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Analogous Reaction for Maximum Sulfonation of Polysulfones

C. Mottet, A. Revillon, P. Le Perchec, M. F. Llauro and A. Guyot

CNRS – Laboratoire des Matériaux Organiques, BP 24, F-69390 Lyon-Vernaison, France

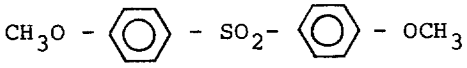
SUMMARY

The sulfonation of the model compounds of the structural units of the polysulfones and bis phenol A polyethersulfones has been conducted up to completion using SO_3 in a dichloroethane solution at room temperature. Whatever the initial structure may be, only one sulfonic group per aromatic ring can be attached. Water soluble polymers with the same degree of sulfonation can be prepared, without chain scission.

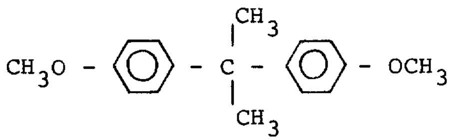
INTRODUCTION

Weakly sulfonated polysulfone are widely used as semi-permeable membranes for water treatment (1).More recently, their interest as ionomer materials has been pointed out (2). We were interested in exploring the properties of polymers with higher degrees of sulfonation, up to the point where they become water soluble. Preliminary studies of the conditions of complete sulfonation, carried out on model compounds for the structure of the polymer are reported here.

Two main families of polysulfone are commercially available. Both involve a bis aryl sulfone unit. One of them contains in addition a bis phenol A group. The model compounds chosen are dimethyl ether of these structures, namely bis(methoxy-4-phenyl)sulfone (I) and bis(methoxy-4-phenyl)-2,2 propane (II).



(I)



(II)

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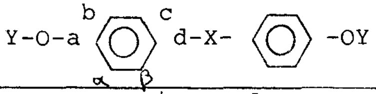
RESULTS AND DISCUSSION

Both I and II have been prepared from the corresponding bis-hydroxyphenyl compounds by reacting with a stoichiometric amount of NaOH in dilute water solution (2.5 10^{-3} N) at 10° C, and then with a slight excess of dimethylsulfate as alkylating agent in methanol followed by a 2 hour reflux treatment. The yields of purified products (recristallization from methanol or vacuum distillation) are respectively 63 and 88 %. The products were characterized by elementary analysis, IR spectroscopy and ^1H and ^{13}C NMR in d_6 dimethyl sulfoxide (Table I).

Table I - NMR data of the models



Nucleus		^1H		^{13}C			
X	Y	α	β	a	b	c	d
$C(CH_3)_2$	H	6.73	7.04	-	-	-	-
	CH_3	6.93	7.23	158	114	128	143
SO_2	H	7.10	7.89	-	-	-	-
	CH_3	7.20	8.06	163	115	129	134

The chemical shifts for ^1H and ^{13}C NMR are given in ppm with TMS as an internal reference.

Sulfonations of I and II have been carried out using SO_3 in dichloroethane (DCE) solution (0.8 mole/kg) slowly added to a DCE solution (0.1 N) of the model, the temperature being kept at 20 °C for 1 or 2 hours and reaching 50 °C to complete the reaction in some cases. After reaction, the solvents are evaporated and the product dissolved in water. When the reaction is not completed (molar ratio SO_3/model lower than 2) a part of the product is not water soluble. The water soluble products, highly hydroscopic, are difficult to purify so that elemental analyses are not reliable, as well as acido-basic titration.

From the ^1H NMR spectra of the aromatic protons, it is clear that (whatever the initial product may be) only one proton per aromatic ring has been substituted, forming a SO_3H group. Both spectra correspond to 6 aromatic protons per molecule, with 3 different protons with ortho (J_1 = 9 Hz) and meta (J_2 = 2 Hz) coupling constants (fig. 1).

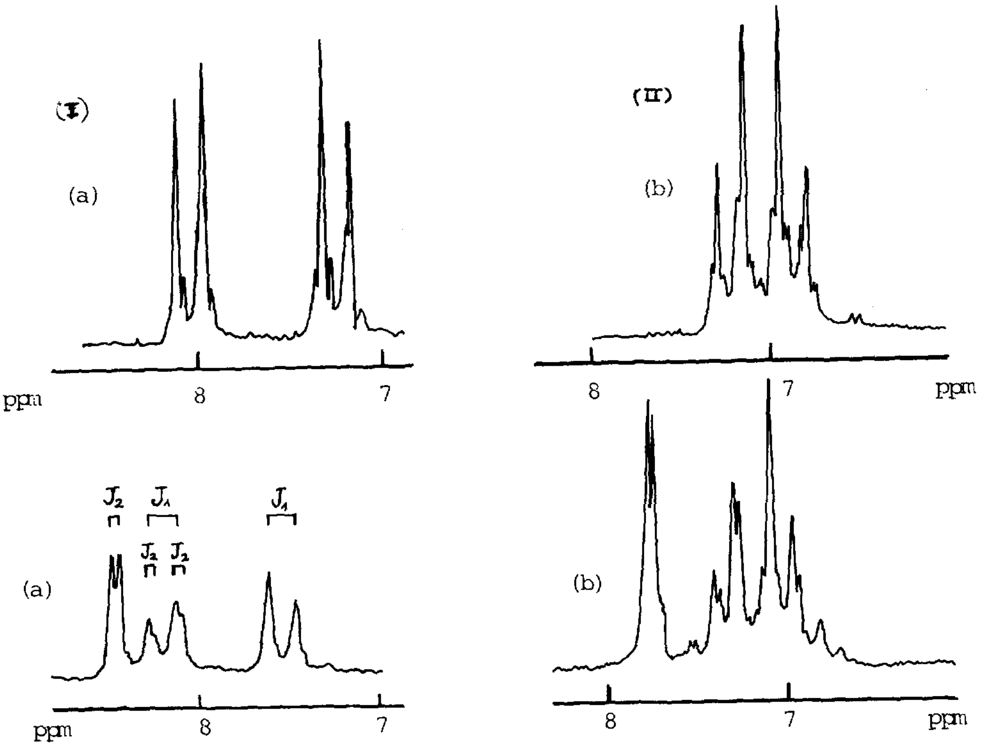
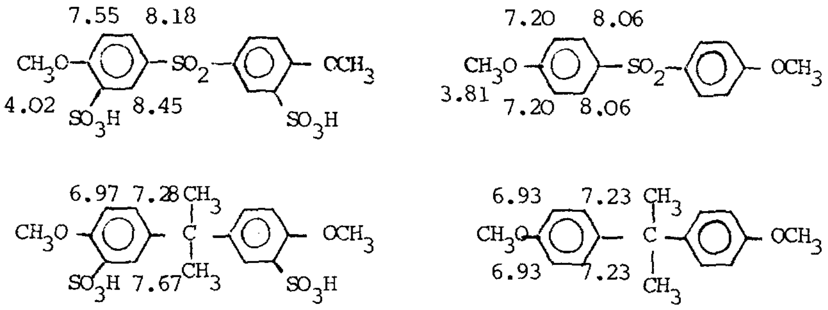


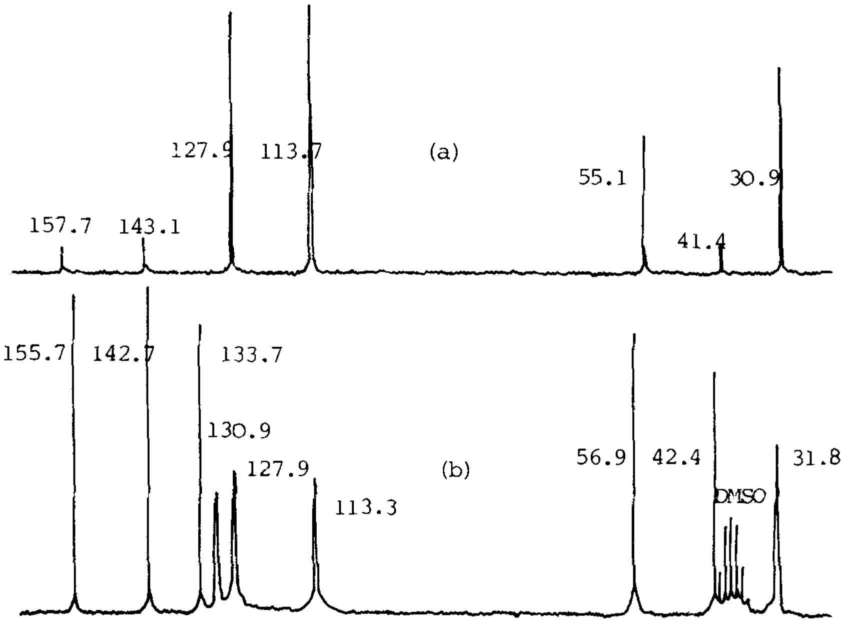
Fig. 1 - NMR spectra of aromatic protons of model compounds before (a) and after (b) sulfonation

The ^{13}C NMR spectra (fig. 2 and 3) showed only two new lines in both cases, a methynic carbon and a quaternary one, confirming a symmetrical structure.

Assignments of the various resonances shown in fig. 3 are summarized as follows (scheme 1 and 2):

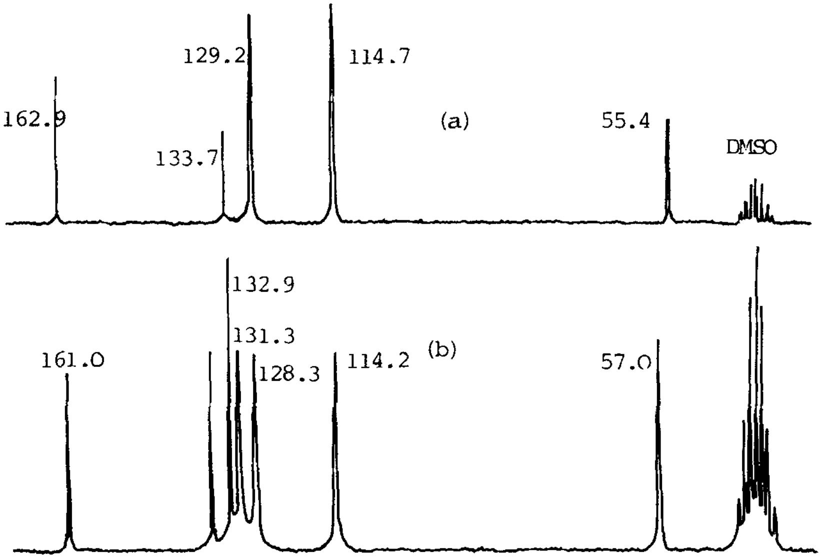


Scheme 1 - Assignment of ^1H resonances



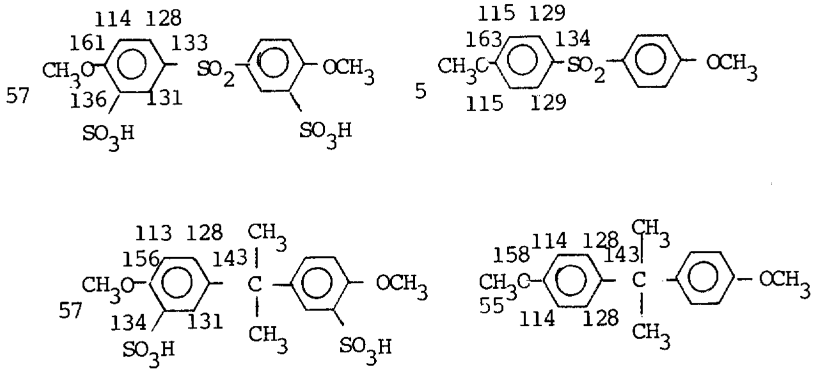
Sulfonation of polysulfones - Fig. 2 -

^{13}C NMR spectra of bis(methoxy-4-phenyl)-2,2 propane before (a) and after (b) sulfonation : d_6 DMSO solution



Sulfonation of polysulfones - Fig. 3 -

^{13}C NMR spectra of bis(methoxy-4-phenyl) sulfone (before (a) and after (b) sulfonation;d_6 DMSO solution



Scheme 2 - Assignment of ^{13} C resonances

The limitation of the sulfonation is most probably caused by steric hindrance more than by electronic induction although the second reason might be valid in the case of the sulfone model.

A commercial polysulfone (UDEL P 1700/1800) containing both structures modelized by I and II, has been sulfonated at 20 C by mixing DCE solutions of polysulfone and SO_3, using a large excess in SO_3 (8 SO_3/structural unit). A solid precipitates, which can be dissolved upon addition of isopropanol. After evaporation, the polymer is dissolved in water ; the water solution is filtrated, evaporated and the solid dried under vacuum to constant weight. The ^{13}C NMR spectra are shown in fig. 4 and are easily interpreted by comparison with the model compounds (fig. 2 and 3).

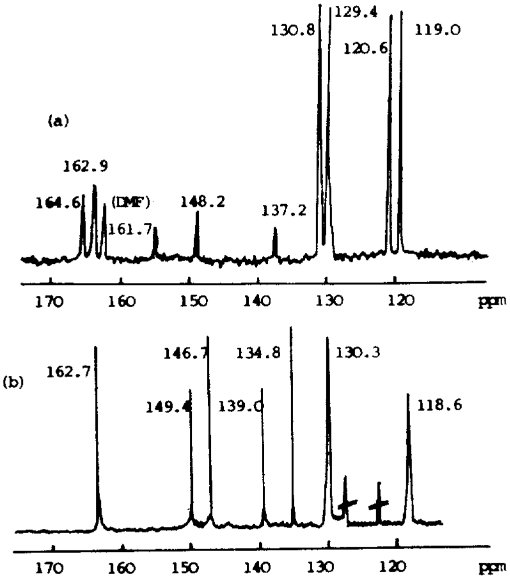
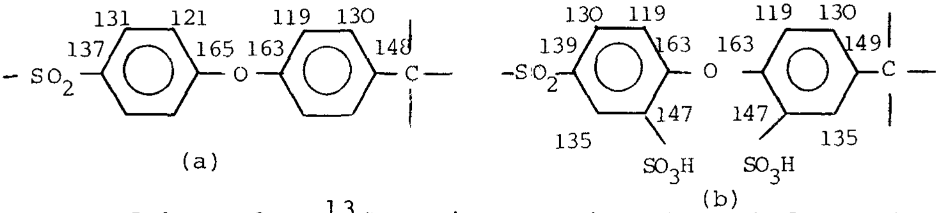


Fig. 4 - ^{13}C NMR spectra of polysulfone before (a) and after (b) sulfontation ; d_6DMF (a) and d_6DMSO (b) solution

Thus, 4 SO_3H are attached per structrural unit. The assignments are as follows (scheme 3) :



Scheme 3 - ^{13}C assignments in polymer before (a) and after (b) sulfonation

The sulfonated polymer is also soluble in dimethyl formamide (DMF), as the initial polymer is. Upon sulfonation, the limiting viscosity number (DMF 25 C) is increased from 0.27 to 0.66. The increase in hydrodynamic values is confirmed by GPC (fig. 5). Both ^{13}C NMR and GPC show that a part of the polymer has not been fully sulfonated.

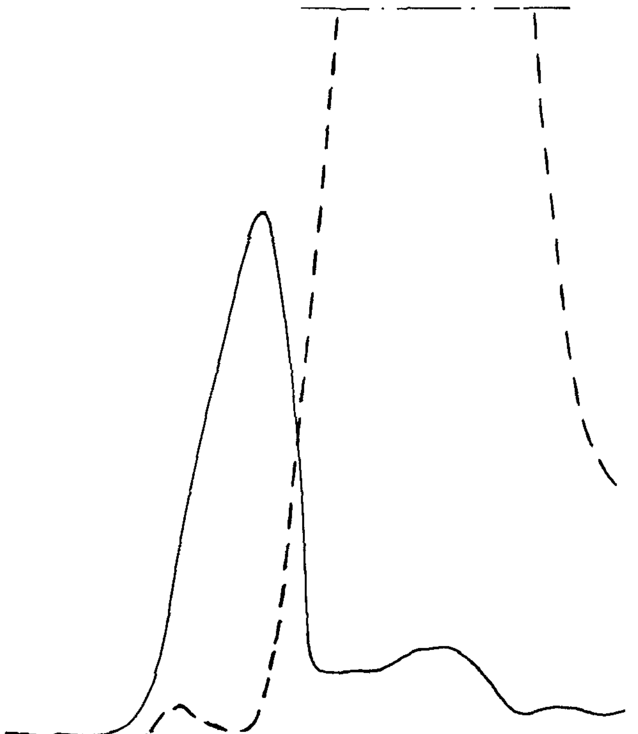


Figure 5 - GPC traces of initial (----) and sulfonated (——) polymer

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