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Aromatic polymers obtained by precipitation polycondensation: 5*. ^{1}H and ^{13}C n.m.r. study of poly(ether ketone ketone)s

M. G. Zolotukhin, D. R. Rueda, M. Bruix, M. E. Cagiao and F. J. Balta Calleja[†]
Instituto de Estructura de la Materia, C.S.I.C., Serrano 119, Madrid 28006, Spain

and A. Bulai
Plastic Institute, Perovskii pr., 35, 111135, Moscow, Russia

and N. G. Gileva
Institute of Organic Chemistry, Prospekt Oktyabrya, 69, Ufa-54, Russia

and L. Van der Elst
Universite de Mons-Hainaut, Department of Organic Chemistry, Place du Parc 20, B-7000, Mons, Belgium
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High molecular weight, linear aromatic poly(ether ketone ketone)s with different iso-/tere-isomer repeating unit ratio (100/0, 50/50, 0/100) have been studied by ^{1}H and ^{13}C n.m.r. spectroscopy. The polymers were obtained in particle form by precipitation electrophilic Friedel–Crafts acylation condensation of iso- and terephthaloyl chlorides with diphenyl ether, 1,4- and 1,3-bis(4-phenoxybenzoyl)benzenes. Conventional ^{1}H and ^{13}C n.m.r. spectroscopy shows *para*-substitution in the diphenyl ether fragments of the main chain. Analysis of the expanded ^{1}H n.m.r. spectra for the ring proton resonances reveals defect *meta*- and *ortho*-structures. The amount and isomer ratio of these defect structures depend on the polymer structure and preparation path. The low field of ^{1}H n.m.r. spectra of polyketones based on 'small monomers' (diphenyl ether and iso- and terephthaloyl chlorides) were found to show additional minor signals corresponding to a different type of defect structure. A possible mechanism of formation of these defect structures is discussed. © 1997 Elsevier Science Ltd.

(Keywords: ^{1}H n.m.r.; ^{13}C n.m.r.; precipitation electrophilic polycondensation)

INTRODUCTION

Aromatic poly(ether ketone)s comprise a class of polymers in which arylene moieties are linked by ether or carbonyl groups[1-4]. These polyketones are semicrystalline, high-temperature and solvent resistant, and as materials are receiving ever-increasingly commercial and academic attention.

Similarly to all semicrystalline polymers, the thermal and mechanical properties of polyketones are dependent upon the morphology and the thermal history of the material. This is the reason for considerable interest in the current literature regarding the determination of their crystal structure and characterization of their morphology[5-9].

Preparation of poly(aryl ether ketone)s by two different approaches has been described in the literature[1-4]. The first approach is a synthesis involving electrophilic aromatic substitution, in which an aryl ketone linkage is formed. The second one is a synthesis involving nucleophilic aromatic substitution, in which an aryl ether linkage is obtained. It is obvious that polyketones obtained by both methods may contain defect structures affecting the polymer properties. Nevertheless, reports on the study of chemical structure of the polyketones are very limited.

One essential reason for this is the difficulty of investigation of the polyketones in solution due to their generally poor solubility. In contrast to poly(aryl ether ketone) oligomers, most of which are soluble in $CDCl_3$ or $C_2D_2Cl_2$ and can be studied by means of ^{1}H and ^{13}C n.m.r. spectroscopy[10], polyketones are normally soluble only in strong acids such as concentrated sulfuric, methane sulfonic or trifluoromethane sulfonic acids. It is to be noted that sulfuric and methane sulfonic acids have been used as solvents for ^{19}F n.m.r. end-group analysis of a poly(aryl ether ether ketone)[11], while sulfuric and trifluoromethane sulfonic acids have been used for complete assignments of the quaternary carbon signals of statistical copolymers of the aryl ether ketone

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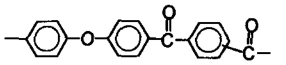
[†] To whom correspondence should be addressed

unit with aryl ether ether ketone, aryl ether ketone ketone and aryl ether sulfones[12].

It is less well known that many poly(aryl ether ketone)s are soluble in mixtures of chlorinated aliphatic hydrocarbons with fluorinated alcohols and acids. Thus, a $CDCl_3/CF_3COOH$ mixture has successfully been used for n.m.r. characterization of chemical microstructure of copolymers of terephthaloylchloride with diphenyl ether and 1,4-diphenoxybenzophenone[13] and polyketones based on 2,6-napthalenedicarboxylic acid[14]. The solvent mixture was found to give low viscous polymer solutions with no chemical degradation (or reaction) of polymer chain affording well-resolved n.m.r. spectra.

In the present paper we report the results of ^1H and ^{13}C n.m.r. studies of poly(aryl ether ketone ketone)s of the following chemical composition:



PEKK

The polyketones were synthesized by precipitation electrophilic polycondensation of iso- and terephthaloyl chlorides with diphenyl ether, 1,4- and 1,3-bis(4-phenoxybenzoyl)benzenes. The use of a high-field 600 MHz n.m.r. spectrometer for the protons has, for the first time, allowed us to obtain a detailed characterization of the chain structure and a quantitative determination of the defect structures.

EXPERIMENTAL

Materials

The polyketones were prepared according to known methods[9,10]. $CDCl_3$ and CF_3COOH were obtained from Aldrich (Madrid). CF_3COOH was distilled prior to use.

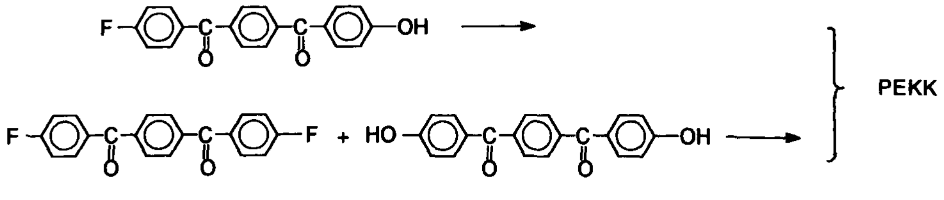
Methods

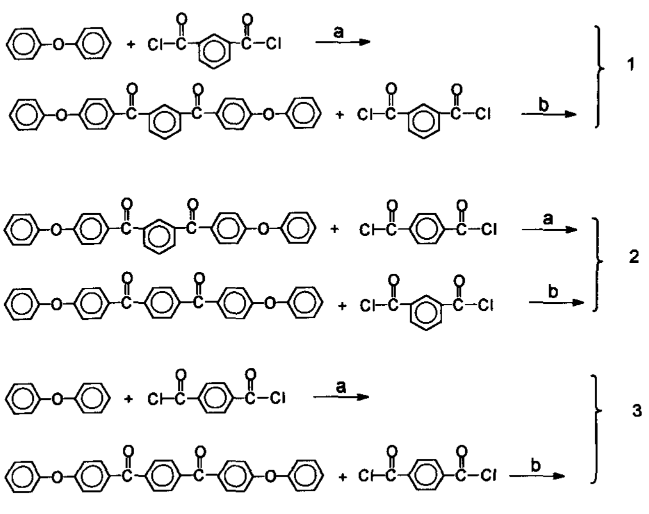
The viscosity of the polymer solutions in 94.5% sulfuric acid was measured at 25°C in a viscometer of the Ubbelohde type. The ^1H and ^{13}C n.m.r. spectra were recorded at room temperature on a Bruker AMX-600 spectrometer operating at 600.13 and 150.92 MHz (for ^1H and ^{13}C frequencies respectively). The polyketones were dissolved in a $CDCl_3/CF_3COOH$ mixture (50/50 v/v) to give 7.5% (w/v) solutions. All chemical shifts cited are referred to tetramethylsilane.

RESULTS AND DISCUSSION

Synthetic aspects

In principle, poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene-carbonyl-1,4-phenylene) can be prepared by both nucleophilic and electrophilic routes. It is easy to show that the nucleophilic route (homopolycondensation as well as polycondensation) involves complex monomers:





Scheme 1

while the electrophilic route is based on simple monomers. Additionally, depending on the monomers used for polycondensation, polyketones of regular structure with different iso-/tere-isomer repeating unit ratio are obtained. Thus, preparation of polyketones with a repeating unit ratio of 100/0, 50/50, 0/100 in the main chain was accomplished via *Scheme 1*.

Each polyketone structure was prepared in two ways: **a** and **b** (*Scheme 1*). A more detailed description of these syntheses is given in a previous paper[15].

The preparation of polyketones performed by precipitation electrophilic polycondensation[14–18] allows the obtaining of high molecular weight polymers in particle form. The polyketone particles are completely soluble in $CDCl_3/CF_3COOH$ mixtures and strong acids, allowing us to carry out n.m.r. spectroscopic measurements on these polyketone solutions.

N.m.r. analysis

The results obtained are discussed according to the order of the preparation of the polymer, from **1a** to **3b**.

To help the reader, for each of the six polymers, the number of the formula scheme (in which the structural formulas of polymer chains of different PEKK are presented), the figure number (in which the proton and carbon spectra are shown) and the table number (in which the signal assignment is given) are collected in *Table 1*.

It is worth mentioning that the conventional ^{13}C and ^1H n.m.r. spectra of the polyketones, obtained by different routes turned out to be practically identical (e.g., each spectrum presented in *Figures 1–6* corresponds to both **a** and **b** polymers).

The assignment of the carbon spectra (*Figures 1–3*) was carried out by the application of a DEPT sequence[19] and on the basis of additive scheme calculations[20] using the substitution increments ((CO)Ph(CO), (CO)PhO and OPh) reported by Ewing[21]

Table 1 Numbers of schemes, figures and tables

Sample	Structural formula of polymer chain	Carbon spectrum	Conventional proton spectrum	Expanded spectra for the ring proton resonances	
				Proton spectrum	Assignment
1a	*Scheme 2*	*Figure 1*	*Figure 4*	*Figure 7a*	*Table 2*
1b	*Scheme 2*	*Figure 1*	*Figure 4*	*Figure 7b*	*Table 2*
2a	*Scheme 3*	*Figure 2*	*Figure 5*	*Figure 8a*	*Table 3*
2b	*Scheme 3*	*Figure 2*	*Figure 5*	*Figure 8b*	*Table 3*
3a	*Scheme 4*	*Figure 3*	*Figure 6*	*Figure 9a*	*Table 4*
3b	*Scheme 4*	*Figure 3*	*Figure 6*	*Figure 9b*	*Table 4*

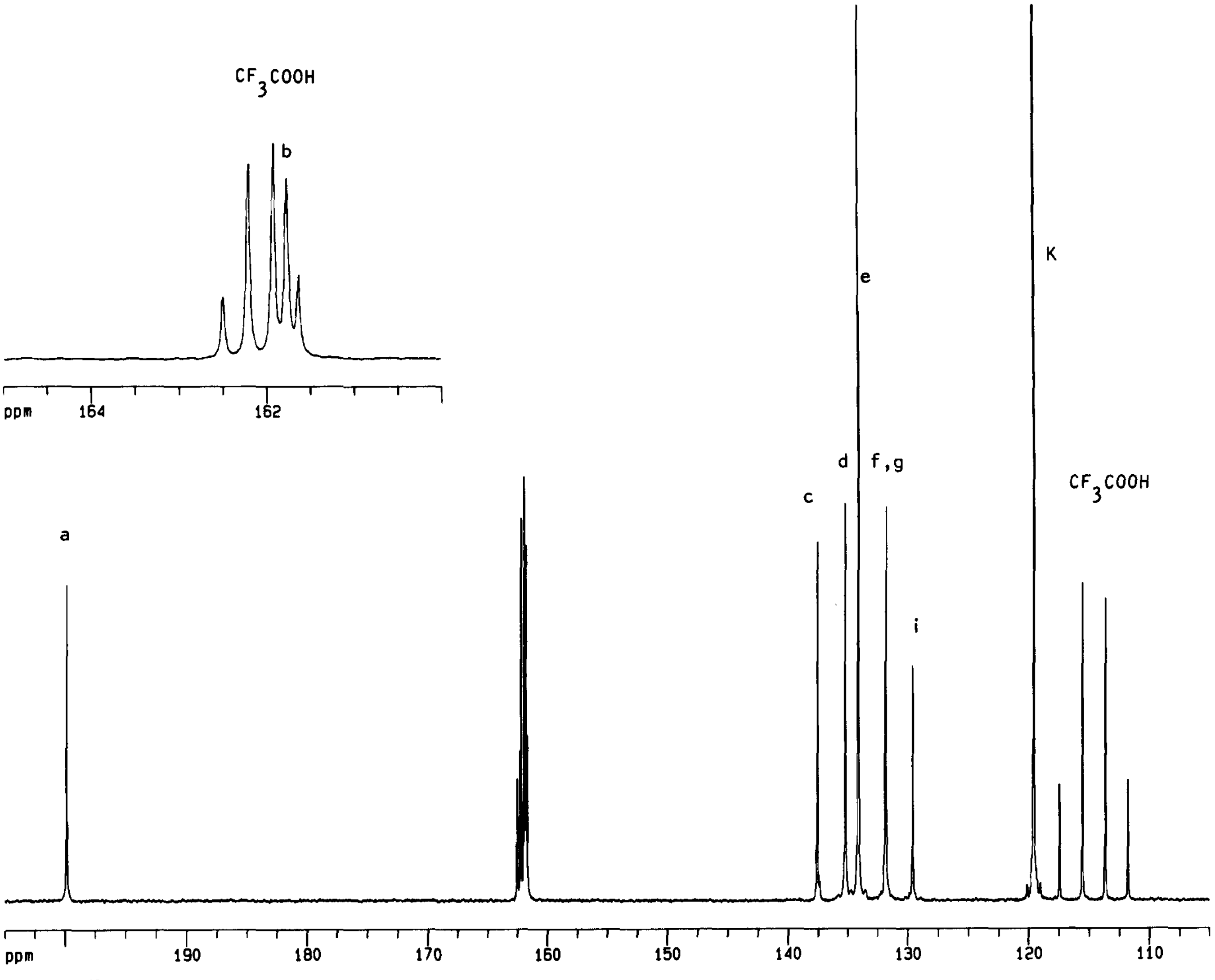


Figure 1 ^{13}C n.m.r. spectrum of samples **1a** and **1b**: carbon designation in accordance with *Scheme 2*

and found from the spectra of the model compounds 1,2-dibenzoylbenzene and 4-methoxybenzophenone presented by Aldrich[22].

As can be seen, all the signals in the ^{13}C n.m.r. spectra of polyketones **1–3** can be completely ascribed to the polymers with *para*-substituted diphenyl ether fragments in the main chains. The assignment of the corresponding proton signals (see *Figures 4–6*) was also made by means of the additive scheme calculations (using the increments reported in ref. 23), and by analysis of the signal multiplicity. At first sight, the ^1H n.m.r. data confirm the high regioselectivity of the polymer syntheses.

However, in the expanded ^1H n.m.r. spectra for the ring proton resonances of the polyketones (*Figures 7–9*), one can observe a number of signals whose intensities are considerably smaller than those of proton signals corresponding to the main structural units (*para*-isomer). These spectra appeared to be very complex due to the carbon-13 satellites which

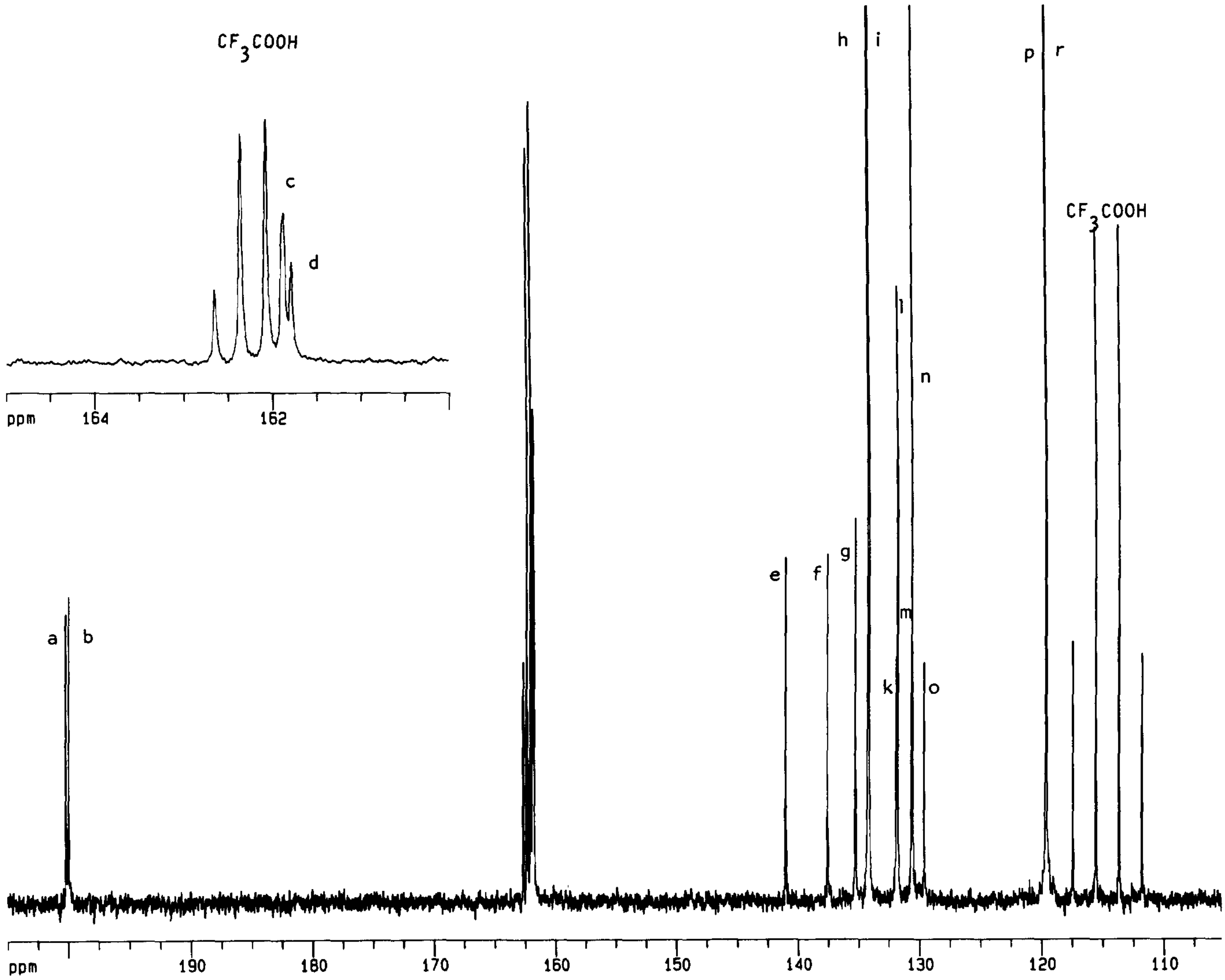


Figure 2 ^{13}C n.m.r. spectrum of samples **2a** and **2b**: carbon designation in accordance with *Scheme 3*

Table 2 The assignment of proton signals of isomer structures and end-units in the spectra of **1a** (*Figure 7a*) and **1b** (*Figure 7b*)

Proton[a]	Chemical shifts δ[b] (ppm)	Signal multiplicity J, Hz[c]
H_4^{p}[d]	7.98	Doublet
H_5^{p}	7.27	Doublet
H_4^{o}	7.98[e]	Doublet
H_5^{o}	7.27[e]	Doublet
H_6^{o}	7.10[f]	Doublet/doublet
H_7^{o}	7.44	Triplet
H_4^{m}	7.70[e]	Doublet
H_5^{m}	6.95	Doublet
H_6^{m}	7.85[e]	Singlet
H_7^{m}	7.70[e]	Triplet
H_1^{k}	8.37 ($R_1 = OCH_3$; $R_2 = -Ph$)	Singlet
H_1^{k}	8.47 ($R_1 = -OCH_3$)	Singlet

[a] Proton designation in accordance with *Scheme 2*
[b] Chemical shift of the multiplet centre
[c] *J ortho–ortho* = 12 Hz
[d] *p*, *m* and *o* refer to *para-*, *meta-* and *ortho*-isomers, respectively
[e] Calculated chemical shifts; experimental values cannot be determined because of signal overlap
[f] In the spectrum of **1a** (*Figure 7a*) signal of H_6^{o} is not observed because of the overlapping with upper field satellite of H_5^{p} signal (at 7.15 ppm)

Table 3 The assignment of proton signals of isomer structures and end-units in the spectra of **2a** (*Figure 8a*) and **2b** (*Figure 8b*)

Proton[a]	Chemical shifts, δ, ppm[b]	Signal multiplicity, J, Hz[c]
H_5^{p}[d]	8.00	Doublet
H_6^{p}	7.30	Doublet
H_7^{p}	7.31	Doublet
H_5^{o}	8.00[e]	Doublet
H_6^{o}	7.31[e]	Doublet
H_7^{o}	7.15	Doublet/doublet
H_8^{o}	7.44	Triplet
H_5^{m}	7.75	Doublet
H_6^{m}	7.00	Doublet
H_7^{m}	7.80[e]	Triplet
H_8^{m}	7.89[e]	Singlet
H_1^{k}	8.37 ($R_1 = OCH_3$; $R_2 = -Ph$)	Singlet

[a] Proton designation in accordance with *Scheme 3*
[b] Chemical shift of the multiplet centre
[c] *J ortho–ortho* = 12 Hz
[d] *p*, *m* and *o* refer to *para-*, *meta-* and *ortho*-isomers, respectively
[e] Calculated chemical shifts; experimental chemical shifts cannot be determined due to signal overlap

Table 4 The assignment of proton signals of isomer structures in the spectra of **3a** (*Figure 9a*) and **3b** (*Figure 9b*)

Proton[a]	Chemical shifts δ (ppm)[b]	Signal multiplicity J, Hz[c]
H_1^p	8.04	Doublet
H_3^p	7.31	Doublet
H_1^o	8.04[e]	Doublet
H_3^o	7.31[e]	Doublet
H_5^o	7.10[f]	Doublet/doublet
H_4^o	7.44[e]	Triplet
H_1^m	7.74	Doublet
H_3^m	7.03	Doublet
H_4^m	7.78	Triplet
H_5^m	7.90[e]	Singlet
H_2^k	8.28 (R_1 = OCH$_3$)	Doublet
H_2^k	8.35 (R_1 = HO–, Cl)	Doublet/doublet

[a] Proton designation in accordance with *Scheme 4*
[b] Chemical shift of the multiplet centre
[c] *J ortho–ortho* = 12 Hz
[d] *p*, *m* and *o* refer to *para*-, *meta*- and *ortho*-isomers, respectively
[e] Calculated chemical shifts; experimental values cannot be determined because of signal overlap
[f] In the spectrum of **3a** (*Figure 9a*), the signal for H_5^o is not observed because of its overlap with the upper field satellite of the H_3^o signal (at 7.17 ppm)

arise from proton coupling to carbon-13[24] and overlap of some signals ascribed to isomer structures.

The assignment of these new signals was made (*Tables 2*, *3* and *4*) on the basis of the following criteria:

(i) a comparison of the spectra of polyketone samples with different molecular weights (analysis of signal intensity and multiplicity), keeping in mind that multiplicity of satellites and the central signal are identical;

(ii) additive scheme calculations based on the chemical shifts of proton signals corresponding to the main *para*-isomer structure (*Figures 4–6*) using substitution increments (CO)Ph(CO) and OPh, also estimated from the conventional proton spectra (*Figures 4–6*).

As a result, signals corresponding to the end-groups, *ortho*- and *meta*-isomer defect structures along with the main signals (*para*-isomer) were identified.

Utilizing the assignments presented in *Schemes 2–4*, the relative signal intensities (known to be proportional to the isomer concentration and to the number of protons corresponding to the signal) are

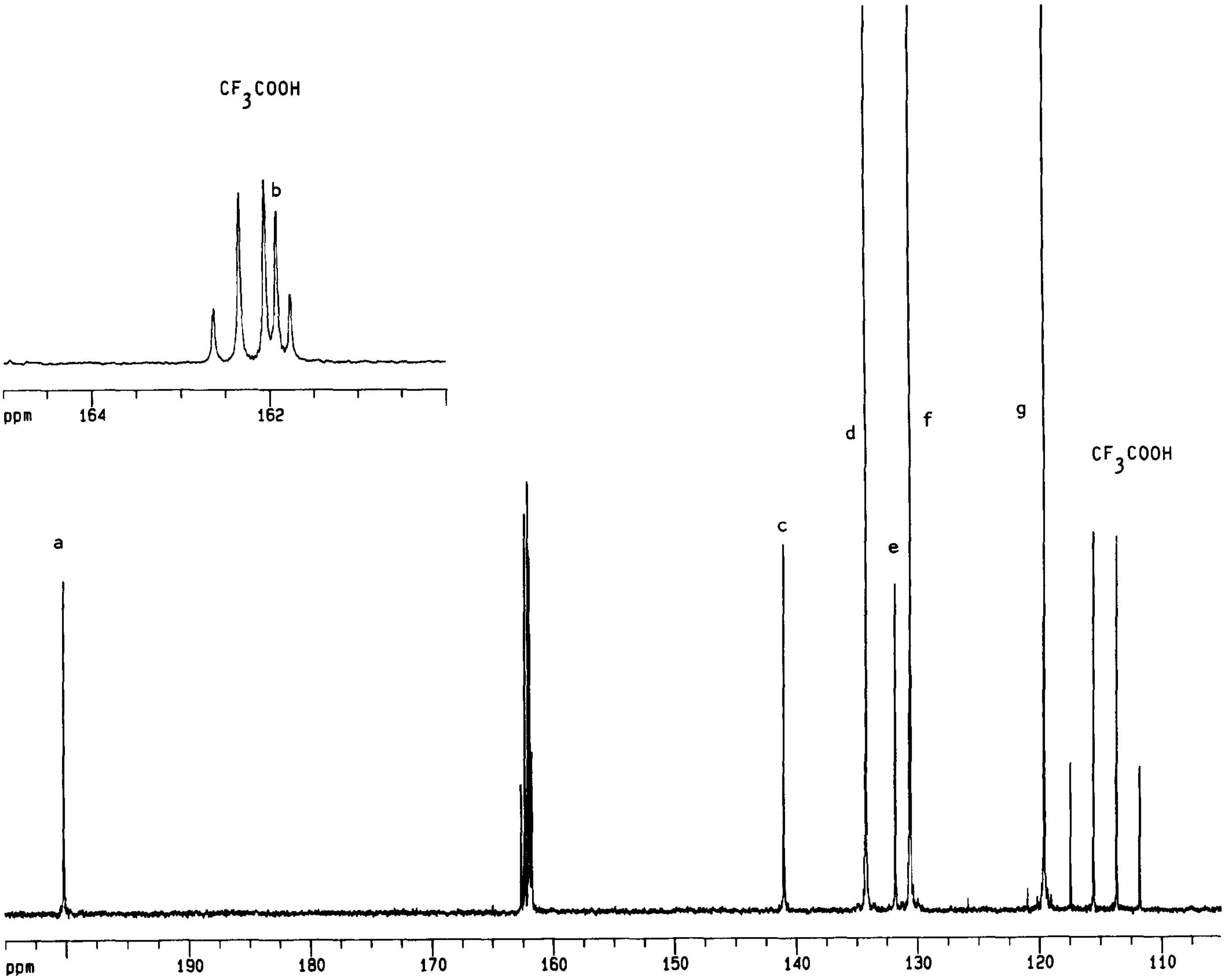


Figure 3 ^{13}C n.m.r. spectrum of samples **3a** and **3b**: carbon designation in accordance with *Scheme 4*

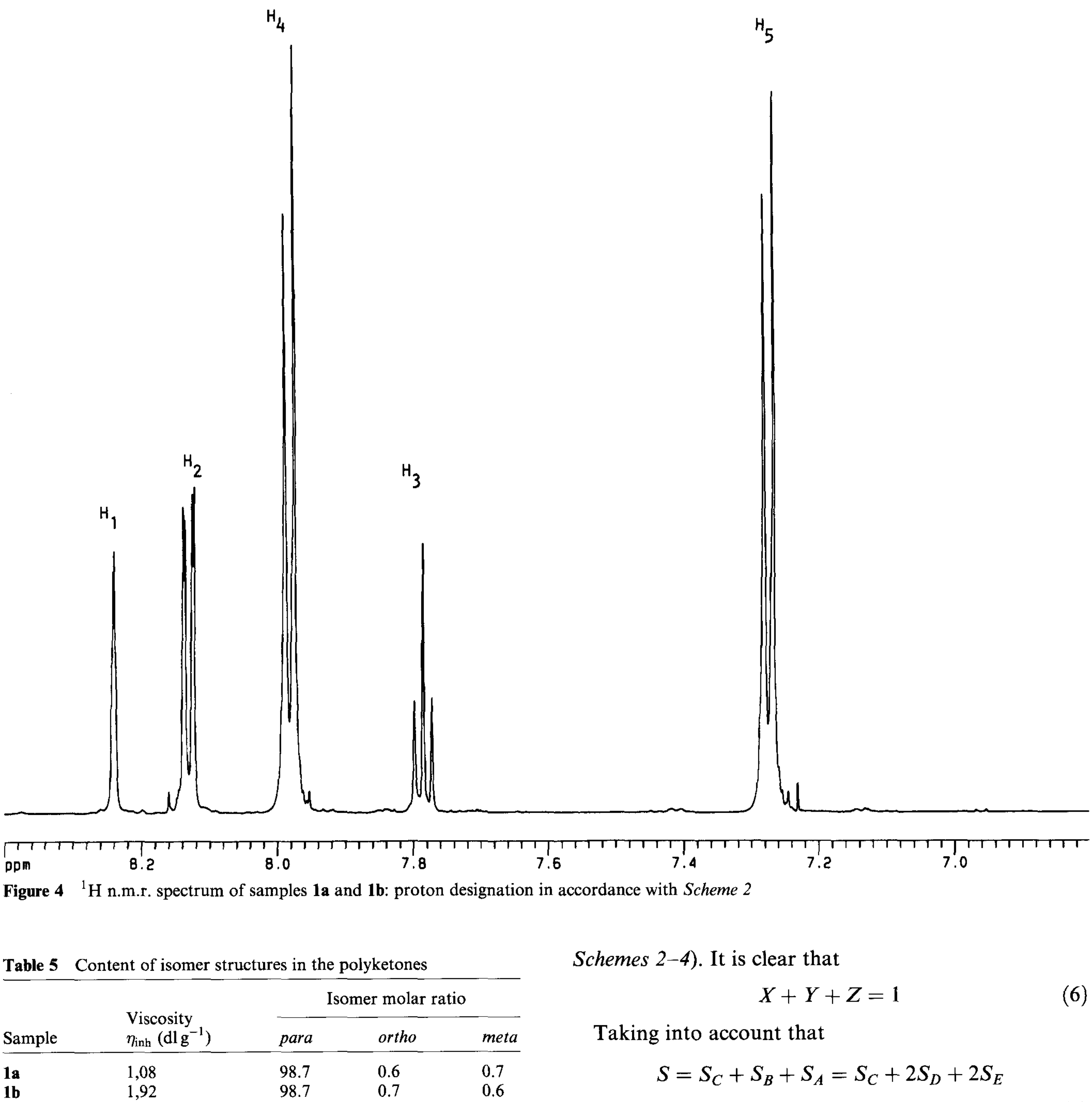


Figure 4 ^{1}H n.m.r. spectrum of samples **1a** and **1b**: proton designation in accordance with *Scheme 2*

Table 5 Content of isomer structures in the polyketones

Sample	Viscosity η_{inh} (dl g^{-1})	Isomer molar ratio *para*	*ortho*	*meta*
1a	1,08	98.7	0.6	0.7
1b	1,92	98.7	0.7	0.6
2a	1,50	97.7	1.9	0.4
2b	1,99	98.0	1.2	0.8
3a	1,24	98.4	0.6	1.0
3b	1,25	93.5	5.3	1.2

given by

$$S_A = 2Z \qquad (\textit{Figure 9}) \tag{1}$$

$$S_B = Y \qquad (\textit{Figures 7, 8b, 9}) \tag{2}$$

$$S_C = 2X + Y \qquad (\textit{Figures 7–9}) \tag{3}$$

$$2S_D = Y \qquad (\textit{Figures 7b, 8b, 9b}) \tag{4}$$

$$S_E = Z \qquad (\textit{Figures 7–9}) \tag{5}$$

where X, Y and Z are the mole fractions of main *para*- and defect *ortho*- and *meta*-structures, respectively (see *Schemes 2–4*). It is clear that

$$X + Y + Z = 1 \tag{6}$$

Taking into account that

$$S = S_C + S_B + S_A = S_C + 2S_D + 2S_E$$
$$= 2(X + Y + Z) = 2 \tag{7}$$

the relationships for calculation of the X, Y and Z values may be expressed as

$$\frac{S_B}{S} = \frac{2 \times S_D}{S} = \frac{Y}{2}; \quad Y = \frac{2 \times S_B}{S} = \frac{4 \times S_D}{S} \tag{8}$$

$$\frac{S_A}{S} = \frac{2 \times Z}{2}; \quad \frac{S_E}{S} = \frac{Z}{2}; \quad Z = \frac{2 \times S_E}{S} = \frac{S_A}{S} \tag{9}$$

$$X = 1 - (Y + Z) \tag{10}$$

and the isomer contents thus calculated are presented in *Table 5*.

It should be noted that Friedel–Crafts aromatic substitution reactions are usually considered not to be very selective, and this is indeed the case for acylation (polyacylation) in which formation of defect *ortho*- and *meta*-isomers is expected.

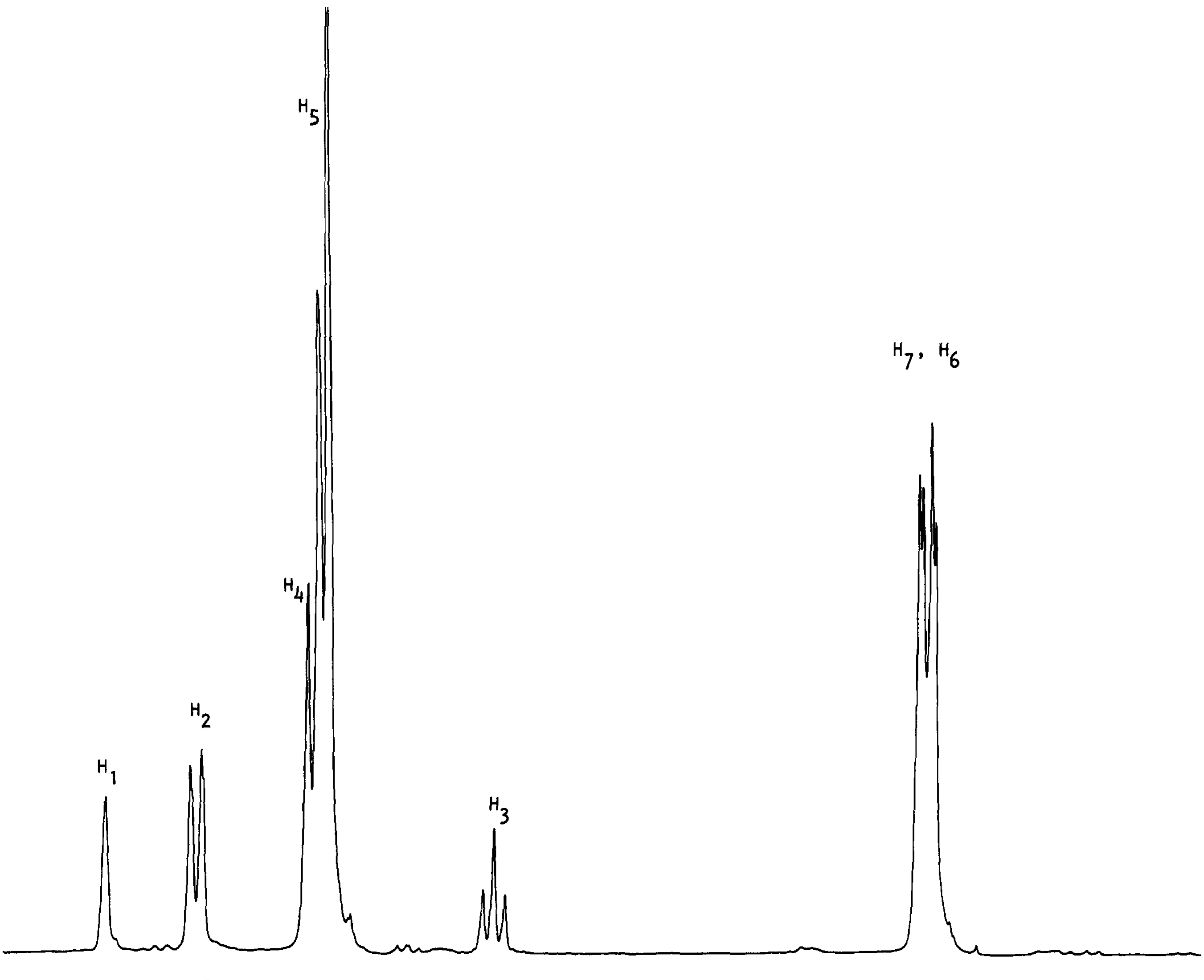


Figure 5 ^1H n.m.r. spectrum of samples **2a** and **2b**: proton designation in accordance with *Scheme 3*

As can be seen from *Table 5*, synthesis of all of the polyketones is accompanied by formation of defect structures.

Defect structures

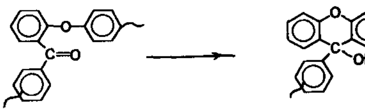
Owing to the large difference between the intensity of n.m.r. signals resulting from the main and defect structures, an accurate determination of the amount of defects cannot be made. However, it is possible to discuss some of the characteristic features and tendencies observed.

From *Table 5* one sees that the total amount of defect structures is approximately similar in all polymer preparations, except for **3b**. For these polymers, the content of defect structures and their ratios do not depend much on polymer viscosity and preparation path. Thus, polyketone **1b**, although of much higher viscosity than **1a**, shows the same content of defect structures. It is possible, therefore, that formation of defect structures takes place during all polymer syntheses.

Polyketone **3b** has the largest abundance of defect structures, due mostly to the presence of *ortho*-isomer.

All the above-mentioned defect structures were identified in our study by n.m.r. spectroscopy. Apart from these, other defect structures have also been mentioned in the literature. Among these are products resulting from alkylating of arylene fragments by chlorinated (dichloroethane) solvents. In this case formation of branched (or even cross-linked) polymers is expected. It is worthy of note that the high solubility of the polyketones obtained points to an absence of cross-linked structures. Further, trisubstituted aromatic rings (or aliphatic protons) were not detected in the n.m.r. spectra.

Another possible type of side reaction in electrophilic acylation is intramolecular cyclization of *ortho*-substituted phenoxy-units resulting in xanthydrol groups[1]:



Evidence for the formation of xanthydrol groups is based on absorption at 455 nm in the visible

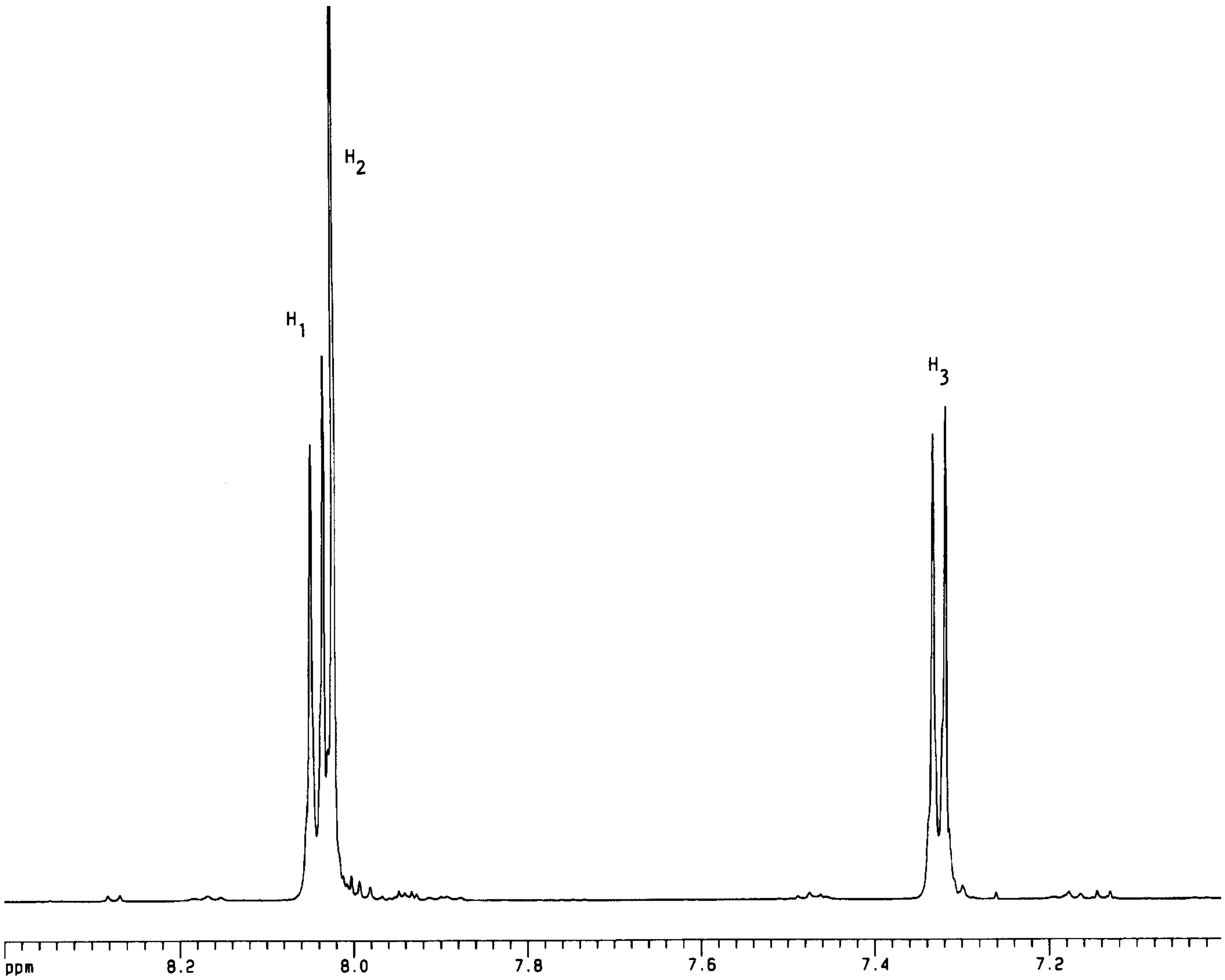
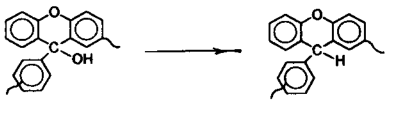


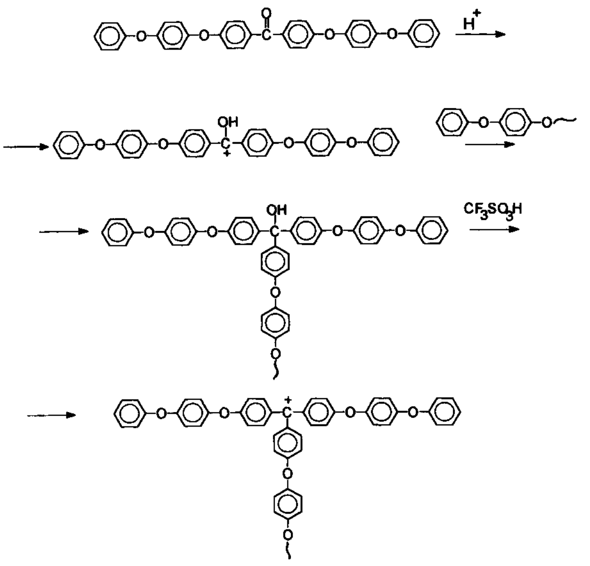
Figure 6 ^{1}H n.m.r. spectrum of samples **3a** and **3b**: proton designation in accordance with *Scheme 4*

absorption spectrum of sulfuric acid solutions of polyketone and on the improved melt stability of the polymer after treatment by formic acid. It is assumed that the treatment results in chemical reduction of xanthydrol groups to the corresponding 9-phenylenexanthenes[1]:



In our case, the n.m.r. spectra do not show signals corresponding to xanthydrol groups. Besides, polyketone **3b**, containing the highest abundance of *ortho*-substituted units, yields only very weakly coloured solutions in sulfuric acid.

Finally, it should be remembered that other electrophiles in the reaction media may compete with the acyl-cation. Protonated ketones are such electrophiles. A study of this type of reaction in trifluoromethanesulfonic acid involving PEEK oligomers has been reported[25]. According to that study, electrophilic attack of the terminal phenyl by the protonated ketone may lead first to a substituted triphenylmethanol, which in strong acids is readily converted into a substituted triphenylmethyl cation:



It should be expected that reactions of this kind occurring during preparation of polyketones **1–3** would result

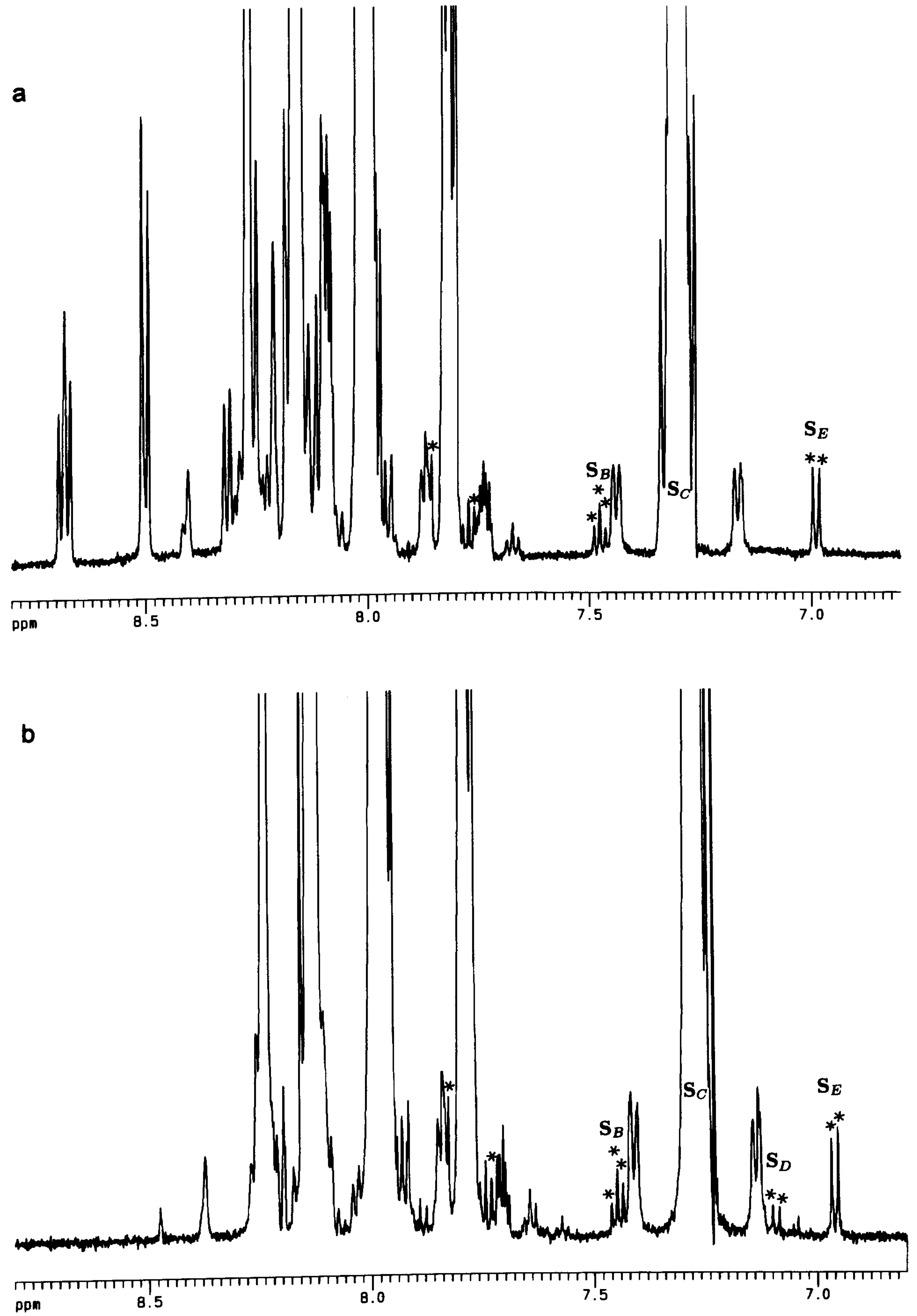


Figure 7 Expanded ^1H n.m.r. spectra for the ring proton resonances of samples **1a** (a) and **1b** (b). Signals of defect structures are marked by *

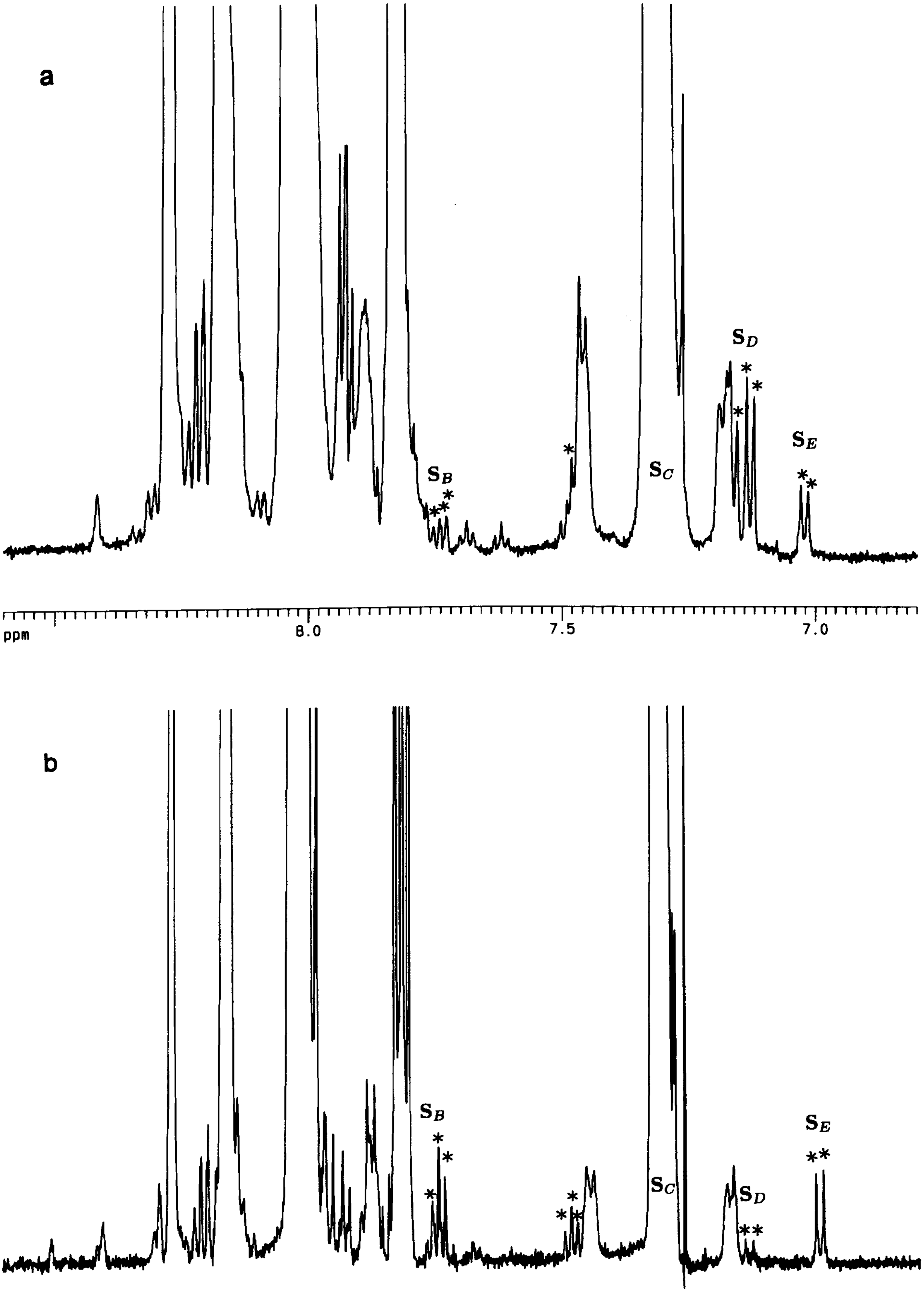


Figure 8 Expanded ^{1}H n.m.r. spectra for the ring proton resonances of samples **2a** (a) and **2b** (b). Signals of defect structures are marked by *

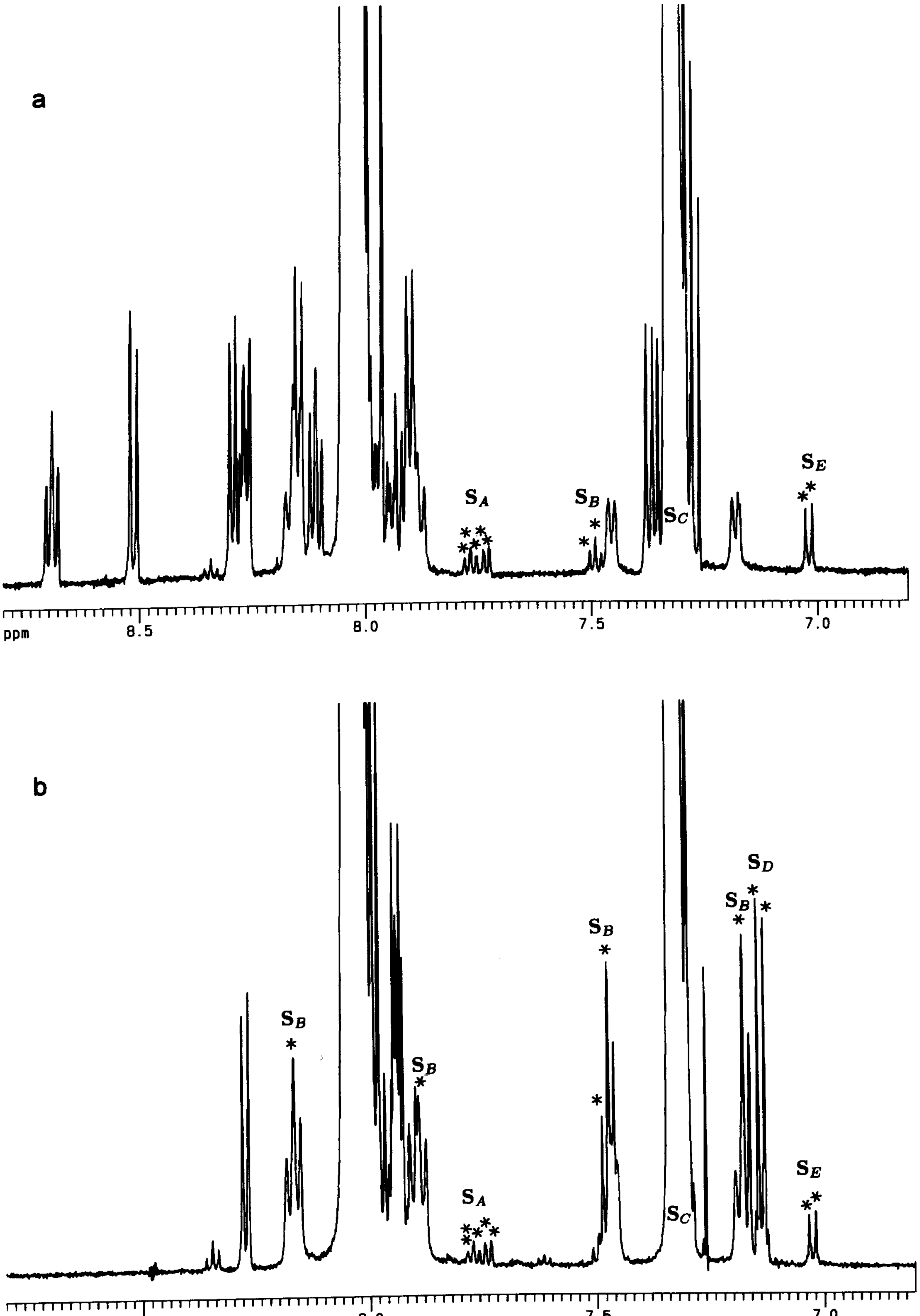
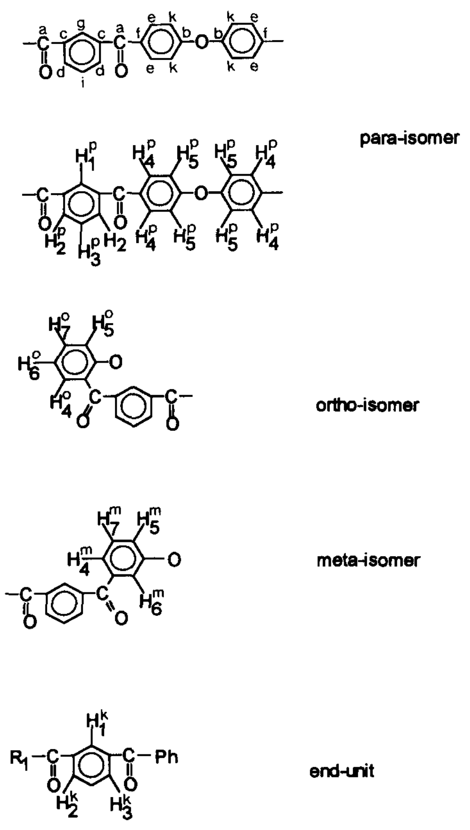
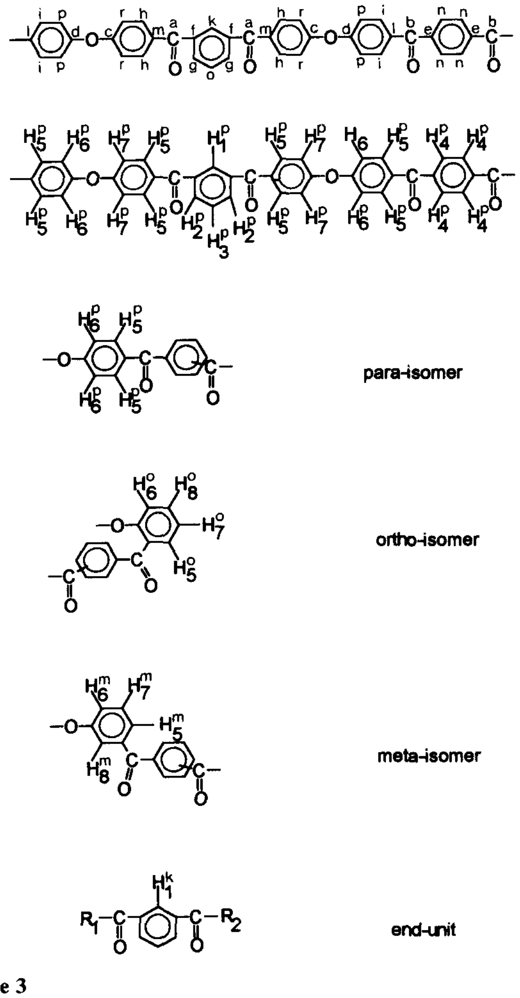


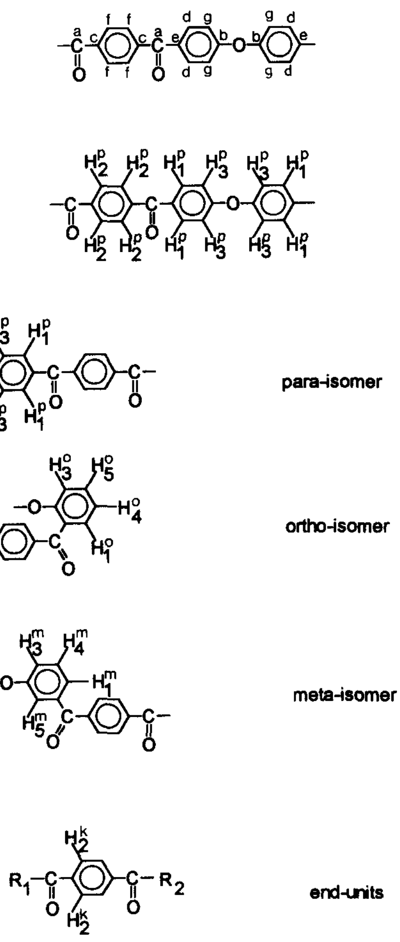
Figure 9 Expanded ^1H n.m.r. spectra for the ring proton resonances of samples **3a** (a) and **3b** (b). Signals of defect structures are marked by *



Scheme 2



Scheme 3



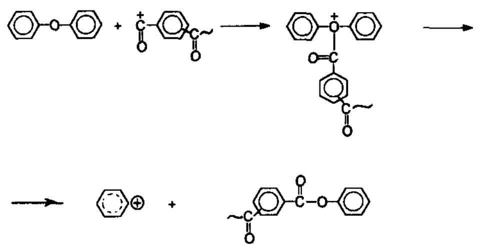
Scheme 4

in branched or, more probably cross-linked structures, which were also not detected in our experiments.

Thus, the only defect structures we could identify by ^1H n.m.r. spectroscopy are *ortho*- and *meta*-isomers and end-groups.

Concerning the expanded ^1H n.m.r. spectra for the ring proton resonances, the presence of two low field signals is to be noted: a triplet at 8.7 ppm and a doublet at 9.5 ppm, in the spectra of polyketones based on iso-/terephthaloyl chlorides and diphenyl ether (**1a** and **3a**).

It is remarkable that the signals are completely identical in both polymers and cannot be attributed to the end-groups. (Obviously the signals can neither be ascribed to xanthydrol groups.) Furthermore, the signals appeared at even lower field than for the protons of isopthaloyl- or terephthaloyl moieties. Taking into account that both polyketone preparation schemes involve diphenyl ether, one may suggest that the signals are due to products of some side reactions of diphenyl ether, for example, from acyl-oxonium complexes converted in arylene fragments containing ester groups:



and a possibility of this type of side reaction in electrophilic polycondensation was reported recently[26]. Calculations reveal that the low field signals (even if the low field triplet presents a superposition of doublet with singlet) may be attributable to arylene rings with keto- and ester-groups. To confirm the suggestion of ester group formation, we have boiled two samples of polyketone **1a** in dilute hydrochloric and potassium hydroxide solutions to hydrolyse the ester groups.

However, after such treatment, the intensity of the signals in the spectra does not change, indicating that they do not correspond to ester-substituted arylene-groups. Another possibility is that heterogeneous hydrolysis of powder polyketones samples was not very effective.

Additional information on the structure of these defect fragments can be drawn from i.r.-data. The i.r. absorption band arising from C=O stretching vibrations (e.g. in ketones, aldehydes or esters) has probably been more extensively studied than any other band. A good deal is now known about the factors which influence its frequency and its intensity[27].

It is, therefore, to be expected that the i.r.-spectrum of polymer **1a** will show absorption bands in the range 1720–1750 cm^{-1}, which is characteristic for the vibration of carbonyl groups in aromatic esters.

In sharp contrast to that, the i.r.-spectrum of the polymer (in the form of film) does not reveal any absorption band in this region. I.r.-spectrum of the thick (80 μm)-film also does not show any band. Moreover, the i.r.-spectra of the polymers **1a** and **1b** are almost identical. Consequently, we can conclude that the signals under question in the n.m.r. spectra of polymers **1a** and **3a** do not correspond to ester groups. (It is very unlikely that the frequency vibrations of these ester groups are lowered by the presence of the substituents on the ring *ortho* to the carbonyl group and overlapped by intensive carbonyl absorption band of diaryl ketone fragments.)

To the best of our knowledge, this type of side reaction in polyketone preparation by electrophilic aromatic polyacylation has not been reported previously. A more detailed explanation of their structure and mechanism of formation will require additional investigation.

CONCLUSIONS

Linear, high molecular weight poly(aryl ether ketone ketone)s with different iso-/tere-isomer repeating unit ratio (100/0, 50/50, 0/100) have been synthesized by electrophilic polycondensation of iso- and terephthaloyl chlorides with diphenyl ether, 1,4- and 1,3-bis(4-phenoxybenzoyl)benzenes. The polymer preparations were performed as precipitation polycondensation and the resulting polymers were obtained in particle form. Conventional ^1H and ^{13}C n.m.r. spectroscopy reveal a linear structure and *para*-substitution of diphenyl ether fragments in the main chain. End-groups, defect *meta*- and *ortho*-structures were identified by means of an analysis of the minor signals observed in the expanded ^1H n.m.r. spectra for the ring proton resonances. The amount and isomer ratio of these defect structures depend on the polymer structure and preparation path. For polyketones **1a**, **1b**, **2a**, **2b**, **3a** the total content of defect structure is *ca.* 2 mol%. Polyketone **3b** possesses the highest abundance of the defect structures. It is likely that the polycondensations involving 'small monomers' (diphenyl ether and iso- and terephthaloyl chlorides) proceed with partial decomposition of the diphenyl ether.

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