^{19}F n.m.r. end-group analysis of a poly(aryl ether ether ketone) (PEEK)

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(*Received 12 February 1988; revised 6 July 1988; accepted 4 August*)

^{19}F n.m.r. spectroscopy of poly(ether ether ketone) (PEEK) and related model compounds has been performed in various solvents including sulphuric acid. Different chemical shifts have been observed on sulphonated samples and long range shielding effects are discussed. An alternative method for the $\bar{M}_n$ evaluation of PEEK is proposed.

(Keywords: poly(ether ether ketone); molecular weight determination; ^{19}F n.m.r. chain-ends characterization)

INTRODUCTION

Owing to its poor solubility, methods for the molecular characterization of PEEK are limited.

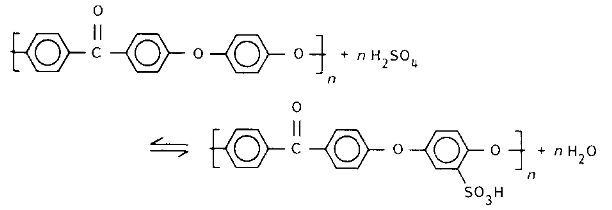
We recently published[1] the results of the molecular weight determination of PEEK based on light scattering in sulphuric acid. Correlations were made by viscometry in sulphuric acid and in a new solvent mixture (50/50 (w/w) phenol/1,2,4-trichlorobenzene). Additionally a gel permeation chromatography (g.p.c.) calibration in this latter solvent was achieved providing weight average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights.

This paper deals with a direct $\bar{M}_n$ determination by nuclear magnetic resonance (n.m.r.) analysis of chain-ends. Osmometry, the alternative way to directly obtain $\bar{M}_n$ has been rapidly discarded owing to the lack of suitable solvent and osmometer membranes.

Poly(aryl ether ether ketone)s are commonly synthesized by nucleophilic aromatic substitution of fluorinated benzophenones[2]. Control of the final molecular weight is achieved by use of an excess of fluorinated species rather than hydroxyl ones because of the propensity of the latter to generate chain branching[3]. It follows therefore that all the PEEK chain-ends should be F atoms and an accurate measurement of fluorine concentration should lead to the $\bar{M}_n$ value. Unfortunately, fluorides are by-products of the synthesis and residues will interfere with elemental analysis for total fluorine content. Spectroscopic analyses (i.r., ^{1}H and ^{13}C n.m.r.) are not sensitive enough to allow the accurate C–F bond analysis at the very low concentration levels necessary to determine medium or high molecular weights. Therefore, we decided to study quantitative ^{19}F n.m.r. spectroscopy. By comparison with other spectroscopic techniques, ^{19}F n.m.r. had the advantage of absolute selectivity on F atoms, leading to enhanced sensitivity and accuracy.

Convenient room-temperature solvents for PEEK are concentrated sulphuric acid and methane sulphonic acid. In a previous paper[1] we used the former, keeping in mind that sulphonation occurred upon PEEK dissolution (*Scheme 1*)[1]:

Scheme 1



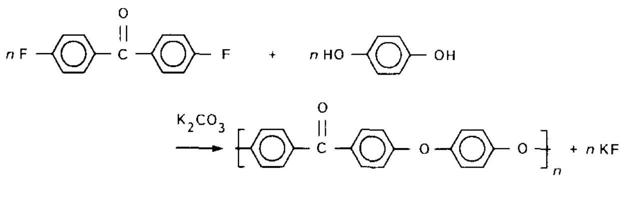
It has been shown that no electrophilic substitution (i.e. no sulphonation) occurred on the phenyl groups directly linked to a carbonyl due to electron withdrawing character of the carbonyl.

EXPERIMENTAL

Polymers

Samples of PEEK used throughout this work were synthesized by nucleophilic aromatic substitution (*Scheme 2*):

Scheme 2



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The reaction was carried out in diphenylsulphone with a slight excess of 4,4'-difluorobenzophenone at temperatures reaching 320°C following a procedure described in detail elsewhere[3]. Except where otherwise stated, a sample having g.p.c. $\bar{M}_w$ and $\bar{M}_n$ of 19 800 and 10 000 was used.

A sample of polyether ketone (PEK) was also used for comparison. Its synthesis was very similar to the PEEK one, except that the main reactant was 4-hydroxy-4'-fluorobenzophenone again in presence of excess 4,4'-difluorobenzophenone.

Model compounds

Three model compounds were also analysed. Their chemical structures are given in *Table 1*. The synthesis of the third model (CMS) was carried out by the same procedure used for PEEK (*Scheme 2*). 4-fluoro- and 4,4'-difluorobenzophenones (CM1 and CM2) were purified by distillation under reduced pressure. The third model compound (CM3) was purified by recrystallization.

Solvents

H_2SO_4 (99–100% UCB) was used as received. Since we observe that significant chemical shifts (up to 1 ppm) in ^{19}F n.m.r. may result from H_2SO_4 concentration modifications (in the range 95–100%), the same H_2SO_4 batch has been used throughout this work, also carefully avoiding the pick up of moisture. No drift in chemical shifts was observed when these precautions were taken.

Other solvents, CH_3SO_3H (98% Janssen Chimica) and dimethyl formamide, DMF (99% Merck) were used as received. The sodium salt of CF_3COOH was used as internal standard in H_2SO_4, CH_3SO_3H and DMF. The dryness of the salt was verified periodically.

Nuclear magnetic resonance ^{19}F

The solutions (*ca.* 5% w/w) in H_2SO_4 or CH_3SO_3H were prepared at room temperature. Sulphonated samples were obtained by precipitation of the H_2SO_4 solution in distilled water, washing and drying[1]. Depending on the duration of the reaction in H_2SO_4, partially (less than 12 h) or completely (more than 1 day) sulphonated samples were obtained. Such sulphonated samples are readily soluble in DMF.

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, 16 K; spectral width, 20 000 Hz; pulse width, 13 μs (90°). The relaxation times for the peaks of the polymer and internal standard were determined by using the inversion recovery method. They are, respectively, 0.3 and 1.1 s. In order to obtain quantitative measurements, a relaxation time of 5.6 s was therefore adopted.

The chemical shifts always refer to the internal standard CF_3COOH. For quantification of the fluorine content, the total peak area corresponding to the analysed sample was integrated and compared with the peak area of the internal standard. The method was optimized with model compounds. It has been found that the best accuracy (±5%) was obtained when the internal standard concentration was adjusted in order to produce a peak area of the same order of magnitude as the area corresponding to the sample (e.g. *Figure 1*).

Table 1 Chemical structure of model compounds

Compound	Chemical structure	Name
CM 1	FØ–CO–Ø	4 fluorobenzophenone
CM 2	FØ–CO–Ø–F	4,4' difluorobenzophenone
CM 3	FØCOØOØOØCOØF	–

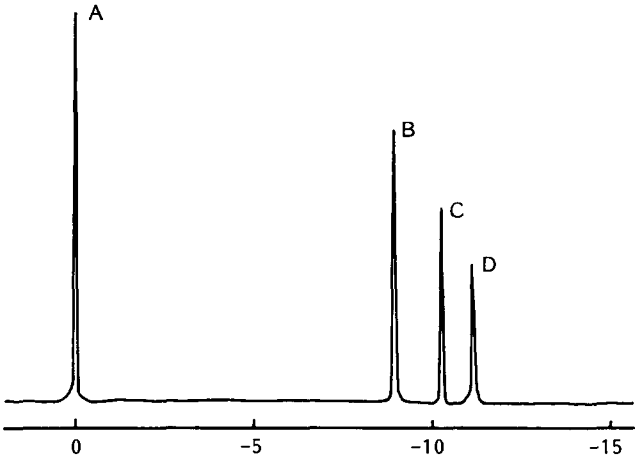


Figure 1 ^{19}F n.m.r. spectra of various model compounds (solvent H_2SO_4 99–100%). A, CF_3COOH; B, F–Ø–CO–Ø; C, F–Ø–CO–Ø–F; D, PEK

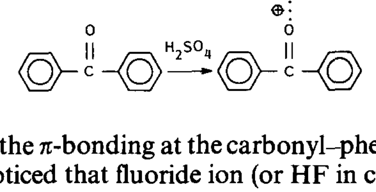
RESULTS AND DISCUSSION

Chemical shifts

The results obtained from ^{19}F n.m.r. analysis of polymers and model compounds can be divided into series with respect to their ease of sulphonation. Non-sulphonable compounds and polymers (i.e. those with carbonyls directly linked to each phenyl) will be discussed first.

For these compounds, the results of ^{19}F n.m.r. analysis in H_2SO_4 are reported in *Table 2* and *Figure 1*. It is observed that each compound is characterized by a different chemical shift. This is a consequence of the long range shielding effect in F atoms which has been extensively studied more than 10 years ago[4–9]. It is known to be due to electronic transmission from one aromatic ring to the following through the π-electron framework. This mechanism is markedly enhanced for compounds like benzophenone by the formation of adducts with Lewis acids. In concentrated H_2SO_4, the carbonyl of benzophenone is protonated in the following way:

Scheme 3



increasing the π-bonding at the carbonyl–phenyl links[9]. It must be noticed that fluoride ion (or HF in conc. H_2SO_4) gives also rise to a shift, but it was observed outside the range considered in this work, and therefore never interfered with our measurements.

The compounds of the second series, i.e. those containing sulphonatable phenyl rings, were analysed for different sulphonation levels resulting from various

Table 2 ^{19}F n.m.r. chemical shifts of samples unable to sulphonate (H_2SO_4 99–100%). Chemical shifts refer to CF_3COOH as internal standard

Compound	Chemical shift (ppm)
CM 1	−9.5
CM 2	−10.3
PEK	−11.2

Table 3 ^{19}F n.m.r. analyses of sulphonable samples in concentrated H_2SO_4. Chemical shifts refer to CF_3COOH

Sample	Sulphonation level	Chemical shifts (ppm)
CM 3	Partial	−12.0 −13.2 −14.7
	Complete	−12.0 −13.2
PEEK (C sample, *Table 6*)	Partial	−12.1 −13.3 −14.8
	Complete	−12.1 −13.3

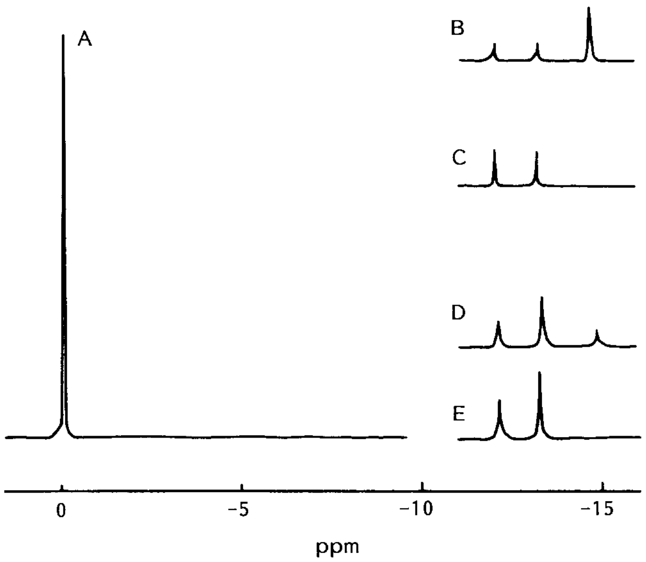
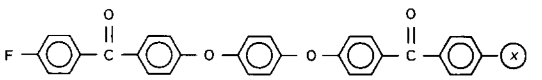


Figure 2 ^{19}F n.m.r. spectra of CM3 and PEEK (solvent: H_2SO_4 99–100%). A, CF_3COOH; B, CM3 partially sulphonated; C, CM3 completely sulphonated; D, PEEK partially sulphonated; E, PEEK completely sulphonated

residence times in H_2SO_4[10,11] (*Table 3* and *Figure 2*). For limited sulphonation reaction, a peak is observed in the −14.8 ppm region and can be attributed to the F atoms belonging to the unsulphonated sequence:

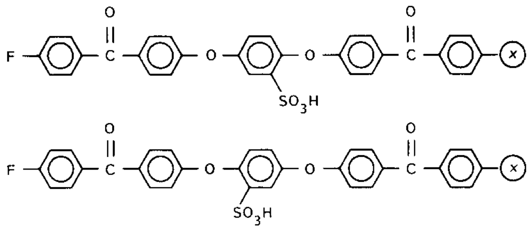
Scheme 4



where *X* stands for another F atom (CM 3) or another PEEK repeat unit. For symmetry reasons, only one peak is observed for CM 3 in this region.

During sulphonation, the first peak (−14.8 ppm) decreases and two new ones arise in the −12.1 and −13.3 ppm regions. These can be attributed to the two non-equivalent sulphonated sequences:

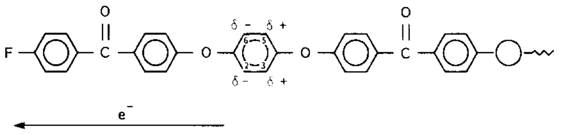
Scheme 5



Sulphonation of the symmetrical model CM3 ($X=F$) gives only one sulphonated species. After sulphonation, however, it becomes unsymmetrical and two different F end-groups are detected. In this case, the intensity of the two n.m.r. peaks is the same.

In the PEEK polymer molecule, there are two possible non-equivalent sulphonation positions, with respect to each F end-group. The two peaks are quite different in size showing evidence of an electronic long range action of the end-groups on the sulphonation reaction itself. In fact, we observed[10,11] an electron-withdrawing force of the F atom, lowering the reactivity of the neighbouring phenyl ring to electrophilic substitution. This effect can be shown as follows:

Scheme 6



Thus, it can be seen that the *ortho* positions (2 and 6) are more reactive than the *meta* positions (3 and 5) to the electrophilic substitution by $-SO_3H$. For this reason, we propose to attribute the higher peak (−13.3 ppm) in ^{19}F n.m.r. spectra to the species sulphonated in the *ortho* position and the lower (−12.1 ppm) to the sequences sulphonated in the *meta* position.

The electron-withdrawing effect seems considerably lower at two repeating unit distance from the end since no other peaks are observed in the PEEK spectrum. Nevertheless, we suspect that the slight chemical shift differences consistently observed between the three peaks of CM 3 and those of PEEK may arise from the same electronic effect. This observation would be, if confirmed, the longest range effect of this kind ever reported.

In *Table 4*, are reported the results of ^{19}F n.m.r. analyses of 4,4′-difluorobenzophenone (CM 2) and PEEK samples in CH_3SO_3H and DMF. For these solvents, only one peak is observed in each case.

In CH_3SO_3H, the peaks corresponding to CM 2 and PEEK lie, respectively, at −15 and −17.8 ppm. This

Table 4 ^{19}F n.m.r. analyses of CM 2 and PEEK samples in various solvents. Chemical shifts refer to CF_3COOH

Sample	Solvent	Sulphonation	Chemical shifts (ppm)
CM 2	H_2SO_4	No	−10.3
	CH_3SO_3H	No	−15.0
	DMF	No	−11.9
PEEK (C sample, *Table 6*)	H_2SO_4	Partial	−12.1 −13.3 −14.8
	CH_3SO_3H	No	−17.8
	DMF	Complete	−11.9

Table 5 Quantitative F end-groups analysis of PEEK (C) sample in various conditions (increasing sulphonation level)

Solvent	Sulphonation	F end-groups concentration (ppm)
CH_3SO_3H	No	3820
H_2SO_4	Partial	3710
H_2SO_4	Complete	3850

Table 6 Comparison between $\bar{M}_n$ values obtained from ^{19}F n.m.r. analysis and g.p.c.

	$\bar{M}_n$	
Sample	G.p.c.	^{19}F n.m.r.
A	4000	3000
B	9800	8500
C	10000	10000
D	12800	13000
E	16300	16500
F	15700	20000
G	17300	22500

difference can be attributed to the shielding effect on the F atom due to the protonation of the carbonyl oxygen. However, this solvent is known to be unable to sulphonate PEEK and, consequently, only one peak is observed for the polymer.

The situation is very different in DMF solution. The only samples of PEEK soluble in this medium are the sulphonated ones. These were sulphonated in H_2SO_4, then recovered, following a procedure described elsewhere[1].

We observe in *Table 4* that the ^{19}F n.m.r. peaks lie exactly at the same chemical shift (-11.9 ppm) for CM 2 and sulphonated PEEK. Indeed, no protonation of the carbonyl oxygen occurs in this case and the transmission of electronic effect through the π-electron framework cannot occur.

Quantitative fluorine analysis

By analysing model compounds of known purity, we verified that the quantitative determination of the F end-group was feasible with an accuracy of $\pm 5\%$.

We have also verified, on PEEK samples, that this accuracy was of the same order of magnitude whatever the sulphonation level. *Table 5* shows the results of F end-groups analyses of the same PEEK sample either unsulphonated (CH_3SO_3H) or sulphonated in concentrated H_2SO_4. Thus, the number of n.m.r. peaks has no influence on the total integrated area.

Therefore, $\bar{M}_n$ values can be calculated on the basis of fluorine end-group determination. In *Table 6*, the values calculated from g.p.c. analyses following our previously published procedure[1] are compared with the ^{19}F n.m.r. values. It can be observed that both methods agree very satisfactorily for the whole range of molecular weights. This agreement is an independent confirmation of the accuracy of our g.p.c. calibration. Moreover, it confirms that the synthesis of this set of PEEK samples was free from loss of fluorine which is sometimes suspected in polyether ether ketone synthesized by nucleophilic substitution[2].

CONCLUSIONS

Despite the poor solubility of PEEK polymers, two independent methods are now available to characterize their number average molecular weight, the g.p.c. as previously published and ^{19}F n.m.r. end-group analysis.

During this latter study, unusually large differences in chemical shifts were observed for very similar polymers and model compounds, when dissolved in H_2SO_4 and CH_3SO_3H. This result is related to very long range shielding effects already pointed out by several authors[4–9] for parent benzophenones in acid solutions. As expected, this effect does not occur in DMF solutions.

From a quantitative point of view, assuming that all the chain ends are aromatic fluorine, ^{19}F n.m.r. is a very reliable method for chain end analysis. This observation provides a good way to control the synthesis of poly(aryl ether ether ketone) and to follow end-group modifications.

ACKNOWLEDGEMENT

The authors are very grateful to Dr A. Bunn for his efficient help in n.m.r. spectra interpretation.

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