

Dichloropentafluoropropanes as solvents for size exclusion chromatography

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Abstract

We have found that HCFC225s (HCFC225ca: 3,3-dichloro-1,1,1,2,2-pentafluoropropane, HCFC225cb: 1,3-dichloro-1,1,2,2,3-pentafluoropropane) are superior mobile phases for size exclusion chromatography (SEC). As alternatives of CFC113, they have been shown to possess a number of excellent properties, such as low flammability, low viscosity, low cost, high purity, and environmental and operational friendliness. In addition, they have distinct advantages for the SEC measurement, because they solubilize some kinds of acrylate such as poly(methyl methacrylate) (PMMA) and commercial monodispersed PMMA can be used to prepare calibration curves necessary for the measurement of equivalent molecular weight of some polymers. Furthermore, we propose an HCFC225/1,1,1,3,3,3-hexafluoroisopropanol mixed solvent for use in the SEC of poly(ethylene terephthalate) (PET) and polyamides. Poly(2-(perfluorooctyl)ethyl acrylate), whose PMMA equivalent weight average molecular weight was 118,100 Da, was evaluated by a multi-angle laser light scattering (MALLS) detector to have an absolute molecular weight of 439,000 Da. The difference can be attributed to the molecular size of the polyfluorinated polymer compared to the non-fluorinated one. The possible application of this novel mobile phase system for molecular size and molecular weight characterization of perfluoropolyethers, PET, nylon 6 and nylon 6,6 are also discussed.

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1. Introduction

Selection of the appropriate mobile phase in size exclusion chromatography (SEC) is a great importance for the accurate estimation of the molecular weight distribution for polyfluorinated polymers. In addition to the high solubility of the sample, several characteristics such as peak shape and reproducibility of measurements, easy selection of a standard polymer for calibration, cost, ease of sample isolation and solvent recycle, and its effect on the operational and global environment should be carefully examined. Generally, several fluorine-containing solvents have been applied to SEC. Popular solvents for the polyfluorinated polymers are, for example, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) [1,2], whose production was halted due to its

role in stratospheric ozone depletion, hexafluoroisopropanol (HFIP), perfluorocarbons, and fluorine containing ethers. However, no solvent completely satisfies the above requirements. For instance, HFIP has disadvantages such as health hazards, high cost, and its inability to dissolve polystyrene. Furthermore in general, perfluorocarbons has a high global warming potential (GWP), and low solubility of poly and non-fluorinated polymers.

On the other hand, HFIP is known to be a good solvent for various non-fluorinated and solvent-restricted polymers such as poly(ethylene terephthalate) (PET) and polyamides. SEC for PET has been carried out using chloroform/HFIP (98/2) [3,4], HFIP [5], and dichloromethane/HFIP (95/5) containing tetraethylammonium chloride [6]. Similarly, polyamides has been analyzed using various mobile phases such as toluene/HFIP(8/2) [7], HFIP containing sodium trifluoroacetate [8,9], or tetraethylammonium nitrate [10]. However, not only HFIP but also the chlorocarbons for HFIP dilution are undesirable for safety and environmental reasons.

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Table 1
SEC measurements of fluorine containing polymers: some representative mobile phases

	HCFC225ca	HCFC225cb	HFIP	Perfluoro compounds	CFC113	THF
Boiling point (°C)	51.1	56.1	58.6	–	47.6	66
Ozone depletion potential (CFC11 = 1)	0.025	0.033	0	0	0.8	0
Global warming potential (CFC11 = 1)	0.04	0.15	–	High	1.4	Low
Standard polymer	PMMA	PMMA	PMMA	None	None	Polystyrene
Solubility of polyfluorinated polymer	High	High	High	High	High	Low
Cost	Low	Low	High	–	–	Low
Remarks			Corrosive irritating		Phased out	

We have found that HCFC225s (HCFC225ca: 3,3-dichloro-1,1,1,2,2-pentafluoropropane $\text{CF}_3\text{CF}_2\text{CHCl}_2$, bp: 51.1 °C, HCFC225cb: 1,3-dichloro-1,1,2,2,3-pentafluoropropane $\text{CF}_2\text{ClCF}_2\text{CFHCl}$, bp: 56.1 °C) are excellent mobile phases for SEC. These solvents, which are the only reasonable substitute for CFC113, have been widely used mainly as cleaning agents. In addition to their low ozone depletion potential (ODP), they also have low GWP and low flammability. They are also particularly suitable as mobile phases of SEC because of their low viscosity, high purity, low cost, and high solubility to wide variety of fluorine-containing polymers. Further, they are certified safe by the Program for Alternative Fluorocarbon Toxicity Testing (PAFT), and having little smell, they offer better operational hygiene.

Another important characteristic of HCFC225s is their ability to dissolve poly(methyl methacrylate) (PMMA). Owing to the insolubility of commercial monodispersed polymers in conventional fluorinated solvents such as CFC113, perfluoroalkanes or fluorine containing ethers, special techniques are necessary for molecular weight determinations of polyfluorinated polymers by SEC using these as mobile phases. These techniques are, for example, using handmade standard polymers for calibration or using absolute molecular weight detectors (viscometry, light scattering). These detectors, however, are relatively insensitive to polyfluorinated oligomers and polymers because of their low refractive index increments compared to the mobile phase (dn/dc). On the other hand, in the case of HCFC225s, PMMA equivalent molecular weights of samples are easily obtained using commercial monodispersed PMMA. Table 1 shows some properties of several representative SEC solvents for polyfluorinated polymers.

One fluorinated acrylic polymer, poly(2-(perfluoroalkyl)ethyl acrylate), is insoluble in practically all common solvents except HCFC225s. This polymer is water and oil repellent and is widely used as a homopolymer or copolymer with non-fluorinated acrylate or vinyl monomers. Meanwhile, perfluoropolyethers (PFPEs), having outstanding characteristics as lubricants of magnetic recording media and aerospace engines, are dissolved in a limited number of fluorinated solvents such as CFC113 [1,2], perfluorobutyl alkyl ether, HFIP, and HCFC225s. Besides, the number average molecular weight (M_n) of PFPEs was conventionally obtained by ^{19}F NMR spectroscopy. The effectiveness of

HCFC225s for SEC of poly(2-(perfluoroalkyl)ethyl acrylate)s and PFPEs has been demonstrated.

Moreover, we propose HFIP diluted with HCFC225s for SEC of PET and polyamides. After testing several mobile phase systems on these difficult-to-manage polymers, suitable mobile phase systems are proposed and their applicability is discussed.

Further, we have tested the applicability of a multi-angle laser light scattering (MALLS) detector for determining the absolute molecular weight of these polymers. In the case of polyfluorinated polymers, PMMA equivalent molecular weights are expected to show considerable differences to the absolute molecular weight because the molecular size of polyfluorinated polymers is presumed to be smaller than that of PMMA having an identical molecular weight. SEC/MALLS evaluation of non-fluorinated polymers in HFIP mobile phase has previously been conducted [11], while in the current work, SEC/MALLS using HCFC225 containing mobile phase is applied to poly and non-fluorinated polymers.

2. Experimental

Since the boiling point of the cb isomer (56.1 °C) is higher than that of the ca isomer (51.1 °C), the former was used in expectation of improved pumping at higher operating temperatures such as 37 °C for higher polymer solubility and lower dissolved gas content. Asahiklin AK-225G[®] (Asahi Glass Co. Ltd., Tokyo, Japan), consisting of about 99.8% HCFC225cb and 0.2% HCFC225ca, was used as the HCFC225cb. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Central Glass Co. Ltd. (Tokyo, Japan), and used without further purification. Monodispersed PMMA mixtures (Easi-Cal PM-1, Molecular weight: mixture of ten standards from 1020 to 1,577,000 Da) were purchased from Polymer Laboratories Ltd. (UK). Perfluoropolyether, Fomblin[®] Z-dol 2000 [$\text{HOCH}_2(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n\text{CF}_2\text{CH}_2\text{OH}$], and AM 2001 [$\text{XCH}_2\text{OCH}_2(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n\text{CF}_2\text{CH}_2\text{OCH}_2\text{X}$, X = aromatic group] were from Ausimont (Milan, Italy). Poly(2-(perfluorooctyl)ethyl acrylate) and poly(2-(perfluorodecyl)ethyl acrylate) were polymerized from the corresponding monomers using azobisisobutyronitrile

Table 2
SEC of PMMA 100 K and poly(2-(perfluorooctyl)ethyl acrylate) in comparison with the detectors and the certification supplied by the manufacturer

	Method	PMMA 100 K				Poly(2-(perfluorooctyl)ethyl acrylate)			
		Injected mass (mg)	Mn (Da)	Mw (Da)	dn/dc (ml/g)	Injected mass (mg)	Mn (Da)	Mw (Da)	dn/dc (ml/g)
RI (positive)	PMMA equivalent	0.200	42,600	82,000		0.200	26,900	118,100	
UV (220 nm)	PMMA equivalent	0.200	39,300	82,400		0.200	22,700	114,600	
ELSD	PMMA equivalent	0.200	23,400	69,200		0.200	20,600	100,400	
MALLS	dn/dc measured	0.196	41,600	79,700	0.157	1.101	93,100	439,000	0.018
Manufacture data (solvent: THF)	GPC		49,000				No data		
	MO		52,000						
	LS			91,000					
	GPC/DV			88,000					

MO: membrane osmometry.

(AIBN) of initiator, in AK-225[®] (Asahi Glass, mixture of HCFC225ca and HCFC225cb). PET, nylon 6, nylon 6,6 and poly(vinyl butyral) (PVB, 13 wt.% hydroxyl, 1 wt.% acetate, 86 wt.% butyral) were from Scientific Polymer Products (Ontario, NY). Poly(butylene terephthalate), Duranex[®] 3300, was from Polyplastics (Tokyo, JAPAN), and polyetherimide, from Polysciences Inc. (Warrington, PA). PMMA 100 K, PET 49 K, and nylon 6 30 K, which are well-characterized molecular weight standard polymers, were from American Polymer Standards Corp. (Mentor, OH). The certifications provided by the manufacturers are listed in Tables 2 and 5 together with analytical results.

The conditions used for the SEC measurement are as follows. The samples to be measured were dissolved in a mixture of HCFC225cb and HFIP by shaking for several minutes and then allowing to stand until the solute was no longer visible (usually overnight). After filtration through a 0.45 μ m pore PTFE membrane (Titan[®] Filtration Systems, Sun Sri, NC), 50 μ l or 100 μ l of each solution was introduced into an HLC-8020 size exclusion chromatograph (Tosoh, Tokyo, Japan) using an auto injector AS-8010, or, a 100 μ l loop injector when accurate volume is required. Besides a differential refractive index (RI) detector, an ultra violet (UV) detector UV-8010 set at 220 nm, and an evaporative light scattering detector (ELSD; Alltech ELSD 500; Alltech Associates Inc., IL) were used. The ELSD drift tube and exhaust temperatures were set at 63 and 38 °C, respectively, and the nitrogen gas flow rate was set at 1.67 dm³/min.

The SEC/MALLS measurement was performed using a three-angle (45°, 90° and 135°) type detector (miniDAWN[®], Wyatt Technology Corporation, Santa Barbara, CA), attached in front of the RI detector. Molecular weight distributions were determined with the ASTRA[®] for Windows (Wyatt Technology) software using specific refractive index increments dn/dc obtained by RI detector (except for PET and polyamides). The latter cases, mass recoveries (RI detection versus sample weight injected) were assumed to be 100%. Detector calibration constants are determined by toluene for miniDAWN, and a characterized narrow distribution polystyrene standard (Mp: 30,300 Da, Polymer

Laboratories) for RI in THF mobile phase. The interdetector volume and accurate injection volume of the loop injector were evaluated using this polystyrene standard to have the reasonable molecular weight and distribution.

Separation columns were equipped with two 30 cm \times (0.75–0.8 cm) columns such as PL gel mixed-C, mixed-E (Polymer Laboratories), TSKgel GMH_{HR}-M (Tosoh Co. Ltd., Tokyo, Japan), or Shodex GPC K-805L (Showa Denko Co. Ltd., Tokyo, Japan) in series with or without a pre-column. The column oven was set at 37 °C and the mobile phase flow rate was 1 ml/min. A flow rate marker for cancellation of minor flow rate fluctuations was not used in these experiments.

3. Results and discussion

3.1. PMMAs as molecular weight standards

PMMA standards were successfully separated using HCFC225cb as the mobile phase. However, the peak symmetry and reproducibility of the chromatograms were rather unsatisfactory, probably because the PMMA adsorb to the stationary phase of the styrene-divinylbenzene copolymer columns.

Using a mixture of 99 vol.% HCFC225cb and 1 vol.% HFIP as the mobile phase overcame this undesirable phenomenon. PMMAs were separated in sharp and symmetrical peaks as shown in Fig. 1, which shows the much improved peak shape achieved on using HFIP. This chromatogram was obtained using two PL gel mixed-C columns. Practically the same separation patterns were obtained using other columns. The result suggests that adsorption of PMMAs to the stationary phase can be avoided by the use of fluorinated polar solvents. The similar effect might be anticipated on addition of non-fluorinated alcohols such as ethanol, but this will reduce the solubility of polyfluorinated polymers. Finally, we obtained each reliable calibration curve for all columns using the third-order correlation with the correlation coefficient of, for example, 0.99986 for 10 PMMA stan-

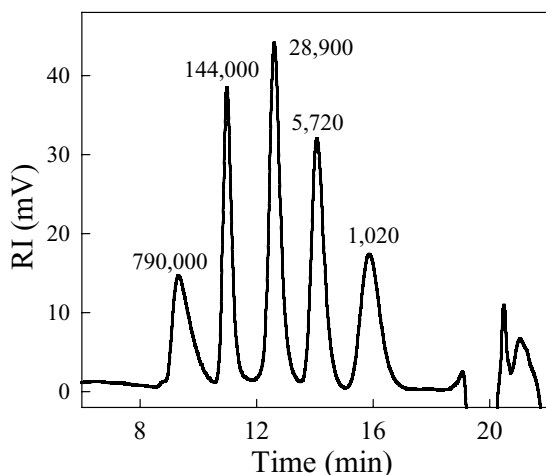


Fig. 1. RI chromatogram and molecular weight of PMMA mixture (Easi-Cal PM-1) in 99 vol.% HCFC225cb/1 vol.% HFIP using two PL gel mixed-C columns.

standards (Easi-Cal). However, the peak shape of PMMA standard by ELSD is not symmetric but rather tails because, besides not optimized detector conditions, this detector might be prone to broaden peaks when using this particular mobile phase. In addition, PMMA standards were separated similarly when another isomer HCFC225ca was used instead of HCFC225cb.

The average molecular weight of the PMMA 100 K standard was obtained using various detectors. The results, with the manufacturer's data for comparison, are shown in Table 2. The "PMMA equivalent" molecular weight obtained by SEC using PMMA molecular weight standards (Easi-Cal) and RI, UV and ELSD detector were lower than the manufacturer's data. Specifically, the difference in PMMA equivalent molecular weight using ELSD is attributed to its tailed peak shape. The dn/dc value of PMMA 100 K in this mobile phase was 0.157, which was sufficient for molecular weight estimation in our system. The absolute molecular weight obtained from the MALLS detector for PMMA 100 K using the dn/dc value was smaller than the manufacturer's data and close to the value obtained using RI and UV detector. Further measurements, for example, a universal calibration, will be required for more detailed discussion.

3.2. SEC of poly(2-(perfluoroalkyl)ethyl acrylate)s

HCFC225s are unique in that they dissolve some kinds of acrylic polymers. As representatives of the class, we chose the perfluorooctyl and decyl homologs for brief investigation. Poly(2-(perfluorooctyl)ethyl acrylate) was dissolved in a mixture of HCFC225cb containing 1 vol.% HFIP, and poly(2-(perfluorodecyl)ethyl acrylate) was in a mixture of 90 vol.% HCFC225cb and 10 vol.% HFIP. The SEC measurements of the samples were carried out using the corresponding mobile phases and two PL gel mixed-C columns. They were detected using RI detector in positive polarity

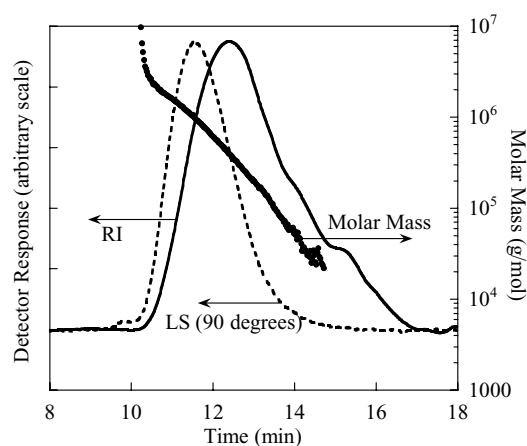


Fig. 2. RI and MALLS (90°) chromatograms of poly(2-(perfluorooctyl)ethyl acrylate) and absolute molar mass vs. retention time in 99 vol.% HCFC225cb/1 vol.% HFIP using two PL gel mixed-C columns.

mode, which implying that the polymers have larger refractive indices than the mobile phase (see Fig. 2). The dn/dc measured was insufficiently high at 0.018 for poly(2-(perfluorooctyl)ethyl acrylate), but the LS chromatogram together with the absolute molar mass versus retention time plot were successfully obtained (Fig. 2). The PMMA equivalent average molecular weight and the absolute one are shown in Table 2. The absolute M_n and M_w values were four times larger than the PMMA equivalent M_n and M_w . This may be attributable to the smaller molecular size of the polyfluorinated polymer.

3.3. SEC of perfluoropolyethers

A mixture of HCFC225cb and 1 vol.% HFIP was utilized as the mobile phase for PFPEs. A chromatogram of Fomblin® Z-dol 2000 using two PL gel mixed-E columns is shown in Fig. 3. Components including low molecular weight oligomers were satisfactorily separated, without interference by system peaks resulting from air or impurities

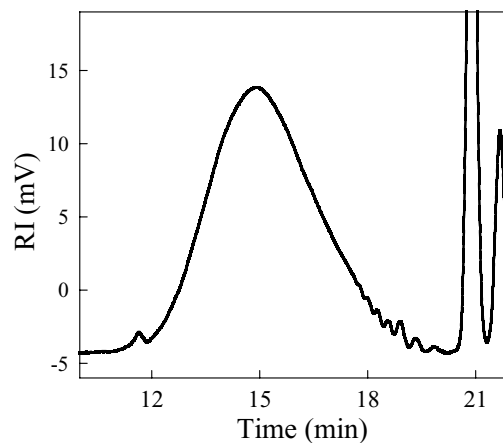


Fig. 3. RI chromatogram of Fomblin® Z-dol 2000 in 99 vol.% HCFC225cb/1 vol.% HFIP using two PL gel mixed-E columns.

Table 3
SEC of PFPEs: dependence on the detector employed

Sample	Injected mass (mg)	Flow rate (ml/min)	RI (negative)			UV (220 nm)			ELSD		
			Mn (PMMA equivalent, Da)	Mw (PMMA equivalent, Da)	Total area (count)	Mn (PMMA equivalent, Da)	Mw (PMMA equivalent, Da)	Total area (count)	Mn (PMMA equivalent, Da)	Mw (PMMA equivalent, Da)	Total area (count)
Z-dol 2000	0.0156	1.0	Not detected	Not detected	1510	Not detected	Not detected	1640	2450	920	
	0.156	1.0	1280	2570	1510	Not detected	Not detected	1500	2390	16,200	
	0.156	0.5	Not measured	Not measured	7690	Not measured	Not detected	1850	2660	11,900	
AM 2001	0.780	1.0	1280	2550		Not detected	Not detected	1300	2420	75,300	
	0.0156	1.0	Not detected	Not detected		910	1530	760	2140	1,480	
	0.156	1.0	Polarity of peak was not constant	Polarity of peak was not constant		880	1540	810	2140	21,500	
	0.780	1.0	Polarity of peak was not constant	Polarity of peak was not constant		870	1540	740	2120	130,900	

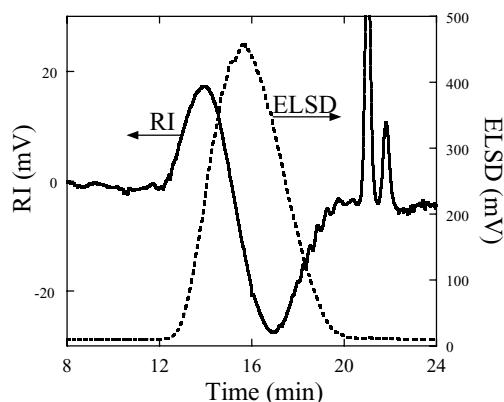


Fig. 4. RI and ELSD chromatograms of Fomblin® AM 2001 in 99 vol.% HCFC225cb/1 vol.% HFIP using two PL gel mixed-E columns.

by using the RI detector in negative polarity mode. The PMMA equivalent molecular weight of this sample was estimated to be 1090 Da for Mn and 2230 Da for the weight average molecular weight (Mw). The Mn of this sample estimated by ^{19}F -NMR was 1888 Da. The difference in Mn arising in both methods might be attributed to use of the non-fluorinated calibration standard (PMMA) for polyfluorinated polymers. Namely, the PFPE molecule is smaller in size than the PMMA of identical molecular weight similarly to the case of poly(2-(perfluorooctyl)ethyl acrylate) noted above.

Fomblin® AM 2001 has aromatic hydrocarbon end groups. Therefore, RI detection was not available because the refractive index varies with molecular weight (see Fig. 4). In the present case having UV absorptive groups, UV detector was effective, however, the chromatogram was not expected to show an accurate distribution of molecular weight because the UV absorptivities of the samples depend on the molecular weight.

When the ELSD was applied to PFPE analyses, higher sensitivity was attained compared to the RI detector (Table 3). Both PFPEs were detected in a 0.0156 mg injection, and Fomblin® AM 2001 was detected independently of the terminal group as shown in Fig. 4 in comparison with RI detection. However, peak areas against sample concentrations were not sufficiently linear compared to RI and UV detector, and were not independent of the mobile phase flow rate because the ELSD detector is not a true mass detector. Thus, RI, UV, and ELSD can be selected in this system to suit the objectives of the PFPE analysis.

3.4. Solubility of non-fluorinated polymers in mixtures of HCFC225cb and HFIP

Solubility tests were conducted at a concentration of 0.2 wt.% non-fluorinated polymers in the mixture of HCFC225cb and HFIP. The results are shown in Table 4. Although no polymer dissolved in pure HCFC225cb, PVB, nylon 6, and nylon 6,6 were dissolved by 10% HFIP/90%

Table 4
Solubility test at a concentration of 0.2 wt.% non-fluorinated polymers to the mixtures of HCFC225cb and HFIP

Sample	HFIP (vol.%) in HCFC225cb		
	0	10	30
Poly(butylene terephthalate)	I	I	I
Poly(vinyl butyral)	I	S	S
Poly(ethylene terephthalate)	I	I'	S
Nylon 6	I	S	S
Nylon 6,6	I	S	S
Polyetherimide	–	I'	S

I: insoluble; I': swelling (no precipitation in 24 h after dilution from 30% solution); and S: soluble.

HCFC225cb, and PET and polyetherimide were not precipitated in the same solvent after dilution from 30% HFIP/70% HCFC225cb solution. Based on these results, 10% HFIP/90% HCFC225cb was applied as the mobile phase for these polymers.

3.5. SEC of PET and polyamides

In general, SEC measurement of PET and polyamides are very difficult because of undesirable effects such as intermolecular interaction (aggregation), intramolecular repulsion of charge, or adsorption of the polymer to separation column.

PET was dissolved in the mixture of 30% HFIP/70% HCFC225cb and injected into the SEC with 10% HFIP/90% HCFC225cb, as the mobile phase. As shown in Fig. 5, the RI chromatogram showed a similar peak pattern to a literature report [4], in which HFIP/chloroform was used as the mobile phase. Since electrolytes are not employed in the mobile phase, excessive peak caused by them were removed compared to a literature report [10], in which peaks assigned to tetraethylammonium nitrate were observed. Furthermore, this system has advantages to be able to use popular high performance columns for such a mobile phase as THF in lower pressure and higher resolution compared with the case

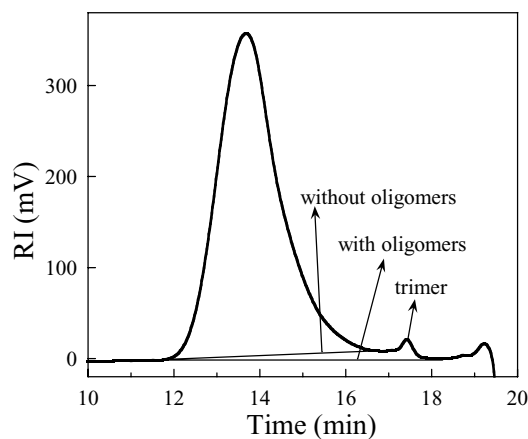


Fig. 5. RI chromatogram of PET 49 K in 90 vol.% HCFC225cb/10 vol.% HFIP using two PL gel mixed-C columns.

of 100% HFIP. These advantages will lead to a more accurate evaluation of the molecular weight.

The average molecular weight of PET and PET 49 K was calculated using a PMMA calibration curve and shown in Table 5 comparing with manufacturer's data and SEC/MALLS results. It should be noted that average molecular weight is greatly influenced by the integration limits of the chromatograms [4]. In the case of PET 49 K standard polymer, the PMMA equivalent Mn and Mw integrated peaks without oligomers were larger than manufacturer's data. Mn was much smaller when integrated with oligomers, which may indicate that the manufacturer's data were based on the integration without oligomer peaks. The larger Mw and Mn obtained by MALLS compared to the PMMA equivalent ones for PET (Scientific Polymer Products) are attributed to the assumption of 100% mass recovery and injection of excessive material.

SEC chromatograms of nylon 6 30 K standard polymer dissolved in various concentrations in 70% HCFC225cb/30% HFIP obtained in the same mobile phase as PET and using RI detector were shown in Fig. 6 together with the molar mass obtained by MALLS. Although the retention time of the peak top was lowered as the increase of injected mass, Mn and Mw calculated by MALLS increased above the injection of 3.23 mg. This may be caused by the change of polymer shape resulting from undesirable effects such as aggregation in the concentrated solution. The Mw obtained by MALLS was about twice that certified by the manufacturer. One reason for this difference may be attributed to the supposition of 100% mass recovery. Another could be due to the employment of the mixed mobile phase, namely, the selective absorption of HFIP onto the polymeric coil in solution resulting in an altered electronic environment between the coil and the mobile phase. The calculated dn/dc values were between 0.069 and 0.072, though the

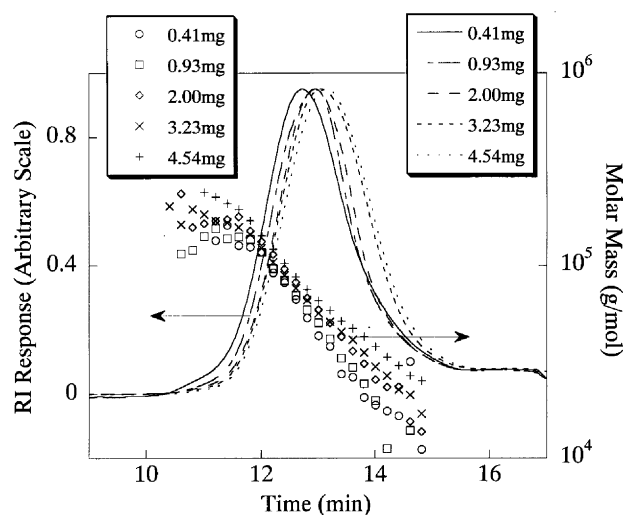


Fig. 6. RI chromatograms of nylon 6 30 K comparing various injected amount and their absolute molar mass vs. retention time in 90 vol.% HCFC225cb/10 vol.% HFIP using two PL gel mixed-C columns.

Table 5

Comparison of measured molecular weights of PET and polyamides using RI and MALLS with certified manufacturer's data

	Method	PET 49 K			Nylon 6 30 K		
		Injected mass (mg)	Mn (Da)	Mw (Da)	Injected mass (mg)	Mn (Da)	Mw (Da)
RI (positive)	PMMA equivalent without oligomers	0.51	30,900	61,900	0.78	20,600	28,600
	PMMA equivalent with oligomers		16,600	59,900		5,100	26,200
MALLS	100% mass recovery	Not measured			0.41	36,500	59,400
					0.93	39,300	52,700
					2.00	37,000	53,000
					3.23	48,500	63,100
				4.54	53,500	71,450	
Manufacture data (solvent: HFIP)	GPC		25,600			17,400	31,400
	LS			49,000			

	Method	PET			Nylon 6,6			Nylon 6		
		Injected mass (mg)	Mn (Da)	Mw (Da)	Injected mass (mg)	Mn (Da)	Mw (Da)	Injected mass (mg)	Mn (Da)	Mw (Da)
RI (positive)	PMMA equivalent without oligomers	0.78	21,000	58,000	0.78	18,200	46,300	0.78	10,900	18,900
MALLS	100% mass recovery	8.55	43,400	66,200	4.01	29,800	39,300	2.85	22,700	34,200

measurement of dn/dc will be needed for a more accurate evaluation. The PMMA equivalent Mw was similar with the manufacturer's data, and Mn was dependent on the integration in analogy with PET 49 K. Anomalous SEC behavior seemed to be suppressed using this mobile phase without adding electrolytes to the mobile phase.

Fig. 7 shows RI chromatograms of PET, nylon 6 and nylon 6,6 (Scientific Polymer Products) and their absolute molar mass versus retention time. The dn/dc values, calculated based on 100% mass recovery, were 0.108 for PET, 0.079 for nylon 6,6 and 0.083 for nylon 6. PET has a higher molar mass at the same retention time than polyamides, which suggests that under these conditions, nylons are more voluminous than PET having an identical molar mass.

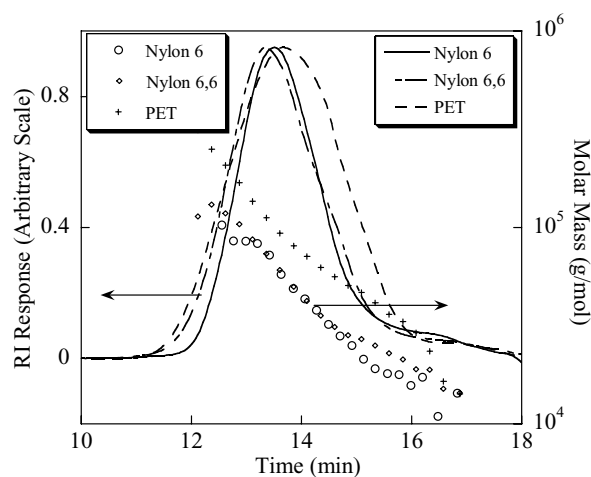


Fig. 7. RI chromatograms of PET, nylon 6 and nylon 6,6 and their absolute molar mass vs. retention time in 90 vol.% HCFC225cb/10 vol.% HFIP using two PL gel mixed-C columns.

4. Conclusions

Dichloropentafluoropropanes, with additional use of hexafluoroisopropanol, have been demonstrated to be a useful SEC mobile phase for some difficult to analyze polymers such as polyfluorinated polymers, PET, and polyamides. By employing this environmental and hygiene friendly solvent, PMMA equivalent molecular weight were readily obtained, and the results were compared among detectors including an absolute molecular weight detector and manufacturer's supplied data. Perfluoropolyethers and polyfluorinated acrylates are among the ideal examples for characterization choosing RI, UV, ELSD, and LS detectors. PMMA equivalent molecular weights of these polymers have shown to be lower than the absolute value, which would be attributed to the smaller molecular size of polyfluorinated polymers compared to the non-fluorinated analogs having the identical molecular weight.

Furthermore, PET and polyamides could be evaluated using dichloropentafluoropropane containing 10% HFIP. Using the MALLS detector, polyamides were shown to be more voluminous than those PET analogs having identical molar mass in the mobile phase.

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