

## Heptane-Soluble Material from Atactic Polypropylene. I. Fractionation and Characterization of Fractions

W. R. MOORE and G. F. BODEN, *Polymer Research Laboratories,  
Department of Chemical Technology, Bradford Institute of  
Technology, Bradford, Yorkshire, England*

### Synopsis

A sample of commercial atactic polypropylene was extracted with ether and the residue extracted with boiling *n*-heptane. Six fractions of the heptane-soluble material, which is very similar to that obtained by heptane extraction of isotactic polypropylene, were obtained by stepwise addition of acetone to a solution in cyclohexane. Densities, melting points, and x-ray photographs of the fractions and the unfractionated material were obtained and infrared absorption spectra used to estimate tacticity. Molecular weights, determined by means of a vapor pressure osmometer, ranged from about 3000 to about 25,000. That of the fraction of highest molecular weight was in good agreement with a separate determination by means of osmotic pressure measurements. Separation in fractionation occurred in order of decreasing molecular weight and increasing crystallinity as estimated from densities and x-ray photographs. Tacticity also seems to increase with decreasing molecular weight. Melting points of the fractions were not entirely in the order expected from their molecular weights and estimated crystallinities, and it is possible that low DP isotactic material may be preferentially concentrated in the highest molecular weight fraction. It is emphasized that the unfractionated material may contain polymers possessing a range of order intermediate between those of purely atactic and purely isotactic polymer and that refractionation may be required in order to characterize the material completely.

### INTRODUCTION

Commercial atactic polypropylene may contain small amounts of material insoluble in diethyl ether, a solvent for the atactic polymer. Most of the ether-insoluble material dissolves in boiling *n*-heptane and in a number of other liquids at room temperature. A small residue which is left after extraction with boiling heptane is soluble only at elevated temperatures. The heptane-soluble material is very similar to that obtained by similar heptane extraction of isotactic polypropylene and which has been termed "stereoblock" polypropylene.<sup>1</sup> However, as Russell<sup>2</sup> has pointed out, such heptane-soluble material is probably better regarded as possessing a range of order intermediate between those of purely atactic and purely isotactic polypropylenes. Low DP isotactic polymer, the solubility of which will depend on its molecular weight, is likely to be present, and imperfect isotactic and/or syndiotactic polymers, the chains of which may contain structural imperfections of purely statistical nature, are also

possible. Stereoblock polymer chains, if present, should contain sequences of each of two kinds of structure—isotactic, syndiotactic, or atactic. A wide variation in the lengths of such blocks may occur. The heptane-soluble material may therefore be a rather complex mixture of chains of differing degrees of stereoregularity. The insoluble residue remaining after extraction with heptane is presumably material of greater stereoregularity and molecular weight. This report is concerned with the fractionation of the heptane-soluble material from atactic polypropylene with respect to molecular weight and the characterization of the fractions in terms of density, crystallinity, tacticity, and molecular weight. A further report (Part II) will be concerned with other aspects of polymer-liquid interaction.

## EXPERIMENTAL

The heptane-soluble material was obtained from a commercial sample of atactic polymer by the method of separation suggested by Natta<sup>3</sup> and elaborated by Russell.<sup>2</sup> The atactic polymer was extracted with diethyl ether for 48 hr. and the residue extracted, under nitrogen, with boiling *n*-heptane for 24 hr. The heptane extract was filtered hot and the filtrate poured into stirred excess acetone giving a fluffy, white precipitate of polymer. This was extracted with diethyl ether for 4 hr. to ensure the removal of any residual atactic polymer and the residue dried *in vacuo* at 50°C. A small residue remained after heptane extraction of the ether-insoluble material. All liquids used in the separation of the heptane-soluble material, its fractionation, and the characterization of the fractions were carefully purified, dried, and fractionally distilled before use.

### Fractionation

Natta<sup>1</sup> and Newman<sup>4</sup> have used extraction by liquids of increasing solvent power to obtain fractions of different stereoregularity. The method of stepwise precipitation was used in this work. Preliminary experiments showed that addition of acetone to a solution of the heptane-soluble material in cyclohexane gave a gel precipitate which could be fairly easily separated from the supernatant liquid. This system has been used in the fractionation of atactic polypropylene.<sup>5</sup> Acetone was slowly added to a well stirred 1% solution of the material in cyclohexane at 35°C. until the mixture was faintly turbid. The mixture was then cooled slowly to 25°C. and kept at this temperature overnight. The gel which separated was removed by centrifuging and decantation, dissolved in cyclohexane, and polymer (fraction 1) precipitated by pouring the solution into stirred excess acetone. The fraction was filtered off, washed with acetone, and dried *in vacuo* at 50°C. Further additions of acetone to the original supernatant and repetition of the process outlined above gave four further fractions (2, 3, 4, and 5). A final fraction was obtained by pouring the final supernatant into excess acetone. The fractionation procedure is summarized

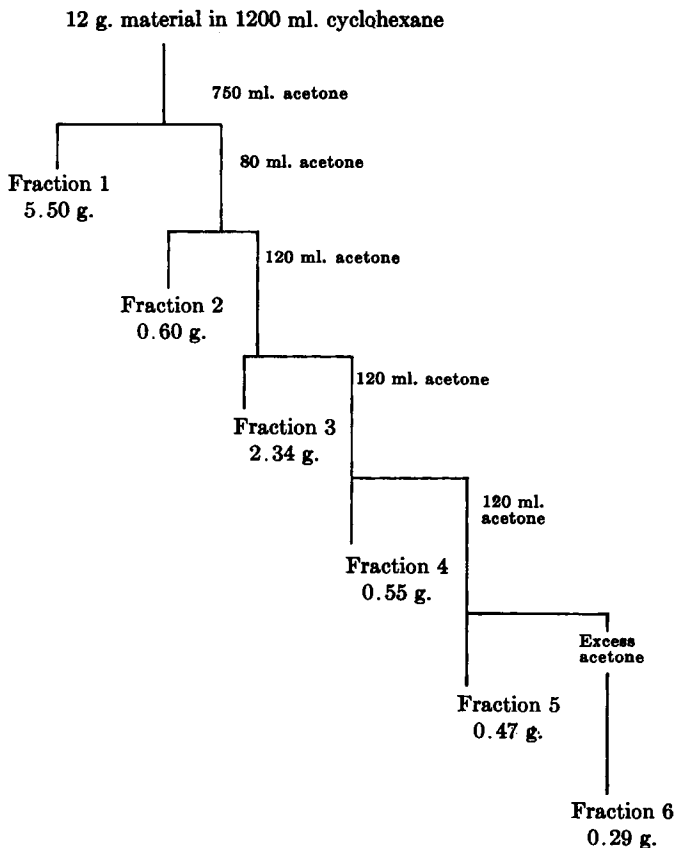


Fig. 1. Summary of fractionation procedure.

in Figure 1. Losses during centrifuging and decantation and possibly some material not finally precipitated account for the discrepancy between the sum of the weights of the fractions and the weight of the unfractionated material.

### Characterization

Films of the fractions and of the unfractionated material were prepared by casting solutions in cyclohexane on mercury, evaporation of solvent, drying under vacuum. Densities of these were determined by a flotation method in ethanol-water mixtures at  $25 \pm 0.02^\circ\text{C}$ . The densities of such mixtures were determined pycnometrically at the same temperature. Densities of the films were reproducible to 0.001 g./ml.

Infrared absorption spectra of fractions 1, 3, and 6 were obtained by using dispersions of the fractions in pressed potassium bromide disks with a Perkin-Elmer Infracord Model 237. The unfractionated material was too hard to mix satisfactorily with potassium bromide. Comparison of the heights of the absorption at  $995\text{ cm.}^{-1}$ , said to be sensitive to changes

in tacticity, and at  $974\text{ cm.}^{-1}$ , said to be insensitive to tacticity changes and used as an internal thickness guide, was used to estimate tacticity.<sup>6</sup> This method, although perhaps not very sensitive at low degrees of tacticity, was preferred to the alternative method<sup>7,8</sup> of comparison of absorptions at  $1150$  and  $947\text{ cm.}^{-1}$ , as the peak at  $1150\text{ cm.}^{-1}$  has been shown<sup>6</sup> to be difficult to resolve.

X-ray diffraction powder photographs of the fractions and the unfractionated material were obtained.

Melting points of the fractions and the unfractionated material were determined by use of a microscope incorporating a heating stage at a heating rate of approximately  $0.5^\circ\text{C./min.}$  Melting points were reproducible to  $1^\circ\text{C.}$

Initially, attempts were made to obtain number-average molecular weights  $\bar{M}_n$  osmotically. Pinner-Stabin osmometers<sup>9</sup> were used statically at  $35 \pm 0.01^\circ\text{C.}$  with cellulose membranes previously treated with 5% aqueous caustic soda and washed with water before conditioning to decalin, the solvent used. Considerable diffusion of polymer through the membranes occurred with solutions of all the fractions with the exception of fraction 1. In this latter case osmotic pressures  $\pi$  of solutions in the concentration range  $0.1\text{--}0.5\text{ g./100 ml.}$  were measured at  $35 \pm 0.01^\circ\text{C.}$  and  $\bar{M}_n$  obtained from a plot of  $\pi/c$  against concentration  $c$  and extrapolation to zero  $c$ .

In all other cases a vapor pressure osmometer (Mechrolab 301A) at  $37 \pm 0.001^\circ\text{C.}$  was used to determine  $\bar{M}_n$ . This instrument, based on the thermoelectric osmometer of Hill<sup>10</sup> and Baldes,<sup>11</sup> measures the steady-state temperature difference between a drop of solvent and a drop of solution suspended side by side in an atmosphere saturated with solvent vapor. The use of thermistors<sup>12</sup> permits detection of very small temperature differences and the determination of molecular weights of up to about 25,000.

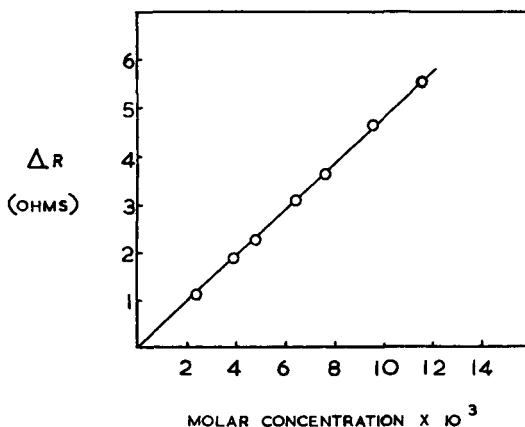


Fig. 2. Calibration graph for vapor pressure osmometer. Glyceryl trioleate in carbon tetrachloride at  $37^\circ\text{C.}$

The instrument was first calibrated with solutions of glyceryl trioleate in each solvent used at molar concentrations between 0.001 and 0.01*M*. Measurements were made of the resistance difference  $\Delta R$  between the thermistors covered with drops of solvent and solution respectively.  $\Delta R$  is proportional to the temperature difference. For each solvent  $\Delta R$  was plotted against molar concentration to obtain a calibration graph, an example being shown in Figure 2. Values of  $\Delta R$  were then obtained for solutions, at different concentrations, of all the fractions and the unfractionated material in carbon tetrachloride and of fraction 3 in cyclohexane and trichlorethylene. The concentration range for the solutions of the fractions was 0.3–2.0 g./100 ml solution.

The solutions used in calibration were assumed to be effectively ideal. It was also assumed that  $\Delta R$  was directly proportional to the vapor pressure difference between solvent and solution and to molar concentration. The assumption of ideality will not, of course, apply to the solutions of the fractions except at infinite dilution. Values of  $\Delta R$  for the solutions of the fractions were used to obtain, from appropriate calibration graphs, apparent molar concentrations from which apparent molecular weights were calculated. These were then plotted against concentration and extrapolated to zero concentration to obtain values of  $\bar{M}_n$ .

An alternative method<sup>13</sup> of treating the results was also used. Assuming a particular value of  $\Delta R$ , for a given solvent, to correspond to the same vapor pressure difference, whatever the solute, such differences can be calculated, by use of Raoult's law, from the calibration data since the solutions used in calibration were assumed to be ideal. Values of  $p/p_0$ , where  $p$  is the vapor pressure of the solvent above the solution and  $p_0$  that of the pure solvent, could therefore be obtained for the solutions of the fractions. The Flory-Huggins equation:

$$\ln (p/p_0) = \ln \phi_1 + (1 - 1/x)\phi_2 + \chi_1\phi_2^2 \quad (1)$$

where  $\phi_1$  and  $\phi_2$  are the volume fractions of solvent and polymer respectively,  $x$  the average degree of polymerization, and  $\chi_1$  the polymer-solvent interaction parameter, may, after substitution of  $V_2/V_1$ , the ratio of molar volumes, for  $x$  be rearranged to give

$$\{ [\ln (p/p_0) - \ln \phi_1]/\phi_2 \} - 1 = - V_1/V_2 + \chi_1\phi_2 \quad (2)$$

A plot of the left-hand side of this equation against  $\phi_2$  should give a straight line with ordinate intercept equal to  $- V_1/V_2$ , from which  $\bar{M}_n$  can be calculated.

## RESULTS

Table I gives densities and melting points of the fractions and the unfractionated material. It also includes percentage crystallinities, estimated from the densities by use of the formula given by Danusso et al.<sup>14</sup> and estimates of tacticity from the infrared absorption measurements.

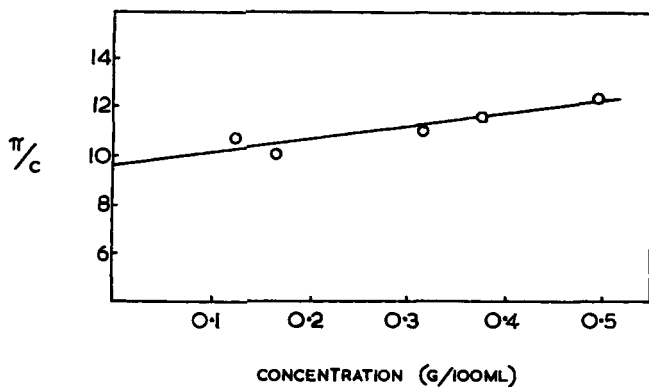


Fig. 3.  $\pi/c$  against  $c$  plot for fraction 1 in decalin at 35°C.

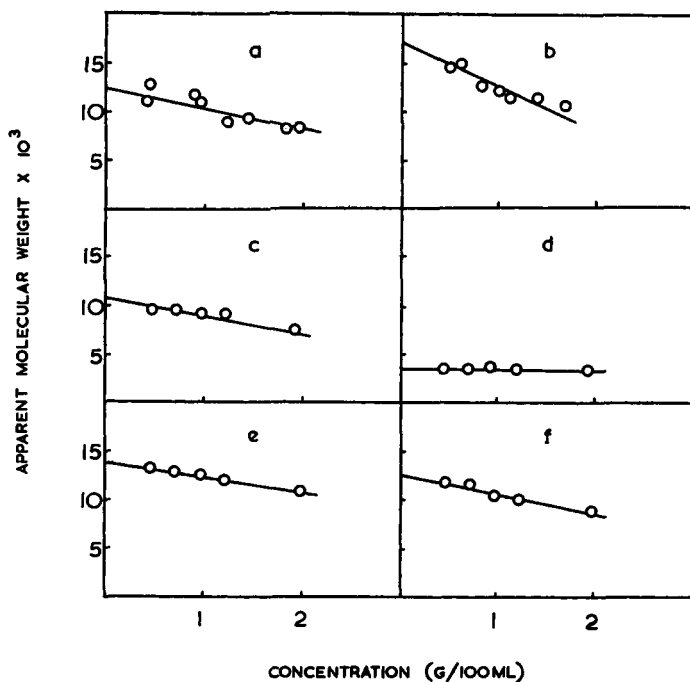


Fig. 4. Plots of apparent molecular weight against concentration at 37°C.: (a) unfractionated material in carbon tetrachloride; (b) fraction 2 in carbon tetrachloride; (c), fraction 4 in carbon tetrachloride; (d) fraction 6 in carbon tetrachloride; (e) fraction 3 in cyclohexane; (f) fraction 3 in trichlorethylene.

The x-ray photographs were in qualitative agreement with the estimates of crystallinity, but quantitative measurements were not possible.

Figure 3 shows a plot of  $\pi/c$  against  $c$  for fraction 1 in decalin at 35°C. Figure 4 shows typical plots of apparent molecular weight, obtained by use of the vapor pressure osmometer, against concentration. Figure 5 shows

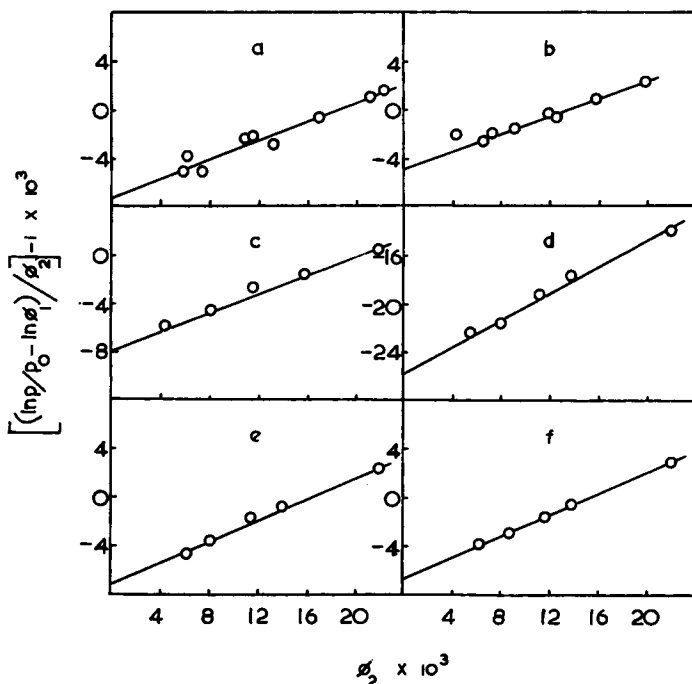


Fig. 5. Plots of left-hand side of eq. (2) against  $\phi_2$ : (a), (b), (c), (d), (e), and (f) as in Figure 4.

TABLE I  
Characteristics of Fractions

Fraction	Density, g./ml.	Melting point, °C.	Crystallin- ity, %	Tacticity, %
1	0.868	132	15.8	16
2	0.869	111.5	16.0	
3	0.871	111.5	20.1	20
4	0.876	111.5	26.2	
5	0.8875	112	41.4	
6	0.888	116	41.8	22
Unfractionated	0.873	125	22.3	

the corresponding plots of the left-hand side of eq. (2) against  $\phi_2$ . Table II gives the molecular weights obtained. The accuracy of these is estimated to be  $\pm 10\%$  for carbon tetrachloride and decalin as solvents and  $\pm 5\%$  in other cases.

## DISCUSSION

Fractionation was with respect to molecular weight rather than structure, and the fractions, like the unfractionated material, may contain polymers of differing degrees of stereoregularity. Low DP isotactic poly-

TABLE II  
Number-Average Molecular Weights

Fraction	Solvent	$\bar{M}_n$		
		Osmotic pressure	From apparent molecular weights	By use of eq. (2)
1	Decalin	27,000		
1	Carbon tetrachloride		24,000	26,000
2	Carbon tetrachloride		17,500	17,000
3	Carbon tetrachloride		12,600	12,600
3	Cyclohexane		13,850	14,000
3	Trichlorethylene		12,750	12,750
4	Carbon tetrachloride		10,700	10,200
5	Carbon tetrachloride		7,300	6,900
6	Carbon tetrachloride		3,400	3,300
Unfractionated	Carbon tetrachloride		12,100	12,100

mer may be preferentially concentrated in the higher molecular weight fractions. Variations in the number of structural imperfections in imperfectly stereoregular chains may lead to a fairly wide distribution of solubilities and melting points, and variations in the length and character of blocks in stereoblock polymer may have similar effects. Tables I and II do, however, suggest some regularities. The crystallinities of the fractions, as estimated from their densities, increase with decreasing molecular weight. Similar results have been obtained by Natta<sup>15</sup> and by Wijga et al.<sup>16</sup> Crystallinity seems to tend to a limiting value as the molecular weight decreases. Natta et al.<sup>17</sup> have recently shown, however, that the crystallinity of isotactic polypropylene increases with decreasing molecular weight down to a molecular weight of about 1000. Below this value crystallinity decreases because of the greater influence of terminal groups. The same may apply in the present case. The weighted average density of the fractions, 0.871 g./ml., is in reasonable agreement with 0.873 g./ml. for the unfractionated material in view of losses during fractionation.

The melting points of the fractions are not generally in the order of their crystallinities. This might perhaps be expected, since melting points will also depend on molecular weight increasing, for a given crystallinity, with increase of molecular weight. The difference of about 20°C. between the melting points of fractions 1 and 2, which have similar degrees of crystallinity, seems too large to be accounted for by difference in molecular weight alone and may be partly accounted for by the preferential concentration of low DP isotactic polymer in fraction 1. The unfractionated material also seems to have a higher melting point than might be expected from its crystallinity. Melting points of the other fractions tend to increase with increasing crystallinity.

Estimates of tacticity agree with those of crystallinity for fractions 1 and 3, but the tacticity of fraction 6 seems to be much less than its crystallinity.



This might be due to insensitivity in the method used to estimate tacticity. It might also perhaps be due to greater mobility of low molecular weight chains permitting closer packing and hence a higher density which might not necessarily represent greater crystallinity. The melting point of fraction 6 seems, however, to suggest a relatively high degree of crystallinity. In view of the possible presence of both isotactic and syndiotactic material in the possible presence of both isotactic and syndiotactic material in the fractions it would be of interest to know what fraction of the crystallinity might be ascribed to each. Such information can be obtained from x-ray studies,<sup>18,19</sup> but the x-ray photographs obtained did not permit this distinction. Nuclear magnetic resonance studies<sup>20</sup> might also be useful in this respect.

The two methods of treating the results obtained with the vapor pressure osmometer give essentially the same molecular weights. The molecular weight of fraction 1, obtained with carbon tetrachloride as solvent, is the same, within experimental error, as that obtained osmotically in decalin. This shows the vapor pressure osmometer to be capable of determining molecular weights as high as 25,000 and also, with the effective identity of the molecular weight in three solvents for fraction 3, suggests the absence of association of polymer.

The overall degrees of stereoregularity of the fractions would not seem to be high, and the molecular weights are less than those commonly obtained for addition polymers. Extraction with heptane is known to yield material of comparatively low stereoregularity from isotactic polypropylene, extraction with higher hydrocarbons being necessary to obtain more stereoregular material. Natta<sup>3</sup> finds that isotactic fractions of polypropylene are usually of relatively high molecular weight but that the molecular weights of fractions of lower degrees of stereoregularity are generally low.

It must again be emphasized that fractionation was with respect to molecular weight rather than structure. If, as is possible, each fraction contains material of differing degrees of stereoregularity and structure, further fractionation with respect to structure would be necessary to characterize the heptane-soluble material completely. Following Natta et al.,<sup>21,22</sup> each fraction might be chromatographically fractionated, first on isotactic and then on syndiotactic polymer. The small amounts of most of the fractions precluded such refractionation.

We are grateful for a Bradford Institute of Technology Scholarship awarded to G. F. B.

### References

1. Natta, G., G. Mazzanti, G. Crespi, and G. Moraglio, *Chim. Ind. (Milan)*, **39**, 275 (1957).
2. Russell, C. A., *J. Appl. Polymer Sci.*, **4**, 219 (1960).
3. Natta, G., *J. Am. Chem. Soc.*, **77**, 1708 (1955).
4. Newman, S., *J. Polymer Sci.*, **47**, 114 (1960).
5. Kinsinger, J. B., and R. E. Hughes, *J. Phys. Chem.*, **63**, 2002 (1959).

6. Luongo, J. P., *J. Appl. Polymer Sci.*, **3**, 202 (1960).
7. Brader, J. J., *J. Appl. Polymer Sci.*, **3**, 370 (1960).
8. Sibilia, J. P., and R. C. Winckhofer, *J. Appl. Polymer Sci.*, **6**, 556 (1962).
9. Pinner, S. H., and J. V. Stabin, *J. Polymer Sci.*, **9**, 575 (1952).
10. Hill, A., *Proc. Roy. Soc. (London)*, **A127**, 9 (1930).
11. Baldes, S. J., *J. Sci. Instr.*, **11**, 223 (1934).
12. Brady, A. P., H. Huff, and J. McBain, *J. Phys. Chem.*, **55**, 304 (1951).
13. Sirrianni, A. F., and I. E. Puddington, *Can. J. Chem.*, **36**, 543 (1958).
14. Danusso, F., G. Moraglio, and G. Natta, *Ind. Plast. Mod. (Paris)* **10**, 43 (1958).
15. Natta, G., *Ric. Sci.*, **28**, 1473 (1959).
16. Wijga, P. W., J. van Schooten, and J. Boerma, *Makromol. Chem.*, **36**, 115 (1960).
17. Natta, G., I. Pasquon, A. Zambelli, and G. Gatti, *Makromol. Chem.*, **70**, 191 (1964).
18. Natta, G., *Makromol. Chem.*, **35**, 94 (1960).
19. Natta, G., P. Corradini, and I. W. Bassi, *J. Polymer Sci.*, **51**, 505 (1961).
20. Bovey, F., and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).
21. Natta, G., M. Pegoraro, and M. Peraldo, *Ric. Sci. Suppl.*, **28**, 1473 (1958).
22. Natta, G., I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, and A. Zambelli, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Natl.*, **28**, 539 (1960).

### Résumé

Un échantillon de polypropylène atactique commercial a été extrait à l'éther et le résidu extrait avec du *n*-heptane à l'ébullition. En ajoutant par fractions de l'acétone à une solution dans le cyclohexane, on a obtenu six fractions solubles dans l'heptane, très semblables à celles obtenues par extraction à l'heptane de polypropylène isotactique. On a obtenu les densités, les points de fusion et les diagrammes aux rayons-X des différentes fractions et du produit non-fractionné, et on a utilisé les spectres d'absorption dans l'infrarouge pour en estimer la tacticité. Les poids moléculaires, déterminés au moyen d'un osmomètre à tension de vapeur, se situaient depuis 3,000 jusque 25,000. La fraction du poids moléculaire la plus élevée est en parfait accord avec une détermination séparée effectuée au moyen de mesures de pression osmotique. La séparation au cours du fractionnement a lieu par ordre de poids moléculaire décroissant et de cristallinité croissante, ainsi que cela a été estimé à partir des densités et des diagrammes aux rayons-X. La tacticité semble également augmenter lorsque le poids moléculaire diminue. Les points de fusion des fractions ne sont pas entièrement dans l'ordre attendu sur la base de leurs poids moléculaires et de leurs cristallinités estimées, et il est possible que le produit isotactique de faible DP se concentre préférentiellement dans la fraction de poids moléculaire la plus élevée. On met l'accent sur le fait que le produit non-fractionné peut contenir des polymères possédant un domaine d'ordre intermédiaire entre celui du polymère purement atactique et celui du polymère purement isotactique. Le refractionnement pourrait être nécessaire en vue de caractériser complètement le produit.

### Zusammenfassung

Eine Probe von handelsüblichem, ataktischem Polypropylen wurde mit Äther und der Rückstand mit siedendem *n*-Heptan extrahiert. Sechs Fraktionen des heptanlöslichen Materials, das dem durch Heptanextraktion von isotaktischem Polypropylen erhaltenen sehr ähnlich ist, wurden durch schrittweisen Zusatz von Aceton zu einer Lösung in Zylohexan erhalten. Dichten, Schmelzpunkte und Röntgenaufnahmen der Fraktionen und des unfraktionierten Materials wurden erhalten und Infrarotabsorptionsspektren zur Bestimmung der Reaktivität verwendet. Die mit einem Dampfdruckosmometer bestimmten Molekulargewichte lagen im Bereich von etwa 3000 bis etwa 25000. Das Molekulargewicht der höchstmolekularen Fraktion stand in guter Übereinstimmung mit dem durch Messung des osmotischen Druckes bestimmten. Die Fraktionierung erfolgte, wie die Dichte und die Röntgenaufnahmen zeigten, nach abnehmen-

dem Molekulargewicht und zunehmender Kristallinität. Ebenso scheint die Reaktivität mit abnehmendem Molekulargewicht anzusteigen. Die Schmelzpunkte der Fraktionen lagen nicht völlig in der aus den Molekulargewichten und Kristallinitäten erwarteten Reihenfolge und es erscheint möglich, dass isotaktisches Material mit niedrigem DP bevorzugt in den höchstmolekularen Fraktionen angereichert wird. Es wird betont, dass unfraktioniertes Material Polymere mit einem Ordnungsgrad zwischen demjenigen von rein ataktischem und rein isotaktischem Polymeren enthalten kann und dass zur vollständigen Charakterisierung des Materials eine Refraktionierung notwendig sein kann.

Received August 20, 1964

Revised December 8, 1964