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HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY OF POLY- AND OLIGOETHYLENE TEREPHTHALATE USING A MIXTURE OF HEXAFLUOROISOPROPANOL AND CHLOROFORM AS THE MOBILE PHASE

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SUMMARY

Solvent systems using a mixture of hexafluoroisopropanol (HFIP) and chloroform ($CHCl_3$) were developed for the analysis of polyethylene terephthalate (PET) and its oligomers by high-performance size-exclusion chromatography (SEC) at room temperature (25°C). The molecular weight distribution of PET and PET film were determined using HFIP–$CHCl_3$ (1:9) and the SEC calibration graph of polystyrenes, which are insoluble in HFIP. These mixed solvents also had considerable advantages with regard to cost reduction and safety in comparison with HFIP alone.

INTRODUCTION

Size-exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), can be used to separate polymers with respect of their molecular size in solution using appropriate calibration graphs based on their elution volumes. SEC columns packed with spherical particles of styrene–divinylbenzene copolymer[1] have been indispensable for the analysis of organic polymeric materials using high-performance liquid chromatography (HPLC) with organic solvents.

The selection of solvents is one of the most important problems in the use of SEC analysis for measuring molecular weight distributions (MWD) of organic materials. With a column packed with styrene–divinylbenzene copolymer, SEC eluents such as tetrahydrofuran (THF), chloroform and toluene have generally been used at room temperature. However, for the analysis of polymers that are insoluble in these common solvents, SEC eluents such as N,N-dimethylformamide, *m*-cresol and *o*-dichlorobenzene have been used at high temperatures.

In SEC measurements of polyethylene terephthalate (PET)[2–4] and polyamides (*e.g.*, nylon)[5–7], various difficulties have been encountered in dissolving these polymers in polar solvents such as *m*-cresol, *o*-chlorophenol and phenol–tetrachloroethane. In addition, the exposure of PET to high temperatures in these solvents during the course of the SEC measurement causes undesirable degradation of the polymer.

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The solvent hexafluoroisopropanol (HFIP)[8,9] is known to dissolve PET and polyamides at room temperature. However, polystyrenes, usually used for preparing SEC calibration graphs to determine the MWD of polymers, are insoluble in HFIP alone. Further, as HFIP is expensive and irritating to the skin and eyes, it is preferable to reduce the amount of HFIP used in any industrial analytical method.

Several attempts have been made to apply SEC to PET and polyamides using solvents mixed with HFIP, such as HFIP–toluene[10], HFIP–pentafluorophenol[11] and HFIP–methylene chloride[12–14]. This paper describes an effective mixed solvent system consisting of a mixture of HFIP and chloroform which permits the successful SEC measurement of various kinds of PET samples at room temperature.

EXPERIMENTAL

Samples and solvents

PET samples with different degrees of polymerization [$\overline{P_n}$ = 150, 110, 52, 35 and 5 (data given by the manufacturer)], two kinds of PET oligomers and PET film were obtained from the Industrial Plant Engineering Office of Hitachi. Epoxy resins, polyester resins and narrow-MWD polystyrene standards were obtained from Shell, NBS, Tosoh and Pressure Chemical, respectively.

THF and chloroform for SEC solvents were obtained from Wako and HFIP from Hidoras Chemical and DuPont. All the SEC solvents were degassed by ultrasonic treatment.

Test of solubility of PET and polystyrene

HFIP–chloroform mixed solvents in the ratios 0.5:9.5, 1:9, 2:8, 3:7, 4:6 and 1:1 (v/v) were prepared to determine the solubility of three kinds of PET samples with different degrees of polymerization ($\overline{P_n}$ = 150, 52 and 5) and two kinds of polystyrene standards (molecular weights $4.98 \cdot 10^5$ and $2.8 \cdot 10^3$). The HFIP–chloroform mixed solvents were added to PET samples and polystyrenes to give a concentration of 0.2% (w/v). The vials containing the solutions were tightly sealed and kept at room temperature (25°C) for one night. The solubility of the samples was also measured in the same manner by using HFIP–THF (1:9 and 1:1).

Preparation of SEC columns

All the packing materials and SEC columns used in this study (Gelpack) were made by Hitachi Chemical.

GL-S300HC-1 series columns with HFIP–$CHCl_3$ (1:9) mixed solvent. Porous spherical particles of styrene–divinylbenzene copolymer with an exclusion limit (M_{lim}) of $1 \cdot 10^3$ were packed in a 500 × 8 mm I.D. stainless-steel column with a slurry prepared by using HFIP–$CHCl_3$ (1:9) (designation: GL-S310HC-1).

GL-S320HC-1 (M_{lim} $5 \cdot 10^3$), GL-S330HC-1 (M_{lim} $2 \cdot 10^4$) and GL-S340HC-1 (M_{lim} $7 \cdot 10^4$) columns were prepared using HFIP–$CHCl_3$ (1:9) in the same manner as described above. A GL-S300MHC-1 column (mixed gel of M_{lim} $7 \cdot 10^4$, $5 \cdot 10^5$, $4 \cdot 10^6$ and $5 \cdot 10^7$) was prepared for measuring the MWD of PET and PET film, because its calibration graph was linear.

GL-S300HC-5 series columns with HFIP–$CHCl_3$ (1:1) mixed solvent. GL-S350HC-5 (M_{lim} $5 \cdot 10^5$) and GL-S360HC-5 (M_{lim} $4 \cdot 10^6$) columns were prepared as described above except that HFIP–$CHCl_3$ (1:1) was used.

GL-A100 series columns with THF solvent. GL-A110 (M_{lim} $1 \cdot 10^3$), GL-A120 (M_{lim} $5 \cdot 10^3$), GL-A130 (M_{lim} $2 \cdot 10^4$), GL-A140 (M_{lim} $7 \cdot 10^4$), GL-A150 (M_{lim} $5 \cdot 10^5$), GL-A160 (M_{lim} $4 \cdot 10^6$) and GL-A100M (mixed gel of M_{lim} $7 \cdot 10^4$, $5 \cdot 10^5$, $4 \cdot 10^6$ and $5 \cdot 10^7$) columns were prepared by packing the particles in 500 × 8 mm I.D. stainless-steel columns as described above except that THF was used as the solvent.

SEC and mass spectrometry

A Hitachi 635 high-performance liquid chromatograph with a UV detector set at 254 nm and a Hitachi 635A high-performance liquid chromatograph with a UV detector set at 250 nm, both instruments also with a refractive index detector, were used. All SEC experiments were carried out at room temperature (25°C).

For column protection, a column packed with HFIP–$CHCl_3$ (1:9) should be used with the same solvent as the SEC eluent, and the same rule should be followed with the HFIP–$CHCl_3$ (1:1) and THF columns. SEC experiments using THF as solvent were carried out under the same analytical condition as for the HFIP–$CHCl_3$ systems.

The number of theoretical plates (N) was determined by using 0.1% or 0.2% (w/v) benzene with UV detection at 254 or 250 nm at a flow-rate of 1.0 ml/min and calculated using the equation $N = 5.54\,(V_R/W)^2$, where V_R is the retention volume and W is the peak width at half-height. The height equivalent to a theoretical plate (HETP) is expressed by L/N, where L is the column length and N is the number of theoretical plates. The column pressure drop (P) was measured at a flow-rate of 1.0 ml/min. M_{lim} was determined from a calibration graph for polystyrene, obtained using the THF solvent column.

The number-average molecular weight (M_n), the weight-average molecular weight (M_w), the Z-average molecular weight (M_z) and the polydispersion index (D) of PET samples were calculated from the following equations: $M_n = \Sigma H_i/\Sigma(H_i/M_i)$, $M_w = \Sigma(H_iM_i)/\Sigma H_i$, $M_z = \Sigma(H_iM_i^2)/\Sigma(H_iM_i)$ and $D = M_w/M_n$, where H_i is peak height and M_i is molecular weight obtained from the calibration graph for polystyrene standards using HFIP–$CHCl_3$ (1:9).

The peaks collected from the SEC fractions of PET samples and oligomers present in PET films were identified using a Hitachi M-60 mass spectrometer.

RESULTS

Test of solubility of PET and polystyrene

The results of the solubility tests on the samples are given in Table I. With HFIP–$CHCl_3$ mixed solvents, PET samples ($\overline{P_n} = 5$ and $\overline{P_n} = 52$) were soluble in the solvents with ratios of 1:9 or higher, while the PET sample ($\overline{P_n} = 150$) was soluble in solvents with ratios of 4:6 or higher. On the other hand, the polystyrene standard of lower molecular weight ($2.8 \cdot 10^3$) was soluble in the solvents at all ratios, while the standard of higher molecular weight ($4.98 \cdot 10^5$) did not dissolve in HFIP–$CHCl_3$ with ratios of 4:6 and 1:1. Unfortunately, we could not find an HFIP–$CHCl_3$ mixture with a ratio in which all the PET samples and polystyrenes were soluble.

None of the PET samples, even that with $\overline{P_n} = 5$, were soluble in the HFIP–THF solvents at the ratios tested. It was evident that HFIP–THF solvents are unsuitable for SEC measurements of PET samples.

TABLE I

TEST OF SOLUBILITY OF PET AND POLYSTYRENE AT A CONCENTRATION OF 0.2% (w/v)

Solvent	*Mixture ratio (v/v)*	*PET*			*PS*	
		$\overline{P_n} = 5$	$\overline{P_n} = 52$	$\overline{P_n} = 150$	$2.8 \cdot 10^3$	$4.98 \cdot 10^5$
HFIP–CHCl$_3$	0.5:9.5	I[a]	I	I	S[a]	S
	1:9	S	S	I	S	S
	2:8	S	S	I	S	S
	3:7	S	S	I	S	S
	4:6	S	S	S	S	I
	1:1	S	S	S	S	I
HFIP–THF	1:9	I	I	I	S	S
	1:1	I	I	I	I	I

[a] I = Insoluble; S = soluble.

In accordance with these results, HFIP–CHCl$_3$ (1:9) and (1:1) were selected for SEC measurements of PET samples.

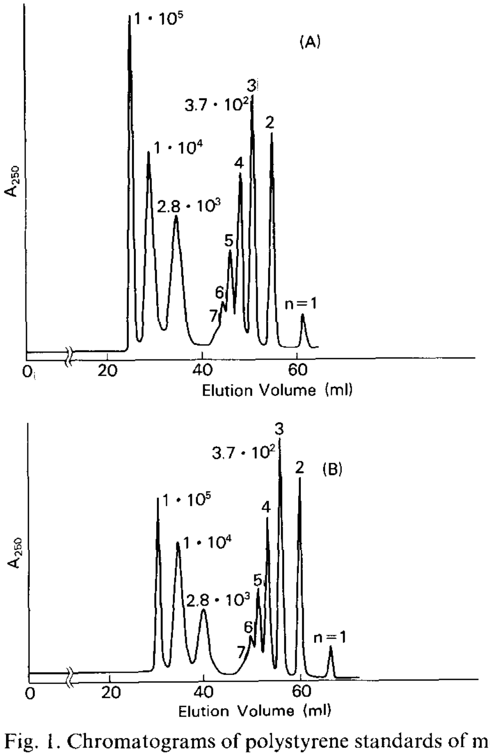

Fig. 1. Chromatograms of polystyrene standards of molecular weights $1.0 \cdot 10^5$, $1.0 \cdot 10^4$, $2.8 \cdot 10^3$ and $3.7 \cdot 10^2$ using (A) HFIP–CHCl$_3$ (1:9) or (B) THF as the mobile phase. HPLC instrument, Hitachi 635A; columns, (A) Gelpack GL-S310HC-1 + GL-S320HC-1 + GL-S330HC-1, (B) Gelpack GL-A110 + GL-A120 + GL-A130; all three columns, 500 × 8 mm I.D.; flow-rate, 1.0 ml/min; detector, UV (250 nm); column temperature, 25°C.

SEC experiments on PET oligomers using the HFIP–$CHCl_3$ (1:9) mixed solvent system

Fig. 1 shows the chromatograms of several kinds of polystyrene standards for the same column combination, using (A) HFIP–$CHCl_3$ (1:9) and (B) THF as the mobile phase. The number of theoretical plates (N) and HETP of system A were 46 000 and 0.003261 cm, respectively. As THF is an excellent solvent for SEC analysis, the column performance of system B was $N = 61\,200$ plates and HETP = 0.002451 cm. The column pressure drops of systems A and B at a flow-rate of 1.0 ml/min were 62 and 36 kgf/cm^2, respectively. The higher pressure drop of system A was due to the high viscosity of HFIP.

However, these differences between the two systems did not affect the efficiency of the SEC separation of polystyrenes, as shown in Fig. 1. Excellent separation, as good as with THF, was obtained with HFIP–$CHCl_3$ (1:9).

Fig. 2 shows the chromatograms of two kinds of PET oligomers of different molecular weights, obtained using HFIP–$CHCl_3$ (1:9). The SEC patterns of the higher molecular weight PET oligomer A and the lower molecular weight PET oligomer B were obtained by UV monitoring at 254 nm at room temperature (25°C). Each peak of PET oligomer B was collected from SEC fractions and identified by mass spectrometry. The formula of PET samples used in this study was determined and found to be that shown in Fig. 2, where n represents the degree of polymerization.

Fig. 3 shows the SEC calibration graphs for polystyrene (PS), isophthalic acid–propylene glycol-type polyester resin [ER(IP/PG)] and bis-phenol-type epoxy resin (Ep) using (A) HFIP–$CHCl_3$ (1:9) and (B) THF with the same column combination. In addition, the SEC calibration graph for PET, obtained from the chromatogram of PET oligomer B shown in Fig. 2, was plotted as shown in Fig. 3. SEC calibration graphs for PS, ER(IP/PG) and Ep were obtained from the chromatograms with both solvent systems. The SEC calibration graph for PET was located between those of PS and Ep.

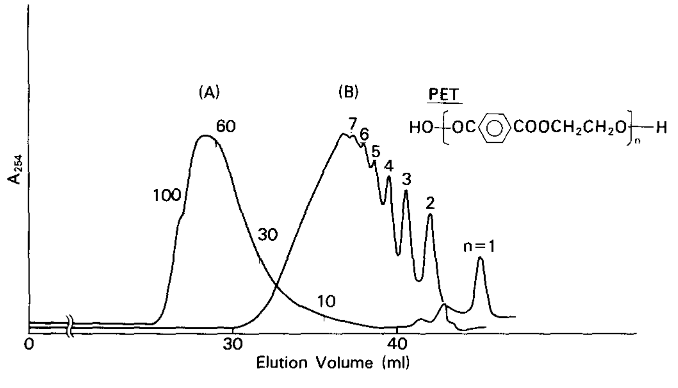

Fig. 2. Chromatograms of PET oligomer A and PET oligomer B using HFIP–$CHCl_3$ (1:9) as the mobile phase. HPLC instrument, Hitachi 635; columns, Gelpack GL-S320HC-1 + GL-S340HC-1 + GL-S340HC-1; all three columns, 500 × 8 mm I.D.; flow-rate, 1.0 ml/min; detector, UV (254 nm); column temperature, 25°C.

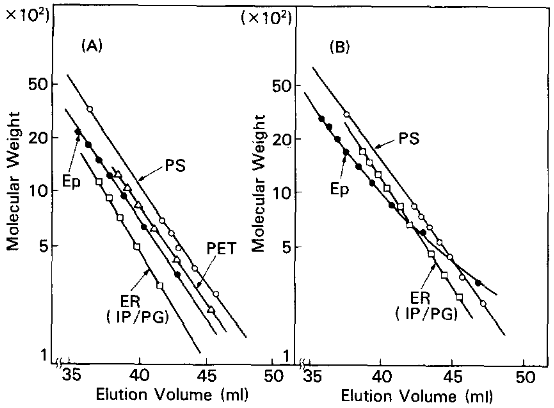

Fig. 3. SEC calibration graphs for (○) PS, (●) Ep, (□) ER(IP/PG) and (△) PET using (A) HFIP–$CHCl_3$ (1:9) and (B) THF as mobile phases. HPLC instrument, Hitachi 635; columns, (A) Gelpack GL-S320HC-1 + GL-S340HC-1 + GL-S340HC-1, (B) Gelpack GL-A120 + GL-A140 + GL-A140; all three columns, 500 × 8 mm I.D.; flow-rate, 1.0 ml/min; detector, UV (254 nm); column temperature, 25°C.

As shown in Fig. 3, all the calibration graphs exhibit good linearity in the HFIP–$CHCl_3$ (1:9) system. In particular, the Ep calibration graph with HFIP–$CHCl_3$ (1:9) shows good linearity in comparison with that obtained with THF. The strong adsorption effect between the sample (Ep) and solvent (THF), which makes the Ep calibration graph non-linear when THF is used, was eliminated by using HFIP–$CHCl_3$ (1:9).

The performances of the column combinations shown in Fig. 3 were $N = 53\,000$ plates, HETP = 0.002830 cm and $P = 56$ kgf/cm^2 in system A and $N = 55\,700$ plates, HETP = 0.002693 cm and $P = 41$ kgf/cm^2 in system B. It is remarkable that the HETP values were almost identical in both systems.

These results indicate that the HFIP–$CHCl_3$ (1:9) has a column efficiency comparable to that of THF and is suitable for SEC measurements of PET oligomers.

SEC experiments on PET polymers and PET films

Fig. 4 shows the chromatograms of three kinds of PET samples, (A) $\overline{P_n} = 150$, (B) $\overline{P_n} = 52$ and (C) $\overline{P_n} = 5$, using HFIP–$CHCl_3$ (1:1) as the mobile phase. SEC patterns of PET samples were obtained by UV monitoring at 254 nm at room temperature. The performances of the column combinations were $N = 25\,200$ plates, HETP = 0.003968 cm and $P = 30$ kgf/cm^2 in HFIP–$CHCl_3$ (1:1) and $N = 36\,300$ plates, HETP = 0.002755 cm and $P = 16$ kgf/cm^2 in THF (Gelpack GL-A150 and GL-A160 columns were used). We also obtained chromatograms of PET films under the same conditions as in Fig. 4.

However, as shown in Table I, the higher-molecular-weight PS was not soluble in HFIP–$CHCl_3$ (1:1). As a result, the MWD of PET samples and PET films could not be determined because the complete SEC calibration graph for PS could not be obtained with this solvent system.

This problem was successfully solved by modifying the method of sample preparation. We found that solutions of PET samples and PET films in HFIP–$CHCl_3$

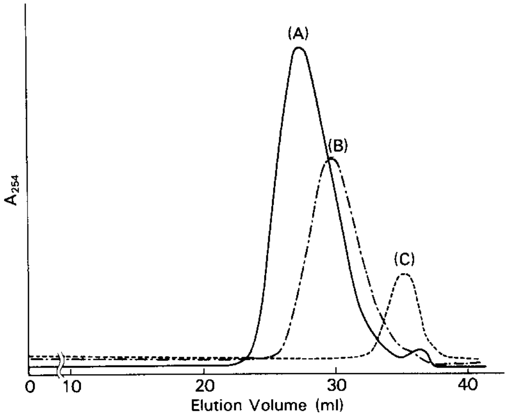

Fig. 4. Chromatograms of PET samples (A) $\overline{P_n}$ = 150, (B) $\overline{P_n}$ = 52 and (C) $\overline{P_n}$ = 5 using HFIP–$CHCl_3$ (1:1) as the mobile phase. HPLC instrument, Hitachi 635; columns, Gelpack GL-S350HC-5 + GL-S360HC-5; column dimensions, 500 × 8 mm I.D. × 2; flow-rate, 1.0 ml/min; detector, UV (254 nm); column temperature, 25°C.

(1:1) could be diluted with $CHCl_3$ to produce HFIP–$CHCl_3$ (1:9) with no polymer precipitation. Injection of these sample solutions into the HPLC instrument caused no problems in operation with HFIP–$CHCl_3$ (1:9).

Table II shows the SEC measurements of five PET samples ($\overline{P_n}$ = 150, 110, 52, 35 and 5) using HFIP–$CHCl_3$ (1:9). The column used for measuring the MWD of PET was Gelpack GL-S300MHC-1, which gave an almost linear calibration graph for polystyrene. The performances of this column were N = 16 300 plates, HETP = 0.003067 cm and P = 11 kgf/cm^2 with HFIP–$CHCl_3$ (1:9) and N = 18 200 plates, HETP = 0.002747 cm and P = 7 kgf/cm^2 with THF (Gelpack GL-A100M column was used).

From the degree of polymerization ($\overline{P_n}$), the number-average molecular weights of PET samples ($\overline{P_n}$ = 150, 110, 52, 35 and 5) were calculated to be 28 948, 21 248, 10 054, 6773 and 983, respectively, from the formula shown in Fig. 2. These M_n data calculated from the degree of polymerization ($\overline{P_n}$) were in good agreement with the SEC results for M_n shown in Table II.

TABLE II

SEC MEASUREMENT OF PET SAMPLES USNG HFIP–$CHCl_3$ (1:9)

SEC conditions: column, Gelpack GL-S300MHC-1 (500 × 8 mm I.D.); eluent, HFIP–$CHCl_3$ (1:9); flow-rate, 1.0 ml/min; detector, UV (250 nm); column temperature, 25°C; HPLC instrument, Hitachi 635A.

PET sample	M_n	M_w	M_z	D
$\overline{P_n}$ = 150	$2.70 \cdot 10^4$	$6.88 \cdot 10^4$	$1.19 \cdot 10^5$	2.55
$\overline{P_n}$ = 110	$2.31 \cdot 10^4$	$5.43 \cdot 10^4$	$9.78 \cdot 10^4$	2.35
$\overline{P_n}$ = 52	$1.11 \cdot 10^4$	$2.76 \cdot 10^4$	$4.76 \cdot 10^4$	2.48
$\overline{P_n}$ = 35	$6.83 \cdot 10^3$	$1.41 \cdot 10^4$	$2.33 \cdot 10^4$	2.06
$\overline{P_n}$ = 5	$5.82 \cdot 10^2$	$8.90 \cdot 10^2$	$1.55 \cdot 10^3$	1.53

These results show that the SEC analysis of all kinds of PET samples and PET films is possible if HFIP–$CHCl_3$ (1:9) is used and that the MWD of these polymers can be determined from the SEC calibration graphs for PS.

SEC experiments on oligomers present in PET films

Oligomers present in the PET samples or PET films can be analysed by SEC measurement of their $CHCl_3$ extracts, using THF as the solvent. The $CHCl_3$ extracts of the PET sample ($\overline{P}_n$ = 5) and the PET film were dissolved in THF after removing $CHCl_3$.

Fig. 5 shows the chromatograms of oligomers present in the $CHCl_3$ extract of the PET sample ($\overline{P}_n$ = 5) and oligomers present in the $CHCl_3$ extract of the PET film using THF. The peak of each SEC fraction was collected and identified by mass spectrometry. The formula of each oligomer was determined and is shown in Fig. 5.

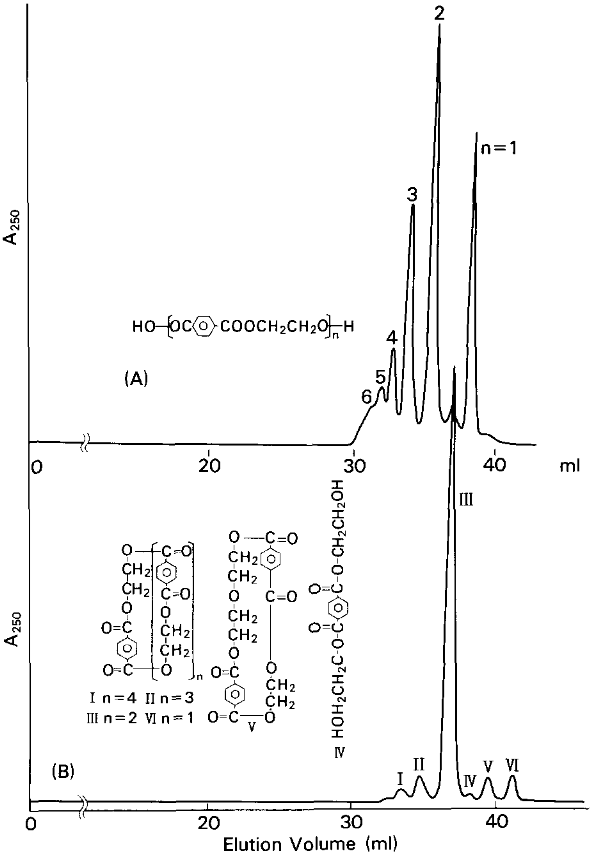

Fig. 5. Chromatograms of oligomers present in PET and PET film using THF as mobile phase. Samples: (A) $CHCl_3$ extract of PET sample ($\overline{P}_n$ = 5); (B) $CHCl_3$ extract of PET film. HPLC instrument, Hitachi 635A; columns, Gelpack GL-A110 + GL-A120 + GL-A130; all three columns, 500 × 8 mm I.D.; flow-rate, 1.0 ml/min; detector, UV (250 nm); column temperature, 25°C.

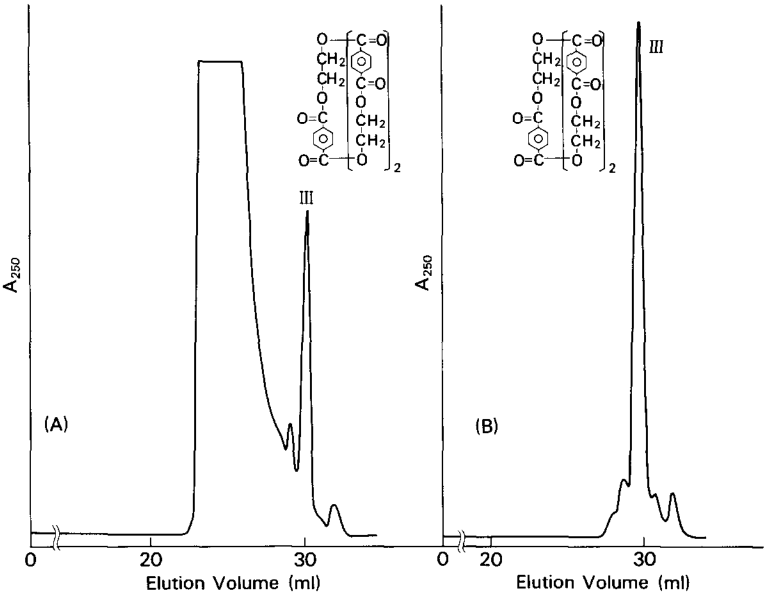

Fig. 6. Chromatograms of PET film using HFIP–$CHCl_3$ (1:9) as the mobile phase. Samples: (A) PET film; (B) $CHCl_3$ extract of PET film. HPLC instrument, Hitachi 635A; columns, Gelpack GL-S310HC-1 + GL-S320HC-1 + GL-S330HC-1; all three columns, 500 × 8 mm I.D.; flow-rate, 1.0 ml/min; detector, UV (250 nm); column temperature, 25°C.

Although this method is effective for identifying the oligomers, it is doubtful that these chromatograms accurately reflect the amount of such oligomers because it was difficult to extract all of the oligomers by the extraction process used. SEC analysis of the PET film oligomer using HFIP–$CHCl_3$ (1:9) was tried in order to overcome this disadvantage.

Fig. 6 shows the chromatograms of PET film and the $CHCl_3$ extract of PET film using HFIP–$CHCl_3$ (1:9). The fractions of the main peaks were collected and identified by mass spectrometry by the same method as with THF. The main oligomer peak of the PET film and the $CHCl_3$ extract of the PET film shown in Fig. 6 was identified as the same cyclic oligomer as peak III in Fig. 5.

DISCUSSION

Even at high temperatures, PET samples and PET films cannot be dissolved in most of the common SEC solvents such as THF, chloroform, toluene, dimethylformamide, dimethyl sulfoxide, anisole, 2-nitropropane, ethyl acetate, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene and acetonitrile. Only a few polar solvents can dissolve PET, *viz.*, trifluoroacetic acid, *m*-cresol, phenol–tetrachloroethane, *o*-chlorophenol, nitrobenzene, HFIP and hexafluoroacetone. Of these solvents, *m*-cresol has been the most commonly used for the SEC analysis of PET at temperatures of 110–135°C. However, there is ample evidence that PET is degraded in *m*-cresol by acid-catalyzed hydrolysis. Further, SEC analysis must be carried out at high temperature to reduce the high viscosity of *m*-cresol. The operation of HPLC under this condition is not easy and it lacks safety, reproducibility and reliability.

Paschke *et al.*[16] reported that SEC of PET using nitrobenzene–tetrachloroethane (0.5:99.5) at room temperature minimizes polymer degradation and distribution equilibration. However, in this instance, PET was first dissolved in pure nitrobenzene at 180–200°C and then diluted with tetrachloroethane, whereas the samples in our study, in which we used the HFIP–$CHCl_3$ to dissolve PET, were prepared under mild conditions at room temperature.

SEC experiments using HFIP alone have been carried out with PET[11], polytetramethyleneterephthalate[15], polyamide 6[5] and polyamide 12[10]. However, the SEC measurement of these polymers in HFIP had the serious disadvantage that polystyrenes, usually used for preparing a calibration graph to determine the MWD of polymers, are insoluble in HFIP.

In our study, we found that the solutions of PET samples in HFIP–$CHCl_3$ (1:1) could be diluted with $CHCl_3$ to give HFIP–$CHCl_3$ (1:9) with no polymer precipitation. We confirmed that this new method of sample preparation could be applied to PET films. The MWD of PET film calculated from the calibration graph for PS under the same analytical conditions as for Table II gave $M_n = 2.33 \cdot 10^4$, $M_w = 5.64 \cdot 10^4$, $M_z = 1.02 \cdot 10^5$ and $D = 2.42$.

We also found that the MWD of PET samples prepared in HFIP–$CHCl_3$ (1:9) by the dilution method described above showed little difference from the MWD of those dissolved in undiluted HFIP–$CHCl_3$ (1:1). For example, the MWDs of the PET sample with $\overline{P_n} = 150$ using HFIP–$CHCl_3$ (1:9) were $M_n = 2.70 \cdot 10^4$, $M_w = 6.88 \cdot 10^4$, $M_z = 1.19 \cdot 10^5$ and $D = 2.55$ when the sample was dissolved and diluted so as to give HFIP–$CHCl_3$ (1:9), and $M_n = 2.55 \cdot 10^4$, $M_w = 6.62 \cdot 10^4$, $M_z = 1.16 \cdot 10^5$ and $D = 2.60$ when the sample was dissolved in HFIP–$CHCl_3$ (1:1). This problem is being studied further and will be the subject of a subsequent paper.

Several SEC experiments using mixed solvents of HFIP with other compounds have been attempted, *e.g.*, HFIP–methylene chloride (30:70)[12–14] and HFIP–pentafluoropropanol (1:1)[11] for PET and HFIP–toluene (20:80)[10] for polyamide 12. In these studies, a refractive index detector, a UV detector and a laser low-angle light scattering photometer[5,11] were used as SEC detectors. For the detector with the HFIP–$CHCl_3$ systems, it has been our experience that a UV detector is to be peferred because of its high sensitivity, high resolution and stability of the baseline.

As HFIP is expensive and irritating to the skin and eyes, the HFIP–$CHCl_3$ system has a considerable advantage in diluting the HFIP with $CHCl_3$, which is much cheaper and safer than HFIP. Moreover, as the HFIP–$CHCl_3$ system can be separated into two phases at low temperature (below 10°C), HFIP–$CHCl_3$ waste solvent can be easily recovered by cooling and redistillation. We were able to re-use the HFIP–$CHCl_3$ solvent as the SEC eluent several times by applying this method.

CONCLUSIONS

HFIP–$CHCl_3$ mixed solvent columns packed with styrene–divinylbenzene copolymer have been developed for SEC measurements of PET, PET film and their oligomers at room temperature. In comparison with THF, HFIP–$CHCl_3$ (1:9) and (1:1) showed sufficient column efficiency. Especially in HFIP–$CHCl_3$ (1:9), the polystyrenes usually used for preparing calibration graphs were soluble and the MWD of PET samples and PET films could be determined. The direct SEC analysis of oligomers present in PET film was also possible with this solvent system.

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REFERENCES

1 J. C. Moore, *J. Polym. Sci., Part A2*, (1964) 835.
2 E. L. Lawton and D. M. Cates, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 9 (1968) 851.
3 R. S. Montserrat, J. P. Selga and V. P. Colomer, *Afinidad*, 38 (1982) 379.
4 N. A. Borshch and N. G. Mal-tseva, *Zh. Anal. Khim.*, 41 (1986) 916.
5 H. Schorn, R. Kosfeld and M. Hess, *J. Chromatogr.*, 282 (1983) 579.
6 R. Panaris and G. Pallas, *Polym. Lett.*, 8 (1970) 441.
7 D. J. Goedhart, J. B. Hussem and B. P. M. Smeets, *J. Chromatogr. Sci.*, 13 (1980) 203.
8 M. Ladika and Z. Mihalic, *Kem. Ind.*, 32 (1983) 433.
9 K. F. Purcell, J. A. Stikeleather and S. D. Brunk, *J. Mol. Spectrosc.*, 32 (1969) 202.
10 M. Sakai and T. Ogawa, *Bunseki Kagaku*, 32 (1983) 258.
11 S. Berkowitz, *J. Appl. Polym. Sci.*, 29 (1984) 4353.
12 B. L. Neff and J. R. Overton, *J. Liq. Chromatogr.*, 7 (1984) 1537.
13 J. R. Overton and H. L. Browning, Jr., *ACS Symp. Ser.*, No. 245 (1984) 219.
14 J. R. Overton and H. L. Browning, Jr., *Org. Coat. Appl. Polym. Sci. Prepr.*, 48 (1983) 940.
15 E. L. Slagowski, R. C. Gebauer and G. J. Gaesser, *J. Appl. Polym. Sci.*, 21 (1977) 2293.
16 E. E. Paschke, B. A. Bidlingmeyer and J. G. Berkmann, *J. Polym. Sci.*, 15 (1977) 983.