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Preparative Gel Permeation Chromatography. I. Polypropylene

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Synopsis

Preparative gel permeation chromatography was used to produce a number of polypropylene reference samples, within the molecular weight range of 10,000–600,000, from commercial materials. Some of these materials were degraded in a controlled manner to give base materials having suitable molecular weight characteristics. A procedure has been developed using a single preparative column packed with equal quantities of Styragel with nominal exclusion limits of 10^2, 10^3, 10^4, and 10^5 nm. The volume of solvent for recovery was minimized by use of higher loading factors than in analytical GPC (some 2–20 times more polymer was thus fractionated in each experiment). Under these conditions the fractions first eluted were sharpest having polydispersities of about 1.5. First fractions, from different base materials, were characterized by analytical GPC, and those of similar molecular weight and polydispersity were combined to give the reference samples. Refractionation was necessary with the highest molecular weight base material because the first stage fractions were not sharp enough. Some of these fractions were recovered at elution volumes where much lower molecular weight material was expected. Comparison with results from the other base materials indicates that the primary cause of the spreading is not overloading. This spreading is explained in terms of slower partitioning of the larger molecules between the interstitial fluid and the gel particles.

INTRODUCTION

Certified reference polymers having sharp molecular weight distribution (i.e., polydispersities $\overline{M}_w/\overline{M}_n$ approaching unity) are required for molecular weight studies on thermoplastics, in particular, for (i) the calibration of analytical gel permeation chromatography (GPC); (ii) the evaluation of Mark-Houwink constants for viscosity measurements; (iii) for theoretical studies on the behavior of polymer molecules in solution; and (iv), if available in sufficient quantity, for the evaluation of the variations of the physical, mechanical, and other properties of polymers with molecular weight. Polystyrene certified reference samples, covering a wide molecular weight range, have been available for some time, and more recently reference samples have also been prepared for high-density polyethylene.[1] In addition, a program has been initiated at the National Physical Laboratory to produce reference samples of other important industrial polymers such as polypropylene, poly(vinyl chloride), and poly(vinyl acetate).

Polystyrene reference materials having narrow molecular weight distributions (i.e., $\overline{M}_w/\overline{M}_n \sim 1.1$) can be prepared economically by anionic polymerization.

Individual batches of 100–1000 g are characterized in terms of molecular weight by light scattering ($\overline{M}_w$) and osmometry ($\overline{M}_n$). (Throughout this paper the term "molecular weight" replaces the more correct "relative molecular mass.") This synthetic method cannot be used with most other polymers; and with high-density polyethylene (HDPE), preparative gel permeation chromatography has been used to recover sharp fractions from commercial broad-MWD materials.[1] Each HDPE reference sample is an individual fraction (1–10 g) characterized by analytical GPC, using a calibration based on particular HDPE fractions which had been characterized in absolute terms.

Preparative GPC was used to prepare the polypropylene reference samples also. Individual small fractions were combined together to give samples of about 10 g, these combined materials being characterized by absolute determination of $\overline{M}_w$ and $\overline{M}_n$.

Preparative GPC is simply analytical GPC carried out on a larger scale. In analytical GPC, the aim is to characterize a sample as accurately as possible using the lowest amount of material, the only constraints being the operational parameters of the instrument. On the other hand, in preparative GPC, the objective is to fractionate as much polymer as possible in an efficient manner. The economics of the fractionation are usually a major consideration, and this leads to compromises over the sharpness of the fractions produced.

Two factors that have an important bearing on the economics of preparative GPC are the columns, which are expensive, and the volumes of solvent that have to be recovered in isolating the fractions. A common procedure in analytical GPC is to use four narrow columns each packed with gels of different porosities (e.g., nominal exclusion limits of 10^2, 10^3, 10^4, and 10^5 nm). In the preparation of the HDPE samples, a similar combination of four columns was used, each with a wider diameter than is customary in analytical GPC. By contrast, in the present work a single wide column was used; but, in order to preserve the ability to fractionate polymers covering an extensive range of molecular weights, it was packed in layers with equal proportions of the same combination of gels used in analytical GPC.

In analytical GPC, typically 0.004 g polymer (2 cm^3 of a 0.2% solution) is eluted through a column combination of total volume about 220 cm^3; and with a broad-MWD sample, the volume of eluant containing polymer is about 110 cm^3, which is approximately equivalent to the so-called pore volume of the column. Thus, during its passage through the column, such a polymer sample becomes considerably diluted. This dilution is important both theoretically and practically since the greater the separation of the polymer molecules, the more efficient the fractionation; and from a practical, particularly the preparative, point of view, the greater the dilution, the more solvent that has to be recovered. In analytical GPC, where conditions are usually highly standardized (i.e., similar combinations of columns of standard dimensions, eluting the same weight of polymer), the dilution is normally not of great interest. But in preparative GPC, where not only the number of columns may be different but also their dimensions and the weight of polymer fractionated can vary considerably, it is important to know this dilution for particular experiments. The volume of eluant containing polymer is approximately half the total volume of the column, and this represents the total dilution of the solid polymer during the operation. It is proposed to call the quantity (column volume/2)/polymer weight the specific

TABLE I
Fractionation of Polypropylene by Preparative GPC

Flask number		1			2			3			4			5			6			7			8			9			10		
Elution volume, cm^3		1,200			1,320			1,440			1,560			1,680			1,800			1,920			2,040			2,160			2,280		
"Calibration," $\overline{M}_w \times 10^{-3}$		581			309			128			62.2			27.8			17.7			11.8			7.43			6.96					
Base material fractionated	Specific dilution, cm^3/g	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$	% w/w	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$
A/2[a]	10,000	4.8	581	2.13	20.1	567	2.04	28.7	385	1.78	18.1	370	1.83	11.6	369	2.39	7.2	393	1.77	4.3			3.0			2.2					
A/5[a]	4,000	2.4			6.2	309	2.09	18.5	256	1.66	24.6	160	1.75	19.4	148	2.21	14.2	136	2.29	7.9			4.2			2.6					
B	2,000	0.1			0.5			5.3	271	1.50	17.3	167	1.47	22.0	97.0	1.65	21.2	58.7	2.40	17.7	69.0	2.63	11.5			4.1					
C	2,000	0.0			1.7			15.6	128	1.41	27.0	90.2	1.57	23.6	74.4	1.80	17.9	77.5	1.82	10.4	76.5	1.95	3.7			0.1					
D	2,000	0.0			0.0			0.0			7.7	62.2	1.33	23.2	55.0	1.35	31.9	40.0	1.48	24.3	27.5	1.60	12.3	25.7	1.91	0.8					
E	2,000	0.0			0.0			0.0			6.1			24.5	43.7	1.34	34.0	37.3	1.45	25.3	21.1	1.62	10.0			0.1					
F	4,000	0.0			0.0			0.0			1.9			18.6	31.4	1.30	39.3	22.8	1.47	28.9	14.8	1.56	10.3	12.3	1.80	0.8					
G	1,000	0.0			0.0			0.0			0.0			6.1	38.4	1.25	19.8	26.8	1.32	31.0	11.8	1.40	27.3	10.9	1.53	16.2	6.96	1.66	1.8	7.01	2.20
H	1,000	0.0			0.0			0.0			0.0			3.7	27.8	1.23	17.4	17.7	1.30	32.1	11.8	1.40	26.8	7.43	1.66	16.2			3.8		

[a] Refractionations of base material A: /2 from flask 2 of first fractionation; /5 from flask 5 of first fractionation.

TABLE II
Degradation of two Commercial Polypropylenes at 135°C

Time, hr	Sharp MWD		Broad MWD	
	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
0	611	4.24	544	7.89
3			372	7.52
17	393	2.62		
20			106	2.84
24			64.0	2.42
44			29.0	1.90
48			24.0	2.00
49	115	1.94		
100	41.9	1.79		

dilution (SD) and express it in cm^3/g. Since in this work the concentrations of the polymer solutions *before* fractionation are usually 1–2% w/w, SD is always $\gg 1$. Thus, for analytical GPC, the SD is about 27,000, and every gram of polymer fractionated in this way involves the recovery of 27.5 liters of solvent. In order to minimize the volume of solvent to be recovered, lower values of SD were used in the present work.

In general, lower values of SD lead to less efficient fractionation; but it has been found in this laboratory, and elsewhere,[2,3] that in preparative GPC the loss of resolution is not uniform over a set of fractions derived from a particular polymer. Usually, the first fractions to be eluted are sharper than the later fractions (see Table I), the differences becoming more pronounced as SD is decreased. Thus, the polydispersities of these first fractions increase comparatively slowly as SD decreases; and, in some cases even with quite low SD values, these first fractions are still quite sharp. The data in Table I from experiments G and H where SD's of 1000 were used (equivalent to fractionating over 20 times the weight of polymer eluted in analytical GPC) include first fractions which nevertheless have polydispersities as low as 1.2–1.3. By combining a number of such first fractions, a reference sample can be prepared; and by fractionating different base materials, one can prepare a series of reference samples covering a wide range of molecular weights.

Commercial polypropylenes generally have broad molecular weight distributions, and only two were found with MWD's narrow enough for the purpose of the present work, one of high molecular weight (base material A in Table III) and the other of very low molecular weight (base material H). Base materials for the intermediate molecular weight ranges were prepared by controlled thermal degradation of some of the higher molecular weight materials. When solutions of polypropylenes are heated, the chain length is reduced and the material gradually changes to a lower molecular weight product with a sharper distribution (see Table II). In this way, a number of base materials were prepared covering a wide molecular weight range (see Table III).

The greater the number of subdivisions of the eluting solution, the sharper the individual fractions. However, each extra subdivision increases the number of individual fractions required to give a combined weight of 10 g. To limit the number of fractionations, in the present work the eluant was subdivided into only 10 to 12 fractions. Even so, 50 or more fractions were required. Combi-

nation of the fractions was carried out in two stages. The same fractions from successive runs were collected in the same flask, the reproducibility of the fractionations being monitored by passing a small amount of the eluant through the differential refractometer of the analytical side of the instrument. Combined fractions were recovered daily and characterized in terms of molecular weight by analytical GPC. Fractions of the same molecular weight were subsequently combined to give the 10-g samples.

EXPERIMENTAL

Preparative GPC

A Waters Associates ANA-PREP gel permeation chromatograph was used with a column of length 1.2 m, I.D. 5.8 cm, and a volume of 3200 cm^3. It had been packed in four equal layers by the manufacturers with Styragels of different porosities expressed nominally as 10^2, 10^3, 10^4, and 10^5 nm. The apparatus was run automatically and programmed such that successive injections occurred after collection of 10 to 12 fractions, each of which had a volume of about 120 cm^3. An injection loop of 150 cm^3 was used with solutions containing 0.1% to 1.0% polymer (i.e., loads of 0.15 to 1.50 g), the lower concentrations with the higher molecular weights. Polypropylene stays in solution only at high temperatures, and these fractionations were carried out at 135°C with 1,2-dichlorobenzene as solvent. Generally, best results were obtained with a volumetric flow rate of 15 cm^3/min,* but slower rates were necessary with the highest molecular weight materials.

Preparative GPC gives reproducible results over a large number of successive runs (see Table IV), but variations can occur and it is necessary to monitor the experiments. This was done in two ways: (i) with individual experiments, by bleeding off a small amount of the eluant and passing it through the differential refractometer of the analytical side of the instrument,[4] and (ii) with the combined fractions by comparisons of the gravimetric data.

Solvent

With preparative GPC, large volumes of solvent are involved (up to 20 liters a day in this work), and this creates problems in relation to toxicity and fire. Generally, with organic solvents it is advisable to take precautions against inhalation of the vapors and absorption through the skin so that, in practice, the major hazard is that of fire. Only a limited number of solvents is available for polypropylene such as 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, tetralin, decalin, etc. 1,2-Dichlorobenzene was chosen for this work, for it is less inflammable than the aromatic hydrocarbons and is more readily available than 1,2,4-trichlorobenzene.

Antioxidant

The antioxidant used in this work was Santonox R, bis(2-methyl-4-hydroxy-5-*tert*-butylphenyl) sulfide. In the analytical experiments, a concentration of 0.05% w/v was used in both the polymer solution and the eluting solvent. In the

* This corresponds to a linear flow rate of 0.56 cm/min, which is much slower than the 2.2 cm/min normally used in analytical GPC.

TABLE III
Polypropylene Base Materials

Base material	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
A	611	4.24
B	188	3.77
C	100	1.90
D	47.4	1.86
E	34.0	2.10
F	24.0	2.00
G	16.6	3.37
H	11.6	1.69

TABLE IV
Reproducibility of Preparative GPC Over 545 Runs.
Polymer Recovered from Flask 4 of Fractionation of Base Material A

No. of runs in combined fraction	% w/w	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
6	19.6		
16	26.7	231	1.94
21	18.2	300	2.47
68	19.6	267	2.04
74	19.2	277	2.92
79	21.3	212	2.02
89	20.8	284	2.39
92	19.6	256	2.51
100	17.2	228	2.47

preparative experiments, the overall concentration was 0.05%, but the Santonox R was dissolved only in the polymer solution. This different procedure had two advantages: (i) it eliminated the necessity of preparing large volumes of solvent containing Santonox R, and (ii) the presence of a high concentration (0.5%) of the antioxidant helped to prevent degradation of the polymer solution, which resided for as long as 24 hr at 135°C in the metal sample chamber before injection. As a further precaution against degradation, this solution chamber was flushed with nitrogen.

Isolation of Fractions

The polypropylene separated as a layer on top of the cold solvent; it was collected by filtration, washed with acetone, and dried at 40°C. The fractions were weighed, and from these gravimetric data, polymer concentration-versus-elution volume graphs were plotted.[4]

Analytical GPC

A Waters Associates 200 instrument was used with four columns (1.2 m × 1 cm) packed with Styragel of nominal exclusion limits 10^2, 10^3, 10^4, and 10^5 nm. The eluting solvent was 1,2-dichlorobenzene containing 0.05% Santonox R, the temperature was 135°C, and the flow rate was 1.4 cm^3/min. Sample concen-

trations were 2–3 mg/cm^3, and the injection volume was 2 cm^3. Column calibration was carried out with narrow molecular weight distribution polystyrene standards (Pressure Chemical Co.) and values of $\overline{M}_w$ and $\overline{M}_n$ were calculated by the universal calibration method, using Mark-Houwink constants for polypropylene[5] and polystyrene.[6] No correction was made for dispersion.

Combinations of Fractions

Fractions having similar molecular weights and polydispersities were combined by dissolution in 1,2-dichlorobenzene containing 0.05% Santonox R at 135°C and recovered in the manner described above. These combined materials were characterized by analytical GPC and subsequently by light scattering $\overline{M}_w$ and osmometry $\overline{M}_n$.[7]

RESULTS AND DISCUSSION

The general method for the preparation of these polypropylene reference materials was the single fractionation of the base materials followed by combination of suitable fractions. The specific dilutions (SD's) were the lowest possible to give fractions having polydispersities of about 1.5. The results are shown in Table I, data from individual fractionations running from left to right across the table and the % figures being wt-% of all the polymer recovered in that particular fractionation.

Low Molecular Weight Samples ($\overline{M}_w < 40{,}000$)

Low molecular weight fractions were prepared from a commercial sample H and a degraded material G, using SD's as low as 1000. The results (see Table I) show that in both cases the first two fractions were sharp (polydispersities between 1.23 and 1.32) with molecular weights $\overline{M}_w$ ranging from 38,400 down to 17,700. With these materials, even some of the later fractions were quite sharp, those of $\overline{M}_w \sim 7000$ having polydispersities of 1.66.

The fractions from the degraded materials tended to be yellow, the problem increasing the greater the degradation. By a combination of (i) reprecipitation and (ii) treating with alumina much of the color was removed but it persisted with the very low molecular weight material.

Intermediate Molecular Weight Samples ($\overline{M}_w$ 40,000–250,000)

In the intermediate molecular weight range, the degraded materials B–E (see Table III) were used. With these base materials, it was necessary to use the higher SD of 2000 (see Table I). Initial fractions were obtained having $\overline{M}_w$'s in the range 40,000 to 270,000 with the polydispersities increasing from 1.3 to 1.5 as the molecular weight increased.

High Molecular Weight Samples ($\overline{M}_w > 250{,}000$)

The commercial sample A was used as base material for the high molecular weight samples. Even with the higher specific dilutions of 4000, the initial fractions from this material had polydispersities of about 1.8, some greater than

TABLE V
Polypropylene Reference Samples[7]

Reference no.	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PP 10A	10.2	7.83	1.30
PP 13A	13.0	10.4	1.25
PP 21B	23.5	17.2	1.37
PP 31B	31.3	23.4	1.34
PP 46B	45.6	33.2	1.37
PP 66C	66.1	46.0	1.44
PP 93C	93.0	59.8	1.56
PP 141D	141.0	93.6	1.51
PP 200D	200.0	131	1.53
PP 241E	241	150	1.61
PP 325E	325	170	1.91
PP 628E	628	400	1.57

2.0. As the use of higher SD's would have involved working with very dilute solutions and small quantities of polymer, it was decided in this case to refractionate.

In order to obtain sufficient material for refractionation, the initial fractionation consisted of nearly 600 repetitive runs. Over this period, the polymer recovered from a particular flask was reasonably reproducible both in respect of wt-% of total polymer recovered and $\overline{M}_w$ (see Table IV).

Polymers from the same flask were combined and refractionated. Although overall the fractions recovered from these refractionations had lower polydispersities, only a few of the initial fractions were less than 1.8 (see Table I). No improvement was observed when a specific dilution of 10,000 (i.e., approaching that used in analytical GPC) was used in the refractionation of the highest molecular weight material $\overline{M}_w \sim 500{,}000$). A second refractionation of some of the lower molecular weight materials ($\overline{M}_w \sim 250{,}000$) produced initial fractions having polydispersities of about 1.5.

Combination of Fractions

Each reference sample was formed by combining ten or more daily combined fractions, each of which itself contained fractions from ten to 20 different runs. To ensure that only similar materials were being mixed, smaller batches were combined and recharacterized before the final combination.

Reference Samples

Fractions were combined to give 11 reference samples covering the molecular weight range of 10,000–600,000 (see Table V). The polydispersities of these materials, although approximately 1.5, increased with molecular weight, a reflection of the increasing difficulty of fractionating higher molecular weight materials.

Spreading of Fractions

In analytical GPC, when a range of polymers of narrow MWD are eluted through the columns, the traces produced are a series of sharp peaks which are

used to calibrate the elution volume in terms of molecular weight. When an unknown polymer is eluted through the column, it is assumed that the broadening of the chromatogram reflects the wider MWD of the sample. Although this is basically true, there are other factors which cause chromatogram broadening, such as (i) diffusion effects, (ii) overloading, and (iii) viscous effects. Corrections can be made for (i) numerically and for (ii) and (iii) by eluting as small a polymer sample as possible. In analytical GPC, it is assumed that the polymer eluting at any point on a trace has a molecular weight corresponding to the calibration value. One advantage of preparative GPC is that one can study this variation of molecular weight with elution volume.

Although the preparative column was not calibrated in the conventional way can be made by using the lowest values of $\overline{M}_w$ (see Table I) for the fraction recovered from a particular flask (i.e., in general those with the lowest polydispersity). Spreading occurs when polymer of higher molecular weight appears at an elution volume (flask number) where polymer of lower molecular weight would have been expected, and thus this calibration can be used to detect it. From the other results in Table I, it would appear that some degree of spreading occurred in most of the fractionations.

In Table I are the results for base material F using a specific dilution of 4000, which is serious overloading by analytical GPC standards. Nevertheless, the fractions have values of $\overline{M}_w$ close to the calibration values and are reasonably sharp. Furthermore, when the load was increased four times (SD 1000) with base material G (very similar to F), the fractions again had $\overline{M}_w$'s close to the calibration values, although the recovered polymer appeared in a slightly larger elution volume. It would appear, therefore, that, in these experiments, the spreading due to overloading is quite small.

On the other hand, the results in Table I for base material A/2 show serious spreading, successive fractions having $\overline{M}_w$ values generally much higher than the calibration values and high polydispersities. The specific dilution in the experiment was 10,000; but if allowance is made for the possibility that only 25% of the gel (that with nominal exclusion limits of 10^5 nm) is available for these high molecular weight molecules, then in respect of fractionation efficiency the effective SD may be 2500. This is similar to the values used with the low molecular weight base materials F and G where no serious spreading was observed. So it would appear that the spreading with base material A/2 is not due to overloading but is associated with its high molecular weight.

The observation in GPC that the polymer molecules emerge in order of decreasing molecular weight is usually explained in terms of differential retardation of the smaller molecules due to the fact that they can penetrate a larger number of pores on the surfaces of the gel particles. Although this simple explanation accounts for most of the GPC phenomena, it does not involve the partitioning process as the polymer molecules enter and leave the gel. When at the same moment two polymer molecules of different size enter the gel through pores of the same diameter, there are three possibilities: (i) the two molecules emerge from the gel at the same time; (ii) the largest molecule emerges first; and (iii) the smaller molecule emerges first. In the case of (i), the rates of retardation of the two molecules will be unaffected; and if (ii) applies, the progress of the smaller molecule through the column will be delayed still further and the effect will enhance, and be indistinguishable from, the usual GPC explanation. However, if the smaller molecule partitions at a faster rate, then the larger molecule will

be differentially retarded, which is the opposite of the usual explanation. Under such conditions, the larger molecules would tend to tail into elution volumes where smaller molecules would be expected, and one would expect the effect to become more pronounced with increasing molecular weight. This would explain why, in these preparative GPC experiments, the first fractions were always sharpest (the higher polydispersities of the subsequent fractions being due to delayed elution of the higher molecular weight polymer) and why the resolution with high molecular weight materials was poor.

The movement of the polymer molecules into and out of the gel is governed by the concentration differential between the interstitial fluid and the inside of the gel. Thus, while the concentration is highest outside, the polymer molecules move into the gel; and when it becomes lower outside, the molecules move out of the gel. The two molecules which enter a gel particle at the same moment are, therefore, subjected to the same forces; and although the smaller molecule will diffuse faster and further into the gel, one might expect it to return to the surface of the particle at the same time as the slower-moving larger molecule. However, on this return journey to the interstitial fluid, there is an important difference. The surface of the gel has a distribution of pore sizes, some larger than the pore through which the two molecules entered the particle, and some smaller. Thus, on the return journey, the smaller molecule has a much larger number of possible exits to the interstitial fluid than the larger molecule, and this would explain faster partitioning of the smaller molecule and thus tailing of the larger molecule.

This model would also explain why the tailing effect becomes more pronounced at higher concentrations since under these conditions the larger molecules would be pushed further into the gel, making it increasingly more difficult for them to find a way out. For example, the further a larger molecule penetrates the gel, the greater the delay through attempting to leave the gel through pores which are too narrow. On the other hand, with the dilute solutions used in analytical GPC, penetration would be minimal, partitioning taking place mainly at the surface of the gel particle.

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