Methyl cyclohexane as a new eluting solvent for the size-exclusion chromatography of polyethylene and polypropylene at 90°C

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Abstract

Size-exclusion chromatography using halogenated aromatic solvents such as trichlorobenzene at 145°C is widely used for industrial polyolefins. Such high temperature operation requires special instrument design and causes many operational problems. In this work, a new eluting solvent, methyl cyclohexane, has been successfully used at 90°C for the size-exclusion chromatography of industrial (high-molecular-mass) grades of polypropylene and polyethylene. Sample preparation involves dissolution in decalin at temperatures as high as 140°C, followed by dilution in methyl cyclohexane at 90°C previous to injection into the SEC column running with methyl cyclohexane as the mobile phase. In addition to permitting operation at 90°C, methyl cyclohexane is less toxic than the usual solvents and has a differential refractive index sensitivity advantage as well. It also provides new opportunities for ultraviolet, fluorescence, and infrared detection for functionalized polyolefins. However, one disadvantage is that polystyrene adsorbs from this solvent on styrene-based packings. Thus, narrow fractions of polyisobutylene (PIB) were used in place of polystyrene for universal calibration. Another disadvantage is that methyl cyclohexane is more flammable than halogenated aromatic solvents. A quantitative assessment of the new solvent system is in progress. Initial results are promising and are presented in this paper.

Keywords: Mobile phase composition; Polyethylene; Polypropylene; Methyl cyclohexane

1. Introduction

Size-exclusion chromatography (SEC) analysis requires polymer molecules to be in true solution. The dissolution of semi-crystalline polyolefins, such as polyethylene (PE) and polypropylene (PP), is particularly difficult and generally requires temperatures above their melting points. Thus, SEC analysis of PE and PP is normally accomplished at 135 to 145°C [1]. Over the past three decades, a number of review papers on high-temperature SEC of these polyolefins have been published [2]. Frequently used solvents in the SEC characterization of PE and PP are o-dichlorobenzene (ODCB), 1,2,4-trichlorobenzene (TCB), chloronaphthalene (CN), decalin, tetralin and xylene [3], with the first two mentioned being the most common [1,2].

A variety of problems have been reported [4]:
– Molecular mass results from SEC increase with increasing temperature. This trend is more pronounced at higher molecular mass, and is particularly noticeable at solution temperatures close to that of the normal crystalline melting temperature of the polymer [5]. It can be

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attributed to the existence of some aggregates in the polymer solution under experimental conditions. At lower temperatures the aggregates are filtered by the SEC columns. At higher temperatures they dissolve and contribute to M_w.

- M_w values obtained from SEC are lower than those from 'off-line' light scattering analyses [6]. This suggests that some high-molecular-mass species were shear degraded cannot be detected either because they re-aggregated during the sample preparation and were filtered out before entering the column or because they were too diluted on passage through the SEC columns to be observed by the detector. Experimental data are less reproducible than with room temperature instruments used for other polymers and column clogging sometimes occurs [4,7].

- ODCB and TCB are highly toxic and have an unpleasant odor. Because of sample handling requirements, this is an important consideration despite the use of well-ventilated, automated instruments.

- The small difference in refractive index (n_d^{20}) between the halogenated aromatic eluting solvents $(n_d^{20}$: ODCB 1.5491, TCB 1.5524) and the polymers $(n_d^{20}$: PP 1.5030, HDPE 1.5450) [8] results in a low sensitivity for the differential refractive index (DRI) detector.

- Degradation of polyolefins may occur at the high (>135°C) SEC operating temperature.

- The lack of spectrophotometric 'windows' in the usual solvents prohibits the use of UV detection and severely limits the use of infrared detection.

Ying et al. [9–11] reported the use of cyclohexane as eluent for the SEC of PP at 70°C. Later, Ibhadon [12] described a similar study using cyclohexane–decalin mixtures at 60°C and extended to a study of the fractionation of PP and ethylene–propylene copolymer samples. Both authors used a similar sample preparation procedure: PP was dissolved in decalin at 140°C for 1–2 h; the solution was diluted with hot cyclohexane and then maintained at about 70°C. Nevertheless, application of this technique directly to the SEC of HDPE and PP samples with high molecular mass (say M_w>250 000) encountered difficult problems because maintaining these polymers in solution requires temperatures above the boiling point of cyclohexane.

The objective of this work is to define a system that will enable reproducible, accurate SEC analyses of industrial (high-molecular-mass) PE and PP at lower temperatures than are conventionally used and with a less toxic mobile phase having a greater refractive index sensitivity.

2. Experimental

2.1. Solvents

Decalin, tetralin, trichlorobenzene, heptane, cyclohexane and methyl cyclohexane were purchased from the Aldrich (Milwaukee, WI, USA) and were used as received.

2.2. Polymers

Linear low density polyethylene (LLDPE) LL6101.00 from Imperial Oil, high density polyethylene (HDPE) PL1840 from Dow Chemicals (Sarnia, ON, Canada), HDPE HIZEX from Mitsubishi Petrochemicals (Japan), PP HGX-010 (MI 1.2) from Phillips (OK, USA) and PP 6823 from Himont (Montreal, PQ, Canada) were the polyolefins analyzed.

2.3. Polymer standards

Poly(isobutylene) (PIB) narrow-molecular-mass distribution fractions from Polymer Standard Service (Houston, TX, USA), polypropylene broad molecular mass distribution standards (PP95K, PP135K, PP180K, PP230K and PP350K) from American Polymer Standards (Mentor, OH, USA) and polystyrene narrow-molecular-mass distribution standards from Polymer Laboratories (UK) were used.

2.4. Solubility evaluation

Samples in the off-line solubility test were prepared by dissolving the polymer in the solvent in a glass vial sealed under dry argon gas. The solutions were heated to 140°C in an oil bath controlled to ±0.1°C and then cooled down. If aggregates were present, then a large increase in light scattering was

observed when a He–Ne laser beam was passed through the solution.

2.5. SEC sample preparation and analysis

A Waters ALC/GPC 150C equipped with a Model 150C differential refractive index (DRI) detector was operated at 90°C using methyl cyclohexane as mobile phase with three 10 μm, 7.5 mm I.D.×300 mm Plgel mixed bed columns (Polymer Laboratories). SEC data were collected by an interface developed at Eastman Kodak Company (Imaging Research and Advanced Development, Rochester, NY, USA). Typical operating conditions are as follows: mobile phase flow-rate: 1.0 ml /min; sensitivity: 128; injection volume: 100 μl; sample concentration: 0.06–0.1 wt%.

The sample preparation procedures developed for PP and PE will be described in Section 3. For calibration, poly(isobutylene) narrow fractions were prepared overnight at ambient temperature without agitation. To ensure data reproducibility, 0.1 wt% butylated hydroxytoluene was added as a stabilizer and flow marker to all samples, although no degradation was evident under the experimental conditions. The prepared samples were then transferred to the SEC injection chamber and injected after 3 h. The resulting logarithm of peak molecular mass versus peak retention volume data was fitted by a cubic polynomial to provide a calibration curve for PIB.

Since narrow standards of PP were unavailable, a numerical optimization search method was used to derive the PP calibration curve from the PIB calibration curve. From the Mark–Houwink equation and assuming the validity of universal calibration, the molecular mass of polypropylene is given by:

$$\log M_{pp} = I + S \log M_{pib} \tag{1}$$

where $S = (\alpha_{pib} + 1)/(\alpha_{pp} + 1)$ and $I = [1/(\alpha_{pp} + 1)]$ $\log (K_{pib}/K_{pp})$. K_{pib}, α_{pib}, K_{pp} and α_{pp} are Mark–Houwink parameters of PIB and PP, respectively, in a given mobile phase. No values for any of these parameters in methyl cyclohexane are available from literature. The parameters S and I were successively guessed using a modified Nelder–Mead Simplex search [13], and substituted into Eq. (1) to obtain a

trial PP calibration curve from the PIB calibration curve. The trial PP calibration curve resulting from each guess was then applied to chromatograms of broad PP standards and the search for S and I continued until the M_w and M_n calculated from the chromatogram matched those known for the standards. The molecular mass averages were compared in an 'objective function', formulated by assuming that the error variance of the averages is proportional to the experimental value of the averages [13].

3. Results and discussion

3.1. Mobile phase selection

A prime requirement for a candidate mobile phase is that it is similar in solubility parameter and polarity to polyolefins. The toxicity and boiling point (b.p.) of the solvent are also of concern. Cyclohexane is a less toxic solvent than halogenated aromatic solvents and has a similar polarity to polyolefins. Also, its solubility parameter (8.2 [cal/cm³]²) is near that of PP (9.2 [cal/cm³]²) [8,14]. However, PP cannot be dissolved directly in cyclohexane because of its high crystallinity and melting point. Dissolving the polymer in decalin at elevated temperature overcomes this problem, and once the crystalline polymer dissolves it does not appear to re-aggregate from either decalin or cyclohexane, or deposit on the PS gel in the column. Also, the SEC can be operated at a lower temperature (70°C). There is no trouble with filter blocking as reported in halogenated aromatic eluents at 145°C, and since the refractive index difference with cyclohexane is greater than that with the usual eluents, sensitivity is improved [9–11]. However, as mentioned earlier, high-molecular-mass polyolefins ($M_w > 250\,000$) require temperatures above the boiling point of cyclohexane to remain in solution.

We have focused upon finding a solvent with similar advantages to cyclohexane, but that can also permit the analysis of higher-molecular-mass polyolefins. Methyl cyclohexane is currently our best candidate: it has a higher boiling point (101°C) than cyclohexane (81°C). Thus, it can be used at higher temperatures. Another advantage is that the refrac-

tive index difference with methyl cyclohexane is even greater than that with cyclohexane. This significantly improves the DRI sensitivity. Furthermore, this new eluent has some potential applications in the analyses of functionalized polyolefins using UV, fluorescence and infrared detection because it has no significant UV absorbance and wider infrared windows, as well as lower operating temperatures than the usual solvents. Further investigations of these attributes are in progress and will be reported soon [15]. A concern with methyl cyclohexane is that its flash point (−3°C) and autoignition temperature (284°C) are much lower than those of trichlorobenzene (flash point: 110°C, autoignition temperature: 571°C). Thus, additional operating precautions are necessary. In the Waters 150C, vapor detectors should be operational, constant ventilation must be assured and considerable vigilance exercised for serious solvent leaks. Use of a nitrogen generator to displace air in the instrument was not used here but can be considered as an additional precaution, especially in heavily used instruments.

3.2. Sample preparation

Recently, Utracki et al. [7] and Grinshpun et al. [16] reported a dissolution procedure to obtain aggregate-free solutions. PE solutions were prepared in TCB by a thermal treatment at 160°C with the addition of antioxidant before operating SEC at 135–145°C. This procedure is not applicable for dissolving PP because PP has a wider crystal melting range (140–170°C) [8] and a poorer thermal stability than PE. Although PP dissolution can be obtained in TCB by controlling the storage time at 145°C with added stabilizers [17], in practice it is inconvenient to determine the optimum time.

In order to find an acceptable sample preparation procedure, the solubilities of PE and PP in different

solvents were qualitatively investigated. As earlier mentioned, this involved observing the light scattering pattern while a He–Ne laser beam passed through the polyolefin solution. The following qualitative solubility results were found:

  – For identical polyolefins at 120°C, the order of decreasing ability to dissolve polyolefins was: decalin, tetralin, TCB.
  – For identical solvents at above 120°C, in decalin, PP is more soluble than PE while, in tetralin, PE is more soluble than PP. In TCB, the solubility of PE was about the same as PP.
  – For dissolution, the following temperatures were required: in decalin greater than 120°C; in TCB greater than 140°C.

Obviously, decalin is a better solvent with an advantage of less toxicity for PE and PP. Table 1 summarizes solubility test results of polyolefins in decalin at different temperatures. Below 70°C, all polyolefin samples are precipitated except PP HGX-010. Above 90°C, all samples remained in solution. It thus appeared that SEC of polyolefins can be run at temperature above 90°C using decalin as the eluent. However, the refractive index of decalin is very close to that of both PE and PP [8]. To overcome this weakness, Ying et al. [9,10] have described a special procedure that involves dissolving PP of moderate molecular mass in decalin at 140°C for 2 h and diluting with hot cyclohexane (70°C) so that the content of decalin is less than 8% by weight. Once the crystalline molecular aggregation is broken, the macromolecules apparently do not re-aggregate in hot cyclohexane because they are solvated by cyclohexane molecules. Another way of dissolving PP is by placing the polymer in cyclohexane under a pressure of 3–4 atm at 140°C for 2–3 h and then cooling to 70°C under normal pressure [11]. SEC can be performed at 70°C using cyclohexane as eluent. However, as already mentioned,

Table 1
The solubility of polyolefins in decalin at different temperatures[a]

	PP HGX-010	PP 6823	LLDPE LL6101.00	HDPE PL1840	HDPE, HIZEX
140°C, 2 h	S	S	S	S	S
90°C, 18 h	S	S	S	S	S
80°C, 22 h	S	S	S	S	I
73°C, 20 h	S	I	I	I	I

[a] Polymer concentration 0.5 wt%. S: soluble, I: insoluble.

higher M_w HDPE and PP (e.g. those with M_w greater than 250 000) do not remain in solution at 70°C.

Methyl cyclohexane and heptane have a higher boiling point and were alternatives. Charlet and Delmas [18] reported the lower critical solubility temperature (LCST) of PE and PP in these two solvents, but no mention on either the upper critical solubility temperature (UCST) or the application of these solvents as a mobile phase in SEC was found. Cyclohexane was replaced with methyl cyclohexane or heptane to dilute decalin solutions with the final concentration of decalin being approximately 2 vol%. The final solutions were maintained at the dilution temperature for three days and then observed with the aid of the He–Ne laser beam to determine possible aggregation. Results are shown in Table 2.

From the above information and Table 2, methyl cyclohexane readily appeared as the best choice. PE and PP samples were prepared by dissolving the polymers in decalin at above 140°C, then diluted to the required concentration with methyl cyclohexane at 90°C previous to injection into the SEC. The SEC was operated at 90°C using methyl cyclohexane as the mobile phase.

3.3. Evaluation of PE and PP chromatograms

Fig. 1 is a plot of chromatogram areas for PP (M_w 230 000) versus the mass of PP injected. The linear relationship indicates no loss of sample injected by adsorption on the column. Also, the number of theoretical plates remained at 24 000±900 during 60 days of consecutive operation (indicating no change in the column characteristics). Fig. 2 shows SEC chromatograms of PP350K and HDPE PL1840. The former has a significantly broader range of molecular
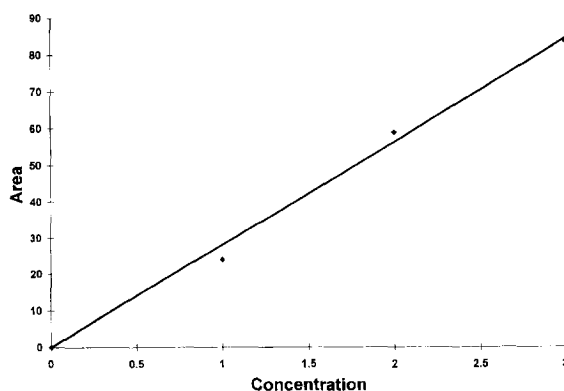

Fig. 1. Area under the chromatograms of polypropylene (M_w 230 000) plotted vs. mass injected, using methyl cyclohexane as the mobile phase at 90°C.
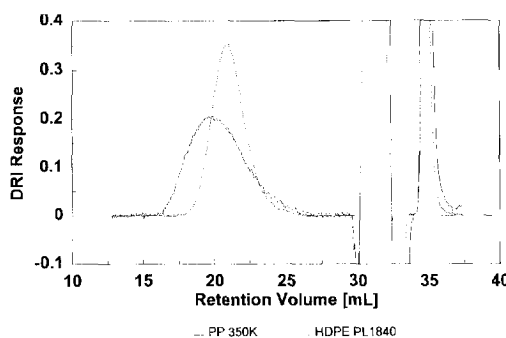

Fig. 2. Chromatograms of polypropylene (PP350K, M_w 350 000, $M_w/M_n = 8.0$) and high density polyethylene (HDPE PL1840, M_w 130 000) using methyl cyclohexane as the mobile phase at 90°C. The sharp peaks at retention volume (~31 ml) result from decalin in the injected sample, while the peaks (~35 ml) from the stabilizer (butylated hydroxytoluene) in the samples were used as flow marker.

Table 2
The solubility of polyolefins in decalin/solvent mixtures[a]

Second solvent in decalin/solvent mixtures[b]	Polyolefins[c]				
	PP HGX-010	PP 6823	LLDPE LL6101.00	HDPE PL1840	HDPE HIZEX
Cyclohexane, 73°C	S	I	I	I	I
Heptane, 90°C	S	I	S	S	I
Methyl cyclohexane, 90°C	S	S	S	S	S

[a] S = soluble, I = insoluble.
[b] Decalin concentration: 2 vol%.
[c] Polymer concentration: 0.4 wt%.

mass than the latter. The large deviation at approximately 30 ml results from the presence of decalin in the injected sample. Identical chromatograms were obtained two months later when the samples were re-injected.

3.4. Calibration

Ying et al. [9] compared the chromatogram of PS sample (M_w 2 300 000) with that of a PP fraction (M_w 103 000), which appeared in the same retention volume region in cyclohexane eluent and found that the peak of PS appeared to be sharpened on the high-molecular-mass side, while that of PP still remained normal. This distortion of PS chromatograms became more pronounced in our experiments with methyl cyclohexane as the mobile phase and can be attributed to adsorption of PS on the column packings. [19]. This is understandable since methyl cyclohexane is a poorer solvent for PS (θ temperature 65°C [9]) than cyclohexane (θ temperature 35°C [9]). Addition of a small amount of a second solvent (such as toluene or trichlorobenzene) to the methyl cyclohexane mobile phase was found to partially suppress this distortion of the PS chromatogram. However, column clogging occurred when injecting PP or PE samples into this mixed mobile phase. In general, polystyrene standards are therefore not suited to the methyl cyclohexane system.

Ying et al. [9–11] used PP fractions to obtain a PP calibration curve. Ibhadon's results [12] were based on the calibration data of Ying et al. In our case, narrow fractions were not available so the calibration

Table 4
Numerical optimization search results for polypropylene calibration

Search Parameters (Eq. 1)	PP95K PP350K	PP230K PP350K	PP95K PP135K	PP95K, PP135K, PP180K, PP230K, PP350K
S	0.9516	0.9412	1.0148	0.9486
I	0.0743	0.1057	−0.1918	0.1001
$K_{pp} \times 10^{4}$ [a]	1.955	1.712	5.528	1.757
α_{pp} [a]	0.776	0.796	0.665	0.782

[a] Based on the assumption that $\alpha_{pib} = 0.69$ and $K_{pib} = 0.000265$ dl/g.

curve was obtained by a numerical search program as described in the Experimental section. Commercially available poly(isobutylene) narrow fractions with peak molecular mass (M_p) from 1150 to 1 020 000 provided the basis for calibration (Table 3). PIB has been shown to not obey universal calibration in tetrahydrofuran at very low molecular masses (<5000) [20]. However, the situation in methyl cyclohexane is not known and much higher molecular masses are the main interest here.

Table 4 shows the values of S and I in Eq. (1) obtained from the search program for different combinations of PP standards. Fox and Flory [21] reported the Mark–Houwink parameters of PIB in cyclohexane at 30°C: $\alpha_{pib} = 0.69 \pm 0.02$, $K_{pib} = 0.000265$ dl/g. Combining these data with the S and I values obtained from the numerical search, Mark–Houwink parameters of PP were calculated and are also shown in Table 4. Although the data of K_{pp} and α_{pp} in Table 4 are only approximate due to

Table 3
Poly(isobutylene) standards used for SEC calibration

Standard	Peak molecular mass ($M_p \times 10^3$)	Polydispersity (M_w/M_n)	Retention volume[a] (ml)
PIB-1	1.15	1.04	27.23
PIB-2	4.20	1.38	25.51
PIB-3	9.40	1.17	24.52
PIB-4	24.40	1.23	23.10
PIB-5	81.60	1.19	21.61
PIB-6	133.00	1.14	20.79
PIB-7	213.00	1.20	20.26
PIB-8	340.00	1.21	19.64
PIB-9	1020.00	1.28	18.55

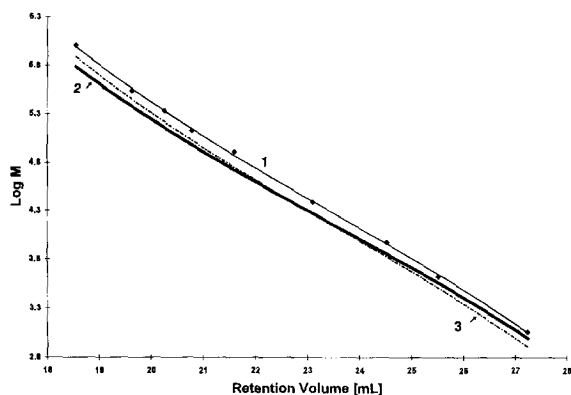[a] After flow-rate correction (ASTM D 5296-92).

Fig. 3. Calibration curves: Curve 1: poly(isobutylene) (PIB) calibration curve obtained by fitting a plot of the logarithm of peak molecular mass vs. peak retention volume for the fractions (peak retention volume data points shown). Curve 2: PP calibration curve obtained from a numerical optimization search for S and I in Eq. (1) while employing five PP broad MWD standards (PP95K, PP135K, PP180K, PP230K and PP350K). Curve 3: PP calibration curve obtained as in curve 2 but employing only two PP broad standards (PP95K and PP135K).

the use of values of K_{pib} and α_{pib} in cyclohexane at 30°C rather than in methyl cyclohexane at 90°C in the calculation, all but one of the values of α_{pp} are above 0.7 and provide some evidence that methyl cyclohexane is a good solvent for PP at 90°C.

Fig. 3 shows the primary calibration curves used in this study. The PIB calibration curve displays the largest molecular masses at each retention volume. It was determined by fitting the peak molecular mass data of the narrow-molecular-mass distribution PIB fractions. Two PP calibration curves determined using Eq. (1) are shown. The one based upon all five PP standards shows a significantly lower slope than the one based upon the two lower-molecular-mass

(narrower-molecular-mass distribution) PP standards. Calibration curves obtained using other combinations of PP standards were near this latter curve.

3.5. Molecular-mass averages and molecular-mass distribution

The molecular mass averages and polydispersity for each of the five PP standards calculated using the calibration curve derived from all of these standards in the numerical optimization search are listed in Table 5. Deviations from the vendor values ranged from -4.3 to 4.2% for M_n and -14.4 to 16.5% for M_w. With regards to utilizing a calibration curve derived using fewer standards, not unexpectedly it was found that a better weight-average molecular mass, M_w, could be obtained using higher-molecular-mass standards only and a better number-average data, M_n, could be obtained by using only lower-molecular-mass standards. Also, the data in Table 5 and the calibration curves in Fig. 3 show that, at least for our standards, the number of broad PP standards used was of secondary importance to the polydispersity of those standards for influencing calibration and molecular-mass averages. The broader the molecular-mass distributions of PP standards, the more satisfactory the resulting calibration curve.

Using the calibration curve obtained from the five PP standards, the molecular-mass distributions of each PP standard was calculated. Two typical molecular-mass distribution curves are shown in Fig. 4. All of these distributions show a long low-molecular-mass tail extending to a molecular mass of 10^3. The high-molecular-mass tail of the highest molecular mass sample, PP350K, extends to a molecular mass

Table 5
Molecular weight results of PP standards compared with vendor values

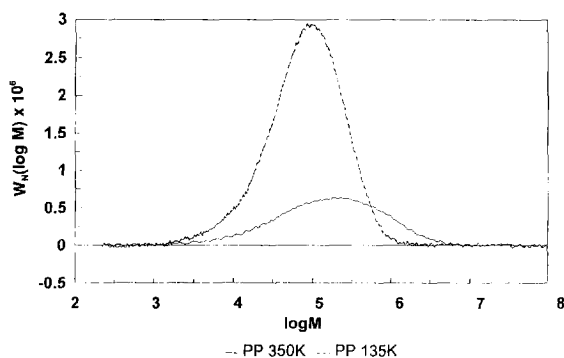|	PP95K	PP135K	PP180K	PP230K	PP350K
M_n (vendor)	28 100	37 000	40 000	41 800	43 500
M_n (calc.)	26 913	38 587	39 312	42 549	43 611
Dev. (%)	4.22	-4.29	1.72	-1.79	-0.26
M_w (vendor)	95 400	136 500	177 100	231 300	348 300
M_w (calc.)	79 704	130 255	171 228	253 156	398 384
Dev. (%)	16.5	4.58	3.32	-9.45	-14.4
M_w/M_n (vendor)	3.40	3.69	4.43	5.53	8.01
M_w/M_n (calc.)	2.96	3.38	4.36	5.95	9.13

Fig. 4. Molecular mass distributions of polypropylene (PP135K and PP350K). The ordinate is the mass fraction of polymer per log M increment.

of approximately 10^7, thus encompassing the whole range of industrial grade PP polymers.

4. Conclusions

Methyl cyclohexane, as a new mobile phase for SEC, permits the analysis of industrial (high molecular weight) polyethylene and polypropylene at 90°C. Samples were prepared by dissolving them in decalin at 140°C followed by diluting with hot methyl cyclohexane at 90°C prior to injecting into the SEC. Compared with the usual halogenated aromatic solvents, this new eluent is less toxic and has a greater differential refractive index sensitivity for polyolefins. Another advantage of this new mobile phase that will be the subject of future publications is that its UV transparency and lower operating temperature make it possible to combine UV and fluorescence detection with high temperature SEC for the analyses of functionalized polyolefins. Such materials are very difficult to characterize at present. The solvent also offers improved windows for infrared analysis.

A notable disadvantage of this solvent is that it is more flammable than halogenated aromatics. No problems in this respect were experienced. However, suitable precautions are required. Also, polystyrene should not be used with this mobile phase in combination with styrene-based column packings because of adsorption. Poly(isobutylene) narrow fractions were used as calibration standards with a set of polypropylene broad standards to obtain the

necessary PP calibration curves by using a numerical optimization method. Using this alternative calibration method, the breadth of the molecular-mass distribution of the PP broad standard was the most important factor in determining the calibration curve: the broader the molecular-mass distribution of the PP broad standards used, the better the results. Using the numerical search method to establish the calibration curve for PP, M_n values were within approximately 4% of the vendor values and M_w were within -9.5% to 16.5%.

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