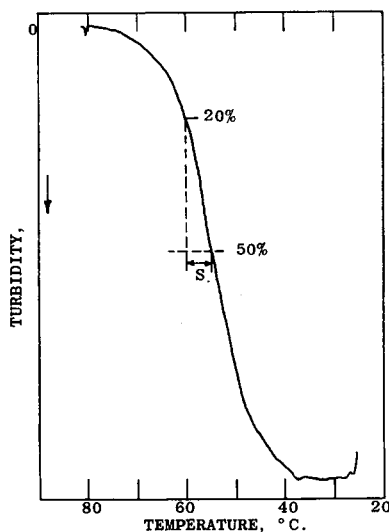


Fig. 4. Chart record from photoelectric turbidimeter X-Y recorder. M_w/M_n of polymer = 8.0.

A parameter designated as S was chosen to be the difference in temperature between points representing 20% of the maximum turbidity and 50% of the maximum turbidity as suggested by Taylor.⁷ This portion of the curve is essentially linear.

Calibration for Measuring Polydispersity

For measuring polydispersity the parameter S is correlated with a parameter determined from the Wesslau equation:⁸

$$I(M) = (1/\beta\sqrt{\pi}) \int_{\infty}^{\ln M} \exp\{- (1/\beta^2) \ln^2 (M/M_0)\} d \ln M$$

where $I(M)$ is an integral distribution function. β is related to the width of the distribution. M_0 is equal to the molecular weight at the midpoint of the probability curve. Wesslau has shown that β is related to the polydispersity in the following manner:

$$\bar{M}_w/\bar{M}_n = \exp \{ \beta^2/2 \}$$

Values of β determined from analysis of fractionation data plotted against S yield a calibration curve by which unknown samples may be analyzed.

EXPERIMENTAL

Polymers studied by this technique included polypropylene, polyethylene, butyl, ethylene-propylene copolymers. Only the ethylene-propylene copolymers (EPR) are discussed in this paper. The samples studied were selected from commercial Enjay EPR as well as some laboratory-prepared copolymers. They have been previously fractionated by the thermal gradient-elution technique.

Choice of Solvent-Nonsolvent System

In fractionation studies the heptane-ethanol solvent-nonsolvent system has been used for EPR.⁹ However, this system forms an azeotrope boiling below the boiling point of either component and therefore is not well suited to the turbidimetric technique because it gives a narrower working temperature range. The heptane-butanol system also forms an azeotrope and is likewise not satisfactory. The heptane-*n*-propanol system was chosen for the studies with EPR because it does not form an azeotrope and therefore gives a working temperature range of 80–25°C.

Effect of Polymer Concentration on Turbidity

Because of the fairly narrow working temperature range, 80–25°C., it has been necessary to study the effect of polymer concentration to provide a suitable, turbid system. Curves in Figure 5 demonstrate the effect of changing the concentration of EPR without changing the concentration of the nonsolvent. When the temperature is decreased below 45°C. some irregularity in turbidity is observed. Furthermore, the irregularity increases as the concentration increases. This phenomenon is attributed to

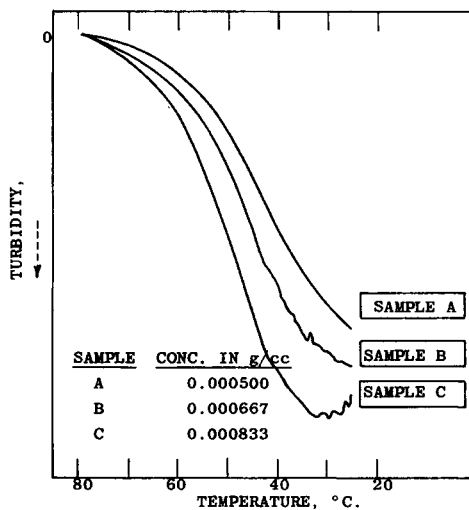


Fig. 5. Effect of polymer concentration on turbidity. Ethylene-propylene rubber.

coagulation of the polymer. As would be expected, the turbidity increases as the concentration increases.

Determination of a Blank

A blank was run on the solvent heptane (see Fig. 6). A recording was made on the heating cycle as well as the cooling. The two curves show a negligible effect of solvent, electronic circuitry cell, optical source, and photocell. The data indicate that errors introduced by the instrument itself are negligible.

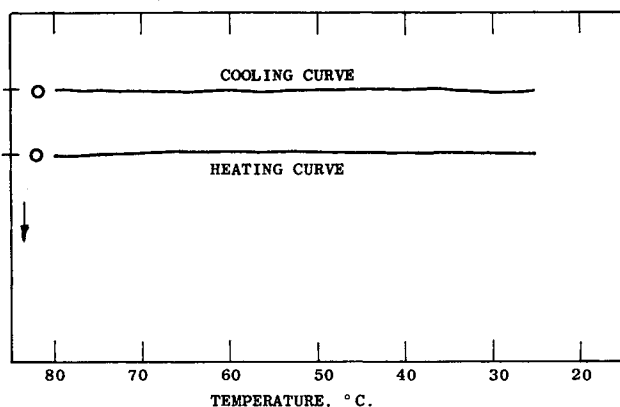


Fig. 6. Solvent blank.

Procedure

The sample (0.125 g.) is dissolved in 50 ml. of heptane. The resulting solution is cooled to room temperature and 20 ml. is transferred to a beaker by means of a pipet. To this beaker is added 9 ml. of *n*-propanol and the solution stirred. Enough of this turbid solution is immediately poured into the cell so that the level of the liquid is just below the tapered fitting of the

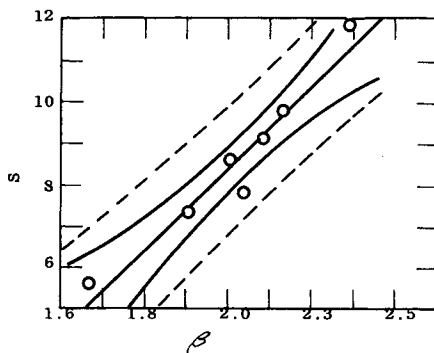


Fig. 7. Calibration curve measuring polydispersity of EPR.

stirring assembly. The stirring assembly is replaced, and the motor of the stirrer is started. The heaters are turned on and the cell is allowed to heat. When the temperature reaches 80°C. and the polymer is entirely dissolved, the stirrer is turned off and the cooling rate switch is actuated and the solution is cooled at a rate of 2.89°C./min. When the temperature reaches 25°C. the chart is removed from the instrument and the 20 and 50% points of maximum turbidity are calculated; the temperature difference represented by the difference in these two turbidities is taken as the parameter S and correlated with the term β from the Wesslau equation, as illustrated in Figure 7. The value β was determined from fractionation data. An excellent correlation coefficient of 0.97 was obtained.

Reproducibility Studies

Data obtained on two samples demonstrating the reproducibility of the instrument are given in Figure 8. The test was carried out in the following manner: A polymer solution prepared as given in the preceding section was placed in the cell, the block allowed to heat until solution was complete, and the temperature lowered in the manner previously described. At the end of the cooling cycle the same solution was again heated and the polymer redissolved and the turbidity obtained in the same manner. Duplicate cooling curves for two samples are shown in this figure and indicate that excellent reproducibility of a sample can be obtained.

To determine the overall experimental reproducibility, three samples were dissolved and carried through the entire procedure as separate samples. Here again the experimental reproducibility of the graphs is excellent.

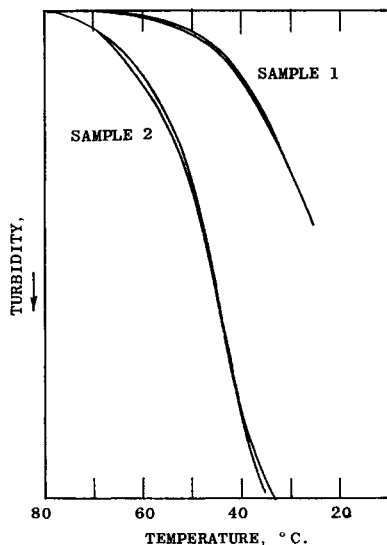


Fig. 8. Duplicate cooling curves for two samples showing excellent instrument reproducibility.

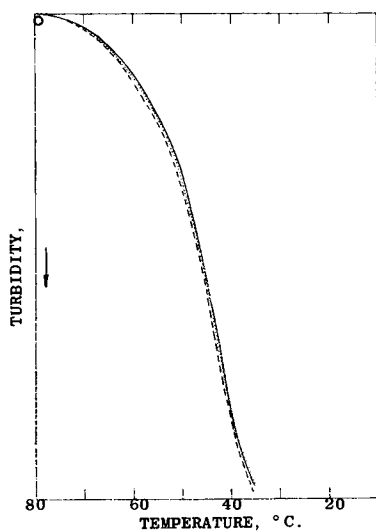


Fig. 9. Three curves showing overall experimental reproducibility.

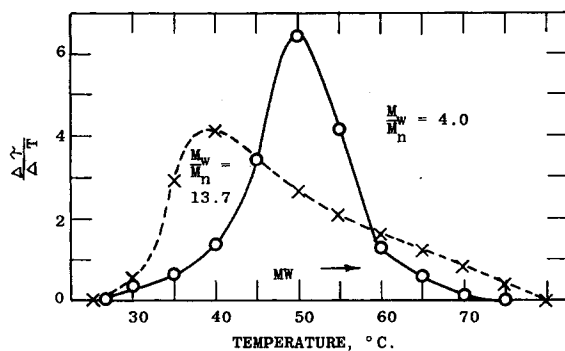


Fig. 10. Differential curves derived from photoelectric turbidimeter plots for ethylene-propylene copolymers of different polydispersities.

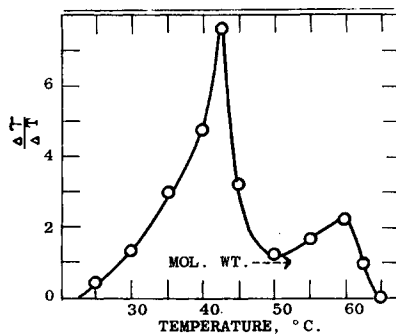


Fig. 11. Differential distribution curve of EPR showing bimodal distribution.

This is shown in Figure 9. Longer-range tests were carried out to demonstrate the reproducibility on a commercial EPR sample which has been analyzed at intervals over a 3-4 month period. In this case the polydispersity index \bar{M}_w/\bar{M}_n was calculated. The results are given in Table I.

TABLE I

Run	\bar{M}_w/\bar{M}_n
1	8.4
2	8.5
3	8.4
4	8.4
5	8.4
6	8.4

Differential Turbidity Curve

Figure 10 shows differential turbidity curves for two polymers, one a narrow distribution and one a wide distribution. Differential curves on a polymer showing a bimodal distribution are illustrated in Figure 11.

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Résumé

Depuis longtemps les chimistes intéressés à la chimie des polymères recherchent une méthode rapide pour déterminer la distribution du poids moléculaire des polymères. La méthode décrite demande moins de deux heures, y compris la dissolution du polymère. C'est une extension de la méthode turbidimétrique présentée par Taylor et Tung en 1961. L'équipement a été complètement remanié et se compose actuellement d'un bloc en cuivre contenant une cellule turbidimétrique, un système optique et un circuit électronique pour mesurer les changements relatifs de la turbidité des solutions de polymères en fonction de la température. Un enregistreur X-Y est employé pour enregistrer la turbidité en fonction de la température. Un paramètre déterminé à partir de l'enregistrement est relié avec une mesure, par un autre moyen, de la distribution du poids moléculaire déterminée sur des échantillons connus pour chaque type de polymère. En se basant sur cette corrélation, des échantillons inconnus peuvent être analysés. L'instrument est facile à manipuler et a présenté une excellente stabilité pendant une durée de deux ans. Les polymères étudiés au moyen de cette technique comprennent le copolymère éthylène-propylène (EPR), le polypropylène, le polyéthylène et le "butyle"; cependant les résultats présentés ici sont uniquement ceux obtenus sur le copolymère éthylène-propylène.

Zusammenfassung

Eine schnelle Methode zur Bestimmung der Molekulargewichtsverteilung von Polymeren war seit langer Zeit das Ziel der Polymerchemiker. Die hier angegebene Methode erfordert einschliesslich der Auflösung des Polymeren weniger als zwei Stunden. Sie bildet eine Weiterentwicklung eines von Taylor und Tung 1961 angegebenen photoelektrischen Trübungsverfahrens. Der Apparat wurde vollständig neu entworfen und besteht jetzt aus einem Kupferblock mit einer Trübigeitszelle, dem optischen System und den zur Messung relativer Trübigeitsänderungen von Polymerlösungen als Funktion der Temperatur notwendigen elektronischen Schaltungen. Zur Auftragung der Trübigeit gegen die Temperatur wird ein *X-Y*-Rekorder verwendet. Ein aus dem Diagramm erhaltener Parameter wird mit einem an bekannten Proben jedes Polymertyps durch andere Mittel bestimmten Mass für die Molekulargewichtsverteilung in Korrelation gesetzt. Auf Grundlage dieser Korrelation können unbekannte Proben analysiert werden. Das Instrument ist leicht zu handhaben und zeigte über einen Zietraum von zwei Jahren ausgezeichnete Stabilität. Nach dem angegebenen Verfahren wurden Äthylen-Propylen Copolymere, Polypropylen, Polyäthylen und Butyl untersucht; es werden aber nur die Ergebnisse am Äthylen-Propylen-Copolymeren hier mitgeteilt.

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