Estimating Elution Fractionation Conditions for Linear Polyethylene and Isotactic Polypropylene

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Synopsis

A technique has been developed which provides a means for estimating polypropylene fractionation conditions in an elution column from a knowledge of the fractionation conditions used to fractionate linear polyethylene in the column and the solution behavior of both polymers in the same solvent–nonsolvent system of varying compositions. The fusion behavior of linear polyethylene and isotactic polypropylene in mixtures of *o*-dichlorobenzene and dimethyl phthalate of varying compositions has been studied by a differential thermal analysis (DTA) technique using concentrations similar to those in an elution fractionation column. The column temperature for fractionating each of these polymers by using *o*-dichlorobenzene and dimethyl phthalate as the solvent and nonsolvent, respectively, was determined from their melting temperatures in dimethyl phthalate. On the basis of the equivalence of the fractional depression in solution temperature of each polymer in the binary liquid mixture, the composition range of solvent–nonsolvent mixtures to be used in fractionating polypropylene was estimated from a knowledge of the polyethylene fractionation conditions together with the DTA data. Although separation depends primarily on molecular weight, the equivalence in fractional solution temperature depression provides a convenient means of correlating fractionation conditions for the polyolefins investigated.

INTRODUCTION

In the last few years there has been a great deal of interest in the elution fractionation of olefin polymers[1] to determine molecular weight distribution and to prepare samples with narrow molecular weight distributions for experimental studies. We found when we recently had to fractionate linear polyethylene and polypropylene into several fractions that simple procedures have not been developed for determining operating conditions in a fractionation column. Variables such as the fractionation temperature, the solvent–nonsolvent system, ratio of polymer to solvent, ratio of solvent to nonsolvent, flow rate of solvent and nonsolvent, and the method of depositing polymer on the support in the column need to be considered.

The determination of a solvent–nonsolvent system, the flow rate, the ratio of solvent to nonsolvent, and the fractionation temperature to employ have in general been done by trial and error. Hall[2] has listed several criteria for the selection of solvent–nonsolvent systems for fractional precipitation which are also helpful criteria for the selection of the solvent

and nonsolvent for elution fractionation.   These criteria are interrelated, and one usually finds that there is a narrow temperature range and a specific range of solvent–nonsolvent compositions for successful operation.   Kenyon and Salyer[3] have shown that fractionation is improved when polymer is deposited on the support material by adding a nonsolvent to a solution of the polymer or by slowly cooling the solution.   Kokle and Billmeyer[4] have reported that resolution can be improved by employing both a low solvent flow rate to reduce the possibility of channeling and a high solvent–polymer ratio.   Crystalline polymers should be fractionated at a high temperature to swell the polymer and to reduce the possibility of crystalline material being present during the fractionation.[6,7]

One method used to determine elution fractionation conditions involves performing successive fractional precipitations of polymer by addition of nonsolvent to a polymer solution.[2]   This method requires considerable time to perform because fractions settle slowly and is especially difficult with olefin polymers because the precipitation must be performed in a closely controlled high temperature bath.   We have found that the determination of operating conditions for an elution column can be simplified by first obtaining the solubility curve for the polymer in dilute mixtures of solvent and nonsolvent.   In this work the solution temperatures of linear polyethylene and isotactic polypropylene were determined as a function of solvent–nonsolvent composition with a differential thermal analysis (DTA) apparatus, and the results were used to estimate operating conditions for fractionating the polymers.

EXPERIMENTAL

Differential Thermal Analysis

A Dupont 900 differential thermal analyzer (DTA) was used to find the solution temperature of linear polyethylene and isotactic polypropylene in mixtures of reagent grade o-dichlorobenzene and dimethyl phthalate.   The solution temperature of polymer in solvent–nonsolvent mixtures is dependent upon the composition of the solvent mixture as well as the relative proportions of polymer and solvent.   In this work solution temperature thermograms were determined in a dilute system at a fixed weight fraction of polymer.

About 1 mg. of polymer was weighed into 4-mm. glass sample tubes and solvent–nonsolvent mixtures of particular compositions were added to make a fixed ratio of weight of polymer to weight of polymer and solvent–nonsolvent mixture of 8%.   Thermograms were obtained by heating the tubes at a rate of 20°C./min. in a nitrogen atmosphere using glass beads as reference.   The thermograms (Figs. 1 and 2) were obtained with a small amount of glass beads added to the sample tube.
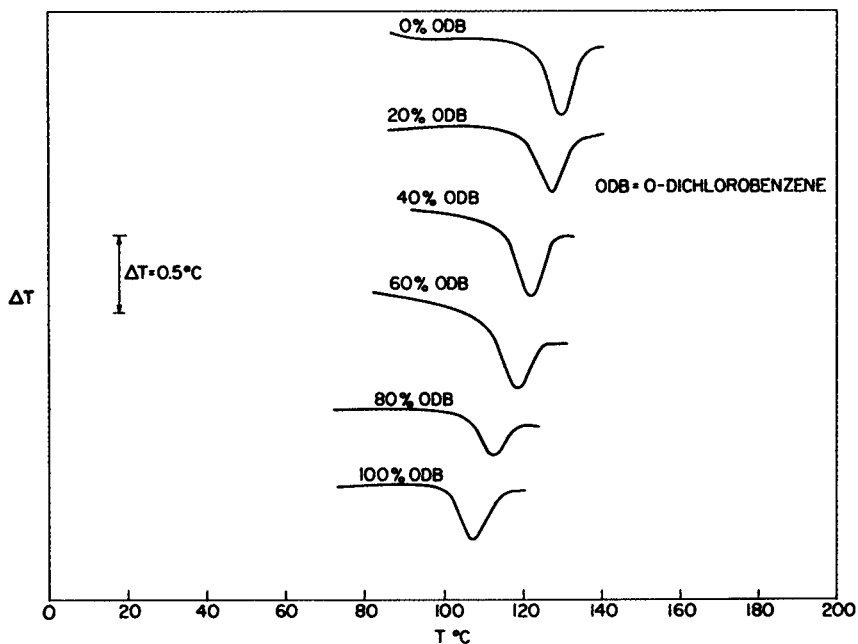
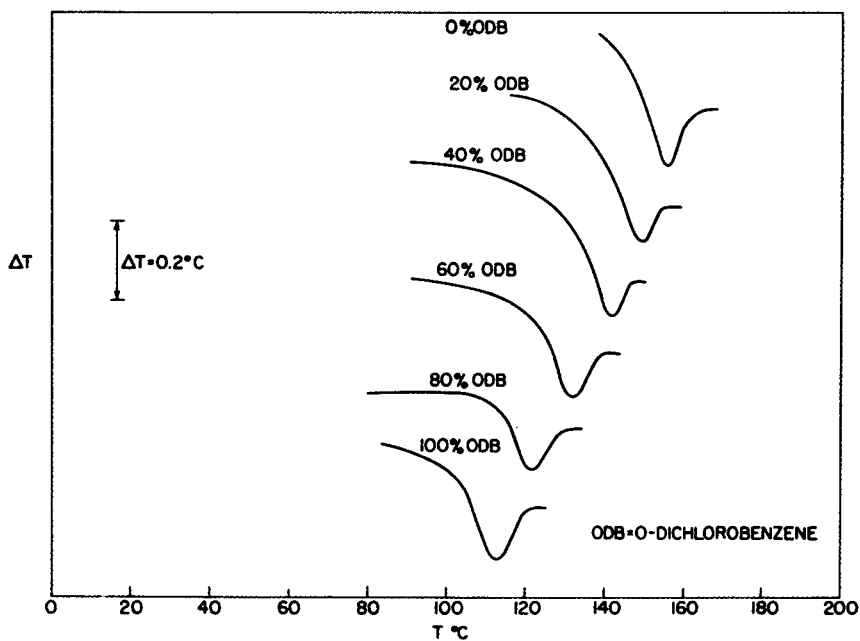Fig. 1. DTA solution thermogram for linear polyethylene in *o*-dichlorobenzene and dimethyl phthalate.

Fig. 2. DTA solution thermogram for isotactic polypropylene in *o*-dichlorobenzene and dimethyl phthalate.

Elution Fractionation of Polymers

The elution fractionation apparatus used in this work was similar to the apparatus developed by Shyluk,[8] with minor modifications. The main portion of the apparatus consisted of a vapor-thermostated glass column with 4-cm. inner diameter and 90 cm. of usable length. The apparatus was constructed of glass with Teflon seals, Teflon tubing, and stainless-steel screening. The solvent flowed upward through the column, and the flow rate was fixed at 5 ml./min. by controlling the head of solvent in the solvent container.

Both polymers were deposited on 100-μ diameter glass beads in a manner similar to the method reported by Kenyon and Salyer.[3] About 1.5 g. of linear polyethylene was dissolved in 160 ml. of o-dichlorobenzene in a 135°C. constant temperature bath. About 650 g. of previously cleaned glass beads was slowly added while the mixture was constantly stirred. The mixture was maintained at 135°C. for 30 min. and then very slowly cooled to room temperature. Polypropylene was deposited on glass beads in a similar manner with the use of a 135°C. bath. The column packing was supported at the bottom of the column by fine stainless steel screening secured between two expandable steel rings which press against the column wall. The column was packed with 15 cm. of uncoated glass beads, which serve as the solvent mixture preheating section, followed by 45 cm. of polymer-coated glass beads. The remainder of the column up to the side arm where effluent is withdrawn was packed with uncoated glass beads. A stainless-steel screen expandable ring assembly, similar to the one employed at the bottom of the column, was placed above the packing just below the side arm to prevent entrainment of glass beads by effluent. The type of packing support assembly used here has advantages over the conventional glass frit support, in that it eliminates clogging at the exit, and since it is movable it provides a means of varying column height and permits the column to be readily cleaned.

Throughout this work the solvent–nonsolvent composition was not varied in a continuous manner, but 200-ml. batches of solvent–nonsolvent mixtures of particular compositions were employed. High-density polyethylene was fractionated first, and the composition range for the solvent–nonsolvent mixtures was established after trial runs. The lower and upper limit of solvent composition were selected as 35% and 70% o-dichlorobenzene, respectively. Intermediate solvent–nonsolvent compositions were so selected as to yield fractions of reasonably uniform weight. The single exception to this method of obtaining the solvent compositions was the first composition which was pure nonsolvent. Polyethylene fractionations were performed at 127°C., and polypropylene fractionations were performed at 152°C., the respective solution temperatures of the polymers in pure nonsolvent as determined by DTA measurements. The results of the polyethylene fractionations together with DTA solution temperature measurements were used to estimate solvent–nonsolvent compositions for

polypropylene fractionations. The method of estimating these composi-
tions will be discussed later. Fractions were precipitated in methanol con-
taining Dry Ice. The precipitates were filtered, repeatedly washed in
methanol, and vacuum-dried overnight.

Polymer Fraction Characterization

Viscosity measurements were made with a dilution-type viscometer of our
own design. Viscosities of polyethylene and polypropylene fractions were
determined in tetralin at 130 and 135°C., respectively. Kinetic energy
and rate of shear corrections were not made. Solution viscosities were
extrapolated to infinite dilution to obtain intrinsic viscosities. Equations
(1)[9] and (2)[10] were used with the intrinsic viscosity values to obtain the
number-average molecular weights of polyethylene and polypropylene
fractions, respectively.

$$[\eta] = 5.10 \times 10^{-4} \bar{M}_n^{0.725} \tag{1}$$

$$[\eta] = 9.17 \times 10^{-5} \bar{M}_n^{0.80} \tag{2}$$

RESULTS

Thermograms in Figures 1 and 2 show a progressive decrease of the solu-
tion temperature of both polymers with increasing concentration of o-di-
chlorobenzene in the solvent–nonsolvent mixture. The solution tempera-
ture is taken as the intersection of tangents drawn from either side of a
thermogram curve. Solution temperature measurements were made on
samples containing 8 wt.-% polymer and 92 wt.-% solvent and nonsolvent.
Duplicate solution temperature measurements agreed within 1°C.

In general the solution temperature is dependent upon the solvent–non-
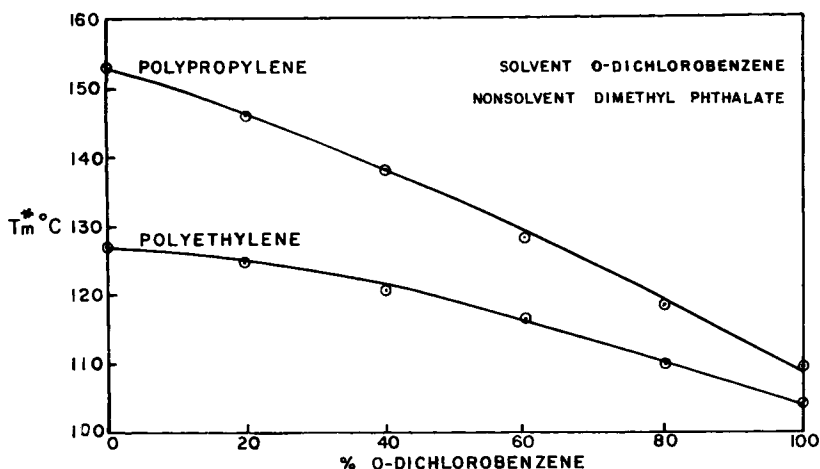solvent composition and the relative amounts of polymer and solvent–

Fig. 3. Solution temperature of polymers in solvent mixtures.

nonsolvent mixture.   A series of measurements was made to determine how
polymer solution temperature changes as the weight per cent of polymer is
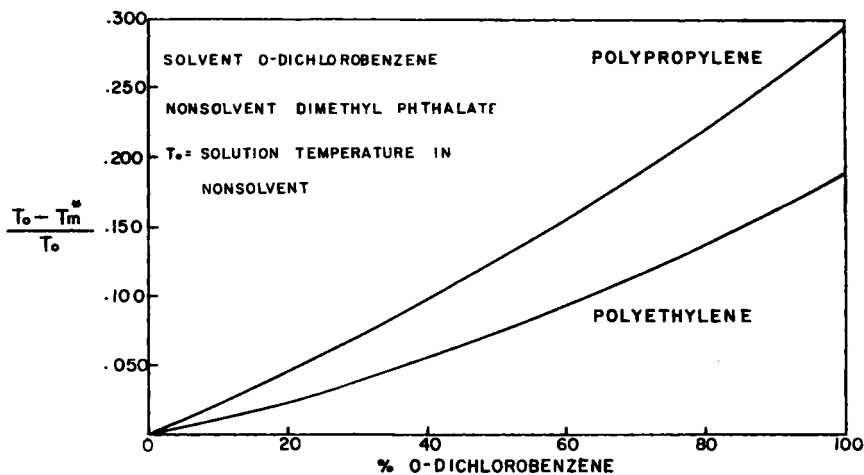reduced from 8%.   These measurements showed no substantial change in

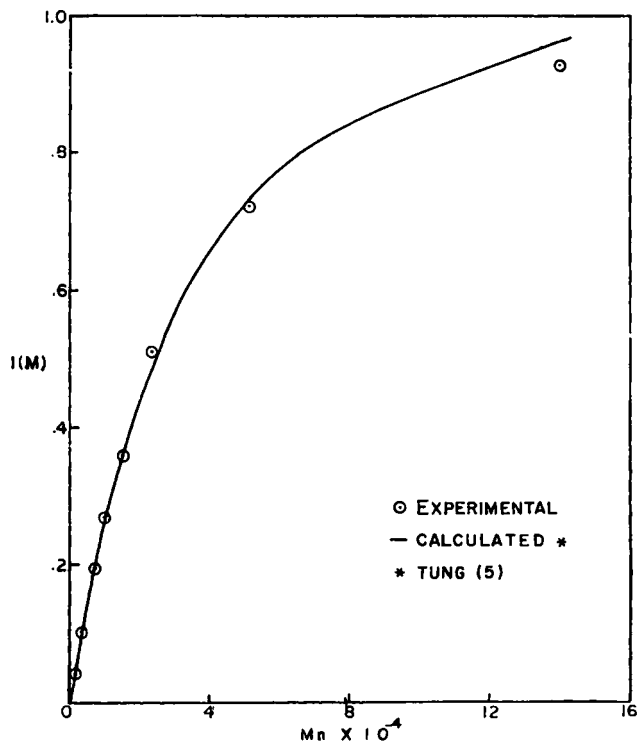Fig. 4. Depression of solution temperature of polymers in solvent mixtures.

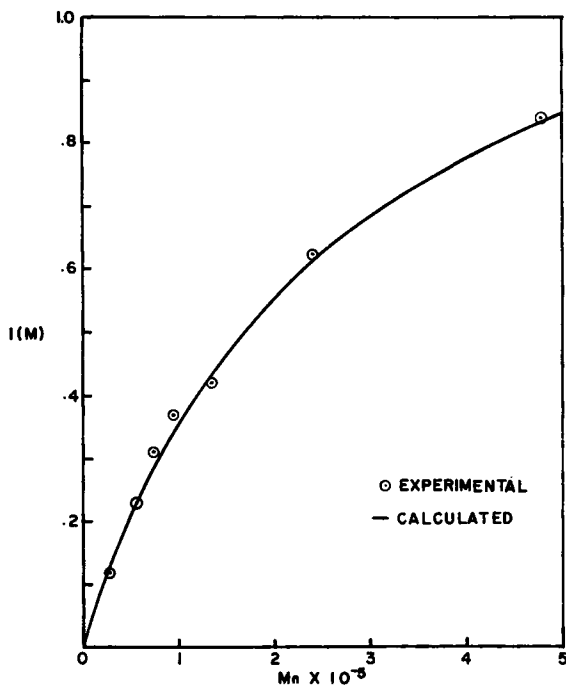Fig. 5. Integral molecular weight distribution curve for polyethylene.

Fig. 6. Integral molecular weight distribution curve for polypropylene.

the solution temperature (less than 1°C.).   This type of behavior has been observed in other polymer–solvent systems.   Mandelkern[11] has reported a decrease of from 1 to 1.5°C. in the solution temperature of linear polyethylene in tetralin as the amount of polymer was decreased from 10% to 0.01%.   Our results indicate that at low concentrations (10% to 0.1%) of these polymers the solution temperature of the polymers is essentially only a function of the solvent–nonsolvent composition and not of the relative amounts of polymer and solvent–nonsolvent mixture.   The solution temperature, $T^*_{m'}$ of each polymer is plotted in Figure 3 as a function of the volume per cent of o-dichlorobenzene in the solvent–nonsolvent mixture for a fixed polymer concentration of 8%.   These curves are essentially the same as those for lower polymer concentrations.   Figure 3 is believed to give a good indication of solution conditions in the fractionation column which operates at a polymer concentration of less than 1%.

A plot of the fractional depression in solution temperature is a useful aid in determining the relative solubility of each polymer in the solvent–nonsolvent system.   The fractional depression in solution temperature, defined as the ratio of the difference between the solution temperature of the polymer in a solvent mixture of a particular composition and that in the pure nonsolvent (dimethyl phthalate) to the solution temperature in the pure nonsolvent, is plotted in Figure 4 as a function of the volume per cent of o-dichlorobenzene in the solvent–nonsolvent mixture.   It can be seen that

at a particular o-dichlorobenzene concentration, the fractional depression in solution temperature of polypropylene is greater than that of polyethylene. It follows then that if a solvent–nonsolvent mixture of a particular composition and volume causes a certain amount of polyethylene to dissolve at 127°C., the same mixture will cause a greater amount of polypropylene to dissolve at 152°C., both temperatures being the melting temperatures of the respective polymers in pure nonsolvent (dimethyl phthalate). To dissolve approximately the same amount of polypropylene a solvent–nonsolvent mixture of lower o-dichlorobenzene concentration has to be used. One method to determine this concentration is to start with the o-dichlorobenzene concentration for polyethylene and basing on the same fractional depression of melting temperature to locate the o-dichlorobenzene concentration for polypropylene on Figure 4.

TABLE I
Estimated Solvent–Nonsolvent Compositions for Fractionation

Solvent composition established in polyethylene fractionation, % o-dichlorobenzene	Solvent–nonsolvent composition for polypropylene fractionation estimated with the aid of Fig. 4, % o-dichlorobenzene
35	20
45	27.5
54	34.5
57	37
60	39
63	41
66	43
70	46

The above considerations can be applied to the estimation of the operating conditions of the elution fractionation of polypropylene when polyethylene fractionation conditions are known and DTA solution data are available. The o-dichlorobenzene concentration range established by the polyethylene fractionation can be used, in conjunction with Figure 4, to estimate a corresponding range for the fractionation of polypropylene at 152°C. based on the same fractional melting temperature depression. Data in the left column of Table I were obtained after trial and error linear polyethylene fractionations were made to determine reasonable operating conditions. The values in the right column of Table I are estimated compositions for a polypropylene fractionation obtained by using the data in the left column and Figure 4. These estimated compositions were slightly adjusted and used to carry out the polypropylene fractionation. The results of one polyethylene and one polypropylene fractionation are given in Tables II and III. Fractions of fairly uniform weights were obtained. The fractions closely follow Tung's[5] molecular weight distribution (Figs. 5 and 6) and show no sign of molecular weight reversal.

TABLE II
Linear Polyethylene Fractionation Results

Solvent composition, % o-dichlorobenzene	Wt. of fraction, polyethylene, mg.	Cumulative wt.-% of polymer eluted
0	31.1	2.2
35	55.4	6.2
45	113.4	14.4
54	129.4	25.4
57	91.5	30.4
60	157.4	41.7
63	257.0	60.2
66	340.8	84.6
70	212.5	100.0

TABLE III
Polypropylene Fractionation Results

Solvent composition, % o-dichlorobenzene	Wt. of fraction, polypropylene, mg.	Cumulative wt.-% of polymer eluted
0	19.2	1.6
25	54.2	6.2
35	132.0	17.4
38	125.0	28.2
39	68.0	33.9
40	72.5	37.5
41	100.6	46.1
42	122.2	56.5
43	141.1	68.4
44	371.4	100.0

The fractionation temperature of 127 and 152°C. are the melting temperatures of the polymers in pure nonsolvent. The operation of the column at these temperatures ensures that none of the polymer is in a crystalline state. The absence of crystalline material thus greatly facilitates the fractionation process. Francis et al.,[12] in an attempt to establish that their column temperature of 127°C., which is below the crystalline melting point of linear polyethylene (131–135°C.), did not interfere with the resolution of the fractionation method, performed fractionations at 127, 142, and 152°C. and found that no difference in resolution is obtained by fractionation at the higher temperatures. They also showed that the polyethylene crystallization temperature was lowered to 123°C. in a 20% cumene–80% butyl cellosolve mixture and thus was safely below the column temperature. In the present study, the column temperatures were quickly determined by the DTA studies, and the results (Fig. 3) clearly indicate that the melting temperature of each polymer is well below the respective column temperature in any of the solvent–nonsolvent mixtures employed. To investigate if the temperatures so determined represent a practical upper limit (i.e., above which the polymer would become so fluid that it leaves the

column unfractionated), the column temperature for one polypropylene fractionation was raised to and maintained at 156°C. As a result, approximately 30% of the total polymer charge was eluted by the first batch of eluent which consisted of pure nonsolvent (dimethyl phthalate). A similar result would be expected with polyethylene fractionation.

CONCLUSIONS

The fractionation temperatures of linear polyethylene and isotactic polypropylene were determined by preliminary DTA studies on the fusion behavior of these polymers in a binary solvent system without actually carrying out trial fractionation runs. When the same solvent–nonsolvent system was used to fractionate both polymers, it was possible to estimate the composition range to fractionate polypropylene from a knowledge of the compositions used during a polyethylene fractionation and solution temperature data from DTA studies. Although separation is dependent on molecular weight, the equivalence in fractional depression in melting temperature was found to provide a means of correlating operating conditions for fractionating both of the polyolefins used in this study. The method immediately narrowed down the composition range to employ when fractionating polypropylene. After small adjustments were made in the estimated compositions, they were used to perform fractionations which yielded fairly uniform fractions.

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Résumé

Une technique a été développée permettant l'estimation des conditions de fractionne-
ment du polypropylène dans une colonne à élution au départ des connaissances des con-
ditions de fractionnement d'un polyéthylène linéaire dans une colonne et le comporte-
ment en solution des deux polymères dans un même système solvant–non-solvant de
compositions variables.   Le comportement à la fusion du polyéthylène linéaire et du
polypropylène isotactique dans un mélange d'ortho-dichlorobenzène et de phthalate de
diméthyle de différentes compositions a été étudié par analyse thermique différentielle
(DTA) utilisant des concentrations semblables à celles dans une colonne de fractionne-
ment par élution.   La température de la colonne pour le fractionnement de chacun
de ces polymères utilisant l'ortho-dichlorobenzène et le phthalate de diméthyle comme
solvant-non-solvant respectivement a été déterminée au départ de la température
de fusion dans le phthalate de diméthyle.   On s'est basé sur l'équivalence de la diminu-
tion fractionnaire à température d'élution de chaque polymère dans des mélanges
liquides binaires, pour estimer le domaine de composition des mélanges solvant-non-
solvant qui devaient être utilisé pour fractionner le polypropylène au départ de la
connaissance des conditions de fractionnement du polyéthylène en même temps que des
résultats de l'analyse thermique différentielle.   Bien que la séparation dépende princi-
palement du poids moléculaire, l'équivalence dans la diminution de température de la
solution fractionnaire procure une méthode convenable pour relier les conditions de
fractionnement des polyoléfines étudiées.

Zusammenfassung

Ein Verfahren zur Bestimmung der Fraktionierungsbedingungen für Polypropylen
in einer Eluierungssäule aus der Kenntnis der für die Fraktionierung von linearem Poly-
äthylen in der Säule eingehaltenen Bedingungen und des Lösungsverhaltens beider
Polymerer im gleichen Lösungsmittel–Fällungsmittelsystem bei variierter Zusammenset-
zung wurde entwickelt.   Das Schmelzverhalten von linearem Polyäthylen und isotak-
tischem Polypropylen in o-Dichlorbenzol-Dimethylphthalatmischungen mit verschied-
ener Zusammensetzung wurde differentialthermoanalytisch (DTA) bei Konzentrationen
ähnlich denjenigen in einer Elutionsfraktionierungssäule untersucht.   Die Säulentem-
peratur für die Fraktionierung jedes dieser Polymeren mit o-Dichlorobenzol und Di-
methylphthalat als Lösungs- bzw.   Fällungsmittel wurde aus der Schmelztemperatur
in Dimethylphthalat bestimmt.   Auf Grundlage der Äquivalenz der relativen Ernie-
drigung der Lösungstemperatur eines jeden Polymeren in der binären Flüssigkeits-
mischung wurde der Zusammensetzungsbereich des bei der Polypropylenfraktion-
ierung zu benützenden Lösungsmittel-Fällungsmittelgemisches aus der Kenntnis der
Polyäthylenfraktionierungsbedingungen und der DTA-Daten bestimmt.   Obgleich die
Trennung primär vom Molekulargewicht abhängt, liefert doch die Äquivalenz der
relativen Erniedrigung der Lösungstemperatur ein bequemes Mittel zur Korrelierung
der Fraktionierungsbedingungen für die untersuchten Polyolefine.