

Size-exclusion chromatography of poly(ethylene terephthalate) and related polymers in methylene chloride–dichloroacetic acid

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ABSTRACT

A solvent mixture of methylene chloride–dichloroacetic acid (DCAA) (80:20, v/v) containing 0.01 M tetrabutylammonium acetate is evaluated as an eluent for room temperature (30°C) size-exclusion chromatography of poly(ethylene terephthalate) (PET). Samples dissolve in less than 1 h at 70°C in 1:2 (v/v) methylene chloride–DCAA and can then be diluted at room temperature to 80% methylene chloride without polymer phase separation. There is no significant degradation of PET during sample preparation, provided the dissolution temperature is lower than 80°C and the water concentration is less than 1%. Accurate absolute molecular mass distributions are obtained using light-scattering detection with a coefficient of variation for weight-average molecular masses of *ca.* ± 2.5%.

INTRODUCTION

Several eluents have been used for size-exclusion chromatography (SEC) of poly(ethylene terephthalate) (PET). The first examples used *m*-cresol at 125–130°C [1,2], although it was later recognized that PET degrades under these conditions. More recently, *o*-chlorophenol at elevated temperatures has been successfully used as a single-component eluent [3]. Mixed eluents such as *o*-chlorophenol–chloroform [4,5], 1,1,2,2-tetrachloroethane–nitrobenzene [6] and 1,1,2,2-tetrachloroethane–phenol [7] allowed room temperature SEC operation, although the samples required extended heating for dissolution and, in at least one method [6], hot filtration. Examples of room temperature dissolution and SEC operation were given by Drott [8], using 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).

Some of the problems associated with calibration standards (polystyrene is insoluble in HFIP) were recently addressed by Mori [9]. Dilution of HFIP with chlorinated hydrocarbons has been more recently developed to defray the high cost of HFIP. These eluents include methylene chloride–HFIP at the azeotropic composition of 71:29 [10,11], 98:2 chloroform–HFIP [12] and 90:10 (v/v) [13]. Semi-micro SEC in 1:1 HFIP–chloroform has been proposed [14] to minimize costs further.

All of the above eluents were developed for use with a concentration-sensitive detector (either refractive index or UV) and narrow standard calibration. Most rely on methods that use Mark–Houwink constants to calculate absolute molecular mass distributions. However, constants may not be available for variants of PET, either linear or branched, or for structurally different crystalline polyesters. Absolute molecular mass distributions for these materials can be measured by SEC with molecular-mass-sensitive

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detection, such as viscometry with universal calibration or light-scattering. To date, we are aware of only one solvent system, HFIP–pentafluorophenol, that has been used with a molecular-mass-sensitive detector (low-angle laser light-scattering, LALLS) [15]. This eluent provides excellent contrast for light-scattering measurements and it is a room temperature solvent for PET samples. Unfortunately, it is quite expensive.

The limited number of applications of either light-scattering or viscometry detection to PET analysis can be partially attributed to the requirements placed by these detector systems on the SEC eluent. For example, viscometry detection is extremely difficult with the 71:29 methylene chloride–HFIP azeotrope because the low-boiling mixture (b.p. 38°C) forms bubbles in the viscometer and is difficult to pump without cavitation. Phenolic solvents are not good candidates for light-scattering detection because their refractive indices are too close to that of PET. They may also cause degradation of styrene-based SEC columns [3], which may cause particle shedding that is unacceptable for both light-scattering and viscometry detectors. Reproducible retention volumes of standards and samples has been raised as a concern for mixed solvents such as HFIP–chloroform [3], particularly for marginally soluble standards such as polystyrene. This may have a larger effect on results obtained from methods that use calibration curves (*e.g.*, viscometry detection using universal calibration) than for light-scattering. In addition, the refractive indices of these solvents differ greatly, which can lead to complications for light-scattering detection such as preferential solvation.

All of the eluents have their advantages and disadvantages. In many instances, the choice of one eluent over another may be driven by resources and requirements of a specific laboratory, *i.e.*, cost, safety, availability of light-scattering or viscometry detection, or routine *vs.* non-routine analysis. In our case, none of the eluents met all of the criteria for multidetector SEC, of which one of the detectors is molecular-mass-sensitive. These criteria are: no degradation of PET, column stability, room temperature operation, compatibility with differential refrac-

tive index (DRI) and UV spectrophotometric detection, compatibility with either light-scattering or viscometry detection, regular PET dilute solution properties (no aggregation), comparative safety and relative low cost. This has led us to investigate the properties of an alternative solvent for PET: dichloroacetic acid (DCAA). Recently, patents have issued on the use of DCAA as a sample solvent for SEC of aromatic polyesters [16] and as an SEC eluent for poly-(aryl sulfones) [17]. Previous investigations of the viscosity behavior of PET in DCAA indicate that it is a good solvent for the polymer and that it does not significantly degrade PET below 80°C [18,19]. However, it is a relatively strong organic acid that can produce severe skin burns, is toxic, and can be corrosive to stainless steel. One compromise is to dilute DCAA with a common HPLC solvent of similar refractive index such that the mixture fulfils most or all of the requirements above. For this, DCAA is diluted with methylene chloride and evaluated for use as an eluent for SEC with molecular-mass-sensitive detectors.

EXPERIMENTAL

Sample preparation

PET samples were synthesized at Eastman Chemical Company (Kingsport, TN, USA). PET 39K was obtained from American Polymer Standards (Mentor, OH, USA). Typically, 25 mg of polyester sample and 3 ml of methylene chloride (J.T. Baker, HPLC grade)–DCAA (Eastman Laboratory Chemicals) (1:2, v/v) were heated for 1 h at 75°C in a sealed 10 ml volumetric flask. The volumetric flask was cooled and diluted to the mark with methylene chloride containing 0.0143 M tetrabutylammonium acetate (TBAA, Aldrich) to give a final concentration of quaternary ammonium salt of 0.01 M. A flow marker, 1-chloro-2,4-dinitrobenzene, was added at a concentration of 0.01% to each sample.

Size-exclusion chromatography

The eluent was prepared at a volumetric ratio of methylene chloride–DCAA (80:20, v/v), containing 0.01 M TBAA. The eluent was continuously sparged with a light stream of helium. The

nominal flow rate was 1.0 ml/min, and samples were injected in a volume of 100 μ l. Three Polymer Labs. (Amherst, MA, USA) Mixed-B columns were converted from THF to methylene chloride and finally to methylene chloride–DCAA (80:20) containing 0.01 M TBAA at 0.5 ml/min. In order and plumbed in series after the columns were a Spectroflow 757 UV detector, an LDC Analytical KMX-6 low-angle laser light-scattering (LALLS) photometer, and a Waters Model 410 DRI detector. The SEC columns and DRI detector were thermostated to 30.0°C. The UV and LALLS detectors were operated at room-temperature. All light-scattering intensities were measured at 6–7° with an aperture of 0.15 mm.

Preliminary experiments were also conducted using a Viscotek Model 100 differential viscometry (DV) detector, connected after the UV detector and in a parallel configuration with the DRI detector. The concentration dependence of viscosity was measured at 30.0°C in a glass Ubbelohde capillary viscometer. Efflux times were long enough to ignore kinetic energy corrections.

RESULTS AND DISCUSSION

Dissolution and solution properties

PET pellets dissolve in approximately 30 min in 1:2 methylene chloride–DCAA at 70°C, depending on the molecular mass of the sample and the size of the pellet. Pulverized or crushed samples dissolve in as little as 10 min. PET samples can be diluted to 95:5 methylene chloride–DCAA containing 0.01 M TBAA at room temperature without polymer phase separation. A solvent mixture consisting of methylene chloride–DCAA (80:20) is a general-purpose eluent for most samples, including solid-stated PET and highly crystalline copolymers. Plots of inherent and reduced viscosities of a solid-stated PET (sample 10388) in methylene chloride–DCAA (80:20) indicated regular dilution behavior that is described by the Huggins–Kraemer equations, and an intrinsic viscosity $[\eta] = 0.882$ dl/g at 30°C. The difference in slopes of the Huggins and Kraemer plots, $k' - k'' = 0.475$ is within experimental error of the predicted value of 0.5.

Chromatography

Chromatograms obtained without TBAA added to the eluent exhibit two kinds of artifacts, neither of which is reproducible. A high-molecular-mass shoulder may appear and/or a high-molecular-mass prepeak. Both artifacts disappear completely upon addition of the quaternary ammonium salt to the eluent (Fig. 1). Preliminary investigations indicate that the TBAA breaks up PET molecular aggregates and also eliminates interactions of PET with the SEC columns. Similar results have been obtained from the addition of lithium bromide to N,N-dimethylformamide [20–23] and sodium trifluoroacetate (NAFAT) to HFIP [8]. As with NAFAT in HFIP, there are no differences in the polymer portion of chromatograms at salt concentrations between 0.01 M and 0.1 M TBAA in methylene chloride–DCAA (80:20). The tetrabutylammonium salt is used because it can be conveniently added to samples as a solution in pure methylene chloride. Tetramethyl- and tetraethylammonium acetates also eliminate prepeaks and shoulders, but they are marginally soluble in pure methylene chloride and must be added as solids to the methylene chloride–DCAA (80:20) sample solvent. It has also been observed that oxidative quaternary ammonium counterions such as nitrate and bromide can cause degradation of polystyrene samples and will cause discoloration of the methylene chloride–DCAA eluent. A peak from the quaternary ammonium

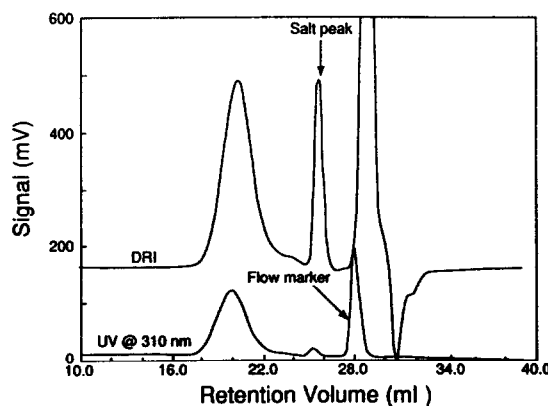


Fig. 1. UV and DRI chromatograms of PET 10388 in methylene chloride–DCAA (80:20) containing 0.01 M TBAA.

salt appears in the DRI chromatogram, which has implications for the calculation of the specific refractive index increment of samples (see below).

Stable baselines and reproducible PET chromatograms are obtained for both DRI and UV detection at 310 nm. The eluent absorbs ultraviolet radiation too strongly to be used at wavelengths shorter than 310 nm. Polystyrene is readily soluble in the eluent at room temperature and is detectable by DRI but not UV at 310 nm.

PET degradation

Sample preparation and analysis conditions that contribute to the degradation of PET are evaluated from normalized SEC chromatograms. Each height, $W(v)$, of a concentration detector chromatogram is divided by the total area under the chromatogram:

$$W_N(v) = \frac{W(v)}{\int_0^\infty W(v) dv} \quad (1)$$

Normalized chromatograms all have an area of unity, which makes them useful for comparisons.

Normalized UV chromatograms of PET injected 15 min, 24 h and 4 days after final dissolution and dilution of the sample are shown in Fig. 2. No significant differences are observed until day 4, at which time there is a minor shift in the molecular mass distribution and an increase

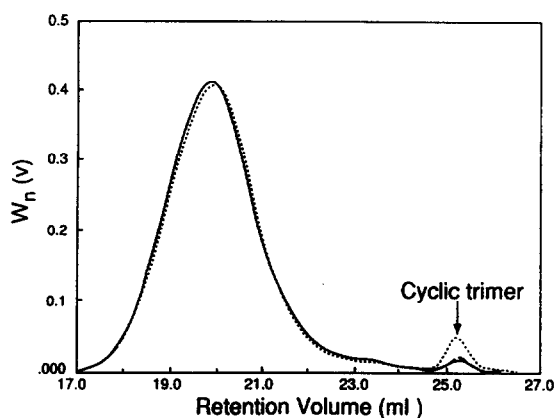


Fig. 2. Normalized UV chromatograms of PET 10388 exposed to eluent after 1 h of dissolution at 70°C. Solid = 0.25 h, dashed = 24 h, dotted = 96 h.

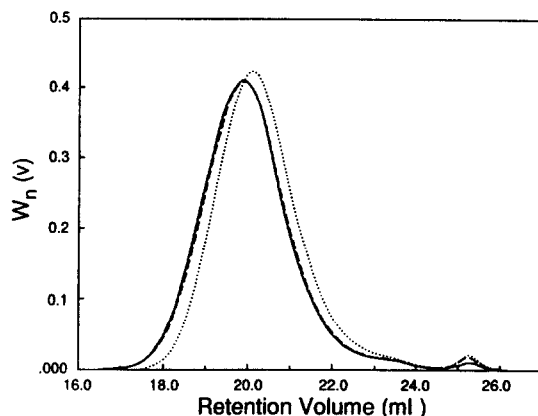


Fig. 3. Normalized UV chromatograms of PET 10388 after 1 h of dissolution at various temperatures. Solid = 70°C, dashed = 80°C, dotted = 105°C.

in cyclic trimer (peak at 25.2 ml). Normalized chromatograms of PET using sample dissolution temperatures of 70, 80 and 105°C are shown in Fig. 3. Identical chromatograms are obtained at 70 and 80°C, while a significant increase in retention time is observed at the 105°C dissolution temperature. This is consistent with the results of Tuzar *et al.* [19], who showed that PET was stable in pure DCAA at temperatures up to 80°C. Dissolution times between 0.75 and 4 h at 70°C have only minor effects on the PET size distribution. Unpublished data also indicate that some PET degradation may be expected in pure DCAA for water concentrations greater than 1.0% [24]. Chromatograms at 0.016, 1.016 and 4.016% (v/v) water concentration in the dissolution solvent confirm that degradation indeed occurs at high water concentrations (Fig. 4). No significant changes in chromatograms are observed for water concentrations in the dissolution solvent of less than 0.5%, which is considerably more than the water concentration of the eluent (0.016%) or pure DCAA (0.076%) measured by Karl Fisher titration.

In all cases, degradation of PET is recognized as a shift in the chromatogram to longer retention volumes and an increase in the concentration of cyclic trimer. This is consistent with ester interchange and hydrolysis, which in dilute solution results in an increase in cyclic trimer content [25-27].

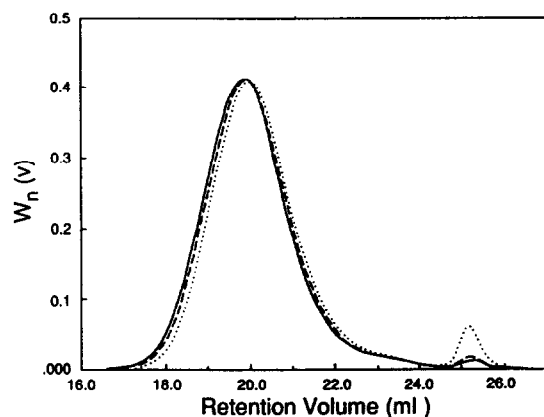


Fig. 4. Normalized UV chromatograms of PET 10388 after 1 h of dissolution at 70°C for increasing concentrations of water in the dissolution solvent. Solid = 0.016% water, dashed = 1.016%, dotted = 4.016%.

The effects of sample preparation and eluent conditions on the weight-average molecular mass (\bar{M}_w) of PET measured by LALLS are summarized in Table I. No significant degradation in molecular mass is observed within the following conditions: water concentrations in the dissolution solvent less than 0.5%, dissolution temperatures less than 80°C, dissolution times less than 2 h, and injection of the sample into the chromatograph less than 4 days after preparation. All of these conditions can readily be met using the procedure described in the EXPERIMENTAL section.

A comparison of the elution behavior of both PET (Fig. 5) and polystyrene (Fig. 6) at eluent compositions of methylene chloride–DCAA (80:20) and (90:10) (both containing 0.01 M TBAA) address the concern of reproducible retention volumes with mixed eluents. PET retention volumes increase slightly with increasing methylene chloride concentration, while polystyrene retention volumes decrease. This implies expansion of polystyrene and contraction of PET in the 90:10 methylene chloride–DCAA eluent. These shifts are consistent with the solvation of polystyrene and PET by the individual solvent components: methylene chloride is a better solvent than DCAA for polystyrene, and DCAA is a better solvent than methylene chloride for PET. The sensitivity of elution

TABLE I
PET DEGRADATION STUDY

	\bar{M}_w
<i>Sample preparation</i>	
<i>% water (v/v)^a</i>	
0.016	72 000 ^b
0.516	71 700 ^b
1.016	65 800 ^b
2.016	63 400 ^b
4.016	59 400 ^b
<i>Sample preparation</i>	
<i>time at 70°C (h)</i>	
0.75	70 800
1	72 000
2	71 200
3	69 400
4	68 900
<i>Time in eluent (h)^a</i>	
0.25	71 600
24	71 800
96	70 000
<i>Sample preparation</i>	
<i>temperature (°C)^c</i>	
60	72 000
70	72 600
85	72 800
105	57 000

^a Samples dissolved by heating at 70°C for 1 h.

^b Weight-average molecular masses measured by LALLS, S.D. \pm 2.5%.

^c Dissolution time 1 h.

volumes to the composition of the eluent is relatively small, fortunately, and the reproducibility of chromatograms is similar to that observed in single-component solvents.

Molecular-mass-sensitive detection: viscometry

Sudden changes in system pressure have deleterious effects on the baseline stability and calibration of viscometry detectors. Pressure changes can arise from leaks, pump failure, and bubble formation before and in the viscometry detector. The methylene chloride–DCAA eluent is prone to all of these: it is difficult to prevent bubble formation in the viscometer at room

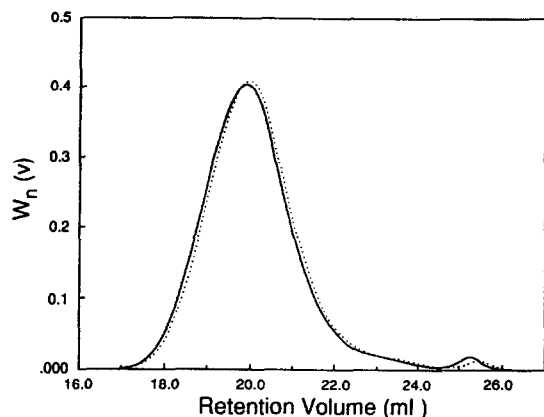


Fig. 5. Normalized UV chromatograms of PET 10388 in methylene chloride-DCAA (80:20) (solid) and methylene chloride-DCAA (90:10) (dotted). Both eluents contain 0.01 M TBAA.

temperature because of the low boiling point of methylene chloride, and the eluent occasionally cavitates in the pump heads, again because of its low boiling point. Also, DCAA tends to cause leaks around old stainless steel fittings, of which there are many in viscometry detectors. Passivation of stainless steel fittings with 6 M nitric acid minimizes this problem but does not completely eliminate it. From a practical standpoint, viscometry detection is only marginally viable with this eluent. Only relationships between viscosity and molecular mass (measured by DV detection) are presented, since they have some practical

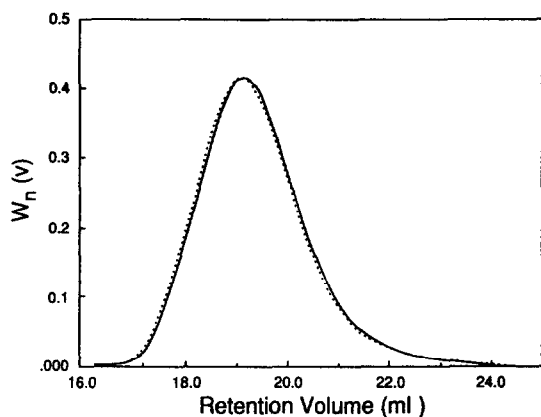


Fig. 6. Normalized chromatograms of NBS 706 in methylene chloride-DCAA (80:20) (solid) and methylene chloride-DCAA (90:10) (dotted).

utility in the routine calculation of absolute molecular masses using only a concentration-sensitive detector. For polystyrene in methylene chloride-DCAA (80:20) containing 0.01 M TBAA at 30°C, and $[\eta]$ in units of dl/g,

$$[\eta] = 0.00014M^{0.70} \quad (2)$$

and for PET,

$$[\eta] = 0.00045M^{0.68} \quad (3)$$

Molecular-mass-sensitive detection: light-scattering

The refractive indices of methylene chloride and DCAA are 1.46 and 1.42, respectively. The refractive index of the 80:20 mixture ($n = 1.43$) is low enough to provide sufficient contrast for DRI and light-scattering detection of PET. In addition, the refractive indices of methylene chloride and DCAA are close to one another, which greatly improves DRI baseline stability. Light-scattering detection involves simpler plumbing than viscometry detection, which minimizes the problems of leaks described above. In the case of LALLS, the weight-average molecular mass at each elution slice of the SEC chromatogram, $M_{w,i}$, is obtained from the excess Rayleigh scattering at each slice, $R_{\theta,i}$,

$$\frac{Kc_i}{R_{\theta,i}} = \frac{1}{M_{w,i}P(\theta)} + 2A_2c_i + 3A_3c_i^2 + \dots \quad (4)$$

where K is the optical constant. At the low concentrations of SEC, the concentration terms of the virial expression are negligible and at small angles the particle function $P(\theta) \sim 1.0$, thereby simplifying the calculation of $M_{w,i}$ to

$$M_{w,i} \approx \frac{R_{\theta,i}}{Kc_i} \quad (5)$$

The whole polymer \bar{M}_w can be obtained from the LALLS chromatogram alone,

$$\bar{M}_w = \frac{1}{Km} \sum R_{\theta,i} \Delta v_i \quad (6)$$

where m is the total sample mass injected and Δv_i is the volume between adjacent data points. The parameters needed are contained in the optical constant K ,

$$K = \frac{2\pi^2 n^2 (\text{dn/dc})_\mu^2 (1 + \cos^2 \theta)}{\lambda_0^4 N_A} \quad (7)$$

where n is the solvent refractive index, λ_0 is the wavelength of light in vacuum (632.8 nm), N_A is Avogadro's number, and $(\text{dn/dc})_\mu$ is the specific refractive index increment at constant chemical potential. Only $(\text{dn/dc})_\mu$ is unknown for polymer samples, but it can be measured from the multidetector SEC experiment.

Specific refractive index increment

The measurement of the specific refractive index increment in solvent mixtures at constant chemical composition, $(\text{dn/dc})_c$, can lead to erroneous results if the solvents differ in refractive index and if one of the solvent components preferentially solvates the polymer. Although the refractive indices of DCAA and methylene chloride are similar, these solvents are not iso-refractive and some concern must be raised about the static measurement of $(\text{dn/dc})_c$ at constant chemical composition. Berkowitz [28] showed that SEC using a DRI detector can be used to measure the specific refractive index increment at constant chemical potential, $(\text{dn/dc})_\mu$. Elution from the SEC column results in an exchange of solvent equivalent to exhaustive dialysis of the polymer solution. From this, the value of $(\text{dn/dc})_\mu$ for a polymer of known molecular mass is determined from the LALLS response [28] for $\cos^2 \theta \approx 1$.

$$(\text{dn/dc})_\mu = \left[\frac{\lambda_0^4 N_A \sum R_{\theta,i} \Delta v_i}{4\pi^2 n^2 \bar{M}_w m} \right]^{1/2} \quad (8)$$

A value of 0.155 is obtained for polystyrene at 632.8 nm is obtained. A response factor for the DRI detector is obtained from the polystyrene chromatogram area, A_{ps} , mass injected, m , and $(\text{dn/dc})_{\mu,ps} = 0.155$,

$$k_{\text{dri}} = \frac{A_{ps}}{m_{ps}} (\text{dn/dc})_{\mu,ps} \quad (9)$$

which is then used to calculate refractive index increments at constant chemical potential of polyester samples, $(\text{dn/dc})_{\mu,pe}$, from their SEC peak areas,

$$(\text{dn/dc})_{\mu,pe} = k_{\text{dri}} \frac{m_{pe}}{A_{pe}} \quad (10)$$

The salt peak at 25.9 ml in Fig. 3 is not included in the integration.

Although the DRI detector measurement is made at a different wavelength than that used by LALLS, this method approximates $(\text{dn/dc})_{\mu,pe}$ to within a few percent provided the value of $(\text{dn/dc})_{\mu,ps}$ at 632.8 nm (LALLS wavelength) is used in eqn. 9.

The measured value $(\text{dn/dc})_\mu = 0.148$ at 632.8 nm for PET in this solvent is higher than the value reported for PET in pure DCAA [29] ($\text{dn/dc} = 0.106$ at 589 nm) by an amount that is consistent with the difference in refractive indices of pure DCAA and methylene chloride–DCAA (80:20). Measurement of $(\text{dn/dc})_c$ at constant chemical composition in a KMX-16 differential refractometer for polystyrene = 0.156 indicates that preferential solvation actually does not seriously affect the measurement.

Absolute molecular mass distributions

Typical LALLS and UV chromatograms used for calculating molecular masses via eqn. 5 are shown in Fig. 7. The molecular mass distribution for a PET sample obtained from SEC-LALLS is shown in Fig. 8. The polydispersity (\bar{M}_w/\bar{M}_n) is considerably larger than 2.0 predicted for a most probable distribution. This is not uncommon in PET because of the presence of cyclic trimer (low-molecular-mass peak in Fig. 8). The dis-

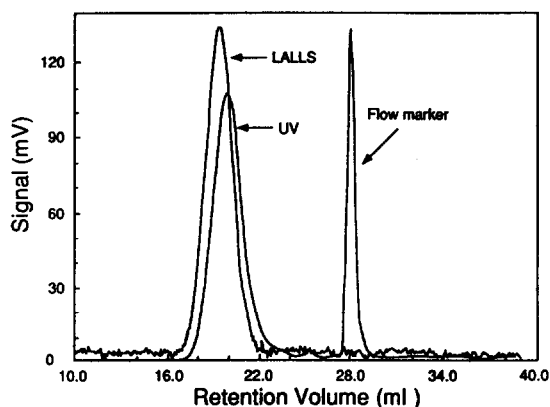


Fig. 7. UV and LALLS chromatograms of PET 10388.

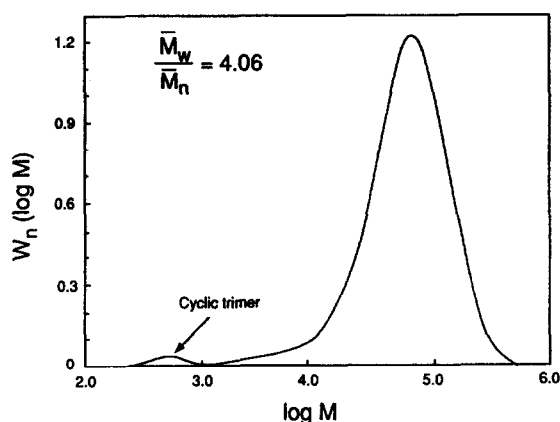


Fig. 8. Absolute molecular mass distribution of PET 10388, including cyclic trimer.

tribution obtained from excluding cyclic trimer gives the expected polydispersity for step-growth polymerization. The values for the whole polymer \bar{M}_w calculated from integration of the LALLS response (eqn. 6) given in Table II are in excellent agreement with the true values (measured by light-scattering for PET 10388, 9902, 7352) and given by the vendor (PET 39K). The coefficient of variation of \bar{M}_w ($\sim \pm 2.5\%$) is comparable to the precision reported for SEC-LALLS results for polystyrene in THF [30].

Application to other polyesters and polymers

This eluent has been successfully applied to the characterization of poly(ethylene 2,6-naphthalate) (PEN). PEN pellets dissolve in approximately 45 min and can be diluted to methylene chloride–DCAA (80:20, v/v) without immediate phase separation; however, some solutions form a gel at room temperature after

TABLE II

MEASURED AND CALCULATED VALUES FOR \bar{M}_w

Sample	Reported \bar{M}_w	\bar{M}_w SEC-LALLS
PET 39K	39 000	36 100 \pm 1000 ^a (2.8%) ^b
PET 10388	69 400	72 000 \pm 1800 (2.5%)
PET 9902	57 600	58 200 \pm 1200 (2.1%)
PET 7352	47 200	49 700 \pm 1300 (2.6%)

^a Sample estimate of the standard deviation, *s*.

^b Coefficient of variation, defined as (*s*/ \bar{M}_w) \times 100%.

1–2 days and should be run within 16 h of sample preparation. The molecular mass dependence of intrinsic viscosity (units of dl/g) of PEN in methylene chloride–DCAA (80:20) at 30°C is

$$[\eta] = 0.00046M^{0.64} \quad (11)$$

From the DRI response and eqn. 9, PEN (dn/dc) _{μ} = 0.195 at 632.8 nm. This large specific refractive index increment provides excellent LALLS response for samples of moderate (\bar{M}_w = 40 000) molecular mass.

This eluent is also suitable for SEC with LALLS detection of other aromatic polyesters, both branched and linear, and readily dissolves oriented films. It also dissolves highly crystalline polycarbonates, but causes molecular mass degradation within 1–2 hours.

CONCLUSIONS

The mixed solvent of methylene chloride–DCAA (80:20) containing 0.01 *M* TBAA has a number of desirable characteristics: it can be used at room temperature with both UV and DRI detectors, it is less expensive than eluents containing HFIP and pentafluorophenol, and degradation of PET is observed only after prolonged heating of samples at temperatures above 80°C or with water concentrations greater than 1% by volume. In addition, no loss of column efficiency and no increase in column back-pressure has been observed in nearly one year of continuous use. To its disadvantage, this eluent is difficult to use with the present design of differential capillary viscometer detectors. This disadvantage is offset by the compatibility of this eluent with light-scattering detection, which allows direct measurement of absolute molecular mass distributions.

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