

Gel Permeation Chromatography of Isotactic Polypropylene Using the Cyclohexane–Decalin Solvent System

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SYNOPSIS

The molecular weight distribution of iPP and its copolymers with ethylene have been studied using cyclohexane/decalin as eluent at 333 K. The fractionation of the polymers using the same solvent system was also investigated. Reproducible and reliable molecular weight distribution and averages have been obtained.

INTRODUCTION

Isotactic PP is a semi-crystalline polymer with attractive high-temperature properties. For its processing and application, the molecular weight distribution is important.¹ The mechanical and thermal properties are also dependent on the molecular weight and its distribution.² Gel permeation chromatography (GPC) has been established as a convenient technique for determining the molecular weight distribution, as well as fractionation of polymers.³ However, for iPP that cannot be dissolved in any solvent at ambient temperatures, the GPC is usually conducted at high temperatures, above 403 K, using solvents such as decalin and *o*-dichlorobenzene, which by virtue of their toxicity usually present handling and technical difficulties. Ying and Ye⁴ reported the use of cyclohexane as a solvent for the GPC of iPP at 343 K. In this paper, I report a similar study using cyclohexane–decalin mixtures at a much lower temperature. This is then extended to a study of the fractionation of iPP and E/P copolymer samples.

EXPERIMENTAL

Materials

Two commercial iPP (Shell KM6001, PXC 32969) and E/P copolymer samples (PXC 22160 and

22156), supplied by Metal Box Wantage and British Sidac, UK, were used.

Sample Preparation

Five to ten polymer pellets were dissolved in 1 cm³ decalin at 413 K for about 1 h and then diluted with 9 cm³ cyclohexane that had been heated to 348 K. The solution was then filtered using filter phials and left in the GPC injector compartment, maintained at 333 K. It was stable for several hours.

Molecular Weight Distribution

Molecular weight distribution determination was carried out on a high-performance GPC, Waters Associate ALC/GPC 150C, interfaced to a BBC-B Plus microcomputer acting as a data station. GPC runs were carried out under the following conditions.

Column and injector compartment temperature: 333 K

Flow rate: 0.5 cm³/min

Sample concentration: 0.1% (w/v)

Sensitivity: 256

Scale factor: 20

Injection volume: 200 μ d m⁻³

The column used was Polymer Laboratory plc crosslinked divinylbenzene/polystyrene mixed analytical column of particle size 1 μ and plate number 9000. The column was calibrated with a series of Polymer Labs narrow distribution polystyrene standards. The iPP calibration curve was obtained

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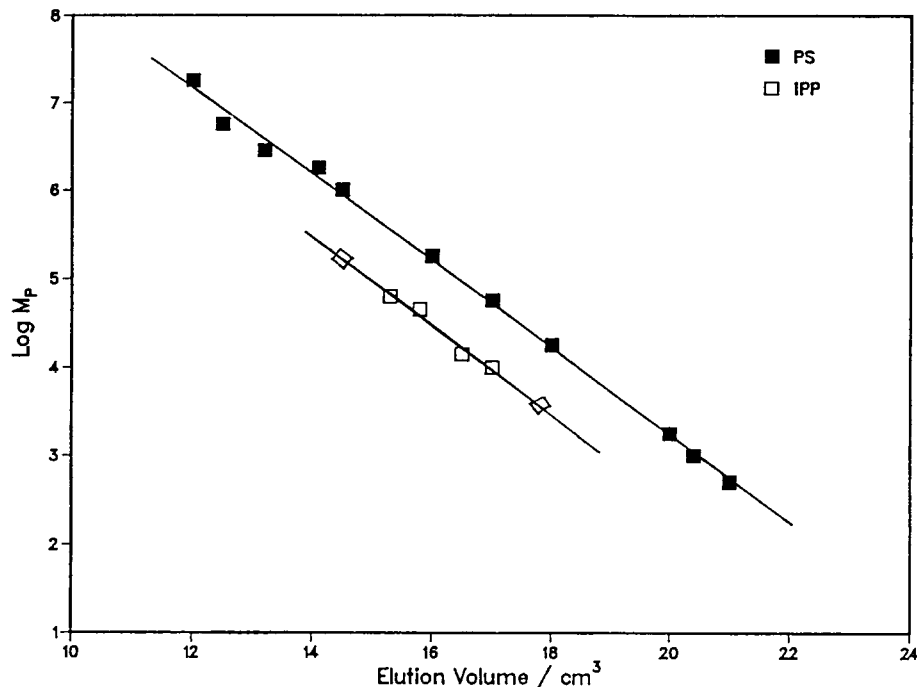


Figure 1 Calibration curves of PS and PP in cyclohexane.

by reinterpreting the data of Ying. The GPC and iPP calibration curves are shown in Figure 1.

To ensure that the molecular weight and averages were reproducible and devoid of significant errors due to baseline uncertainties and data imprecision,^{5,6} each sample was run as many times as possible.

FRACTIONATION

Fractionation of polymer samples was carried out using a computer program written in this laboratory for this purpose.⁷ The program was loaded with times for the collection of each fraction by the fraction collector, which consisted of a circular carousel with 12 boiling tubes. The movement of the carousel was controlled by the BBC-B Plus microcomputer using its internal lock. A pulse from the computer that occurred as injection was made triggered the start of fraction collection. Polymer was recovered by filtering through a porosity 3 glass frit and drying to a constant weight in a vacuum oven at 313 K.

RESULTS AND DISCUSSION

As a preliminary investigation, the cloud point⁸ of a solution of iPP in varying amounts of cyclohexane/decalin mixtures was determined. Ten mg sample was dissolved in varying amounts of decalin

at 413 K and diluted to the appropriate composition with cyclohexane at 343 K. The temperature of the solution was then lowered by natural cooling and the temperature at which phase separation first oc-

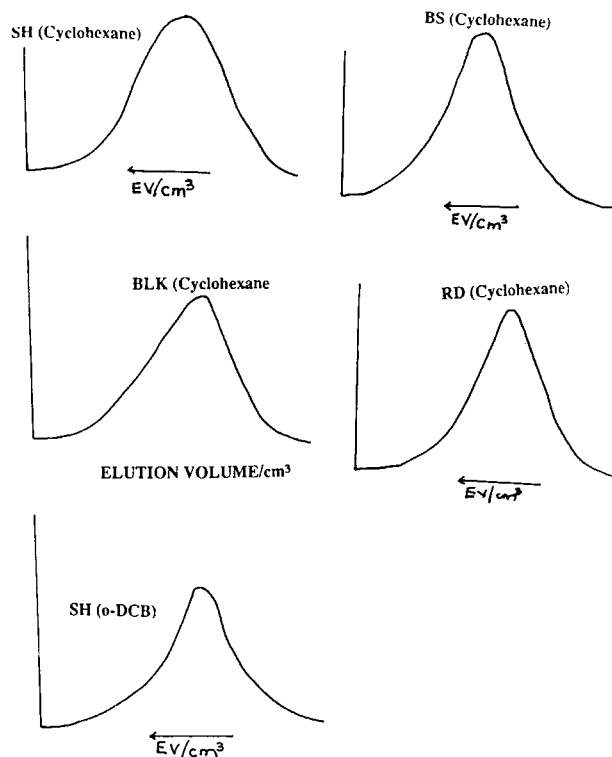


Figure 2 GPC traces.

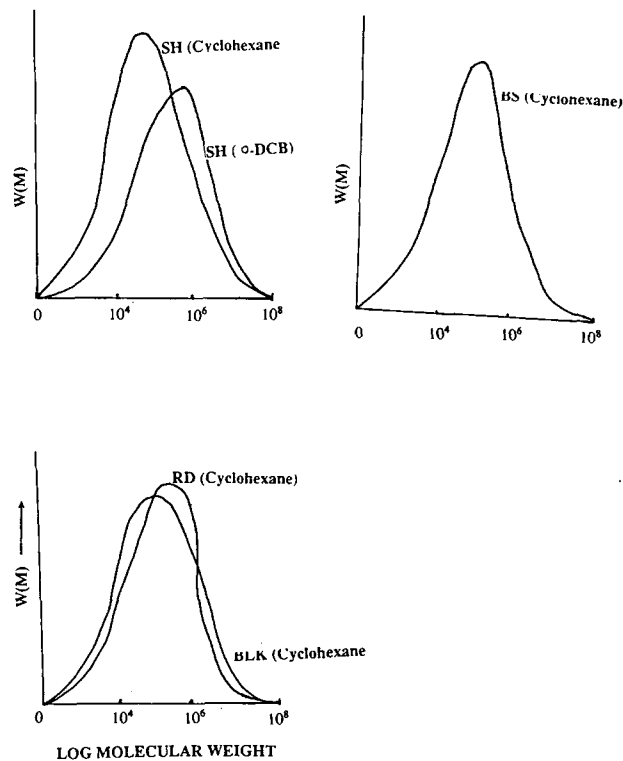


Figure 3 Molecular weight distributions.

curred was determined. Based on this study, 333 K was considered a suitable temperature at which to carry out the GPC runs, as a homogeneous phase could not be obtained below this temperature.

It was reasoned that if iPP was first dissolved in decalin at 413 K and the solution then diluted with hot cyclohexane above 333 K, the molecules of the polymer already dispersed in decalin would not readily crystallize from solution. One advantage of this is the greater refractive index difference between iPP and cyclohexane than that between iPP and halogenated aromatic solvents, respectively. Thus, more dilute solutions could be used in the GPC analysis.

The GPC traces and the molecular weight distribution determined in *o*-DCB at 413 K and cyclohexane at 333 K are shown in Figures 2 and 3 for the purpose of comparison, while the molecular weight averages are shown in Table I.

The breadth of the distribution as determined by the ratio, M_w/M_n , and the molecular weight averages determined in the two solvents were highly reproducible. Experimental differences do not appear to have affected the results. The high molecular weight tail of the iPP and copolymer samples extended to a molecular weight of about 10^7 which appears general for iPP samples.

Fractionation results for samples PXC22156 (block copolymer) and KM6001N (commercial iPP sample) are given in Tables II and III.

The fractionation was reasonably successful given the difficult experimental conditions associated with fraction collection and column blockage, although the latter effect was minimized by using a precolumn

Table I Molecular Weight Averages Calculated from the Molecular Weight Distribution Determined by GPC

Sample	Solvent	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Dispersity
KM6001N	Cyclohexane	102	22	4.58
KM6001N	Cyclohexane	103	22	4.57
KM6001N	Cyclohexane	104	22	4.59
KM6001N	Cyclohexane	106	23	4.60
PXC32969	Cyclohexane	148	31	4.85
PXC32969	Cyclohexane	147	30	4.83
PXC32969	Cyclohexane	146	31	4.80
PXC22160	Cyclohexane	105	30	3.54
PXC22160	Cyclohexane	108	32	3.55
PXC22156	Cyclohexane	197	45	4.37
PXC22156	Cyclohexane	195	43	4.40
KM6001N	<i>o</i> -DCB	120	34	3.56
KM6001N	<i>o</i> -DCB	127	35	3.61
PXC22156	<i>o</i> -DCB	165	45	3.66
PXC22156	<i>o</i> -DCB	169	46	3.64
PXC22160	<i>o</i> -DCB	160	49	3.30
PXC22160	<i>o</i> -DCB	156	43	3.60

PXC32969 and KM6001N are iPP; PXC22160 and PXC22156 are random (RD) and block (BLK) copolymer samples.

Table II Fractionation of Sample KM6001N

Ref. No.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Dispersity
SH1	76	23	3.30
SH2	55	21	2.60
SH3	46	20	2.3
SH4	43	19	2.2
SH5	35	17	2.0
SH6	28	16	1.50
SH7	18	14	1.3
SH8	16	13	1.23
SH9	13	11	1.21

SH = iPP, KM6001N.
Homopolymer $M_w/M_n = 4.58$.

Table III Fractionation of Sample PXC22156

Ref. No.	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Dispersity
BLK1	175	50	3.5
BLK2	149	46	3.2
BLK3	142	44	3.1
BLK4	130	42	3.1
BLK5	104	32	3.0
BLK6	75	32	2.3
BLK7	46	28	1.6
BLK8	32	24	1.3

BLK = block copolymer, PXC 22156.
Homopolymer $M_w/M_n = 4.37$.

filter. It might be useful, however, to bypass the refractive index detector (RID) during fraction collection. This could have accounted for the small variation in the number average molecular weight compared to the weight average of the fractions.

CONCLUSION

The molecular weight distribution and fractionation of iPP and its copolymers with ethylene have been studied using cyclohexane as solvent for the GPC runs. Reproducible results have been obtained. The technique of using cyclohexane as solvent for the GPC of iPP at low temperatures is an attractive alternative to *o*-DCB and other toxic halogenated aromatic solvents normally used at 413 K. Molecular weight fractions have also been obtained that are useful for studying the effect of molecular weight on polymer properties such as crystallization behaviour.

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