Sequence Analysis of Fluorine-Containing Polyarylethersulfone Copolymers by ^{13}C–NMR*

ZHONGGANG WANG,[†] TIANLU CHEN, and JIPING XU

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,
Changchun 130022, People's Republic of China

SYNOPSIS

HexafluorobisA polyethersulfone-cardo polyethersulfone, random and block copolymers with different segment lengths were synthesized by a reaction of 4,4'-(hexafluoroisopropylidene)diphenol and 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone with bis(4-chlorophenyl)sulfone. Their NOE-suppressed quantitative ^{13}C–NMR spectra were recorded on a 400 MHz NMR spectrometer. The ^{13}C–NMR signals of tertiary carbon atom and quaternary carbon atom, on the benzene ring adjacent to sulfone group, appeared to be sensitive to sequence variation. Degrees of randomness of the copolyarylethersulfone synthesized were 0.96, closing to 1, and 0.39, as well as 0.55, far smaller than 1, indicating random distribution and regular distribution of the comonomers, respectively. The number average sequence lengths, calculated by ^{13}C–NMR spectra, were shorter than expected, due to the transetherification reaction. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The ^{13}C–NMR method, used to analyze the microstructure of the copolymer, has proved to be successful, and a number of articles concerning the determination of the monomer composition and sequence distribution of the copolyester have been published.[1-9] However, few NMR investigations dealing with other kinds of condensation aromatic copolymers have been reported in the literature.

Fluorine-containing polymers have received the major emphasis, due to their unique physical properties.[10-12] Recently, a series of fluorine-containing polyarylethersulfone and cardo polyarylethersulfone homopolymers, as well as their random and block copolymers with different segment length, were synthesized in our laboratory. In order to interpret and understand their physical and mechanical properties, it is important to know the monomer composition and sequence distribution in this copolyarylethersulfone system. The chemical structure of the copolymers can be written as below:
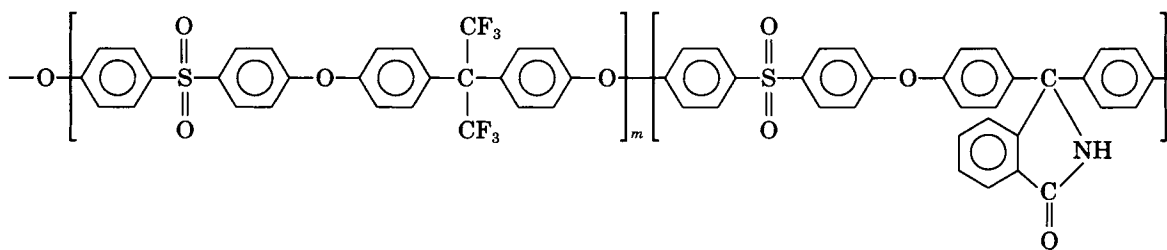
Scheme 1

Previously, the ^{13}C–NMR investigation of aromatic copolymers was restricted to the signals of the quaternary carbon atoms,[13,14] by resolution-increased and NOE-suppressed quantitative ^{13}C–

Table I   Values of $\eta_{sp/c}$ of Polymers Synthesized

Samples	PES-H	Random	Block I	Block II	PES-F
$\eta_{sp/c}$	0.59	0.55	0.46	0.42	0.61

$\eta_{sp/c}$ were measured in DMF at 25°C, unless indicated otherwise; $\eta_{sp/c}$ of PES-F was measured in chloroform. Random: 50/50 PES-H/PES-F random copolymer; Block I: block copolymer with PES-H/PES-F segment length ratio 10/9; Block II: block copolymer with PES-H/PES-F segment length ratio 5/4.

NMR spectra, as this article reported, signals of the tertiary carbon atoms could also be used for the sequence analysis of copolymers. Results, calculated from the two kinds of carbon atom signals, were consistent.

Differential scanning calorimetry (DSC) and dynamic mechanical analysis techniques have long been used to distinguish block copolymers from random copolymers,[15-17] but the distinction between random and block copolymers in the DSC spectra or dynamic mechanical spectra is often confusing when the two segments of block copolymer are compatible. In this article is presented a first report on using the ^{13}C–NMR method to qualitatively and quantitatively discriminate block copolymer from random copolymer.

EXPERIMENTAL

Materials

4,4'-(Hexafluoroisopropylidene)diphenol (6 FA) was purchased from Aldrich Chemical Corp. and was used as received, 3,3'-bis(4-hydroxyphenyl)-1-isobenzopyrrolidone (HPP) was synthesized in our laboratory[18] with mp 283–285°C, bis(4-chlorophenyl)sulfone (DCDPS) with mp 146–148°C; DMSO was vacuum-distilled before use.

The detailed synthesis procedures of copolyarylethersulfone samples have been reported previously.[19] A random copolymer was prepared from DCDPS, 6 FA, and HPP at 2 : 1 : 1 molar ratio in the DMSO/K_2CO_3 system. Two block copolymers, with PES-H/PES-F segment length ratios 10/9 and 5/4, were synthesized by a reaction of hydroxy-terminated oligomers and chlorine-terminated oligomers. The values of η_{sp}/c are listed in Table I.
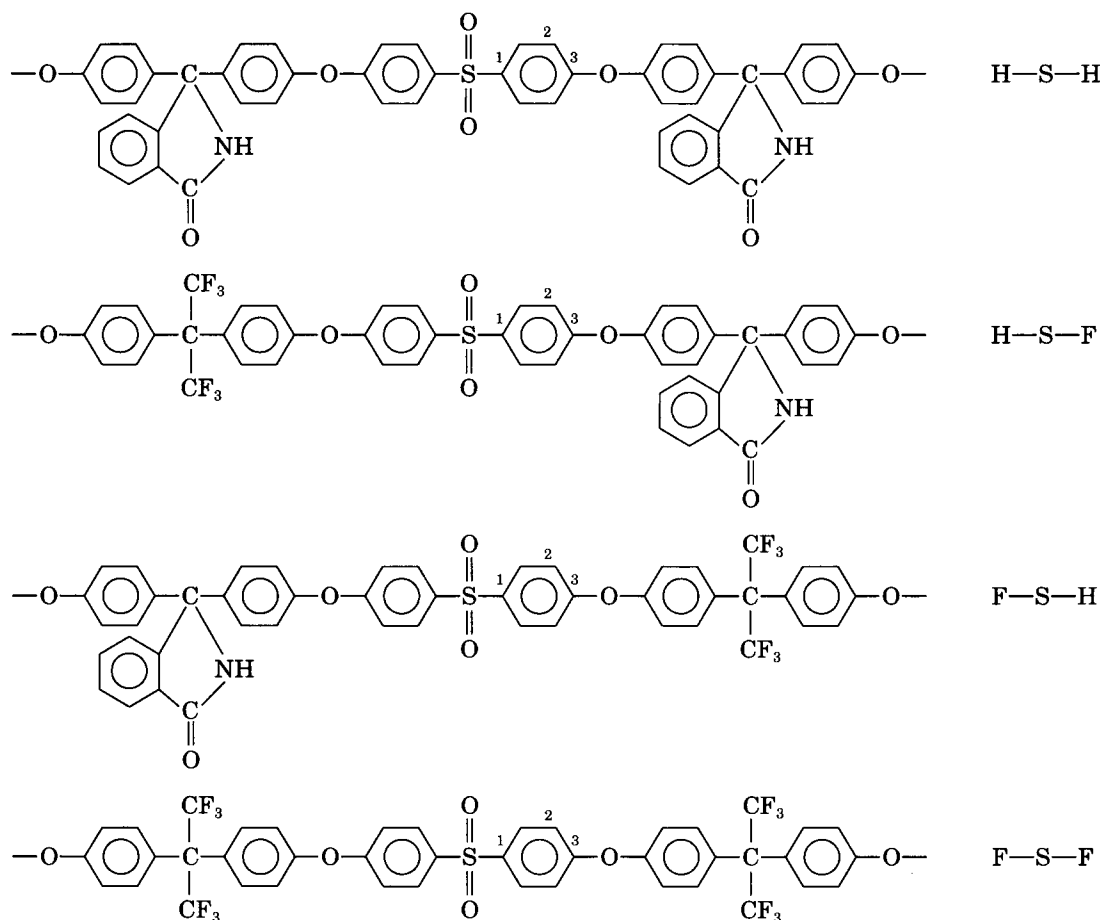
^{13}C–NMR spectra were determined on a Unity-400 NMR spectrometer (Brucker) at room temperature. All the samples, except PES-F, were determined in DMSO solution, chemical shifts referred to the central peak of the DMSO-d_6 multiplet (39.6 ppm). PES-F homopolymer was determined in DCCl$_3$, using TMS as an internal standard. The quantitative, NOE-suppressed ^{13}C–NMR spectra were obtained with 0.5 s acquisition times, at a 2500 Hz sweep width.

RESULTS AND DISCUSSION

The various resonance signals of the two homopolymers are assigned in Table II. Chemical shifts of the C_1, C_2, and C_3 atoms in copolymers can readily be assigned, by comparison with that of the homopolymers. In the case of the copolyarylethersulfone system studied, the three diad sequences for the copolymers synthesized are as follows:

Table II.   Chemical Shifts Assignment of PES—F and PES—H Homopolymers

Chemical Structure	Assignment

PES—H:

C_1: 154.124	C_2: 118.288	C_3: 129.162
C_4: 139.847	C_5: 69.701	C_6: 149.710
C_7: 131.169	C_8: 132.496	C_9: 128.939
C_{10}: 123.651	C_{11}: 124.948	C_{12}: 168.537
C_{13}: 161.216	C_{14}: 130.253	C_{15}: 120.238
C_{16}: 135.508		

PES—F:

C_1: 155.663	C_2: 122.545	C_3: 129.198
C_4: 132.013	C_5: 118.737	C_6: 125.390
C_7: 160.634	C_8: 130.081	C_9: 119.904
C_{10}: 136.238		

H—S—H

H—S—F

F—S—H

F—S—F

Scheme 2

Long-range effects on the chemical shift make the signals of C_1, C_2, and C_3 atoms split into multiplets, indicating that these carbon atoms' signals do show absorptions that are sensitive to the sequence variation (see Fig. 1). For C_1 and C_2 atom signals, the middle two absorptions have the same chemical shift as the singlets observed in the homopolymers and the remaining two absorptions are new absorptions, attributable to sequences HSF and FSH; the signals of HSF and FSH sequences of the C_2 atom overlap into one singlet, so that the integral C_2 atom absorptions of copolymers appear as a triplet. For the 50 : 50 HPP-DCDPS-6FA random copolymer, the absorption intensities, corresponding to HSF and FSH sequences, are nearly identical with that corresponding to the HSH and FSH sequences. However, for the two block copolymers, as the segment length increases, the absorption intensities of the asymmetric HSF and FSH sequences decrease greatly (see Figs. 2 and 3). Hence, we can qualitatively discriminate between random and block copolymers by ^{13}C-NMR spectroscopy directly.

Concentrations of various diad sequences can be calculated from the relative areas of the resonance signals. The probabilities of diad sequence are the numerical areas of the respective resonance signals. Chemical shifts and probabilities of various diad sequences of C_1 and C_2 atoms are presented in Tables III and IV. The degree of randomness and average sequence length are calculated from ^{13}C-NMR spectra,[14] which spectra show that the copolymer information follows Bernouillian statistics.

Molar ratios of HPP and 6 FA, in the copolymers, are presented below:

$$P_H = \tfrac{1}{2} P_{HSF} + P_{HSH} \qquad (1)$$

$$P_F = \tfrac{1}{2} P_{HSF} + P_{FSH} \qquad (2)$$

where P_{HSF}, P_{HSH}, and P_{FSF} are the probabilities of asymmetric sequences and symmetric sequences, respectively.
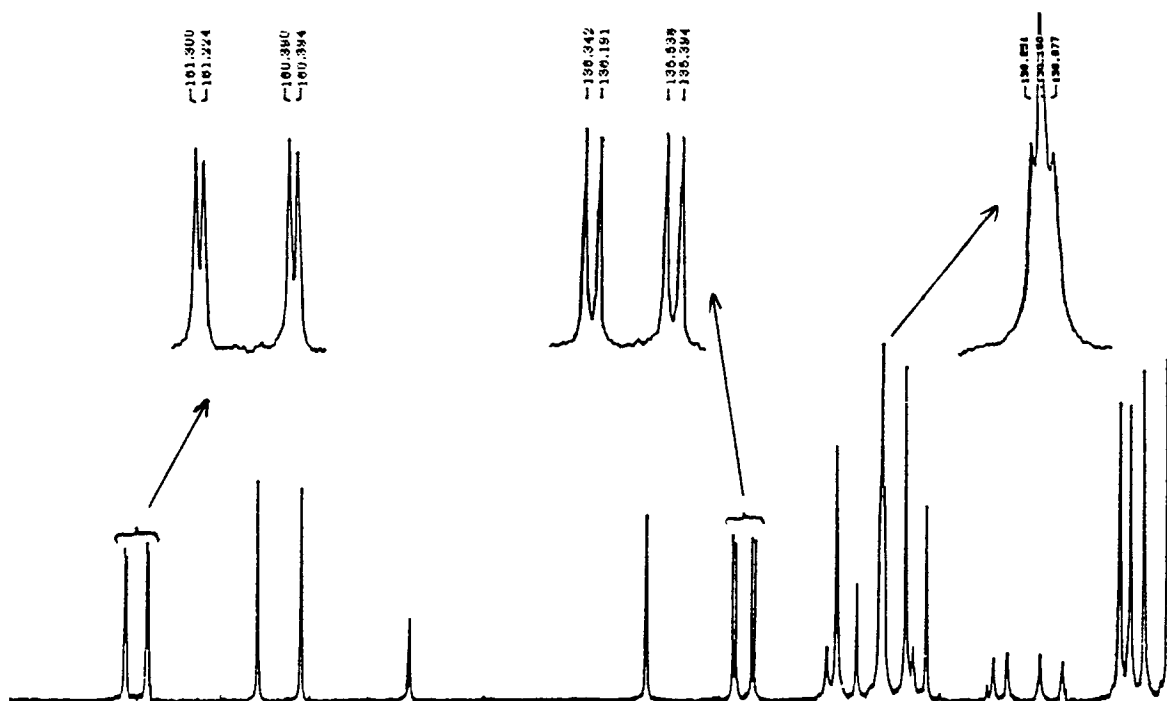
$$P_{HF} = P_{HSF}/2P_H \qquad (3)$$

Figure 1 ^{13}C-NMR spectra of 50 : 50 PES-H/PES-F random copolymer.

$$P_{FH} = P_{FSH}/2P_F \qquad (4)$$

where P_{HF} is the probability of an HS unit being followed by an FS unit and P_{FH} is the probability of the reverse sequence.

The degree of randomness (B) is defined as:

$$B = P_{HF} + P_{FH} \qquad (5)$$

where $B = 1$, $B < 1$, and $B = 0$ correspond to random copolymers, block copolymers, and a mixture of two homopolymers, respectively.
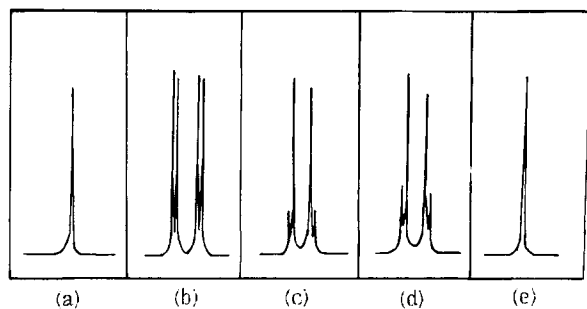
Number average sequence lengths of HS and FS units are defined as:

$$L_{HS} = 1/P_{HF} \qquad (6)$$

$$L_{FS} = 1/P_{FH} \qquad (7)$$

Figure 2 Detailed C_1 and C_3 ^{13}C-NMR spectra of copolymers at 100.6 MHz: (a) PES-F, (b) 50 : 50 random copolymer, (c) block copolymer with PES-H/PES-F segment length ratio 10 : 9, and (d) block copolymer with PES-H/PES-F segment length ratio 5 : 4.
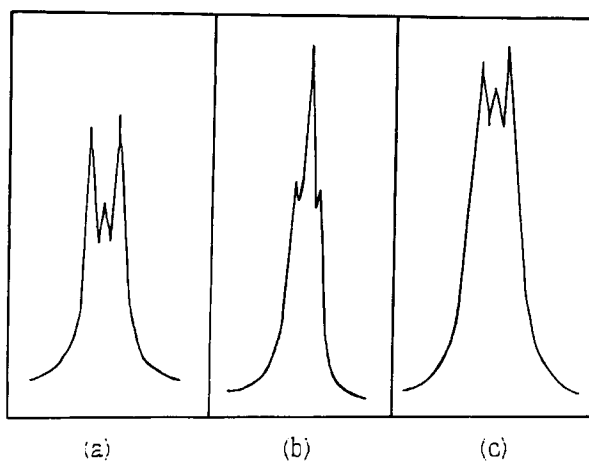

Figure 3 Detailed C_2 ^{13}C-NMR spectra of copolymers at 100.6 MHz: (a) block copolymer with PES-H/PES-F segment length ratio 10 : 9, (b) 50 : 50 random copolymer, and (c) block copolymer with PES-H/PES-F segment length ratio 5 : 4.

Table III Chemical Shifts and Absorption Area for C_1 Atom

| Assignment | δ (ppm) | Diad Probabilities | | |
		Random	Block I	Block II
HSH	135.538	26.54	44.28	43.80
HSF	135.394	23.40	9.22	12.74
FSH	136.342	24.51	10.21	13.97
FSF	136.191	25.55	36.28	29.50

Block I and Block II have been explained in Table I.

Degrees of randomness and number average sequence lengths, calculated from the above equations, are listed in Table V. The data in Table V show the value, B, of a random copolymer is 0.96, within the experimental error of 1, whereas the values of B of two block copolymers are 0.39 and 0.55, respectively, which are far smaller than 1. The degree of randomness data, calculated with a tertiary carbon atom and a quaternary carbon atom, are in good agreement.

Number average molecular weights of hydroxy-terminated and chlorine-terminated oligomers are evaluated by the following equations.

$$M_{W,OH} = L_{HS} \times M_{W,HS} \qquad (8)$$

$$M_{W,Cl} = L_{FS} \times M_{W,FS} \qquad (9)$$

where $M_{W,OH}$ and $M_{W,Cl}$ represent number average molecular weights of hydroxy-terminated and chlorine-terminated oligomers, respectively, $M_{W,HS}$ and $M_{W,FS}$ represent molecular weight of HS and FS repeating units, respectively.

The molar fractions (P) and number average molecular weights of two oligomers are presented in table VI.

An important point to note is that the calculations above assume that the bisphenol monomers

Table IV Chemical Shifts and Absorption Area for C_2 Atom

| Assignment | δ (ppm) | Diad Probabilities | | |
		Random	Block I	Block II
HSH	130.077	24.04	37.38	30.20
HSF and FSH	130.160	47.61	21.40	27.80
FSF	130.251	28.35	41.22	42.00

Block I and Block II have been explained in Table I.

Table V Values of Sequence Distribution Calculated by ^{13}C–NMR Spectra

Polymer	B*	B**	L_{LS}	L_{FS}	L_{FS}/L_{HS}
PES-H	0	0	—	—	—
Random	0.96	0.95	2.1	2.1	1.00
Block I	0.39	0.42	5.6	4.7	0.85
Block II	0.55	0.54	4.2	3.2	0.76
PES-F	0	0	—	—	—

Block I and Block II have been explained in Table I; B* and B** are calculated from C_1 and C_2 resonance signals, respectively.

Table VI Monomer Compositions and Number Average Molecule Weights of Oligmers

| Polymer | Molar Fraction of HPP (%) | | $M_{w,OH}$ | $M_{w,cl}$ |
	Feed	Calculated		
PES-H	100	100	—	—
Random	50	50.5	—	—
Block I	52.6	54.0	2976.9	2587.4
Block II	55.6	57.3	2232.7	1760.6
PES-F	0	0	—	—

Block I and Block II have been explained in Table I.

have the same reactive activities, but, in fact, the reactive activities of bisphenol monomers of the HPP and 6 FA used are different, due to the electronic effect and steric hindrance effect, so that the deviation from the theoretical calculation is unavoidable. Furthermore, especially in the course of the syntheses of the above block copolymers, the reaction mixture thus contains phenoxide end groups, which can cleave oxygen-aryl bonds with para sulfone function. This process is known as transetherification[20] and it might result in the randomization of the PES-F and PES-H segments to some extent. For this reason, the number average sequence lengths, calculated by the above equation, are shorter than expected.

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