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# Molecular characterization of poly(p-phenylene sulfide) (PPS) from size exclusion chromatography of a modified PPS and dilute solution properties

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A new method for poly(p-phenylene sulfide) (PPS) molecular mass characterization by size exclusion chromatography (s.e.c.) at 75°C based on a derivatization procedure, improving the polymer solubility, is proposed. This procedure leads to the preparation of a poly(p-phenylene sulfoxide) (PPSO) polymer. As complete oxidation is achieved, the reproducibility of the chemical modification is ensured as well as the increase of molecular mass. Furthermore, the molecular mass distribution is preserved for all that the PPS macromolecule only contains sulfide linkages and halogenoaryl chain ends. Molecular characterization of PPSO by light scattering, viscometry and s.e.c. is described. A Mark–Houwink–Sakurada relationship in m-cresol + 0.1 M LiBr is established. From specific and universal calibrations, absolute molecular masses of PPSO are obtained by s.e.c. The study of PPSO conformation in dilute solution reveals that the PPSO macromolecule can be considered as a freely rotating chain with *ca* 104–110° valence angles. The σ factor is close to 1. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

The determination of the molecular mass distributions of poly(p-phenylene sulfide) (PPS) by size exclusion chromatography (s.e.c.), which has become indispensable for predicting and correlating performance as well as understanding polymerization mechanisms, is precluded by its intrinsic high chemical resistance. Indeed, PPS characterization in solution must be carried out at temperatures above at least 200°C when the upper working temperature of the majority of commercial instruments is limited to 150°C. Consequently, PPS molecular mass characterization by s.e.c. would be greatly facilitated by the availability of a derivatization procedure improving the polymer solubility.

In the area of polymer characterization in dilute solution, several papers reported that chemical modification of a polymer is an interesting way to improve its solubility. Several authors[1–8] showed that aliphatic and aromatic polyamides become soluble on N-trifluoroacetylation in ordinary organic solvents such as acetone,

methylene chloride, tetrahydrofuran, etc. This functionalization leads to nearly quantitative conversion (≥98%) without polymer degradation and consequently allows reliable mass evaluation by light scattering, osmometry, viscometry and s.e.c. Moreover, Daoust and co-workers[9–13] proposed a derivatization method for poly(ether ether ketone) and HTX by sulfonation with concentrated sulfuric acid and demonstrated that the molecular characteristics of the original polymer can be found from the analytical results describing the derivative polymer.

In a previous paper[14], it has been shown, notably with the help of model compounds, that PPS can be transformed into poly(p-phenylene sulfoxide) (PPSO) with nitric acid. The increase in molecular mass due to oxidation is a constant value equal to 1.15 obtained from the ratio between oxidized repeat unit molecular mass (124) and the non-oxidized one (108). Furthermore, it has also been demonstrated that the molecular mass distribution is preserved for all that the PPS macromolecule only contains sulfide linkages and halogenoaryl or thiophenate chain ends.

The present paper comprises two parts. The first part is essentially devoted to the description of a s.e.c. method

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| Samples | $\eta_{inh}$ (dl g$^{-1}$) |
| --- | --- |
| PPS 2 | 0.09 |
| PPS 3 | 0.15 |
| PPS 5 | 0.25 |
| PPS 6 | 0.33 |
| PPS 7 | 0.38 |
| PPS 8 | 0.48 |

for PPSO. The nature of the s.e.c. solvent is discussed. Light scattering and viscometry results are presented mainly in order to obtain absolute molecular masses of PPSO samples from specific and universal s.e.c. calibrations. Molecular characteristics of the initial PPS samples are then calculated from molecular masses of the PPSO samples by applying the increase in molecular mass factor equal to 1.15. Afterwards, the weight average molecular masses obtained, using this derivatization method and inherent viscosities determined in 1-chloronaphthalene above 200°C, are used to establish a Mark–Houwink–Sakurada relationship. This latter relationship is then compared with viscosity laws given in the literature.

In the second part, the conformational behaviour of PPSO in dilute solution in *m*-cresol and in acid media is approached.

## EXPERIMENTAL

### *Products*

*Polymers.* PPS: the 22 linear experimental PPS samples used in this study were supplied by Solvay S.A. in the form of fine powder. Low and high molecular mass samples were prepared following the procedures described, respectively, in refs 15 and 16. The inherent viscosities of these samples (PPS1–PPS22), determined at 206°C and at $10 g l^{-1}$ in 1-chloronaphthalene, ranged from 0.05 to 0.48 dl g$^{-1}$. PPSs 2, 3 and 5–8 were selected as standards (*Table 1*).

PMMA: 12 practically isomolecular poly(methyl methacrylate) samples with molecular masses ranging from 3800 to 1 400 000 were used as primary s.e.c. standards. They were provided by Polymer Laboratories Ltd (part No. 2020-0101).

*Solvents.* Methanesulfonic acid (CH$_3$SO$_3$H) (Merck, ref. 0275472 > 98%) and HNO$_3$ (Merck, ref. K13487756, 65% PA) were used as received. *m*-Cresol (Merck, ref. 809691) was the solvent selected for s.e.c. and some viscometric analyses. It was purified by distillation under reduced pressure. It was used after filtration through a 0.45 μm filter (Millipore, ref. HVHP 04700). Lithium bromide was supplied by Merck (ref. 5669).

### *Modified PPS preparation*

Dried PPS (3 g dl$^{-1}$) is introduced in a mixture of 58 ml of HNO$_3$ and 100 ml of CH$_3$SO$_3$H conditioned at a temperature of 0°C. The sample reacts for a period of 24 h. PPS is not soluble in this medium. Dissolution only occurs after oxidation by HNO$_3$. Consequently, in order to facilitate the reaction and dissolution procedures, PPS powder is used and the medium is vigorously stirred

during the gradual addition of PPS and during the whole reaction time. The resulting oxidized PPS (PPSO) is then precipitated by dropwise addition of 10 ml of the reaction medium to 100 ml of de-ionized water at 4°C. After filtering under air pressure with a hydrophilic membrane (Millipore, ref. GVUP, pore size 0.22 μm), the polymer is washed thoroughly with H$_2$O to remove acid residues completely. The sample is then dried in an oven at 100°C *in vacuo* during 16 h.

### *Techniques*

*Light scattering (LS).* LS measurements on PPSO standards were performed at room temperature on a Fica 42000 Photo Gonio Diffusiometer fitted with a He–Ne laser source of 4 mW at 632.8 nm wavelength, vertically polarized. The solvent used was CH$_3$SO$_3$H. The solutions were clarified by centrifuging at 15 000 rev min$^{-1}$ for 4 h. For all the samples, no LS asymmetry was detected and the measurements were carried out at an angle of 90°. For samples having a weight average molecular mass below around 15 000, anisotropy has to be taken into account and the intensities were corrected by using a depolarization ratio ($\rho_v$) of around 0.04. Refractive index increments (d$n$/d$c$) were measured with a previously calibrated Brice–Phoenix differential refractometer working at 632.8 nm. The values are between 0.247 and 0.251 ml g$^{-1}$.

*Viscometry. PPS in 1-chloronaphthalene*: the inherent viscosity of each PPS sample was measured in 1-chloronaphthalene at a concentration of $10 g l^{-1}$ and at a temperature of 206°C using an Ostwald viscometer in an oil bath.

*PPSO*: (1) From the reaction medium ($C_i = 3.0 g dl^{-1}$ of dried PPS in the HNO$_3$/CH$_3$SO$_3$H mixture), kept at 0°C, 7 ml was taken and introduced into the capillary viscometer set in a water bath thermostated at 25°C. Two other solutions were also prepared by adding each time 3.5 ml of the solvent mixture. In order to assure a constant temperature, each solution was maintained in the viscometer until the measured time of flow was reproducible. For the calculation of the inherent and reduced viscosities, the change in mass concentration due to oxidation was taken into account. This correction of the concentration was easily applied. Indeed, the concentration in oxidized species ($C_m$) is related to the initial concentration in non-oxidized species ($C_i$) by

$$C_m = 1.15 C_i \qquad (1)$$

It must be noted that volume modification due to the different experimental temperatures (0 and 25°C) were neglected.

(2) In CH$_3$SO$_3$H: 0.3 g of dried PPSO was dissolved in 10 ml of CH$_3$SO$_3$H during 24 h at room temperature. Three viscometric measurements were performed at 25°C: the first one with 7 ml of the initial solution and the two others with solutions obtained by subsequent dilutions with 3.5 ml of solvent made within the viscometer.

PPSO and PMMA in *m*-cresol + LiBr (0.1 M): viscosity measurements of the six PPSO standards and of six PMMA standards dissolved in *m*-cresol + LiBr (0.1 M) were performed in a constant-temperature oil bath at 75 ± 0.1°C. The initial solution concentrations

were prepared at about $0.3\,g\,dl^{-1}$ for PPSO and at $\pm 0.33$ to $\pm 0.16\,g\,dl^{-1}$ for PMMA (depending on the molecular mass of each sample) and were further diluted in three stages. Volume modification due to the experimental temperature was taken into account.

All the PPSO and PMMA solution viscosities were determined in an Ubbelohde viscometer modified by Desreux[9]. The intrinsic viscosities were taken as the arithmetical mean of the reduced and inherent viscosities extrapolated to zero concentration.

*Size exclusion chromatography.* The s.e.c. chromatograph was the Millipore-Waters 150C instrument. It was connected to a Microvax 2000 computer from Digital for the acquisition and treatment of the data. Two sets of columns were used. The first set consisted of two mixed-bed Shodex columns from Showa Denko (ref. AD 80M/S). For the second set, one $500\,\text{Å}$ ultrastyragel column from Millipore-Waters (ref. P/N 85501) was added to the two previous columns in order to improve the separation of the low molecular masses. The solvent was *m*-cresol + LiBr (0.1 M). The working temperature was 75°C. The PPSO sample concentration and flow rate were, respectively, $2\,g\,l^{-1}$ and $0.5\,ml\,min^{-1}$.

## RESULTS AND DISCUSSION

*Molecular mass characterization*

### Molecular mass characterization of PPSO

*PPSO light scattering characterization:* The molecular characteristics of the six PPSO standards were determined from LS experiments. It must be recalled that the angular distribution of the scattered light for all the solutions is symmetrical around $\theta = 90°$ $(I_{135}/I_{45} = 1)$ and so far can be considered as independent of the observation angle $\theta$. *Table 2* reports the values for the weight average molecular masses $(\bar{M}_w)$, the refractive index increments $(dn/dc)$, the depolarization factor $(\rho_v)$ and the second virial coefficients $(A_2)$. Below *ca* 15000, the $(\bar{M}_w)$ values were corrected using the Cabannes factors $(3 + \rho_v)/(3 - 4\rho_v)$ due to the anisotropy detected for the two lowest molecular masses (PPSO 1 and 2 samples).

*Choice of the s.e.c. solvent:* As PPSO is soluble in *m*-cresol at 70°C, this solvent was used as the s.e.c. mobile phase. *Figure 1a* presents the s.e.c. chromatogram of a PPSO sample performed in pure *m*-cresol at 75°C. The chromatogram exhibits a major peak between the exclusion and permeation volumes, but also a smaller one close to the exclusion volume. Such behaviour was reported for weakly charged polyelectrolytes in organic polar solvents[9,12]. This effect, appearing at high dilution, could be attributed to the presence of some presumably 'adsorbed' ionic residues coming from the mixture of acids used to modify the original PPS sample and/or to the nature of the PPS chain ends. As a consequence, it was then decided to add a salt to the s.e.c. solvent—in all cases LiBr at a concentration of 0.1 M. *Figure 1b* shows the s.e.c. analysis of the same PPSO sample with *m*-cresol + LiBr (0.1 M) as solvent. It can be observed that classical elution and peak shape are obtained with these new experimental conditions.

*Mark–Houwink–Sakurada (MHS) relationships:* Three viscosity laws for PPSO were determined: the first one in the reaction medium (58 ml $HNO_3$/100 ml

**Table 2** Molecular characteristics of PPSO standards from light scattering experiments

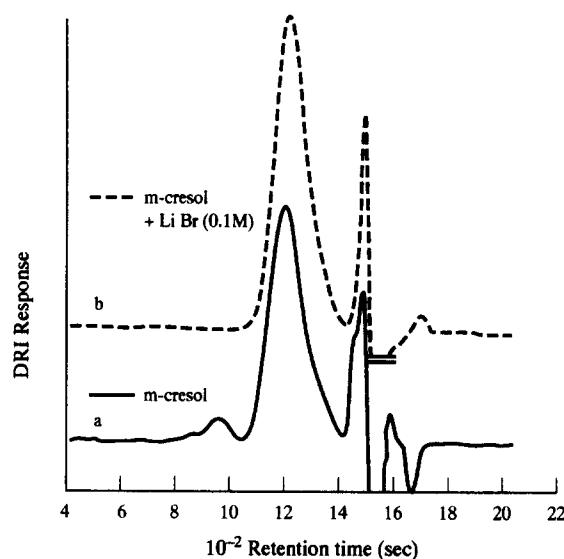| Samples | $\bar{M}_w$ | $dn/dc$ $(ml\,g^{-1})$ | $\rho_v$ | $10^3 A_2$ $(mol\,ml\,g^{-2})$ |
|---|---|---|---|---|
| PPSO 2 | 6600 | 0.248 | 0.05 | 6.5 |
| PPSO 3 | 13600 | 0.251 | 0.04 | 8.8 |
| PPSO 5 | 19300 | 0.247 | (<0.015) | 7.9 |
| PPSO 6 | 26800 | 0.251 | (<0.020) | 8.0 |
| PPSO 7 | 27900 | 0.251 | (<0.015) | 6.7 |
| PPSO 8 | 36800 | 0.251 | (<0.015) | 6.3 |



**Figure 1** Size exclusion chromatography of a PPSO sample in (a) *m*-cresol and (b) *m*-cresol + LiBr (0.1 M) (column set: two Shodex mixed bed)

$CH_3SO_3H$) at 25°C, the second in $CH_3SO_3H$ at 25°C and the third one in *m*-cresol + LiBr (0.1 M) at 75°C. The values of the intrinsic viscosities $[\eta]$ and of the weight average molecular masses $(\bar{M}_w)$ of the different PPSO standards are given in *Table 3*. The MHS relationships for PPSO in these media could then be deduced from these values:

In $CH_3SO_3H$ at 25°C: $\quad [\eta] = 6.17 \times 10^{-5}\bar{M}_w^{0.93}(dl\,g^{-1})$ (2)

In 58 ml $HNO_3$/100 ml $CH_3SO_3H$ at 25°C:

$$[\eta] = 44.95 \times 10^{-5}\bar{M}_w^{0.66}(dl\,g^{-1}) \qquad (3)$$

In *m*-cresol + LiBr (0.1 M) at 75°C:

$$[\eta] = 20.84 \times 10^{-5}\bar{M}_w^{0.72}(dl\,g^{-1}) \qquad (4)$$

It must be noted that the viscosity law in $CH_3SO_3H$ [equation (2)] was obtained with the six PPSO standards characterized by LS. Afterwards, the $\bar{M}_w$ values of PPSOs 1 and 4 were calculated from equation (2) and used to establish the two other viscometric relationships (3) and (4). It must also be noted that no polyelectrolyte behaviour of PPSO dissolved in $HNO_3/CH_3SO_3H$ or in $CH_3SO_3H$ was detected during the viscometric work.

On the other hand, the viscosity law for the polymer used as reference for primary s.e.c. calibration, viz. PMMA, was determined in *m*-cresol + LiBr (0.1 M) at

Table 3 Weight average molecular masses ($\bar{M}_w$), intrinsic viscosities ($[\eta]$) in $CH_3SO_3H$, in $HNO_3/CH_3SO_3H$ and in $m$-cresol + salt, root mean square of the unperturbed end-to-end distances $[(\langle r^2 \rangle_0)^{1/2}]$, unperturbed gyration radii in weight $[(R_{G,w})_0]$, viscometric radii of gyration ($R_{G,\eta}$) and viscometric expansion factors ($\alpha_\eta$)

| PPSO samples[a] | $\bar{M}_w$ | | | $[\eta]$ (dl g⁻¹) | | | $(\langle r^2 \rangle_0)^{1/2}$ (Å) | |
|---|---|---|---|---|---|---|---|---|
| | LS | Viscometry[b] | S.e.c. | $CH_3SO_3H$ ($T=25°C$) | $HNO_3/CH_3SO_3H$ ($T=25°C$) | $m$-Cresol + LiBr (0.1 M) ($T=75°C$) | $HNO_3/CH_3SO_3H$ | $m$-Cresol + LiBr (0.1 M) |
| PPSO 1 | | 3800 | | 0.13 | 0.10 | — | 49 | 44 |
| PPSO 2 | 6600 | | | 0.23 | 0.15 | 0.12 | 65 | 58 |
| PPSO 3 | 13 600 | | | 0.39 | 0.22 | 0.20 | 93 | 83 |
| PPSO 4 | | 16 100 | | 0.50 | 0.24 | 0.22 | 101 | 90 |
| PPSO 5 | 19 300 | | | 0.61 | 0.29 | 0.24 | 111 | 99 |
| PPSO 6 | 26 800 | | | 0.75 | 0.36 | — | 130 | 117 |
| PPSO 7 | 27 900 | | | 0.83 | 0.38 | 0.32 | 134 | 119 |
| PPSO 8 | 36 800 | | | 1.16 | 0.44 | 0.43 | 153 | 137 |
| PPSO 9 | | | 10 300 | — | 0.19 | | 81 | 72 |
| PPSO 10 | | | 11 900 | 0.37 | 0.20 | — | 87 | 78 |
| PPSO 11 | | | 12 300 | 0.38 | 0.22 | | 89 | 79 |
| PPSO 12 | | | 15 100 | 0.47 | 0.23 | | 98 | 87 |
| PPSO 13 | | | 16 400 | 0.54 | 0.27 | — | 102 | 91 |
| PPSO 14 | | | 17 800 | 0.51 | 0.27 | | 107 | 95 |
| PPSO 15 | | | 21 200 | 0.61 | 0.30 | | 116 | 104 |
| PPSO 16 | | | 22 300 | — | 0.32 | | 119 | 106 |
| PPSO 17 | | | 24 800 | 0.69 | 0.33 | | 126 | 112 |
| PPSO 18 | | | 25 000 | — | 0.35 | | 126 | 113 |
| PPSO 19 | | | 26 100 | 0.81 | 0.35 | | 129 | 115 |
| PPSO 20 | | | 26 800 | 0.71 | 0.36 | — | 131 | 117 |
| PPSO 21 | | | 26 800 | 0.80 | 0.34 | — | 131 | 117 |
| PPSO 22 | | | 26 900 | — | 0.34 | — | 131 | 117 |

| PPSO samples[a] | $(R_{G,w})_0$ (Å) | | $R_{G,\eta}$ (Å) | | $\alpha_\eta$ | |
|---|---|---|---|---|---|---|
| | $HNO_3/CH_3SO_3H$ | $m$-Cresol + LiBr (0.1 M) | $HNO_3/CH_3SO_3H$ | $m$-Cresol + LiBr (0.1 M) | $HNO_3/CH_3SO_3H$ | $m$-Cresol + LiBr (0.1 M) |
| PPSO 1 | 20 | 18 | 24 | — | 1.20 | — |
| PPSO 2 | 27 | 24 | 33 | 32 | 1.22 | 1.33 |
| PPSO 3 | 38 | 34 | 48 | 48 | 1.26 | 1.41 |
| PPSO 4 | 41 | 37 | 53 | 52 | 1.29 | 1.41 |
| PPSO 5 | 45 | 40 | 58 | 57 | 1.29 | 1.43 |
| PPSO 6 | 53 | 48 | 70 | — | 1.32 | — |
| PPSO 7 | 55 | 49 | 73 | 71 | 1.33 | 1.45 |
| PPSO 8 | 62 | 56 | 84 | 86 | 1.35 | 1.54 |
| PPSO 9 | 33 | 29 | 41 | — | 1.24 | — |
| PPSO 10 | 36 | 32 | 44 | — | 1.22 | — |
| PPSO 11 | 36 | 32 | 46 | — | 1.28 | — |
| PPSO 12 | 40 | 36 | 51 | — | 1.28 | — |
| PPSO 13 | 42 | 37 | 54 | — | 1.29 | — |
| PPSO 14 | 44 | 38 | 56 | — | 1.27 | — |
| PPSO 15 | 47 | 42 | 61 | — | 1.30 | — |
| PPSO 16 | 49 | 43 | 64 | — | 1.31 | — |
| PPSO 17 | 51 | 46 | 67 | — | 1.31 | — |
| PPSO 18 | 51 | 46 | 68 | — | 1.33 | — |
| PPSO 19 | 53 | 47 | 69 | — | 1.30 | — |
| PPSO 20 | 53 | 48 | 69 | — | 1.30 | — |
| PPSO 21 | 53 | 48 | 69 | — | 1.30 | — |
| PPSO 22 | 53 | 48 | 69 | — | 1.30 | — |

[a] PPSO 1, PPSO 2, etc., are oxidized forms of PPS 1, PPS 2, etc., respectively
[b] From equation (2)

75°C to allow the establishment of the s.e.c. universal calibration. The molecular masses and the intrinsic viscosities obtained for the selected PMMA standards are presented in *Table 4*. The expression of the PMMA viscosity law is

$$[\eta] = 10.78 \times 10^{-5} M_p^{0.74} \, (\text{dl g}^{-1}) \qquad (5)$$

*S.e.c. molecular mass characterization:* (a) Establishment of the specific calibration curve: The determination of absolute PPSO molecular masses from s.e.c.
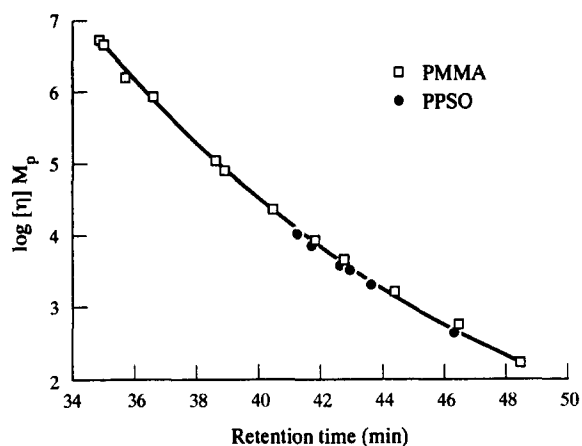


**Figure 2** S.e.c. universal calibration curve (column set: two Shodex mixed bed and one 500 Å ultrastyragel)

**Table 4** Molecular masses ($M_p$) and intrinsic viscosities ([$\eta$]) of six poly(methyl methacrylate) standards in *m*-cresol + LiBr (0.1 M) at a temperature of 75°C

| Samples | $M_p^a$ | [$\eta$] (dl g$^{-1}$) |
|---|---|---|
| PMMA 1 | 7600 | 0.07 |
| PMMA 2 | 13900 | 0.13 |
| PMMA 3 | 24300 | 0.22 |
| PMMA 4 | 62600 | 0.42 |
| PMMA 5 | 153700 | 0.83 |
| PMMA 6 | 685000 | 2.07 |

$^a$ Molecular mass at the top of the chromatographic peak

experiments can be achieved from a specific calibration curve constructed with the broad PPSO standards characterized by LS. To reach this objective, a PMMA calibration curve was first established with practically isomolecular samples covering a molecular mass domain as wide as possible. In fact, the molecular masses of the PMMA standards ranged from 3800 to 1 400 000. Afterwards, the different PPSO standards were chromatographied and weight average molecular masses were calculated in PMMA equivalents. These $\bar{M}_w$ values and the LS ones were then used to apply an iterative procedure, described in detail elsewhere[17], which has allowed the determination of the PPSO specific calibration. This specific calibration has given the molecular masses collected in *Table 5*. A good agreement (<5.5%) was obtained between the calculated $\bar{M}_w$ values and the results from the LS measurements. Such a calibration has also allowed the determination of the molecular masses at the top of the chromatographic distribution ($M_p$).

(b) Establishment of the universal calibration curve: The $M_p$ values have been used to demonstrate that PMMA and PPSO macromolecules followed the concept of the universal calibration when *m*-cresol + LiBr (0.1 M) at 75°C and a gel of styrene and divinylbenzene are, respectively, the s.e.c. mobile and stationary phases.

If the s.e.c. fractionation of PMMA and of PPSO results only from pure size exclusion, the universal calibration method can be applied. In other words, this means that, in this case, a sole relationship exists between the PMMA and PPSO macromolecules' hydrodynamic volumes represented by the product [$\eta$] $M_p$ and the s.e.c. retention times[18]. *Figure 2* shows the universal calibration curve obtained from PMMA standards with three columns, viz. two Shodex mixed bed and one 500 Å ultrastyragel. On this curve are also reported the [$\eta$] $M_p$ data due to the PPSO standards. It can be seen that all the PPSO points fall on the curve within the limit of experimental accuracy. In a first step, this result indicates that the separation is only performed from size exclusion phenomena without any side interaction in this s.e.c. system. In a second step, this result confirms the validity of the PMMA and PPSO MHS relationships.

**Table 5** Comparison between molecular masses obtained from s.e.c. by using the specific and universal calibrations

| | $\bar{M}_w$ | | S.e.c. Specific calibration | | | | | S.e.c. Universal calibration | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Samples | LS | Viscometry$^a$ | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_z$ | $M_p$ | $H^b$ | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_z$ | $H^b$ |
| PPSO 1 | — | 3800 | — | — | — | — | — | — | — | — | — |
| PPSO 2 | 6600 | — | 6300 | 2100 | 15600 | 5200 | 3.0 | 6300 | 2100 | 15700 | 3.0 |
| PPSO 3 | 13600 | — | 13400 | 3800 | 33900 | 12300 | 3.5 | 13800 | 3900 | 35600 | 3.5 |
| PPSO 4 | — | 16100 | 18000 | 5100 | 48600 | 16300 | 3.5 | 18000 | 5100 | 48000 | 3.5 |
| PPSO 5 | 19300 | — | 19600 | 5100 | 62200 | 17000 | 3.8 | 20600 | 5300 | 63000 | 3.9 |
| PPSO 6 | 26800 | — | — | — | — | — | — | — | — | — | — |
| PPSO 7 | 27900 | — | 29500 | 6500 | 89900 | 26500 | 4.5 | 29400 | 6500 | 89000 | 4.5 |
| PPSO 8 | 36800 | — | 35600 | 7200 | 104300 | 30700 | 4.9 | 36200 | 7200 | 102000 | 5.0 |

$^a$ From equation (2)
$^b$ H = $\bar{M}_w/\bar{M}_n$
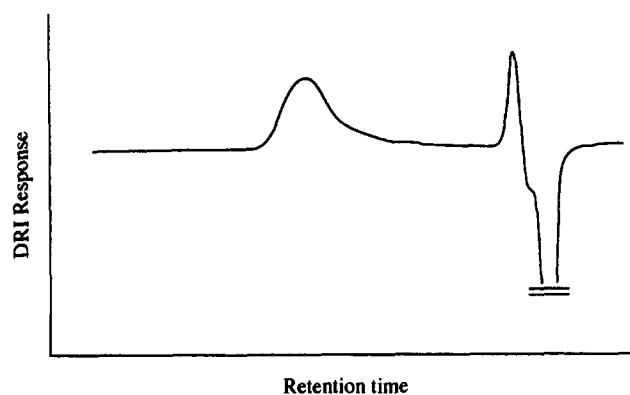
**Figure 3** Chromatogram of a PPSO sample obtained with the second set of columns used in this work
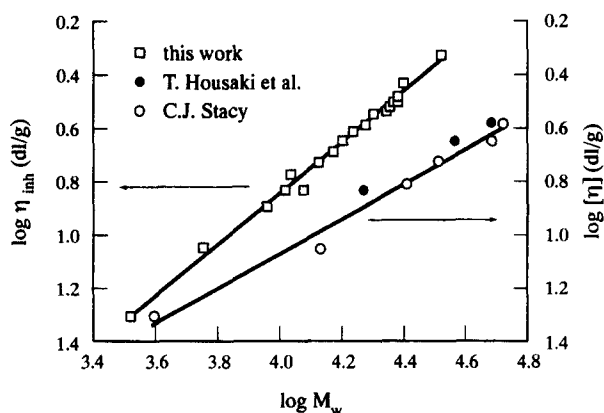


**Figure 4** Log–log plot of inherent ($\eta_{inh}$) and intrinsic [$\eta$] viscosities *versus* weight average molecular masses ($\bar{M}_w$) for various PPS samples in 1-chloronaphthalene at a temperature of 206 or 208°C

**Table 6** Weight average molecular mass ($\bar{M}_w$) and intrinsic viscosity ([$\eta$]) values of PPS samples available in the literature

| Samples | $\bar{M}_w$ | [$\eta$] (dl g$^{-1}$) |
|---------|-------------|-------------------------|
| PPS I[a] | 4000 | 0.05 |
| PPS II[a] | 13 300 | 0.09 |
| PPS III[a] | 24 800 | 0.16 |
| PPS IV[a] | 31 600 | 0.19 |
| PPS V[a] | 46 900 | 0.23 |
| PPS VI[a] | 50 400 | 0.27 |
| PPS A[b] | 18 100 | 0.149 |
| PPS B[b] | 35 700 | 0.228 |
| PPS C[b] | 46 700 | 0.273 |

[a] From ref. 19
[b] From ref. 20

*Table 5* summarizes the PPSO molecular masses calculated from the universal calibration curve. From this table it appears that the agreement between the values determined from universal or specific calibrations is very satisfying. *Figure 3* represents the chromatogram of a PPSO sample analysed with the set of three columns.

*Molecular characteristics of the initial PPS samples.* As the increase of molecular mass due to the derivatization is known, the absolute molecular characteristics of an original PPS sample can be found from the absolute molecular characteristics of the same derivatized sample if the molecular mass distribution of the PPS sample is preserved. Consequently, the PPS molecular masses of the standards and of other experimental samples have been determined by applying the 1.15 correction factor. The $\bar{M}_w$ values in PPSO equivalents of all these samples, before dividing by 1.15, are given in *Table 3*. The inherent viscosities ($\eta_{inh}$) of all these PPS samples determined in solution in 1-chloronaphthalene at a concentration (c) of 10 g l$^{-1}$ and at a temperature of 206°C are presented in *Table 1*. As Stacy[19] reports that the plots of ln $\eta_{inh}/c$ *versus* c have very low slopes over the whole range of intrinsic viscosity and concentration, the inherent viscosity values can be assimilated to intrinsic viscosity values, at least in a first approximation. This should normally allow the determination of practically accurate MHS constants of PPS in 1-chloronaphthalene at a temperature of 206°C. The viscosity law so-obtained is

$$[\eta] = 1.75 \times 10^{-5}\bar{M}_w^{0.98} \ (\mathrm{dl\,g^{-1}}) \tag{6}$$

*Figure 4* illustrates this relationship.

In other respects, values of weight average molecular mass and of intrinsic viscosity of some PPS samples made by the Phillips process are reported in papers of Stacy[19] and Housaki and Satoh[20]. These values are shown in *Table 6* and plotted in *Figure 4*. Furthermore, Stacy[19] proposes the following viscosity law for PPS in 1-chloronaphthalene at 208°C:

$$[\eta] = 8.91 \times 10^{-5}\bar{M}_w^{0.747} \ (\mathrm{dl\,g^{-1}}) \tag{7}$$

From the comparison between the relationships (6) and (7) and, of course, between the two straight lines of *Figure 4*, it has to be deduced that, for the same intrinsic viscosity, the derivatization method leads to a lower molecular mass than the one which can be obtained by using the literature data. This discrepancy between the two classes of results could be explained by the presence of weak linkages in the PPS macromolecules that induce chain scissions during the oxidation reaction in the acid medium. One fault in the PPS chemical structure which could be considered is the disulfide group. In this connection it must be emphasized that, though authors suggest the appearance of disulfide linkages during the PPS synthesis by founding upon the envisaged mechanisms, disulfide structures have never been analytically detected.

*Dilute solution properties of PPSO*

*Unperturbed dimensions.* When radius of gyration values cannot be obtained from LS characterization, viscosity measurements can be used to determine unperturbed dimensions. However, direct experimental determination is often difficult as a $\theta$ solvent is not always available and polymers tend to crystallize out from 'poor solvents'. To overcome these difficulties, many viscometric expressions based on the two-parameters theory have been developed, assuming different approximations in the mathematical procedure in order to determine unperturbed dimensions and also interaction parameters from measurement of intrinsic viscosity in good solvents. In this field, one of the most well-known viscometric treatments is the Burchard–Stockmayer–Fixman (BSF) plot[21,22] of

$[\eta] M^{-0.5}$ *versus* $M^{0.5}$:

$$[\eta]M^{-0.5} = K_\theta + 0.51\phi_0 BM^{0.5} \qquad (8)$$

where $K_\theta$ is the MHS $K$ for a $\theta$ solvent, $\phi_0$ is a universal constant equal to $2.5 \times 10^{21}\,\mathrm{mol}^{-1}$, and B is the interaction parameter, related to $A_2$.

From the value of $K_\theta$ and from the Fox–Flory equation[23], the unperturbed dimensions can be evaluated by

$$K_\theta = \phi_0(\langle r^2\rangle_0/M)^{3/2} \qquad (9)$$

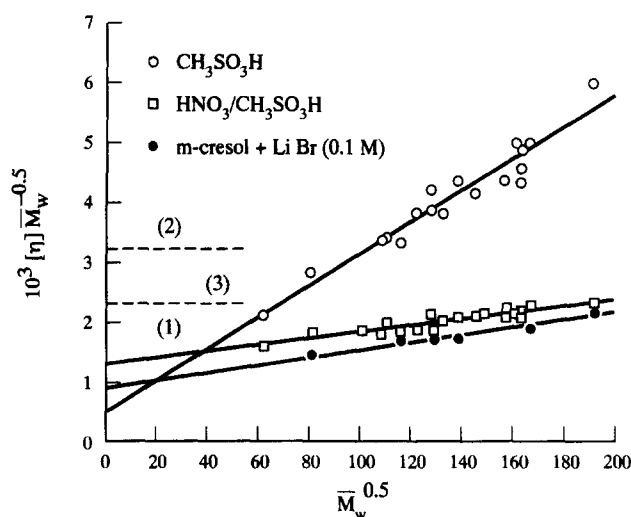where $\langle r^2\rangle_0$ is the mean-square end-to-end distance of the chain in the unperturbed state. Yamakawa[4] has



**Figure 5** Intrinsic viscosity and molecular mass data plotted according to the treatment of Burchard–Stockmayer–Fixman used to estimate unperturbed dimensions for PPSO in $CH_3SO_3H$, in $HNO_3/CH_3SO_3H$ and in *m*-cresol + salt. Horizontal lines indicate the limits of applicability of equation (10) in the text: (1) for PPSO in $CH_3SO_3H$; (2) for PPSO in $HNO_3/CH_3SO_3H$; (3) for PPSO in *m*-cresol + salt
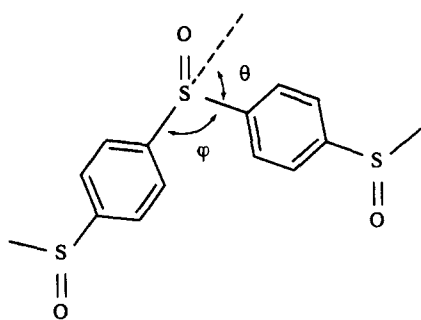


**Figure 6** Representation of PPSO as a chain of virtual bonds ($\varphi$ = valence angle; $\theta = \pi - \varphi$)

suggested a modification of equation (8):

$$[\eta]M^{-0.5} = 1.05 K_\theta + 0.287\phi_0 BM^{0.5} \qquad (10)$$

valid for $[\eta]/[\eta]_0 < 2.5$, where $[\eta]_0$ is the intrinsic viscosity in a $\theta$ solvent.

In order to improve the accuracy of the results which can be obtained by applying the BSF treatment modified by Yamakawa to PPSO, intrinsic viscosities of other PPSO samples have been determined in the $HNO_3/CH_3SO_3H$ mixture and in $CH_3SO_3H$. *Table 3* summarizes the viscometric values, and *Figure 5* shows the plots of $[\eta]\, \bar{M}_w^{-0.5}$ *versus* $\bar{M}_w^{0.5}$ for PPSO in $CH_3SO_3H$, in $HNO_3/CH_3SO_3H$ and in *m*-cresol + LiBr (0.1 M). The horizontal lines indicate the upper limits for application of equation (10). Since all the data points of the PPSO/$CH_3SO_3H$ system fall outside the application limit, only the results concerning the PPSO $HNO_3/CH_3SO_3H$ and *m*-cresol–salt systems have been considered. Linear regressions fit to these data have yielded

in $HNO_3/CH_3SO_3H$:

$$[\eta]\, \bar{M}_w^{-0.5} = 134.06 \times 10^{-5} + 5.22 \times 10^{-6}\bar{M}_w^{0.5} \qquad (11)$$

in *m*-cresol + salt:

$$[\eta]\, \bar{M}_w^{-0.5} = 94.81 \times 10^{-5} + 6.10 \times 10^{-6}\,\bar{M}_w^{0.5} \qquad (12)$$

*Table 7* presents the values of $K_\theta$ and $\langle r^2\rangle_0/M$. Since

$$\langle r^2\rangle_0 = 6(R_{G,w}^2)_0 \qquad (13)$$

the unperturbed gyration radii in weight can be calculated. *Table 3* gives the results of $(\langle r^2\rangle_0)^{1/2}$ and of $(R_{G,w})_0$ for the various PPSO samples.

*Perturbed dimensions and viscosity expansion factor.* A viscosity average radius of gyration $(R_{G,\eta})$ was determined from the intrinsic viscosity values by the Fox–Flory equation:

$$[\eta] = \phi'(R_{G,\eta})^3/\bar{M}_w \qquad (14)$$

in which $\phi' = 6^{3/2}\phi_0$. Flory's viscosity constants $\phi_0$ and $\phi'$ were determined by using the relationship derived by Ptitsyn and Eizner[25]:

$$\phi' = \phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)6^{3/2} \qquad (15)$$

where $\phi_0$ is a universal constant equal to $2.5 \times 10^{21}\,\mathrm{mol}^{-1}$, $\epsilon = (2a - 1)/3$, and $a$ is the exponent of the corresponding MHS relationship. The Flory constant is assumed to show no significant change with the molecular mass.

The values calculated for $R_{G,\eta}$ are reported in *Table 3*.

**Table 7** $K_\theta$, $\langle r^2\rangle_0/M$, characteristic ratios ($C_\infty$), valence angles ($\varphi$) and conformational factors ($\sigma$) of PPSO in $HNO_3/CH_3SO_3H$ and in *m*-cresol + salt

| Solvents | $10^5 K_\theta$ (dl mol$^{1/2}$ g$^{-3/2}$) | $\dfrac{\langle r^2\rangle_0}{M}$ (Å$^2$ mol g$^{-1}$) | $C_\infty$ | $\varphi$ (degree) | $\sigma$ |
|---|---|---|---|---|---|
| $HNO_3/CH_3SO_3H$ | 128.7 | 0.639 | 2.03 | 110 | 1.00 |
| *m*-Cresol + LiBr (0.1 M) | 90.3 | 0.507 | 1.61 | 104 | 0.99 |

$(R_{G,W})_0$ and $R_{G,\eta}$ have then allowed the determination of the viscometric expansion factors $\alpha_\eta$, also given in *Table 3*.

*Conformation.* The evaluation of the chain flexibility was done via the determination of the characteristic ratio ($C_\infty$) and the conformational parameter ($\sigma$).

The PPSO chain (*Figure 6*) can be represented by one sequence length $l$ and one valence angle $\varphi$. It must be noted that no values of $l$ and $\varphi$ are available in the literature. Consequently, the bond length $l$ calculated from the known covalent bond lengths was found to be equal to $6.25\text{Å}$ admitting for the C-SO length an average value between the C-SO$_2$ ($1.73\text{Å}$) and C-S ($1.75\text{Å}$) bond lengths. Concerning the valence angle, Unwin and Wardd[26] and Attwood *et al.*[27] reported that PPS and polysulfone valence angles are respectively equal to $110°$ and $105°$. It can thus be expected that the PPSO valence angle is in the same range.

The characteristic ratio $C_\infty$ and the conformation parameter $\sigma$ were determined by equations (16) and (17), respectively:

$$C_\infty = \frac{\langle r^2 \rangle_0}{nl^2} \tag{16}$$

$$\sigma = \frac{\left(\dfrac{\langle r^2 \rangle_0}{M}\right)^{0.5}}{\left(\dfrac{\langle r^2 \rangle_{0,f}}{M}\right)^{0.5}} \tag{17}$$

where $n$ is the number of main-chain bonds and $\langle r^2 \rangle_{0,f}$ is the mean square end-to-end distance calculated on the assumption of a freely rotating chain. As $n$ is also equal to:

$$n = M/m_0 \tag{18}$$

with the $m_0$ the molecular mass per repeat unit, equation (16) becomes

$$C_\infty = \frac{\langle r^2 \rangle_0}{M} \frac{m_0}{l^2} \tag{19}$$

and, by introducing equation (9) into equation (19):

$$C_\infty = \left(\frac{K_\theta}{\phi_0}\right)^{2/3} \frac{m_0}{l^2} \tag{20}$$

The $C_\infty$ values obtained for PPSO in HNO$_3$/CH$_3$SO$_3$H and in $m$-cresol + salt are shown in *Table 7*.

In the case of a freely rotating chain with one valence angle, $C_\infty$ can also be expressed by

$$C_\infty = \frac{1 + \cos\theta}{1 - \cos\theta} \tag{21}$$

where $\theta$ is the bond angle supplement.

Relationship (21) has allowed the calculation of the valence angle $\varphi$ (*Table 7*). It is equal to $110°$ and $104°$ for PPSO in HNO$_3$/CH$_3$SO$_3$H and in $m$-cresol + salt, respectively. In other respects, by using the values $\varphi = 110°$ and $\varphi = 104°$ with equation (22):

$$\frac{\langle r^2 \rangle_{0,f}}{M} = \frac{nl^2 \dfrac{1 - \cos\varphi}{1 + \cos\varphi}}{M} \tag{22}$$

Equation (17) has allowed the determination of the $\sigma$ values presented in *Table 7*, viz. $\sigma = 1$ and $\sigma = 0.99$ for PPSO in HNO$_3$/CH$_3$SO$_3$H and in $m$-cresol + salt, respectively.

As a conclusion of the study of the PPSO behaviour in dilute solution, it can be deduced from the results that the values of $C_\infty$ and $\sigma$ are typical of a freely rotating chain with a valence angle between $104°$ and $110°$. These values of $C_\infty$ and $\sigma$ can be compared with those reported in the literature for polymers with $X-\phi-X$ sequences[28-35].

## CONCLUSIONS

Due to the high solvent resistance of linear PPS, the development of analytical methods suitable for the determination of molecular masses and their distributions was difficult.

This paper presents a useful s.e.c. of PPS at a temperature of 75°C based on a chemical derivatization procedure leading to the preparation of a PPSO polymer. This method requires dissolution of a PPS sample in a mixture of acids (viz. nitric acid/methanesulfonic acid) at 0°C, complete oxidation and recovery of the modified sample. Methanesulfonic acid was the solvent used for PPSO light scattering characterization. $m$-Cresol was selected as s.e.c. solvent. However, a salt has to be added to the solvent owing to an anomalous chromatographic elution curve attributed to the nature of the macromolecule chain ends and/or to ionic residues adsorbed on the polymer.

The s.e.c. method of PPSO was standardized via the universal calibration established with PMMA standards and the viscosity laws of PMMA and PPSO in $m$-cresol + LiBr (0.1 M) at 75°C. Compared to the specific calibration, the universal calibration gives very accurate molecular masses. Viscometric laws of PPSO in methanesulfonic acid and in the nitric acid/methanesulfonic acid mixture have also been determined.

However, the principal aim of the derivatization method is to give the possibility of finding the absolute molecular characteristics of the initial linear PPS sample. This objective involves ensuring that the molecular distribution of the initial PPS sample is not modified during the oxidation reactions. The results obtained in this work do not allow us to certify that this indispensable condition is respected. Indeed, the PPS weight average molecular masses found by applying the derivatization correspond to lower intrinsic viscosity values than the ones experimentally determined (thus, before chemical modification) if a viscosity law reported in the literature is taken as a reliable reference. In other words, this observation suggests that chain scissions occur when the linear PPS samples used in this work are transformed into PPSO samples. One could explain this unexpected chemical behaviour by the presence of weak linkages in the PPS main chain. That is the reason why the stability of disulfide structures in the reaction medium is presently studied, notably with the help of a model compound. In addition, a synthesis work on linear PPS samples which do not contain other linkages than sulfide ones is also in progress. These two methods of research should bring interesting information and, of course, will lead to another paper.

In the second part of the present paper, the behaviour

of PPSO in dilute solution in the nitric acid methanesulfonic acid mixture and in *m*-cresol + LiBr (0.1 M) was examined. As it was impossible to measure molecular dimensions from LS experiments, viscometric data were exploited in order to calculate more particularly unperturbed dimensions, the characteristic ratio and the conformation parameter.

All the results obtained demonstrate that the PPSO macromolecule can be considered as a freely rotating chain with approximately 104–110° valence angles. Lastly, the exponent of the MHS expression for PPSO in *m*-cresol + salt clearly proves that the macromolecule is a flexible coil in a good solvent.

## ACKNOWLEDGEMENTS

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