Chemical modification of poly(ether ether ketone) for size exclusion chromatography at room temperature: 1. Absolute molecular-mass determination for sulfonated PEEK

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A new method for poly(ether ether ketone) (PEEK) molecular-mass characterization by room-temperature (r.t.) size (steric) exclusion chromatography (s.e.c.) based on a derivatization procedure that improves the polymer solubility is described. Upon dissolution in 99.5% sulfuric acid at room temperature, PEEK is chemically modified by sulfonation of phenyl rings without polymer degradation. As complete sulfonation is achieved, the reproducibility of the chemical modification is ensured as well as the increase of molecular mass. Sulfonated PEEK is soluble at room temperature in different solvents suitable for s.e.c. *N*-Methyl-2-pyrrolidine (NMP) is selected as PEEK s.e.c. solvent. Owing to the polyelectrolyte nature of sulfonated PEEK, a salt (0.1 M LiBr) is added to NMP. Various broad-dispersity PEEK standards are used to establish specific and universal calibrations. The viscosity laws of sulfonated PEEK in NMP + LiBr (0.1 M), in methanesulfonic acid (MSA) and in 99.5% H_2SO_4 are determined. As sulfonated PEEK is a hygroscopic polymer, some spectroscopic methods are developed to determine the absolute concentration of the standards in order to perform accurate viscometric experiments giving the Mark–Houwink–Sakurada parameters in NMP–salt and in MSA. The s.e.c. universal calibration curve is constructed with poly(methyl methacrylate) narrow-dispersity standards.

(Keywords: sulfonated PEEK; molecular-mass determination; size exclusion chromatography)

INTRODUCTION

Interest in materials exhibiting high thermal stability, environmental resistance, excellent mechanical properties and low density has greatly increased over the past years[1]. These products are notably sought as replacements for metals in structural applications where specific toughness, stiffness and strength are of the greatest importance[2]. Potential commercial uses of such materials include more particularly the areas of transportation and aerospace industries. To satisfy this demand, some new polymers have been introduced into the market that show substantial improvements over metals[3–5]. Among them, poly(oxy-1,4-phenylene oxy-1,4-phenylene carbonyl-1,4-phenylene) (poly(ether ether ketone) or PEEK), a highly aromatic semicrystalline thermoplastic, has currently received considerable attention.

The physico-chemical properties of PEEK make this material an interesting high-temperature resistant polymer that finds increasing use in various applications such as electrical and electronic parts, wires and cables in nuclear plants, underground railways, military equipment, as well as advanced structural composites for aircraft[6–8].

The remarkable solvent resistance of PEEK[9] is an attractive characteristic when the polymer is used in agressive environments. But the very poor solubility of PEEK is a major drawback for its characterization, especially for the determination of molecular masses and molecular-mass distributions, which are very important parameters controlling the end-use properties of the polymer. In this field, the first complete size (steric) exclusion chromatography (s.e.c.) of PEEK was reported by Devaux *et al.*[10]. This latter method works under rather drastic conditions, including the use of a phenol/1,2,4-trichlorobenzene mixture at high temperature. As these analytical conditions cannot be used in a routine procedure, a continuation of this work based on a polymer derivatization concept was undertaken with the aim to improve the dissolution properties of PEEK and, consequently, to develop a room-temperature (r.t.) s.e.c. of PEEK.

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Such a chemical derivatization for s.e.c. characterization must fulfil some specific criteria:

(i) No polymer degradation can occur during the derivatization process.

(ii) The chemical modification must be complete and reproducible.

(iii) The change in molecular mass due to the chemical modification must be known.

(iv) The derivative polymer must be chamically stable and soluble in a classical room-temperature s.e.c. solvent without any degradation.

(v) The derivative polymer cannot undergo any column retention effect. Preferably, in order to apply the universal calibration principle, a suitable reference polymer, soluble in the same solvent, should be commercially available.

If the above criteria are satisfied, the molecular characteristics of the original polymer can be found from the analytical results describing the derivative polymer.

It will be demonstrated that sulfonation of PEEK is a chemical method that allows all of the above criteria to be fulfilled.

We present two papers dedicated to this particular method, which will improve PEEK characterization in dilute solution.

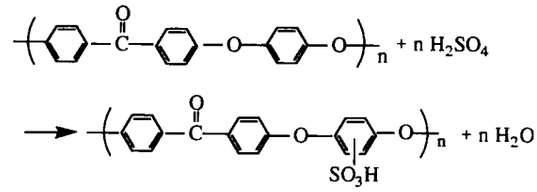
This first paper is essentially devoted to the development of a reliable s.e.c. method of totally sulfonated PEEK at room temperature. A preliminary section treats the present state of PEEK sulfonation in the scientific literature in order to select the more appropriate sulfonating agent and to determine experimental conditions that allow a reproducible preparation of the modified polymer. Afterwards, the nature of the s.e.c. solvent is discussed and viscometry results are presented mainly with a view to obtaining absolute molecular masses from universal s.e.c. calibration.

The second paper[11] of this series treats more particularly the assessment of the validity of this chemical derivatization applied to PEEK from the perspective of its molecular-mass characterization by s.e.c. It will also be shown that this derivatization method is suitable to determine the molecular-mass parameters of PEEK as the matrix of a carbon-fibre composite.

LITERATURE SURVEY ON POLY(ETHER ETHER KETONE) SULFONATION

Bishop *et al.*[12], Jin *et al.*[13] and Devaux *et al.*[10] reported the sulfonation of PEEK upon dissolution in chlorosulfonic and sulfuric acids. In addition to sulfonation, Bishop and Jin revealed that chlorosulfonic acid induces crosslinking of PEEK via the condensation of $-SO_3H$ groups and formation of sulfone links. They also suggested that the same reactions might occur with 100% sulfuric acid. However, these authors asserted that sulfone formation and chemical degradation of PEEK dissolved in aqueous H_2SO_4 have never been detected even upon standing for long periods. From this viewpoint, concentrated sulfuric acid, as long as the concentration of the acid is kept below 100% to prevent crosslinking, can be considered as a suitable reagent giving rise to sulfonated PEEK without changing the molecular distribution of the original polymer. For this reason, 99.5% H_2SO_4 was selected as the sulfonating agent in this work.

Sulfonation of PEEK at room temperature in concentrated sulfuric acid is an electrophilic reaction and, as desulfonation is negligible[14,15], can be represented as follows:



The sulfonation process is limited to one sulfonate group per repeat unit and is located at one of the four chemically equivalent positions of the phenyl ring surrounded by two ether linkages. The other phenyl rings are deactivated by the neighbouring ketone.

To ensure the reproducibility of the derivatization procedure, only fully sulfonated PEEK samples were prepared and analysed by s.e.c. Therefore, the increase in molecular mass due to sulfonation is a constant value equal to 1.278 obtained from the ratio between the sulfonated repeat-unit molecular mass (368) and the unsulfonated one (288).

As shown by Devaux *et al.*[10], complete sulfonation of PEEK upon dissolution in 99.5% H_2SO_4 is very quickly achieved. These authors performed a kinetic analysis of PEEK sulfonation in 99.5% concentrated sulfuric acid at room temperature. During this work, it was observed that the maximum sulfonation level corresponding to one $-SO_3H$ per structural unit was achievable in less than one day following proper experimental conditions.

Owing to this chemical modification leading to an amorphous polymer, the solubility of PEEK is greatly improved. Indeed, fully sulfonated PEEK becomes soluble in several ordinary strong polar organic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), pyridine and *N*-methyl-2-pyrrolidone (NMP)[9]. The latter solvent was selected for the present s.e.c. experiments.

EXPERIMENTAL

Products

PEEK powder samples. Eleven experimental PEEK samples supplied by ICI were used throughout this work. They were synthesized following a nucleophilic procedure[9] in order to cover a wide range of molecular masses ($\bar{M}_n$ from ~3000 to ~27 000). Four of them (PEEK 1, 2, 3 and 4) were selected as s.e.c. standards. Their weight-average molecular masses after complete sulfonation are 72 200, 47 500, 28 900 and 18 300 respectively[10]. As these samples were not fractionated, they can be qualified as broad molecular-mass distribution calibration agents.

Model compound. In the low-molecular-mass range, $LiO\phi CO\phi O\phi SO_3Li$ was used for PEEK s.e.c. specific calibration. The synthesis of this model compound was performed following a procedure reported by Leblanc[16].

Calibration agents. Ten practically isomolecular poly(methyl methacrylate) (PMMA) samples with molecular masses ranging from 2400 to 1 400 000 were used as primary s.e.c. standards. They were provided by Polymer Laboratories Ltd (part No. 2020-0101).

Solvents

For u.v. spectroscopy and viscometric experiments and for totally sulfonated PEEK preparation, sulfuric acid

(UCB, 99–100%, p.a., ref. 1102) was used without further purification. During this study, care was taken to avoid picking up moisture, which modifies notably the solvent sulfonation properties[13–15].

Methanesulfonic acid (MSA) (Fluka, ref. 64280, puriss., >99% (T)) was selected for ^{19}F n.m.r. and viscometry analyses. It was used as received.

Hydrochloric acid (min. 37%) was a Merck product (ref. 1027).

N-Methyl-2-pyrrolidone (NMP) from GAF Corporation was the solvent selected for s.e.c. and some viscometric analyses of sulfonated PEEK. It was purified by distillation under reduced pressure at 100°C over calcium hydride to avoid hydrolysis. The solvent was used after filtration through a 0.45 μm filter (Millipore, ref. HVHP 04700). Lithium bromide (LiBr) was supplied by Merck (ref. 5669).

Selected procedure for fully sulfonated PEEK preparation

PEEK (around 3 g dl^{-1}) dissolved in 99.5% concentrated sulfuric acid is reacted for periods ranging from 3 to 4 days.

PEEK dissolution is not instantaneous and sulfonation only occurs after dissolution. Consequently, heterogeneous mixtures can be obtained if care is not taken. Dried PEEK powder is thereby used to keep the dissolution process as short as possible (less than 1 h) relative to the total sulfonation time. Furthermore, the medium is vigorously stirred during the gradual addition of sulfuric acid and shaken during the whole reaction time.

The obtained sulfonated polymer is precipitated with at least a five-fold volume of a stirred mixture of deionized water and hydrochloric acid (50/50 vol.) at 0°C. The polymer is then shredded to obtain a fine powder, filtered, thoroughly washed with water/HCl to eliminate H_2SO_4 residue and dried at room temperature for about 2 days. The so-prepared sulfonated PEEK (H-SPEEK) can be used in this free acid form for viscometry and room-temperature s.e.c. analyses.

If H-SPEEK has to be stocked for a long time or has to undergo thermal treatments in the solid state, it is preferable to perform a neutralization of the polymer. For example, to obtain a Li-SPEEK sample, a stirred H-SPEEK/water mixture (5 g dl^{-1}) is neutralized with LiOH (0.1 M). This Li-SPEEK mixture is then filtered and washed with cold water. Afterwards, the polymer salt can be dried overnight at 100 to 120°C under vacuum.

The sulfonation level of each sulfonated sample was checked by ^{13}C n.m.r. using deuterated dimethylsulfoxide (DMSO-d_6) as solvent[9].

Dissolution procedures

In concentrated sulfuric acid. Sulfuric acid solutions of PEEK for u.v. spectroscopy and viscometry were obtained by vigorous shaking for a period of about 36 h at room temperature. Owing to sulfonation, the molecular mass and thereby the mass concentration of a PEEK sample increase as soon as a macromolecule is dissolved in H_2SO_4. This change in mass concentration was taken into account when H_2SO_4–PEEK solutions were used for u.v.-visible (absorbance law determination) and viscometry (reduced and inherent viscosity calculations) characterizations. This correction of concentration due to sulfonation was easily applied. Indeed, the concentration in sulfonated species (C_s) is related to the initial concentration in unsulfonated species (C_u) by:

$$C_s = 1.278 C_u \quad (1)$$

In N-methyl-2-pyrrolidone. For viscometry and s.e.c. experiments, H-SPEEK or Li-SPEEK was dissolved in NMP–LiBr (0.1 M) at room temperature during 12 h with strong mechanical shaking. The solution was then heated for 1 h at 80°C. It was verified that s.e.c. characterization of H-SPEEK or Li-SPEEK samples gives identical results[17]. Furthermore, no degradation was detected by s.e.c. experiments if H-SPEEK or Li-SPEEK/NMP–salt solutions stay from 1 to 10 h at 180°C[17].

In methanesulfonic acid (MSA). ^{19}F n.m.r. and viscometry solutions of H-SPEEK and ^{19}F n.m.r. solutions of PEEK were prepared at room temperature with shaking for a period of about 24 h.

Viscometry

The viscometry measurements were carried out with an Ubbelohde viscometer modified by Desreux. The intrinsic viscosity was taken as the arithmetic mean of the reduced and inherent viscosities extrapolated to zero concentration.

Data for universal calibration study were obtained at 25°C with solutions of poly(methyl methacrylate) (PMMA) (initial concentration ~0.7 g dl^{-1}) and of the four Li-SPEEK standards (initial concentration ~0.6–0.8 g dl^{-1}) in NMP–LiBr (0.1 M). The solvent used for the determination of t_0 and for the different dilutions of Li-SPEEK solutions was maintained for 1 h at 80°C (see Li-SPEEK solution preparation).

The viscometry measurements of H-SPEEK samples in methanesulfonic and sulfuric acids were carried out at 25°C with solutions of initial concentration around 1 g dl^{-1}.

In NMP, H_2SO_4 and MSA, four solutions were used to give a wide coverage of the concentration scale.

U.v.-visible spectroscopy

U.v.-visible spectra were recorded with a Philips PU 8720 UV/VIS scanning spectrophotometer in the 200–600 nm wavelength range. The choice of the s.e.c. u.v. detector wavelength was based on the u.v. spectrum of H-SPEEK in the NMP–salt solvent[9].

^{19}F nuclear magnetic resonance

Spectra were obtained with a Bruker WM 250 spectrometer working at 235.34 MHz for ^{19}F. The experimental conditions were as follows: *FT* size, 16K; spectral width, 20 000 Hz; pulse width, 13 μs (90°). The relaxation times for the peaks of the polymer and internal standard FϕSO$_2\phi$F were determined by using the inversion recovery method. They were, respectively, 0.3 and 1.2 s. In order to obtain quantitative measurements, a relaxation time of 5.6 s was therefore adopted. The polymer concentration was around 5 g dl^{-1}. The solvent was MSA.

The polymer fluorine content $[F]_P$ (expressed in ppm) was determined following a procedure described in a previous paper[18] using the relationship:

$$\frac{S_{IS}}{S_P} = \frac{[F]_{IS}}{[F]_P} \quad (2)$$

where S_{IS} is the peak area of the internal standard, S_P is the peak area of the polymer and $[F]_{IS}$ is the fluorine content of the internal standard.

DETERMINATION OF THE ABSOLUTE MASS CONCENTRATIONS OF H-SPEEK SAMPLES

The H-SPEEK standards were characterized by u.v.-visible spectroscopy and ^{19}F n.m.r. with a view to calculating a correction factor allowing the determination of the absolute mass concentration (C_S) required for accurate viscometry measurements.

U.v.-visible spectroscopic measurements

The calibration of the u.v. spectrophotometer at 411.2 nm was determined with six solutions of fully sulfonated PEEK-9 sample in 99.5% H_2SO_4 at concentrations ranging from ~ 1 to 15 mg l^{-1}. Such solutions were prepared from weighing unsulfonated and dried PEEK powder. The concentration modification due to complete sulfonation was taken into account. The relationship between the absorbance (A) and the concentration (C_s) expressed in mg l^{-1} is:

$$A = 12.970 \times 10^{-5} C_s \quad (3)$$

Afterwards, each H-SPEEK sample was dissolved in the same batch of 99.5% H_2SO_4 at a concentration of around 50 mg dl^{-1}. The solution was then diluted in order to obtain an apparent concentration (C_a) below 15 mg l^{-1}. *Table 1* shows their absorbance values (A) at $\lambda = 411.2$ nm. The true concentration (C_s) was then obtained from equation (3) and compared with the experimental concentrations (C_a). The ratio between C_s and C_a represents the correction factor (f_{uv}) (*Table 1*).

^{19}F n.m.r. measurements

The fluorine contents of the unsulfonated PEEK $[F]_u$ and sulfonated PEEK $[F_a]_s$ standard samples were measured by ^{19}F n.m.r. in CH_3SO_3H. If $[F]_u$ is an absolute value, it is obvious that $[F_a]_s$ is an apparent content depending on the purity of the sulfonated sample. These values were then used to calculate a concentration correction factor (f_{nmr}) by applying the expression:

$$f_{nmr} = \frac{1.278\,[F_a]_s}{[F]_u} \quad (4)$$

where 1.278 is the constant corresponding to the increase of polymer concentration due to sulfonation. The results are presented in *Table 2*.

Table 1 U.v.-visible spectroscopy correction factor (f_{uv}) allowing the determination of the absolute mass concentration of a sulfonated PEEK standard solution

Sample	C_a[a] (mg l^{-1})	A[b]	C_s[c] (mg l^{-1})	f_{uv}
H-SPEEK-1	2.14	0.179	1.38	0.64
H-SPEEK-2	5.82	0.609	4.69	0.80
H-SPEEK-3	5.08	0.514	3.96	0.78
H-SPEEK-4	14.64	1.480	11.41	0.78

[a] Experimental concentration
[b] Absorbance at $\lambda = 411.2$ nm in 99.5% H_2SO_4
[c] Absolute concentration

Table 2 ^{19}F n.m.r. correction factor (f_{nmr}) allowing the determination of the absolute mass concentration of a sulfonated PEEK standard solution

Sample	$[F]_u$[a] (ppm)	$[F_a]_s$[b] (ppm)	F_{nmr}
H-SPEEK-1	722	376	0.67
H-SPEEK-2	805	466	0.74
H-SPEEK-3	2615	1649	0.81
H-SPEEK-4	5938	3439	0.74

[a] Absolute fluorine content of an unsulfonated sample
[b] Apparent fluorine content of a sulfonated sample

Size (steric) exclusion chromatography (s.e.c.)

Two mixed-bed columns set in an oven were used. They were supplied by Millipore-Waters (Shodex columns from Showa Denko, ref. AD 80 M/S). The working temperature was 25°C. The solvent NMP + LiBr 0.1 M was continuously degassed by He. The flow rate was 0.5 ml min^{-1}. The chromatogram was obtained using a u.v. detector (Perkin Elmer model LC 55) working at a wavelength of 270 nm and a 410 Millipore-Waters differential refractometer (d.r.i.). The s.e.c. apparatus was connected with a MicroVAX 2000 computer from Digital for acquisition and treatment of the data. The injection conditions were: sample size, 50 μl; Li-SPEEK concentration, 0.5 g l^{-1} (u.v. detection), 1 g l^{-1} (d.r.i. detection).

RESULTS AND DISCUSSION

Solvent for s.e.c.

The viscometric characterization of sulfonated H-SPEEK-9 sample in NMP clearly shows a particular polyelectrolyte behaviour (*Figure 1*). Indeed, the reduced viscosity increases markedly with decreasing concentration, showing an unusual but typical polyelectrolyte upward curvature[19].

On the other hand, if pure NMP is used as s.e.c. mobile phase, the chromatogram of H-SPEEK-9 sample appears distorted (*Figure 2*). The macromolecules elute predominantly near the exclusion volume and there is little or no separation on the basis of molecular mass.

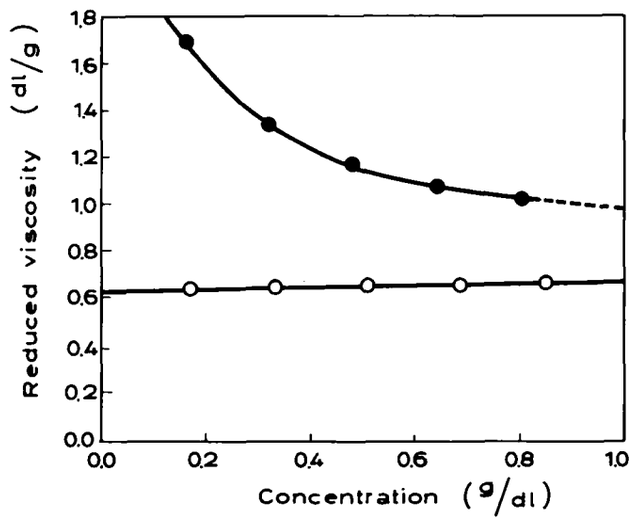


Figure 1 Variation of reduced viscosity *versus* concentration for H-SPEEK-9 in *N*-methyl-2-pyrrolidone (●) and Li-SPEEK-9 in *N*-methyl-2-pyrrolidone + LiBr (0.1 M) (○)

In viscometry at high concentrations of H-SPEEK, the polyelectrolyte molecules overlap one another and no possibility is offered for the counter-ions to leave the domain of a given macromolecule. The molecules are not appreciably expanded and the specific viscosity varies as usual. When the solution is diluted to concentrations in the range of those commonly used for s.e.c. experiments, the molecules are expanded. Regions appear that are not occupied by polymer molecules, and mobile counter-ions will diffuse from the molecular domain into the bulk of the solvent. The development of this net negative charge due to loss of counter-ions is responsible for molecular expansion. The reduced viscosity then undergoes a marked increase with dilution, reaching values at high dilution that are many times the intrinsic viscosity expected for the polymer in the absence of charges.

In s.e.c. not only can chain expansion give rise to larger hydrodynamic volumes, but also, as reported in the literature, even for styrene–divinylbenzene copolymer gel, repulsion between the polyion and some charged groups on the packing can lead to exclusion of the polyion from the pores. This effect, called 'ion exclusion', is a well known phenomenon in which the diffusion of the ionic species into the interior of the gel is restricted by electrostatic repulsion.

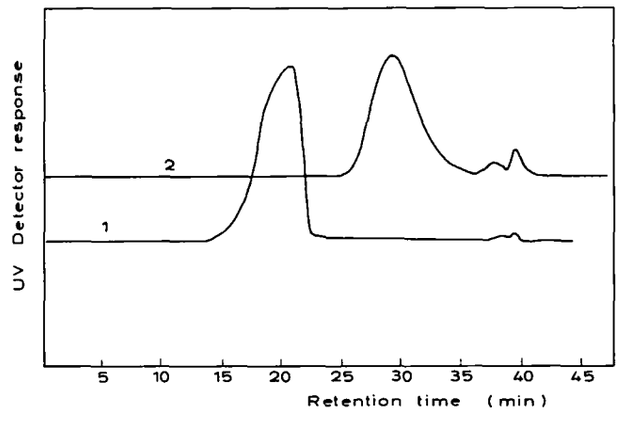


Figure 2 Room-temperature size exclusion chromatograms of totally sulfonated PEEK-9 in *N*-methyl-2-pyrrolidone without (chromatogram 1) and with (chromatogram 2) 0.1 M LiBr ($\bar{M}_w = 24\,000$, $\bar{M}_n = 12\,700$)

The addition of a strong electrolyte such as LiBr to the solvent overcomes 'ion exclusion' and suppresses the loss of counter-ions from the charged sites on the polymer. This allows a return of the polymer to normal physical and thermodynamic solution properties. Classical elution and peak shape (see *Figure 2*) are then observed[20–23]. In the same way, the plot of the reduced viscosity against concentration becomes linear (*Figure 1*) and correct intrinsic viscosities $[\eta]$ can be obtained.

Mark–Houwink–Sakurada (MHS) relationships for totally sulfonated PEEK

As a preliminary to measuring the intrinsic viscosities of the H-SPEEK standards in NMP + LiBr and in MSA, the accurate mass concentration of each H-SPEEK sample was sought. Indeed, H-SPEEK is hygroscopic[24] and, in addition, owing to the sulfonation method followed, may contain some residual impurities (for example, H_2SO_4 molecules absorbed on H-SPEEK macromolecules). The problems of both moisture and impurities were overcome by determining absolute mass concentrations by u.v.-visible and ^{19}F n.m.r. experiments. This work (see 'Experimental' part) has allowed the determination of the concentration correction factors, which are shown in *Tables 1* and *2*. From the comparison between the values given by u.v.-visible spectroscopy and ^{19}F n.m.r., it can be seen that both methods give very similar results, which have been averaged for each sample and used during the viscometric work.

The molecular masses and the intrinsic viscosities of the Li-SPEEK standards dissolved in NMP–LiBr (0.1 M) and of the H-SPEEK standards dissolved in MSA are given in *Table 3*. The Mark–Houwink–Sakurada relationships for the fully sulfonated PEEK polymer at temperatures of 25°C could then be deduced from these values:

in NMP + LiBr (0.1 M)

$$[\eta] = 4.87 \times 10^{-5} \bar{M}_w^{0.938} \text{ (dl g}^{-1}\text{)} \quad (5)$$

in CH_3SO_3H

$$[\eta] = 5.77 \times 10^{-5} \bar{M}_w^{0.900} \text{ (dl g}^{-1}\text{)} \quad (6)$$

Figure 3 illustrates the molecular-mass dependence of $[\eta]$ for Li-SPEEK in the NMP–salt medium.

Table 3 Weight-average molecular masses and intrinsic viscosities of Li-SPEEK[a] and H-SPEEK samples in *N*-methyl-2-pyrrolidone–LiBr (0.1 M), in methanesulfonic acid and in concentrated sulfuric acid at 25°C

		$[\eta]$ (dl g^{-1})		
Samples	$\bar{M}_w$	NMP + LiBr	CH_3SO_3H	99.5% H_2SO_4
Li-SPEEK-1	73 400	1.68		
H-SPEEK-1	72 200		1.30	1.29
Li-SPEEK-2	48 300	1.28		
H-SPEEK-2	47 500		1.02	1.04
H-SPEEK-11[b]	36 200[b]			0.72
Li-SPEEK-3	29 400	0.78		
H-SPEEK-3	28 900			0.62
H-SPEEK-9	24 800[c]		0.50	0.51
Li-SPEEK-4	18 600	0.47		
H-SPEEK-4	18 300		0.40	0.38

[a] $(\bar{M}_w)_{\text{Li-SPEEK}} = (378/368)\,(\bar{M}_w)_{\text{H-SPEEK}}$ taking into consideration the ratio between the molecular masses of the structural units
[b] See *Table 4*, sample PEEK-3 in ref. 10
[c] See second paper of this series[11]

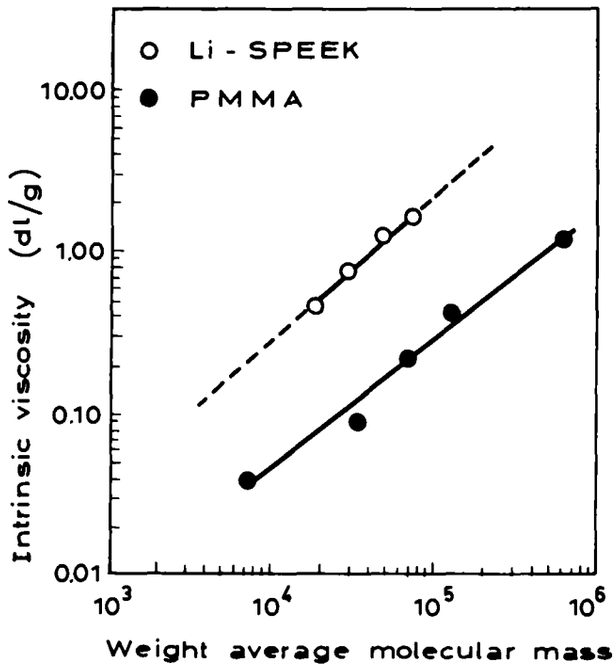


Figure 3 Logarithmic plot of the intrinsic viscosity against the weight-average molecular mass in *N*-methyl-2-pyrrolidone + LiBr (0.1 M) at 25°C for Li-SPEEK and PMMA standards

Table 4 Comparison between molecular masses obtained from room-temperature s.e.c. using the specific and universal calibrations

	Specific calibration			Universal calibration		
Samples	$\bar{M}_w$	$\bar{M}_n$	H	$\bar{M}_w$	$\bar{M}_n$	H
Li-SPEEK-1	73 000	35 200	2.1	71 900	31 300	2.3
Li-SPEEK-2	49 700	23 200	2.1	50 900	23 100	2.2
Li-SPEEK-3	30 500	17 400	1.8	31 600	16 300	1.9
Li-SPEEK-4	18 100	9 800	1.9	18 800	10 000	1.9
Li-SPEEK-5	48 900	20 700	2.4	47 500	21 000	2.3
Li-SPEEK-6	35 200	17 600	2.0	34 300	17 400	2.0
Li-SPEEK-7	31 300	15 000	2.0	30 200	15 600	1.9
Li-SPEEK-8	24 000	12 700	1.9	23 200	12 200	1.7
Li-SPEEK-9	23 900	12 900	1.9	24 000	12 300	2.0
Li-SPEEK-10	8 500	4 400	1.9	8 200	5 100	1.6

In other respects, the work of Devaux *et al.*[10] concerning the viscometric study of totally sulfonated PEEK dissolved in 99.5% H_2SO_4 at 25°C was carried out mainly to improve the values of the Mark–Houwink–Sakurada constants. Six samples were used to reach this objective. Their intrinsic viscosities are gathered in *Table 3*. They lead to the establishment of a new viscosity law:

$$[\eta] = 4.86 \times 10^{-5} \bar{M}_w^{0.917} \text{ (dl g}^{-1}\text{)} \quad (7)$$

It must also be noted that no polyelectrolyte behaviour of sulfonated PEEK dissolved in H_2SO_4 and in CH_3SO_3H was detected during the viscometric work.

S.e.c. of sulfonated PEEK

The s.e.c. experimental conditions of SPEEK having been optimized and the viscosity law of Li-SPEEK determined, the next step was the establishment of the universal[25] and specific calibration curves.

The specific calibration was obtained following an iterative procedure described elsewhere[10] using a poly(methyl methacrylate) (PMMA) calibration and five standards (Li-SPEEK 1 to 4 and $LiO\phi CO\phi O\phi SO_3Li$). It allowed the calculation of the results reported in *Table 4*.

There have been a number of attempts to apply the 'universal calibration' concept to a polyelectrolyte when an organic polar solvent containing a salt is used as mobile phase and while a successful size exclusion separation can be made for the polyelectrolyte[26–29]. In this case, polystyrene standards do not provide pure size exclusion but PMMA standards do well. Indeed, it was found that Li-SPEEK and PMMA verified the same relationship between $[\eta]M_p$ and the elution volume[30]. The viscosity law of PMMA was determined in *N*-methyl-2-pyrrolidone–LiBr (0.1 M) at 25°C (*Table 5* and *Figure 3*):

$$[\eta] = 5.33 \times 10^{-5} M^{0.749} \text{ (dl g}^{-1}\text{)} \quad (8)$$

After the establishment of the universal calibration and with the help of the MHS parameters of sulfonated PEEK, the average molecular masses of the four Li-SPEEK standards were calculated. The results are presented in *Table 4*.

In order to assess the reliability of the determination of absolute molecular mass of totally sulfonated PEEK measured by the s.e.c. universal calibration method, six other experimental samples were analysed. Their molecular data are also presented in *Table 4*.

Finally, it must be noted that the chemical stability of the sulfonated polymer in solution in 99.5% H_2SO_4 was checked. Indeed, different samples of PEEK-9 dissolved from 15 days to 4 months in H_2SO_4 were analysed by this room-temperature s.e.c. method. The results are shown on *Figure 4*. The difference between weight-

Table 5 Molecular masses and intrinsic viscosities of five PMMA standards in *N*-methyl-2-pyrrolidone–LiBr (0.1 M) at 25°C

M_p[a]	$[\eta]$ (dl g^{-1})
610 000	1.18
127 000	0.42
67 000	0.22
34 500	0.09
6 950	0.04

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

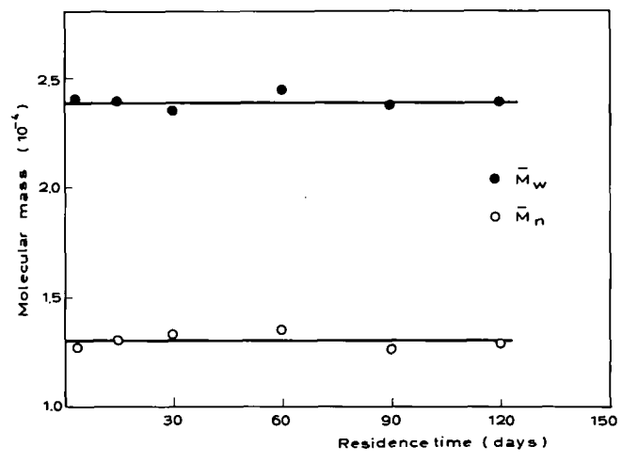


Figure 4 Weight-average and number-average molecular masses of Li-SPEEK-9 samples after different residence times in 99.5% H_2SO_4

average and number-average molecular masses ($\bar{M}_w$ = 23900 and $\bar{M}_n$ = 13000) always remains in the limit of experimental accuracy (below 5%).

CONCLUSION

Owing to the high solvent resistance of a PEEK macromolecule, the development of analytical methods for determination of molecular mass and molecular-mass distribution was difficult.

This paper presents a new, useful and accurate size (steric) exclusion chromatography method for PEEK at room temperature based on a chemical derivatization procedure. This method requires dissolution of the sample in 99.5% H_2SO_4 at room temperature, complete sulfonation and recovery of the modified polymer. Several solvents of sulfonated PEEK are compatible with the packings of the columns used in s.e.c. (NMP, DMF, DMSO, DMAc). In this work, NMP is selected, but a salt must be added to the solvent owing to the polyelectrolyte nature of the sulfonated polymer. Owing to the u.v.-visible properties of the sulfonated PEEK NMP–salt solution, the macromolecules can be detected by a u.v. spectrometer, which has a higher baseline stability and sensitivity than the d.r.i. one. This s.e.c. method is also standardized via the universal calibration established with PMMA standards and the viscosity laws of Li-SPEEK and PMMA in NMP–LiBr (0.1 M). Compared to the specific calibration, the universal calibration gives accurate molecular masses.

Finally, viscometric laws of sulfonated PEEK in methanesulfonic acid and concentrated sulfuric acid are also established.

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