Molecular Mass Determination and Dilute Solution Properties of Polyether from Bisphenols and 4,4'-Dichlorodiphenyl Sulfone

Y. Charlier, P. Godard,† and D. Daoust*

Université Catholique de Louvain, Laboratoire des Hauts Polymères, 1, B-1348 Louvain-la-Neuve, Belgium

C. Strazielle

Institut Charles Sadron, rue Boussingault 6, F-67083 Strasbourg, France

Received December 7, 1993; Revised Manuscript Received April 5, 1994®

ABSTRACT: Molecular characterization of PES by light scattering, viscometry, and size exclusion chromatography (SEC) is described. A Mark-Houwink-Sakurada relationship in NMP + 0.1 M LiBr is established. From specific and universal calibrations, absolute molecular masses of PES are obtained by SEC. Number average molecular masses from SEC and ^{1}H NMR are compared. The study of PES conformation in dilute solution reveals a high flexibility of the PES chain in a good solvent. The σ factor is close to 1, and the Kuhn statistical element contains approximately six repeat units.

Introduction

In the area of high-temperature resistant polymers, poly(ether sulfones) take an important place. Among them poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES) is currently one of the most developed. This polymer is synthesized by polycondensation of 4,4'-dichlorodiphenyl sulfone with 4,4'-dihydroxydiphenyl sulfone in a high boiling point dipolar aprotic solvent.[1] As can be seen from its structure (Chart 1), PES is a polymer containing stiff sequences along with ether bonds which are known to be totally flexible.[2] Owing to its amorphous character, PES easily dissolves in classical polar solvents such as dimethyl sulfoxide (DMSO), sulfolane, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*'-dimethylformamide (DMF), dimethylacetamide (DMAc), ... PES is also "sensitive" to methylene chloride and acetone.

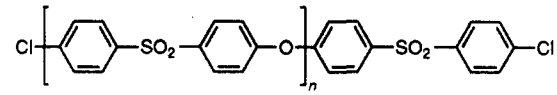
Due to its high T_g (±225 °C), PES is of particular interest for high-temperature applications. Its mechanical properties remain attractive up to 200 °C. PES exhibits toughness and impact resistance at low temperature and deformation resistance at high temperature.[3]

From a general point of view, the determination of the molecular masses and their distribution is often very important in macromolecular engineering. In this field, size exclusion chromatography (SEC) is of great interest. However, SEC is intrinsically a relative method and needs some calibration to obtain absolute characterization.

Very few data are available[4] about PES SEC. One of the reasons is that no isomolecular standards or viscosity laws are available to allow the establishment of PES calibration curves.

This paper is devoted to the development of a SEC method for PES molecular mass characterization in order to routinely obtain absolute molecular mass values. Toward this goal, established techniques like light scattering (LS) and viscometry will be used to determine absolute weight average molecular masses of PES samples selected as standards, and consequently, a Mark-Houwink-Sakurada relationship. These preliminary experiments must allow the establishment of specific and universal calibration procedures. A second objective of the work is to analyze the conformational behavior of PES in dilute solution in a good solvent.

Chart 1. PES Chemical Structure



Experimental Section

1. **Material.** Since only high molecular mass PES are commercially available (PES 3-5), samples of lower molecular mass (PES 1 and 2) were prepared by transetherification of PES 3 in the presence of a calculated amount of sodium phenoxide. PES 3-5 are commercial grades supplied by ICI under the trade name Victrex 3600 P, 4100 P, and 5200 P, respectively.

2. **Solvents.** The solvents *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) were distilled in the presence of calcium hydride under vacuum and stored over molecular sieves. They were used with or without salt (LiBr, 0.1 M).

3. **Calibration Agents.** Ten practically isomolecular poly(methyl methacrylate) (PMMA) samples with molecular masses ranging from 2400 to 1 400 000 g/mol were used as primary SEC standards. They were provided by Polymer Laboratories Ltd. (reference 2020-0101).

4. **Light Scattering.** Light scattering measurements were performed at room temperature on centrifuged solutions with a Fica 50 instrument equipped with vertically polarized light at 546 nm. The refractive index increments (dn/dc) measured at 546 nm with a Brice-Phoenix differential refractometer were 0.158 mL/g in NMP + LiBr (0.1 M), 0.165 mL/g in NMP, 0.189 mL/g in DMF + LiBr (0.1 M), and 0.192 mL/g in DMF. The depolarization factor (ρ_v) was calculated from the ratio between the horizontal and vertical light components. To improve the dissolution process, the solutions were heated for 30 min at 90 °C before centrifugation at 14 000 rpm for 2 h.

5. **Viscometry.** The viscosity measurements were carried out with the AVS 350 Duran Schott automatic viscometer at a temperature of 25 °C. The samples were previously dissolved in NMP + LiBr (0.1 M) at 80 °C for 45 min.

6. **Size Exclusion Chromatography.** Two mixed bed Shodex columns (reference AM 80M/S) from Showa Denko were set in an oven at a temperature of 25 °C. The solvent NMP + LiBr (0.1 M) was continuously degassed by He at a flow rate of 0.8 mL/min. The chromatograms were obtained using a Perkin-Elmer UV detector (Model LC55) working at a wavelength of 270 nm and a 410 Millipore-Waters differential refractometer (DRI). The SEC apparatus was connected with a Microvax 2000 computer from Digital for the acquisition and the treatment of

* To whom all correspondence should be addressed.
† Research Associate of the National Fund for Scientific Research (FNRS).
® Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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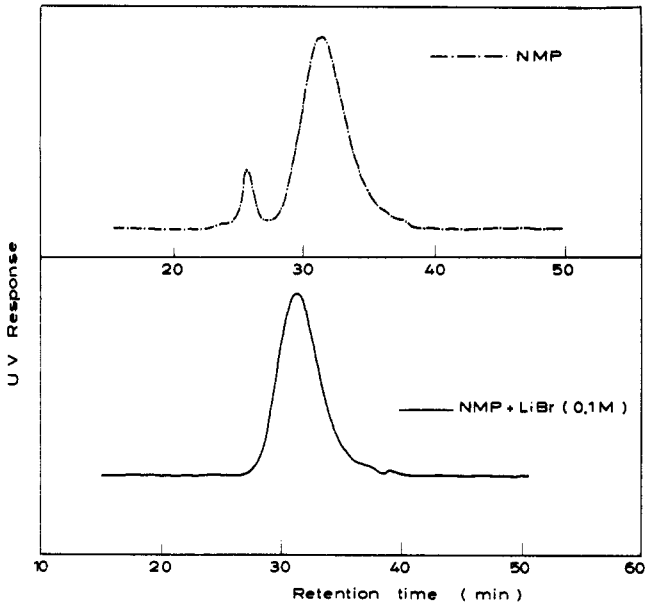

Figure 1. Steric exclusion chromatography of PES 3: (a, top) in pure NMP; (b, bottom) in NMP + LiBr (0.1 M).

the data. The injection conditions were as follows: sample size, 50 μL; PMMA concentration, 2 g/L (DRI detection); PES concentration, 0.4 g/L (UV detection).

7. **^{1}H NMR.** ^{1}H NMR spectra of PES were taken in DMSO-d_6 at room temperature on a Bruker AM 500. Typical experimental conditions were as follows: concentration, ±20 g/L; scan frequency, 500 MHz; spectral width, 8000 Hz; pulse width, 15 μs; relaxation delay, 2 s; shift reference, TMS.

Results and Discussion

A. Molecular Mass Characterization. 1. Choice of the Solvent. Figure 1a reports the SEC analysis of a PES 3 sample performed in pure NMP. The chromatogram exhibits a major peak between the exclusion and permeation volumes and also a smaller one close to the exclusion volume. It must be noted that a similar observation was also made when working with pure DMF. Such unexpected chromatograms showing multiple peaks were also observed for other polar polymers such as PVDF,[5] polyurethanes,[6] polyacrylonitriles,[7,8] polyamides,[9] .... In the case of PES, this effect has also been previously mentioned.[4] The proposed interpretation was based on chain branching.

To more fully understand this phenomenon, a viscometric study of PES in pure NMP was undertaken. An unusual upward curvature of the reduced viscosity versus concentration was observed (Figure 2). Such behavior was already reported for weakly charged polyelectrolytes in organic polar solvents.[10-13] This effect, appearing at high dilution, could be attributed to the presence of presumably "adsorbed" ionic residues coming from the synthesis[1] (salt like Na_2CO_3). The polyelectrolyte nature of the effect is clearly demonstrated from the result of salt addition on the viscosity plot (Figure 2). The dependence between reduced viscosity and concentration is linear and correct intrinsic viscosities can then be determined.

Therefore, it was decided to use NMP + LiBr (0.1 M) as the SEC mobile phase. Figure 1b shows the SEC analysis of the same PES sample in NMP + LiBr (0.1 M). In NMP (or DMF) containing salt, no peak appears close to the exclusion volume. In fact, classical elution and peak shape are obtained.

2. Light Scattering Characterization. The weight average molecular masses ($\bar{M}_w$) of the five PES samples were determined from light scattering experiments. The

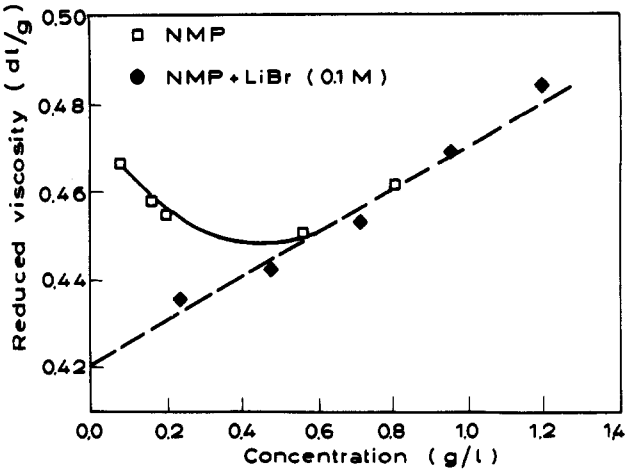

Figure 2. Variation of reduced viscosity versus concentration for PES 3 in pure NMP and NMP + LiBr (0.1 M).

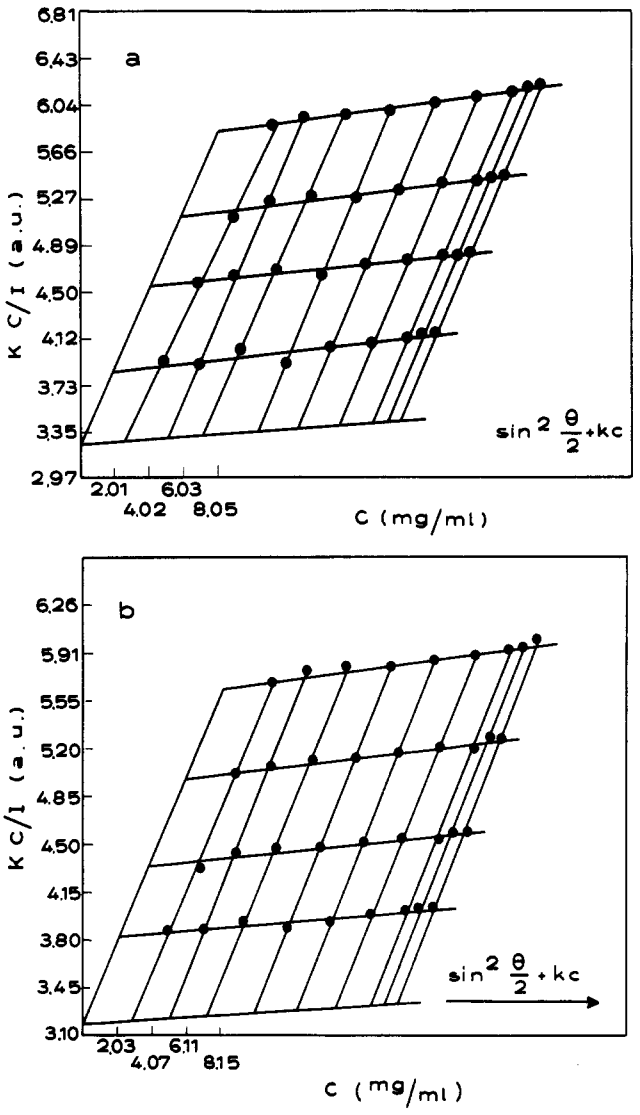

Figure 3. Zimm plots of PES 3: (a, top) in pure NMP; (b, bottom) in NMP + LiBr (0.1 M).

measurements were carried out mainly in NMP + LiBr (0.1 M) but also in pure NMP. The Zimm plots obtained in both LS conditions are reported in Figure 3 for PES 3. They show identical results. Indeed, no polyelectrolyte effect is observed because the lowest LS concentration remains above the minimum value for which this effect can appear.

Table 1. Characteristic Light Scattering Parameters of DCDPS[a] and of PES Standards and Intrinsic Viscosities of PES Standards in NMP + LiBr (0.1 M)

	ρ_v	$\bar{M}_w$ (g/mol)	$\bar{n}_w$	$10^4 A_2$ (mol mL^{-1} g^{-2})	δ^2	$[\eta]^b$ (dL/g)
DCDPS	0.375	216	1		1.25	
PES 1	0.067	6 000	26	9.1	0.12	0.12
PES 2	0.053	12 200	53	5.1	0.09	0.17
PES 3	0.01	31 300	135	14.9	0.02	0.42
PES 4		35 500	153	16.0		0.50
PES 5		50 000	216	15.6		0.54

[a] 4,4'-Dichlorodiphenyl sulfone. [b] At 25 °C.

Table 2. Light Scattering Characterization of the PES 5 Sample in Various Experimental Conditions

solvent	$\bar{M}_w$	$10^4 A_2$ (mol mL^{-1} g^{-2})
NMP	50 400	15.6
NMP + LiBr (0.1 M)	50 000	15.6
DMF	49 000	8.9
DMF + LiBr (0.1 M)	50 300	7.4

On the other hand, it can be seen that the angular distribution of the scattered light is symmetrical around $\theta = 90°$ ($I_{135°}/I_{45°} = 1$) and thus can be considered as independent of the observation angle θ. This indicates the absence of any aggregate in the range of the concentrations used.

Table 1 reports the values of the depolarization factor (ρ_v), of the weight average molecular mass ($\bar{M}_w$), of the weight average number of repeat units ($\bar{n}_w$), and of the second virial coefficient (A_2) for the five PES samples. The $\bar{M}_w$ values were corrected using the Cabannes factors $(3 + 3\rho_v)/(3 - 4\rho_v)$ due to the anisotropy observed for the low molecular mass PES.

In order to check the reliability of the LS results from PES–NMP solutions, supplementary analyses were also performed in pure DMF or in DMF + salt.

Table 2 gives the weight average molecular mass ($\bar{M}_w$) and the second virial coefficient (A_2) for PES 5 in various conditions. A good reproducibility is obtained whatever the nature of the solvent.

3. Mark–Houwink–Sakurada Relationship (MHS) in NMP + LiBr (0.1 M). No Mark–Houwink–Sakurada relationship for PES in this peculiar solvent is available in the literature. Therefore, the intrinsic viscosities were measured for the five PES standards in NMP + LiBr (0.1 M). The values, presented in Table 1, were calculated from arithmetical mean of the reduced and inherent viscosities extrapolated to zero concentration. From Table 1, a MHS relationship for PES in NMP + LiBr (0.1 M) at 25 °C was deduced. This can be expressed by the following equation:

$$[\eta] = K\bar{M}_w^{\alpha} = 1.33 \times 10^{-4}\bar{M}_w^{0.77} \quad (1)$$

where $[\eta]$ is given in dL/g. The MHS constants K and α are equal to 1.33×10^{-4} and 0.77 ± 0.02, respectively. The high value of the parameter α indicates that NMP + LiBr (0.1 M) is a good solvent for PES and could be correlated to the high value of A_2 obtained from light scattering. Figure 4 illustrates this viscosity law.

4. SEC Molecular Mass Characterization. Establishment of the Specific Calibration Curve. The determination of absolute molecular masses from SEC analysis necessitates the use of calibration agents. Ten practically isomolecular PMMA were chosen as standards to cover a domain of molecular mass as wide as possible. Their molecular masses range from 2400 to 1.4×10^6 g/mol. By using these standards, a PMMA specific calibration was performed.

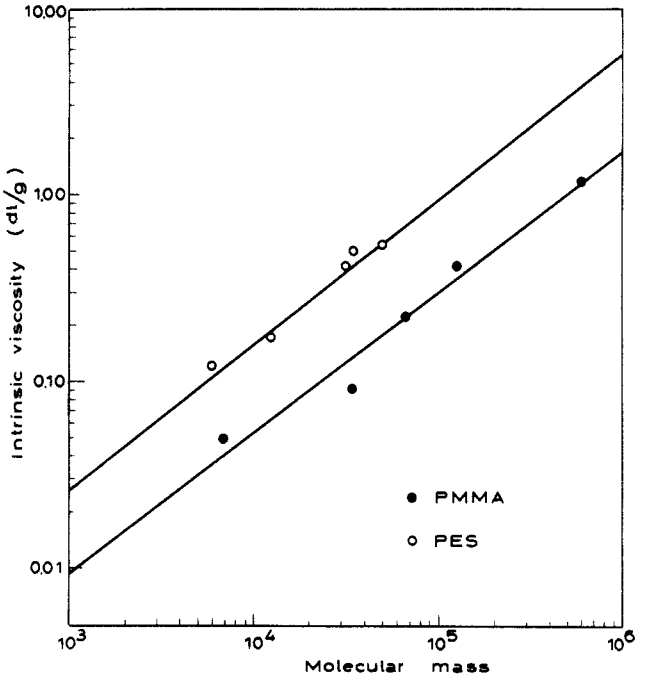

Figure 4. Logarithmic plot of intrinsic viscosity against molecular mass in NMP + LiBr (0.1 M) at 25 °C for PES and PMMA standards.

Table 3. PES Molecular Masses Obtained from Light Scattering (LS) and from Specific and Universal SEC Calibrations

	$\bar{M}_w$ (g/mol)				
samples	from LS	from PMMA calibration	from PES specific calibration	from universal calibration	M_p[a] (g/mol)
PES 1	5 970	10 450	5 400	5 900	4 460
PES 2	12 260	21 650	11 200	11 700	9 900
PES 3	31 200	59 400	30 600	30 200	27 100
PES 4	35 500	70 100	36 100	35 400	31 200
PES 5	50 000	97 600	50 400	48 300	48 000

[a] Molecular mass at the top of the chromatographic molecular distribution (from the specific calibration).

From the chromatographic analyses of the five PES standards and using the PMMA specific calibration, it was easy to determine the PES molecular masses at the peak maximum (M_{p_1}) in PMMA equivalents and their weight average molecular masses ($\bar{M}_{w_1}$). As weight average molecular masses from light scattering and from PMMA calibration do not agree, the molecular mass at the top of the peak must be corrected using the following relationship:

$$M_{p_2} = M_{p_1}\frac{\bar{M}_{wLS}}{\bar{M}_{w_1}} \quad (2)$$

These five corrected M_{p_2} values allowed the construction of a new calibration curve. This iterative process, more completely described elsewhere,[14] was repeated until the calculated $\bar{M}_w$ value was very close to the light scattering one. Table 3 reports the values obtained using such a procedure for the establishment of the specific PES calibration.

Good agreement (around 5%) was obtained between the calculated $\bar{M}_w$ values and the ones measured by light scattering. This calibration also has allowed the determination of the peak top molecular mass values (M_p) reported in Table 3. These values were used for the determination of the universal calibration curve.

Table 4. Intrinsic Viscosities ([η]) of PMMA Standards in NMP + LiBr (0.1 M) at 25 °C

samples	M_p[a]	[η] (dL/g)
PMMA 1	6 950	0.05
PMMA 2	34 500	0.09
PMMA 3	67 000	0.22
PMMA 4	127 000	0.42
PMMA 5	610 000	1.18

[a] Molecular mass at the top of the chromatographic peak.

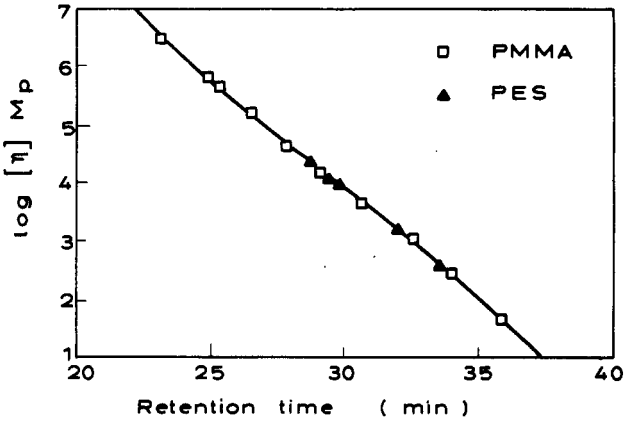

Figure 5. Universal calibration curve.

Establishment of the Universal Calibration Curve. The establishment of the universal calibration curve necessitates the determination of the Mark–Houwink–Sakurada relationship for PMMA in NMP + 0.1 M LiBr. The intrinsic viscosities measured at 25 °C for the five PMMA standards are presented in Table 4. The MHS relationship can be written as follows:

$$[\eta] = KM^{\alpha} = 5.4 \times 10^{-5} M_p^{0.75} \qquad (3)$$

where [η] is expressed in dL/g, K and α being equal to 5.4×10^{-5} and 0.75 ± 0.02, respectively (Figure 4).

When, in SEC, the separation results only from pure size exclusion, a relationship between the hydrodynamic volume, represented by the product $[\eta]M_p$, and the SEC retention time (RT) can be obtained.[15]

The values of $[\eta]M_p$ were calculated for each PMMA and PES standard and are related to the SEC retention time at the peak maximum. Figure 5 shows the universal calibration from PMMA standards. As the five PES standards do not cover a wide range of molecular masses, it was then not reasonable to calculate the universal calibration curve from PES standards. However, it is very important to observe from Figure 5 that for the five PES standards, the log $[\eta]M_p$ values versus the RT are located on the universal calibration curve established with PMMA standards. This confirms the validity of the Mark–Houwink–Sakurada relationships presented before. This also indicates that, in these SEC operation conditions, the separation is performed only from size exclusion phenomena without any side interaction. PMMA standards have been preferred to polystyrene standards because polystyrene exhibits some retention effects, especially in the range of low molecular masses.[16]

Table 3 gives the PES weight average molecular masses calculated from the universal calibration. As can be observed, the agreement between the values obtained from specific or universal calibrations seems to be very good. Moreover, the SEC $\bar{M}_w$ values are very close to the ones obtained from light scattering.

5. Number Average Molecular Masses from ^{1}H NMR. PES 3–5 samples contain chloride aryl sulfone chain ends.[1] These samples were analyzed by ^{1}H NMR in order to determine the number of chain ends and consequently the $\bar{M}_n$ values (Figure 6). The results are presented in Table 5, where the SEC $\bar{M}_n$ values are also given.

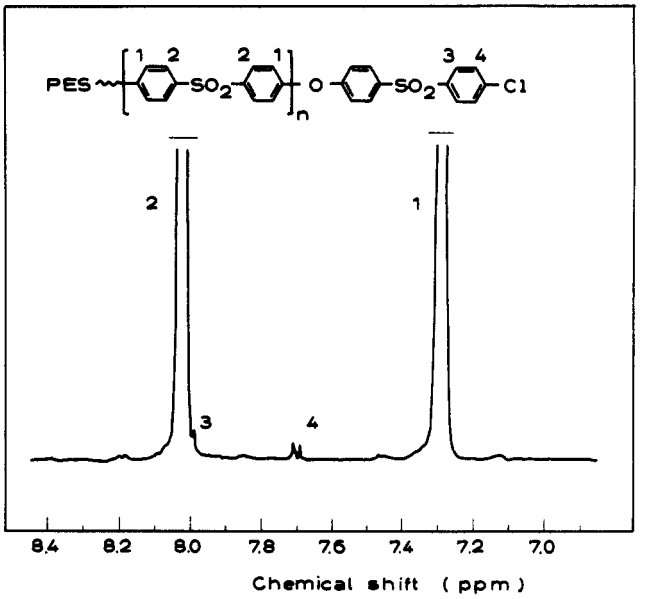

Figure 6. ^{1}H NMR spectrum of PES 5 in DMSO-d_6.

Table 5. Number Average Molecular Masses ($\bar{M}_n$, g/mol) from ^{1}H NMR and SEC Experiments

samples	^{1}H NMR	SEC
PES 3	14 200	13 900
PES 4	18 100	15 700
PES 5	25 000	20 200

This table shows that the agreement between ^{1}H NMR and SEC $\bar{M}_n$ is very satisfactory for the PES 3 sample. For the higher molecular mass samples, a difference of between 15 and 25% was found. It is obvious that the measurement of chain end content becomes less accurate as the molecular mass increases. On the other hand, it is also possible that some hydroxyl chain ends are present in some PES samples.

However that may be, the excellent correspondence between ^{1}H NMR and SEC values for PES 3 confirms the validity of the SEC method developed in this work.

B. Dilute Solution Properties. 1. Unperturbed Dimensions. The evaluation of unperturbed chain dimensions is performed more conveniently and accurately from the measurement of the polymer intrinsic viscosity at or near the Θ conditions. However the identification of a Θ solvent is not always easy for polycondensates. Furthermore, the root-mean-square radius of gyration ($R_{G,z}$) determined by light scattering is a z-averaged quantity. It is thus strongly affected by the molecular mass distribution. It is also well-known that measurements of $R_{G,z}$ less than about 15 nm are impractical with conventional light sources. Consequently, light scattering characterization is often confined to the higher molecular masses where the contribution of the excluded volume interaction is most significant. This explains why viscometric experiments carried out in rather good solvents are used to approach the unperturbed dimensions.[17]

In this field, the extrapolation procedure to a molecular mass of zero is performed to remove the excluded volume interactions. One of the most frequently used viscometric treatments is the Burchard–Stockmayer–Fixman plot of $[\eta]M^{-0.5}$ versus $M^{0.5}$.[18,19]

$$\frac{[\eta]}{\bar{M}_w^{0.5}} = K_\Theta + 0.51B\Phi_0\bar{M}_w^{0.5} \quad (4)$$

where K_Θ is the MHS K parameter for a Θ solvent and B the polymer–solvent interaction parameter related to A_2.

From the value of K_Θ and from the Fox–Flory equation, an unperturbed dimension $\langle r_o^2\rangle$ can be evaluated by using

$$K_\Theta = \Phi_0\left(\frac{\langle r_o^2\rangle}{\bar{M}_w}\right)^{3/2} \quad (5)$$

where $\langle r_o^2\rangle$ is the average unperturbed mean-square end-to-end distance and Φ_0 is the Flory constant, for which the most used value is 2.5×10^{21} with $[\eta]$ expressed in dL·g^{-1}.[20,21] From the results reported in Table 1, the following BSF relationship was determined (Figure 7):

$$[\eta]/\bar{M}_w^{0.5} = 8.7 \times 10^{-4} + 7.95 \times 10^{-6}\bar{M}_w^{0.5} \quad (6)$$

Using 8.7×10^{-4} for K_Θ, one calculates $A = [\langle r_0^2\rangle/\bar{M}_w]^{0.5}$ equal to 0.704 Å. The scattering of the calculated points (see Figure 7) does not justify a correction for molecular mass heterogeneity.

Since

$$\langle r_o^2\rangle = 6(R_{G,w}^2)_o \quad (7)$$

the unperturbed weight average gyration radii $(R_{G,w})_o$ can be calculated. Table 6 summarizes the results of $(\langle r_o^2\rangle)^{1/2}$ and of $(R_{G,w})_o$ for PES 3–5.

2. Perturbed Dimensions, Viscosity Expansion Factor, and Interaction Parameter χ. A viscosity average radius of gyration $(R_{G,\eta})$ which can be considered as a combination of the radius of gyration R_G (from angular dependence of light or neutron scattering intensity) and of the hydrodynamic radius R_H (from diffusion and sedimentation coefficients)[22,23] was calculated from the intrinsic viscosity using the Fox–Flory equation:[21]

$$[\eta] = \Phi'\frac{R_{G,\eta}^3}{\bar{M}_w} \quad (8)$$

Flory's viscosity constant Φ' was determined by using the relationship derived by Ptitsyn and Eizner:[24]

$$\Phi' = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)6^{3/2} \quad (9)$$

where Φ_0 is 2.5×10^{21}, $\epsilon = (2\alpha - 1)/3$, and $\alpha = 0.77$ obtained from the Mark–Houwink–Sakurada relationship (1). The Flory constant is assumed to show no significant change with the molecular mass.

The values calculated for $R_{G,\eta}$ are presented in Table 6. From $(R_{G,w})_o$ and $R_{G,\eta}$ values, the viscometric expansion factors α_η were determined and reported in Table 6.

Alternatively, the interaction parameter χ can also be evaluated by using the BSF treatment. Indeed, eq 4 contains the parameter B equal to

$$B = \frac{2\bar{\nu}_2^2}{N_A V_1}\left(\frac{1}{2} - \chi\right) \quad (10)$$

where $\bar{\nu}_2$ is the polymer specific volume, N_A is Avogadro's number, and V_1 is the solvent molar volume.

Using a B value of 6.24×10^{-27} (see eq 6) and taking into account that $\bar{\nu}_2 = 0.81$ cm^3·g^{-1} and $V_1 = 96$ cm^3·mol^{-1}, a value of 0.22 is calculated for the interaction parameter χ.

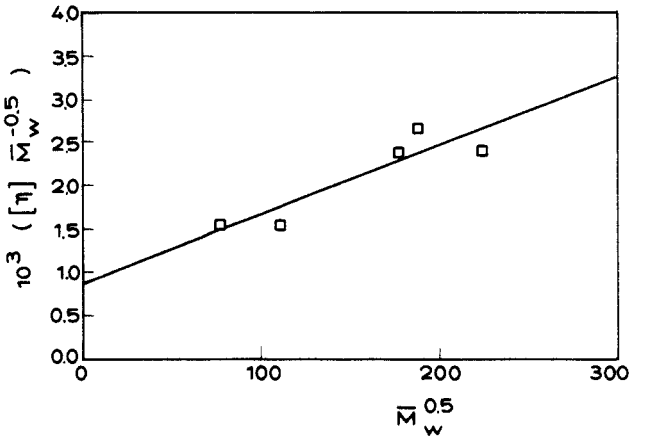

Figure 7. Burchard–Stockmayer–Fixman treatment for PES in NMP + LiBr (0.1 M).

Table 6. Average Unperturbed Root-Mean-Square End-to-End Distances $(\langle r_0^2\rangle)^{1/2}$, Gyration Radii, and Viscometric Expansion Coefficients (α_η) for PES 3–5

samples	$(\langle r_0^2\rangle)^{1/2a}$	$(R_{G,w})_0{}^b$	$R_{G,\eta}{}^c$	α_η
PES 3	124	51	83	1.63
PES 4	133	54	92	1.70
PES 5	157	64	106	1.66

[a] From the BSF viscometric treatment. [b] From eq 7. [c] From eqs 8 and 9.

A value of χ equal to 0.25 has also been calculated for PES 3–5 samples from the second viral coefficient A_2 of Flory and Krigbaum by means of the $F(X)$ function.[21]

3. PES Conformation. Several methods can be used to evaluate the chain flexibility or rigidity. In this work, this was performed using the value of exponent α of the MHS law, light scattering data (gyration radius and chain anisotropy), the evaluation of the conformation factor (σ) and of the characteristic ratio (C_∞) and of the Kuhn segment length $(l\mathrm{k})$ [or the persistance length (q)].[17,25]

Viscometry Law. From relationship 1 it appears that the value of the exponent α of the viscosity law of PES in NMP–salt falls between 0.5 and 0.8. In fact, it is equal to 0.77. This is consistent with the model of the flexible coil in a good solvent.

Optical Anisotropy. The values of the optical anisotropy (δ^2) of PES standards were calculated from relationship

$$\delta^2 = \frac{5\rho_v}{3 - 4\rho_v} \quad (11)$$

with ρ_v the depolarization factor.

They are noted in Table 1. Anisotropy of the PES monomer unit was estimated from the measurement of the depolarization factor of 4,4′-dichlorodiphenyl sulfone (DCDPS). Indeed, the molecular structure of this molecule is nearly identical to the one of the monomer unit.

It can be observed that the depolarization factor (ρ_v) and, consequently, the anisotropy of the molecule (δ^2) markedly decrease and tend toward a negligible value when $\bar{M}_w$ increases.

Figure 8 compares the experimental variation of δ^2 with the theoretical variation for semirigid (curve b) and rigid (curve c) polymers. It can be deduced that the behavior of PES in solution is typical of flexible chains.

Conformation Factor (σ) and Characteristic Ratio (C_∞). The effect of the steric hindrance on free rotation about a bond can be described by the conformation factor (σ) which is given by

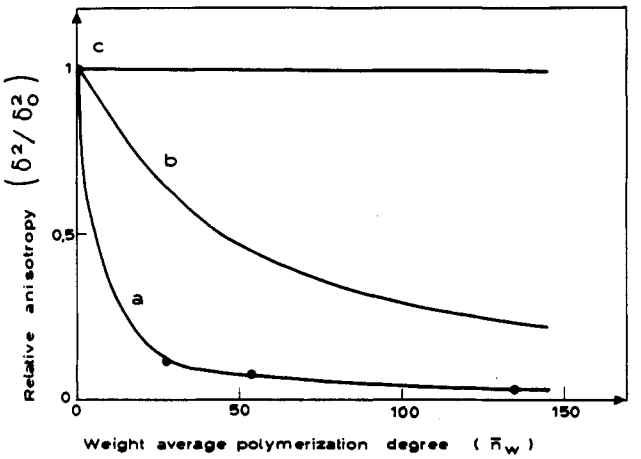

Figure 8. Variation of the relative anisotropy (δ^2/δ_0^2) with respect to the weight average number of repeat units ($\bar{n}_w$): (a) experimental results; (b) theoretical curve for a semirigid chain; (c) theoretical curve for a rigid chain.

$$\sigma = (\langle r_o^2\rangle/M)^{0.5}/(\langle r_o^2\rangle_f/M)^{0.5} = A/A_f \qquad (12)$$

where $\langle r_o^2\rangle_f$ is the mean-square end-to-end distance calculated using the assumption of a freely rotating chain and by taking into account the valence angles between successive bonds.

The PES chain can be characterized by one sequence length l (O–Φ–SO_2) and two valence angles θ_1 and θ_2 (Figure 9). The bond length l, calculated from the known covalent bond lengths, is found to be 5.87 Å. The valence angles θ_1 and θ_2 are equal to 104 and 123°, respectively,[26] according to results of X-ray structural analysis. It is questionable whether these angles would be the same in solution.

$\langle r_o^2\rangle_f$ is evaluated from the model of the freely rotating chain using the following equation[27]

$$\frac{\langle r_o^2\rangle_f}{N} = l^2\frac{(1-\cos\theta_1)(1-\cos\theta_2)}{1-\cos\theta_1\cos\theta_2} \qquad (13)$$

where the number of sequences N is equal to $2M/m_o$, m_o being the molecular mass of the repeat unit (equal to 232). The calculation gives $\langle r_o^2\rangle_f/N = 76$ Å^2 and $A_f = 0.809$ Å.

In this respect, the σ value calculated using eq 13 is 0.9 ± 0.1. This value indicates a behavior of a freely rotating chain and can be compared to those reported in the literature for polymers with X–Φ–X sequences. For these polymers, σ values close to 1 are often reported.[27-34] More specifically, the published values of σ are 1.05 for Bisphenol A polysulfone,[27] 1.30 for Bisphenol A polycarbonate (PC),[28] 1.00 for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO),[29] 1.10 for poly(2,6-diphenyl-1,4-phenylene oxide),[29] and 1.00 for poly(*p*-phenylene sulfoxide) (PPSO).[34]

Similarly, the value of the characteristic ratio for PES

$$C_\infty = \frac{\langle r_o^2\rangle}{Nl^2} = \frac{\langle r_o^2\rangle}{M}\frac{m_o}{2l^2} = 1.668 \qquad (14)$$

is typical of a freely rotating chain with approximately 104.5° valence angles. This last value is determined by assuming $C_\infty = (1-\cos\theta)/(1+\cos\theta)$ and corresponds to the θ_1 valence angle at the level of the sulfone group.

Persistence and Kuhn Segment Lengths. The rigidity of the PES macromolecule can be determined by an estimation of its persistance length in two ways.

Firstly, the Krakty–Porod model describes the polymer macromolecule as a Gaussian distribution of equivalent Kuhn segments:[35]

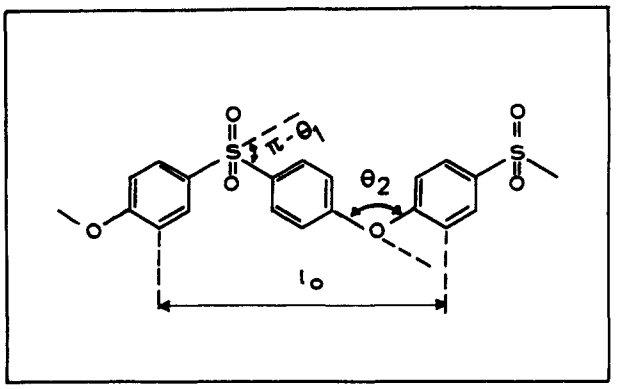

Figure 9. Representation of the repeat unit of the PES chain.

$$R_{G,w}^2 = \frac{n_k l_k^2}{6} \qquad (15)$$

where n_k and l_k are the Kuhn segment number and length, respectively. It must be noted that $n_k l_k = L$ is the contour length of the macromolecule, which is of course proportional to the molecular mass, and that the persistance length q is defined as half the Kuhn length. As L is also identical to

$$L = \bar{n}_w l_o \qquad (16)$$

with $l_o = 9.78$ Å[38] (see Figure 9), and where $\bar{n}_w$ is the weight average degree of polymerization (see Table 7), eq 16 gives

$$l_k = \frac{6(R_{G,w})^2}{\bar{n}_w l_o} \qquad (17)$$

Equation 17 establishes a dependence between the length of the statistical element and the weight average radius of gyration.

Considering the most probable mass distribution ($\bar{M}_w/\bar{M}_n = 2$ and $\bar{M}_z/\bar{M}_w = 1.5$),[36] the following relationship can be deduced:

$$(R_{G,w})^2 = \frac{2}{3}(R_{G,z})^2 \qquad (18)$$

Substituting the values of $R_{G,z}$ (reported in Table 7) in eq (18) and using equation 17 gives the values of l_k for PES 3–5. They are presented in Table 7.

It must be noted that l_k can also be determined from the model of the wormlike chain. In this case, Benoît and Doty have given the following relationship for the radius of gyration of a wormlike chain.[37]

$$(R_{G,w})^2 = \frac{Lq}{3} - q^2 + \frac{3q^3}{L} - \frac{2q^4}{L^2}\left[1-\exp\left(-\frac{L}{q}\right)\right] \qquad (19)$$

where $q = l_k/2$ is the persistence length. The values of l_k are summarized in Table 7.

Both models estimate the average Kuhn statistical length to be $l_k = 57 \pm 2$ Å, meaning that the statistical element possesses six repeat units. Such a value confirms the flexibility of the PES chain in the NMP + LiBr (0.1 M) solvent.

It must be emphasized that these results obtained from geometrical dimensions are totally in agreement with the l_k value of 55 Å deduced from hydrodynamic properties (viz. intrinsic viscosity, sedimentation, and diffusion coefficient[38]).

Conclusions

PES molecular mass characterization was performed using light scattering, viscometry, and size exclusion

Table 7. Kuhn Statistical Element (l_k)

samples	$R_{G,z}$[a] (Å)	$\bar{M}_w$[a] (g/mol)	R_{Gw}[b] (Å)	$\bar{n}_w$[c]	l_k[d] (Å)	l_k[e] (Å)
PES 3	135	31 200	110	135	55	58
PES 4	145	35 500	118	153	56	58
PES 5	170	50 000	139	216	55	56

[a] From light scattering experiments. [b] From eq 18. [c] Weight average polymerization degree. [d] From eq 17. [e] From eq 19.

chromatography (SEC). NMP was selected as the SEC solvent. In pure NMP, bimodal SEC curves were observed, probably due to weak polyelectrolyte effects. This particular behavior was confirmed by viscometric experiments and necessitated addition of salt in the solvent. The SEC method was then standardized via the universal calibration established with PMMA standards and via the viscosity laws of PMMA and PES in NMP + 0.1 M LiBr at a temperature of 25 °C.

In other respects, number average molecular masses determined by ^{1}H NMR analyses support the reliability of light scattering, viscometry, and SEC measurements.

Afterward, PES conformation in dilute NMP + LiBr solutions was investigated. This study has led to the conclusion that the macromolecule in solution has the behavior of a flexible coil. The value of the conformational parameter σ is close to 1, and the length of the Kuhn statistical element corresponds to about six repeat units.

Acknowledgment. We are greatly indebted to Miss C. Fagoo and Mrs. A. F. De Mahieu for their contribution in the experimental work. We acknowledge the National Fund for Scientific Research and the European Community for the financial support of this research. We would also like to thank Imperial Chemical Industries for supplying the polymers used. Finally, we wish to express our gratitude to Mrs. A. Becquevort for her patient manuscript typing and to Mr. F. Gerardis for drawing the figures.

References and Notes

(1) British Patent 1.586.972, 1981.
(2) Tonelly, A. E. *Macromolecules* **1973**, *6* (4).
(3) Gotham, K. V.; Turner, S. *Polymer* **1974**, *15*, 665.
(4) Attwood, T. E.; King, T.; McKenzie, I. D.; Rose, J. B. *Polymer* **1977**, *18*, 665.
(5) Daoust, D.; Godard, P.; Paulus, G. To be published.
(6) Hann, N. D. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1331.
(7) Cha, C. Y. *J. Polym. Sci.* **1969**, *B7*, 343.
(8) Coppola, G.; Fabbri, P.; Polleri, B. *J. Appl. Polym. Sci.* **1972**, *16*, 2829.
(9) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley-Interscience Publication, John Wiley & Sons: New York, 1979; p 390.
(10) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(11) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1757.
(12) Lantman, C. W.; McKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D.; Wignall, C. D. *Macromolecules* **1988**, *21*, 1344.
(13) Lutringer, G.; Meurer, B.; Weill, G. *Polymer Commun.* **1990**, *31*, 235.
(14) Devaux, J.; Delimoy, D.; Daoust, D.; Legras, R.; Mercier, J. P.; Strazielle, C.; Nield, E. *Polymer* **1985**, *26*, 1994.
(15) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci.* **1967**, *B5*, 753.
(16) Daoust, D.; Godard, P. To be published.
(17) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(18) Burchard, W. *Macromol. Chem.* **1960**, *50*, 20.
(19) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.
(20) Roovers, J.; Cooney, J. D.; Toporowski. *Macromolecules* **1990**, *23*, 1611.
(21) Flory, P. J. *Principles of Polymer Chemistry*; Cornwell University Press: Ithaca, NY, 1953; pp 528 and 628.
(22) Weill, G.; des Cloizeaux, J. *J. Phys.* **1979**, *40*, 99.
(23) Reed, W. F.; Snehasish Ghosh; Ghouti Medjahdi; François, J. *Macromolecules* **1991**, *24*, 6189.
(24) Ptitsyn, O. B.; Eizner, Y. E. *Zh. Tekh. Fiz.* **1959**, *29*, 1117.
(25) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Hadjichristidis, N.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2614.
(26) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hay, L. R. J.; Staniland, P. A. *Polymer* **1981**, *22*, 1096.
(27) Allen, G.; McAinsh, J.; Strazielle, C. *Eur. Polym. J.* **1969**, *5*, 319.
(28) Berry, G. C.; Nomura, H.; Mayhan, K. G. *J. Polym. Sci.* **1967**, *A-2*, 1.
(29) Akers, P.; Allen, G.; Bethell, M. *Polymer* **1968**, 575.
(30) Wallach, M. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 860.
(31) Wallach, M. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 52.
(32) Schulz, G. V.; Horbach, A. *Makromol. Chem.* **1959**, *29*, 93.
(33) Sitaramaiah. *J. Polym. Sci., Part A* **1965**, 2743.
(34) Daoust, D.; Godard, P.; Bebelman, S.; Coisne, J. M.; Strazielle, C. To be published.
(35) Porod, G. *Monatsh. Chem.* **1949**, *80*, 251. Krakty, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(36) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *43*, 25.
(37) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(38) Berg, A. A.; Monakov, Y. B.; Salazkin, S. N.; Rafikov, S. R.; Budtov, V. P.; Grigoreva, V. P.; Filatova, E. S.; Yegorov, A. Y. *J. Polym. Sci. USSR* **1983**, *25* (10), 2375.