

Viscosity–Molecular Weight Relationships for Poly(ethylene Terephthalate) in Hexafluoroisopropanol–Pentafluorophenol Using SEC–LALLS

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Synopsis

Viscosity–molecular weight characterization of poly(ethylene terephthalate) (PET) in hexafluoroisopropanol (HFIP), pentafluorophenol (PFP), and HFIP/PFP is reported for the first time using size exclusion chromatography–low angle laser light scattering (SEC–LALLS) measurements. These strong solvents are capable of dissolving PET under very mild conditions and therefore minimize polymer degradation. In addition these solvents are capable of dissolving PET samples which have poor solubility in more traditional PET solvents such as orthochlorophenol (OCP) and phenol/tetrachloroethane (PTCE). By combining molecular weight information, obtained without the need of any SEC calibration curves, with intrinsic viscosity measurements, on several broad molecular weight PET samples, the Mark–Houwink coefficients for the five PET–solvent systems mentioned above have been determined. The coefficients correspond to those which would be obtained by using a large number of relatively monodisperse samples of PET covering a molecular weight range of about 2×10^3 to 2×10^5 . Data is also provided which shows that intrinsic viscosities for PET in HFIP, PFP, HFIP/PFP, OCP, and PTCE can be determined from a single viscosity measurement at a finite concentration. Data for interconverting intrinsic viscosities determined in any of these five solvents is also given.

INTRODUCTION

In conducting molecular weight characterization studies on linear and branched PET, difficulties have at times been encountered in dissolving these polymers in such traditional solvents as orthochlorophenol (OCP) and phenol/tetrachloroethane (PTCE). In addition the exposure of PET to the high temperature required to dissolve this polymer in these solvents and to conduct size-exclusion chromatography (SEC) promotes the risk of polymer degradation.^{1,2} Hexafluoroisopropanol (HFIP), a known solvent for PET,^{3–5} a mixed solvent of HFIP with pentafluorophenol (PFP), and PFP have been found to be superior solvents capable of dissolving PET at room temperature or in the case of PFP at 60°C (an elevated temperature is required for PFP since it is a solid at room temperature) with no signs of polymer degradation. We have observed that in dissolving PET samples which are difficult to solution in OCP or PTCE that solutioning proceeds in the order of HFIP to HFIP/PFP to PFP with PFP being the best in terms of ease and speed. In this study we have used these solvents for the first time to characterize a series of linear PETs in terms of molecular weight and molecular weight distribution using SEC coupled to a low angle laser

light scattering (LALLS) detector.⁶ By combining the molecular weight information with intrinsic viscosity measurements the Mark-Houwink coefficients for these PET-solvent systems have been evaluated. Good agreement between calculated intrinsic viscosities (determined using these Mark-Houwink coefficients and SEC-LALLS chromatograms) and experimentally measured values of this parameter indicate that these coefficients are applicable over a molecular weight range from 2×10^3 to 2×10^5 . In addition we have also provided the appropriate information for interconverting viscosities between the five solvent systems mentioned above.

EXPERIMENTAL

Samples, Sample Preparation, and Solvents

Four linear unfractionated PET samples were used in this study. They were obtained from the Celanese Corp. The intrinsic viscosity of these samples, measured in OCP at 25°C, ranged in value from 0.20 to 0.92 dL/g. They are referred to in this report as samples 1-4 in order of increasing viscosity. All PET solutions were made on a wt/vol basis and dissolved by agitating solutions at room temperature in the case of HFIP and HFIP/PFP or in an oil bath at a temperature of 60°C for PFP or 120°C for OCP and PTCE. All solutions were filtered through either a 5.0 or 0.5 μm fluoropore filter (Millipore Corp.) before use. HFIP, PFP, and OCP were obtained from Dupont, Fairfield Chemicals, and Aldrich, respectively. These solvents were distilled once before use. Phenol/1,1,2,2-tetrachloroethane (60/40) and tetrahydrofuran (THF) were obtained from AquAir Corp. and Burdick and Jackson Lab., respectively, and used as received. HFIP/PFP (50/50) was made on a volume basis. All solvents used for SEC were degassed and filtered through a 5.0 μm fluoropore filter. Waste HFIP, PFP, and HFIP/PFP were saved and redistilled.

Instrumentation, Experimental Conditions, and Data Analysis for SEC-LALLS

SEC runs were made on a Waters 201 chromatography unit which consisted of a M-6000A pump, U6K injector, and a R401 differential refractive index (DRI) detector. SEC columns used for work conducted in HFIP consisted of a bank of three Dupont columns (SE-4000, SE-1000, and SE-100) while work conducted in HFIP/PFP used a bank of four columns obtained from Dupont and Waters (SE-4000, SE-1000, SE-100, and 60 \AA μ -Porasil). On-line light scattering measurements of SEC eluant and static measurement were made on a Chromatix KMX-6 Light Scattering Photometer equipped with a 5 mm stainless steel flow-through cell. All experiments were conducted in a fume hood at ambient temperature ($23 \pm 2^\circ\text{C}$) at flow rates of 1.2 mL/min in the case of HFIP and 0.5 mL/min in the case of HFIP/PFP. Light scattering measurements were made at a forward scattering angle of 6-7° (in air). The volume of sample injected into the SEC columns was 150 μL . The solvents used during SEC experiments were constantly agitated and kept under dry argon. Analog signals from the DRI

and LALLS detectors were recorded on a dual pen strip-recorder and then manually digitized. The excess Rayleigh ratio, $R_\theta(\text{rt})$, and the corresponding concentration $c(\text{rt})$ at various retention times, rt , across the chromatogram were then calculated via eq. (6) and (10) given in the paper by McConnell.⁷ The weight-average molecular weight $\bar{M}_w(\text{rt})$, at various rt values, were calculated using the following equation:

$$Kc(\text{rt})/R_\theta(\text{rt}) = 1/\bar{M}_w(\text{rt}) + 2A_2c(\text{rt}) \quad (1)$$

where $K = 2\pi^2 n_0^2 (1 - \cos^2 \theta) (dn/dc)^2 / N_{\lambda_0}$ (n_0 = solvent refractive index, dn/dc = the specific refractive index increment of PET in the solvent used and λ_0 = is the wavelength, in vacuum, of the incident light). An average value for the second virial coefficient A_2 of $2.9 \pm 0.4 \times 10^{-3} \text{ mol} \cdot \text{cc} \cdot \text{g}^{-2}$ was determined from static light scattering experiments and used for PET in both HFIP and HFIP/PFP. Although we have used an average value for A_2 , this parameter is in fact a weak function of molecular weight⁸ having a functional form given by

$$A_2 = \alpha M^{-\beta} \quad (2)$$

From experimental data on a number of different polymers⁹ β was found to have an average value of 0.23. Molecular weight calculations which incorporate this molecular weight dependence of A_2 were found to differ by only a few tenths of a percent, at most, from values calculated using this average value for A_2 .

Differential Refractometry

The specific refractive index increment, dn/dc , used for PET in HFIP was $0.257 \pm 0.004 \text{ cc g}^{-1}$.¹⁰ The partial specific refractive index increment measured at constant chemical potential, $(\partial n/\partial c)_\mu$, for PET in HFIP/PFP was $0.242 \pm 0.008 \text{ cc g}^{-1}$. This value was determined using the procedure developed by Berkowitz (10), which employed polystyrene in THF as well as PET in HFIP as the calibrating standards. This value differs considerably from the specific refractive index increment at constant chemical composition, $(\partial n/\partial c)_c$, of $0.277 \pm 0.010 \text{ cc g}^{-1}$ measured on a KMX-16 differential refractometer (Chromatix). Hence, substantial preferential solvation effects exist for this polymer-solvent system indicating the importance in using $(\partial n/\partial c)_\mu$ to obtain the correct molecular weight from light scattering measurement in mixed solvents.¹¹⁻¹⁴

Viscosity Measurements

All viscosity measurements, except for those made in PFP, were conducted at $25.00 \pm 0.02^\circ\text{C}$. In the case of PFP, viscosity measurements were made at a temperature of $60.00 \pm 0.02^\circ\text{C}$. All measurements were made over the concentration range of 0.1–1.0% wt/vol in Ubbelohde type viscometers either manually or automatically using an automatic viscometer (Schott America). Intrinsic viscosities were determined from the average

intercept obtained from plots of the data using the Huggin and Kraemer equations.^{15,16} In all cases good agreement between intercepts were obtained.

RESULTS

Molecular Weights

Values determined for \bar{M}_w , the number-average molecular weight, \bar{M}_n , and the molecular weight distribution, $MWD = \bar{M}_w/\bar{M}_n$, by SEC-LALLS for PET samples 1-4 in both HFIP and HFIP/PFP are given in Table I. The stability of PET in HFIP and PFP is demonstrated by the results given in Table II. Data shows that even after approximately 2 days at either room temperature in the case of HFIP/PFP or at 60°C in the case of PFP the calculated weight-average molecular weight of PET sample 4 is in good agreement with the value obtained after a very short exposure to these solvents. The stability of the porous silica column packings in both of these solvents is also very good. This is indicated by the negligible change in column performance after more than 2 years of work with the same column banks. Although SEC-LALLS gives the correct \bar{M}_w , independent of column resolution and band broadening effects,^{17,18} the \bar{M}_n obtained from this technique will be biased toward values higher than the true value.^{6,17-19} This is due to the limitation in the assumption that the instantaneous polydispersity within the flow-through cell is low enough that $M(rt) = \bar{M}_n(rt) = \bar{M}_w(rt)$, which results from imperfect column resolution and the poor response factor of the light scattering photometer at low molecular weights. Consequently, the MWD obtained will be biased low.

Mark-Houwink Coefficients

The Mark-Houwink equation

$$[\eta] = K\bar{M}_v^a \quad (3)$$

relates the intrinsic viscosity $[\eta]$ of a polymer to its viscosity average molecular weight \bar{M}_v . The coefficients K and a in eq. (3) are commonly obtained from the intercept and slope, respectively, of plots of $\log[\eta]$ (where $[\eta]$ is

TABLE I
PET Molecular Weights Determined in HFIP and HFIP/PFP by SEC-LALLS

Sample	\bar{M}_n^a		\bar{M}_w^b		MWD ^c	
	HFIP	HFIP/PFP	HFIP	HFIP/PFP	HFIP	HFIP/PFP
1	4700	4800	6900	6300	1.5	1.3
2	13,000	12,100	23,100	22,200	1.8	1.8
3	20,300	22,400	40,900	38,500	2.0	1.7
4	36,500	45,600	65,800	69,400	1.8	1.5

^a The percent fractional error (in terms of 1 standard deviation) for this parameter varied over the range ± 3 -12%.

^b The percent fractional error (in terms of 1 standard deviation) for this parameter varied over the range ± 2 -6%.

^c From the stated uncertainty in \bar{M}_n and \bar{M}_w , the percent fractional error (in terms of 1 standard deviation) for this parameter varied over the range ± 4 -14%.

TABLE II
Effect of Temperature and Time on Weight-Average Molecular Weight of PET (Sample 4) in HFIP/PFP

Average value determined in HFIP/PFP	20 h at room temperature in HFIP/PFP	40 h at room temperature in HFIP/PFP	1 h at 60°C in PFP	40 h at 60°C in PFP
69,400 ^a	64,400	69,900	67,700 ^b	70,500 ^b

^a Value obtained from Table I.

^b Samples were diluted 1:1 with HFIP after incubating in PFP.

the intrinsic viscosity determined on the unfractionated polymer sample) vs. $\log M$ (where M would usually correspond to number or weight average molecular weight for the unfractionated polymer samples). Correct values for K and a , however, are only obtained when the calibrating samples are monodisperse.^{20,21} To obtain the correct coefficients, a number of relatively monodisperse PET samples must be prepared over a wide range of molecular weights. The intrinsic viscosity and molecular weight of these samples must then be determined. This clearly represents a large project to carry out. Fortunately, this can be done very simply and quickly by realizing the SEC fractionates polymer samples such that the polydispersity of the material passing through the SEC detector at any instant is very low. Since the LALLS detectors yield the absolute molecular weight of this relatively monodisperse fraction, the only information lacking is the corresponding $[\eta]$ value for each fraction. To obtain this information, $[\eta]$ values were calculated for each unfractionated PET sample by using the $c(rt)$ and $M_w(rt)$ data, obtained from the SEC-LALLS experiment, in eq. (4)

$$[\eta] = \frac{\sum_i c_i [\eta]_i}{\sum_i c_i} = \frac{\sum_{rt} c(rt) K \{M_w(rt)\}^a}{\sum_{rt} c(rt)} \quad (4)$$

and an optimization search procedure which determines the best K and a values, which minimize δ^2 (the sum of the deviations between experimental and calculated $[\eta]$ values squared):

$$\delta^2 = \sum_i ([\eta]_{\text{expt}} - [\eta]_{\text{calcd}})_i^2 \quad (5)$$

The optimum Mark-Houwink coefficients for all five solvents are given in Table III. A summary of measured and calculated intrinsic viscosities for

TABLE III
Mark-Houwink Coefficients for PET in Various Solvents

Solvent	K^a	a
OCP	6.31×10^{-4}	0.658
PTCE	7.44×10^{-4}	0.648
HFIP	5.20×10^{-4}	0.695
PFP	3.85×10^{-4}	0.723
HFIP/PFP	4.50×10^{-4}	0.705

^a Values for K are in units of $\text{dL} \cdot \text{g}^{-1}$.

each solvent is also given in Table IV. In conducting routine viscosity measurements on a large number of samples, the time required to evaluate intrinsic viscosities via dilution series is too long. A single point measurement would be preferable. Such a procedure has been developed,^{22,23} which employs the following equation:

$$[\eta] = (2\{\eta_{sp} - \ln \eta_{rel}\})^{0.5}/c \quad (6)$$

where η_{rel} is the relative viscosity and η_{sp} is the specific viscosity. In this procedure a single viscosity measurement conducted at a finite concentration will yield $[\eta]$. The application of this equation to any polymer-solvent system is valid given that it satisfies several requirements.²⁴ The feasibility of using eq. (6) for calculating $[\eta]$ of PET in the solvent systems studied in this paper is verified by the good agreement of these calculated values with values determined at zero concentration (see Table IV).

TABLE IV
Summary of Experimental and Calculated Intrinsic Viscosities^a for PET in Various Solvents

Sample	$[\eta]_{\text{expt}}^b$	$[\eta]_{\text{expt}}^c$	$[\eta]_{\text{SEC-LALLS}}^d$	Solvent
1	0.20	0.19	0.20	OCP
2	0.44	0.44	0.44	OCP
3	0.62	0.63	0.63	OCP
4	0.92	0.91	0.92	OCP
1	0.21	0.20	0.22	PTCE
2	0.46	0.46	0.47	PTCE
3	0.65	0.65	0.67	PTCE
4	0.98	0.96	0.97	PTCE
1	0.22	0.22	0.22	HFIP
2	0.54	0.53	0.54	HFIP
3	0.79	0.79	0.78	HFIP
4	1.09	1.10	1.13	HFIP
1	0.20	0.20	0.21	PFP
2	0.53	0.53	0.52	PFP
3	0.79	0.78	0.78	PFP
4	1.08	1.10	1.16	PFP
1	0.22	0.24	0.22	HFIP/PFP
2	0.56	0.56	0.54	HFIP/PFP
3	0.81	0.78	0.80	HFIP/PFP
4	1.15	1.14	1.19	HFIP/PFP

^a All intrinsic viscosities are reported in units of dL g⁻¹.

^b Intrinsic viscosities were obtained by extrapolation to zero concentration. The percent fractional error (in terms of 1 standard deviation) observed for this parameter was less than or equal to $\pm 3\%$.

^c Intrinsic viscosities were calculated from eq. (6) using viscosity data obtained at 0.5% wt/vol. The percent fractional error (in terms of 1 standard deviation) observed for this parameter was less than or equal to $\pm 3\%$.

^d These intrinsic viscosities represent the average of values calculated from SEC-LALLS runs in HFIP and HFIP/PFP. The percent fractional error (in terms of 1 standard deviation) observed for this parameter was less than or equal to $\pm 5\%$.

In order to permit the interconversion of $[\eta]$ for PET between the five solvents discussed in this paper, plots of $[\eta]$ in OCP vs. $[\eta]$ in HFIP, PFP, HFIP/PFP, or PTCE were made and fitted to a second order polynomial of the following form:

$$[\eta]_{\text{OCP}} = a' + b'[\eta] + c'[\eta]^2 \quad (7)$$

The coefficients for eq. (7) for each of the four plots are given in Table V. By using these coefficients and the quadratic equation $[\eta]$ determined for PET in one solvent can be converted to the corresponding $[\eta]$, which would be obtained in any of the other four solvents. The agreement of these calculated $[\eta]$ with experimentally measured values has been found to average $\pm 2-3\%$.

DISCUSSION

It has been our experience that HFIP, HFIP/PFP, and PFP are excellent solvents for PET samples, especially for samples which are difficult to dissolve in such common PET solvents as OCP or PTCE. We have observed that in dissolving PET that the solutioning power of these solvents proceeds in the order of HFIP to HFIP/PFP to PFP, with PFP being the best in terms of ease and speed. In addition, these solvents drastically reduce the risk of hydrolytic degradation from the exposure of PET to the high temperatures normally required to dissolve this polymer in traditional PET solvents and for conducting SEC measurements.^{1,2} Although claims have been made that HFIP degrades PET,³ we have not observed any instability with either HFIP or PFP. We have also shown that combined SEC-LALLS and intrinsic viscosity measurements (for unfractionated samples) can readily provide the correct Mark-Houwink coefficients, corresponding to those which would be obtained by using a wide range of relatively monodisperse PET samples, in a short period of time. The good agreement between calculated (determined using the Mark-Houwink coefficients obtained in this study and SEC-LALLS chromatograms) and measured intrinsic viscosities indicates that these coefficients are applicable over the molecular weight range of about 2000-200,000. The feasibility of such a method has been reported previously^{25,26} using normal SEC. SEC-LALLS, however, provides these parameters without any need for calibration curves. Although no corrections were made for band-broadening effects,^{27,28} the resolution provided by the SEC columns and the small difference between \bar{M}_v and \bar{M}_w for values of α encountered in this work make corrections for calculating $[\eta]$ negligible. Furthermore, development and commercialization of an on-line

TABLE V
Values for Coefficients in Eq. (7) for Various Solvents

Solvent	a'	b'	c'
PTCE	-0.02675	1.07766	-0.11495
HFIP	0.06823	0.57189	0.19283
PFP	0.08986	0.51523	0.23593
HFIP/PFP	0.05804	0.61361	0.11654

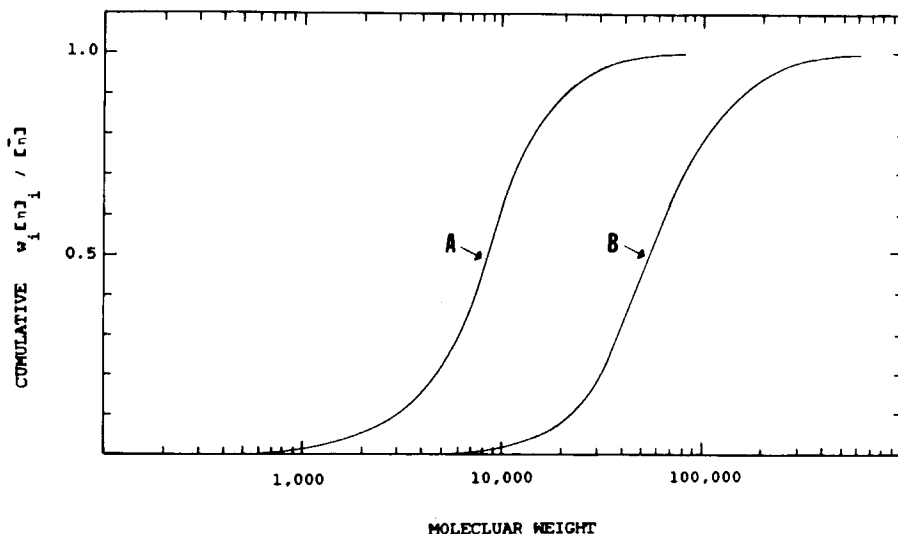


Fig. 1. Plots of cumulative weight viscosity fraction vs. molecular weight for (A) sample 1, which has the lowest viscosity, and (B) sample 4, which has the highest viscosity.

viscometer²⁹ for SEC units will eventually allow direct evaluation of these coefficients during SEC experiments using a three detector system. It should be noted that several samples covering a molecular weight range as wide as possible should be used since for any given sample the major contribution to $[\eta]$ is made by a rather limited molecular weight range (see Fig. 1). This is due to the molecular weight dependence of viscosity and the form of the concentration distribution as a function of molecular weight.

A major drawback in the use of HFIP and PFP is their extreme high cost. However, most of the waste solvent can be recovered by redistillation resulting in a considerable cost reduction. Furthermore, the use of small amounts of solvent normally required for viscosity measurements and with the development of SEC columns having small total volumes³⁰ the actual cost can be further reduced.

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