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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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### SYNTHESES OF BRANCHED POLY(ETHER KETONE)S WITH PENDANT FUNCTIONAL GROUPS BASED ON 1,1,1-*TRIS*(4-HYDROXYPHENYL)ETHANE

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Online publication date: 10 July 2002

**To cite this Article** Fritsch, Detlev , Vakhtangishvili, Lali and Kricheldorf, Hans R.(2002) 'SYNTHESES OF BRANCHED POLY(ETHER KETONE)S WITH PENDANT FUNCTIONAL GROUPS BASED ON 1,1,1-*TRIS*(4-HYDROXYPHENYL)ETHANE', Journal of Macromolecular Science, Part A, 39: 11, 1335 – 1347

**To link to this Article:** DOI: 10.1081/MA-120015734

**URL:** <http://dx.doi.org/10.1081/MA-120015734>

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JOURNAL OF MACROMOLECULAR SCIENCE®  
Part A—Pure and Applied Chemistry  
Vol. A39, No. 11, pp. 1335–1347, 2002

## SYNTHESES OF BRANCHED POLY(ETHER KETONE)S WITH PENDANT FUNCTIONAL GROUPS BASED ON 1,1,1-*TRIS*(4-HYDROXYPHENYL)ETHANE

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### ABSTRACT

1,1,1-Tris(4-hydroxyphenyl)ethane, THPE, was silylated with chlorotrimethylsilane and the silylated THPE was polycondensed with 1,4-bis(4-fluorobenzoyl)benzene, BFBB, in dry N-methylpyrrolidone. The resulting poly(ether ketone) had a moderate molecular weight and contained a significant fraction of cyclic oligomers and polymers. The pendant trimethylsiloxy group allowed an in situ alkylation with chloropropionitrile, allylbromide, 3,4-dichlorobenzyl chloride, 4-nitrobenzyl bromide, 1,3-propane sultone and 1,4-butane sultone. The latter alkylating agents yielded poly(ether ketone)s having pendant sulfonic acid groups. Further functional groups were introduced by acylation of the pendant free OH-group (resulting from the hydrolysis of the Me<sub>3</sub>SiO group) with acetic anhydride, methacrylic anhydride, cinnamoyl chloride and undecenoyl chloride.

*Key Words:* Poly(ether ketone)s; Polyelectrolytes; Alkylation; 1,1,1- Tris(4-hydroxyphenyl)ethane; Cyclization

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## INTRODUCTION

Aromatic poly(ether ketone)s have been commercialized over the past twenty years, and have attracted much interest from the viewpoint of fundamental research and technical application.<sup>[1-3]</sup> Poly(ether ketone)s combine several useful properties such as high melting temperatures (when crystalline) and thus, high heat distortion temperatures (>300°C). They possess a high thermal stability, a high stability against oxidation, and thus, a low inflammability, and are resistant to hydrolysis. This last property is particularly useful when applications as membranes, polymeric reagents or polymeric catalysts are taken into consideration.

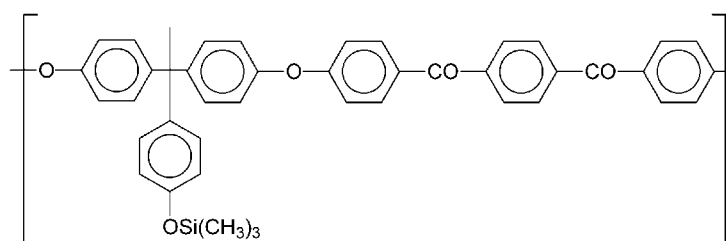
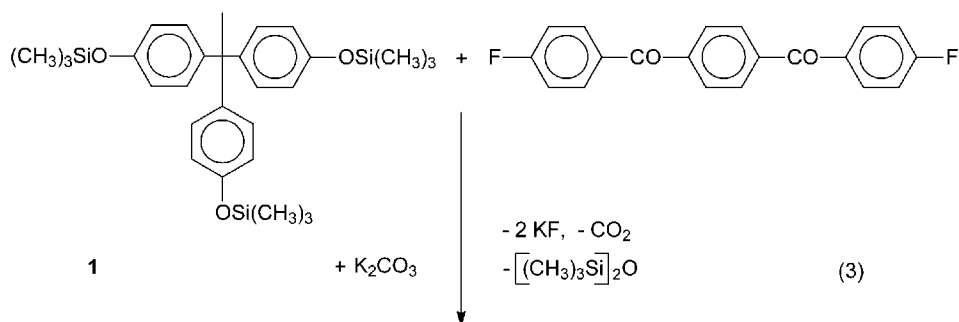
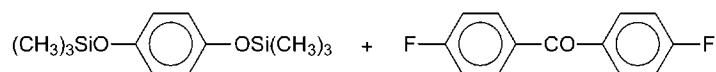
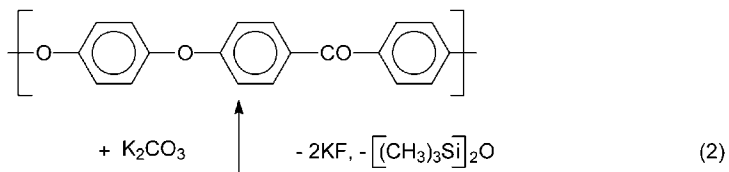
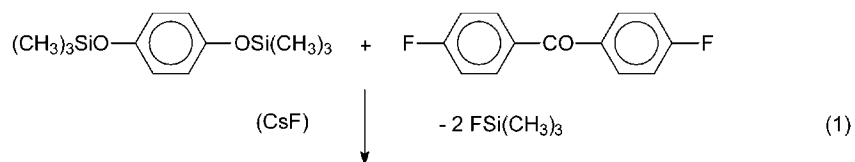
Poly(ether ketone)s are usually prepared by polycondensation of aromatic difluoroketones with the potassium salts of diphenols or with free diphenols in the presence of  $K_2CO_3$ .<sup>[1-5]</sup> The second method has the advantage of "one-pot procedure", but water is liberated in equimolar amounts and may cause hydrolytic side reactions. Anyway, both methods require an inert polar and high boiling reaction medium such as diphenylsulphone, N-methylpyrrolidone (NMP) or dimethylsulfoxide (DMSO). An alternative approach is based on silylated diphenols, which allow polycondensations to be conducted in the melt when CsF is used as catalyst (Eq. (1)).<sup>[6]</sup> Polycondensations of silylated diphenols promoted by  $K_2O_3$  in an inert, polar solvent are likewise feasible and have the advantage that the formation of water is avoided (Eq. (2)).

The present work had the purpose of synthesizing branched poly(ether ketone)s having pendant functional groups starting out from 1,1,1-tris(4-hydroxyphenyl)ethane (THPE). For reasons discussed below, the silyl method was used throughout this work (Eq. (3)).

## EXPERIMENTAL

### Materials

1,1,1-Tris(4-hydroxyphenyl)ethane, THPE, 3-chloropropionitrile, 4-nitrobenzyl-bromide, 3,4-dichlorobenzylchloride, undecenoylchloride, and annamoyl chloride were purchased from Aldrich Co. (Milwaukee, WI) and used as received. Fluorobenzene, terephthaloyl chloride, alkylbromide and ethacrylic anhydride were purchased from Acros Organics (Geel, Belgium) and again used as received.  $K_2CO_3$  p.a. grade (E. Merck KG, Darmstadt, Germany) was used as received. Chlorotrimethylsilane and triethylamine were gifts of Bayer AG (Leverkusen, Germany) and used as received. N-Methylpyrrolidone (NMP) was a gift of BASF AG (Ludwigshafen, Germany) and was twice distilled over  $P_4O_{10}$  in vacuo. 1,3-Propane sultone, and 1,4-butane sultone were purchased from Aldrich Co. and used as received.



### Monomers

#### A) Sililyted THPE

The triphenol was silylated with chlorotrimethylsilane and triethylamine in refluxing toluene and distilled at  $10^{-3}$  mbar over a "short-path apparatus" as described previously.<sup>[7]</sup>

**B) 4,4'-bis(4-Fluorobenzoyl)Benzene (BFBB)**

This monomer was prepared by  $\text{AlCl}_3$  catalyzed Friedel crafts acylation of fluorobenzene with terephthaloyl chloride as described in the literature.<sup>[8]</sup>

**Synthesis of Poly(Ether Ketone) 4**

Silylated THPE (20 mmol), BFBB (20 mmol) and  $\text{K}_2\text{CO}_3$  (21 mmol) were weighed into a 250 mL three-necked flask which was equipped afterwards with a mechanical stirrer and a reflux condenser. Dry NMP (150 mL) was added and the reaction mixture was heated in an oil bath to 140–145°C for 48 h. Afterwards the reaction mixture was precipitated into water. The isolated polymer was dried in vacuo, dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  and trifluoroacetic acid (TFA, volume ratio 4:1) and precipitated into methanol. After drying at 120°C in vacuo a glass transition temperature of 203°C was determined by DSC with a heating rate of 20°C/min.

**Alkylation**

Silylated THPE (10 mmol), BFBB (10 mmol) and  $\text{K}_2\text{CO}_3$  (11 mmol) were polycondensed in dry NMP (80 mL) at 145°C as described above. After cooling to 60°C, an alkylating agent (11 mmol) and dry  $\text{K}_2\text{CO}_3$  (55 mmol) were added and the reaction mixture was stirred at 60°C for 24 h. The reaction mixture was then poured into water and the precipitated polymer was (after drying) reprecipitated from  $\text{CH}_2\text{Cl}_2$ /TFA and methanol.

All other alkylations were conducted analogously with the temperatures listed in Table 2.

**Acylations**

The poly(ether ketone) 4 (10 mmol) and an acylating agent (11 mmol) were weighed into a 250 mL three-necked flask (under dry nitrogen). Dry  $\text{CH}_2\text{Cl}_2$  (100 mL) was added at once, and dry pyridine (20 mmol) was added dropwise with stirring. Stirring was continued for 4 h at 20°C and for 1 h with reflux. The reaction mixture was then cooled and poured into methanol. The precipitated polymer was isolated by filtration, washed with methanol and dried at 80°C *in vacuo*.

**Measurements**

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C.

The DSC measurements were conducted with a PERKIN ELMER DSC-7 in aluminum pans under nitrogen with a heating and cooling rate of 20°C/min. The 400 MHz <sup>1</sup>H NMR spectra were recorded on a Bruker “Avance” FT NMR spectrometer in 5 mm o.d. sample tubes using a CDCl<sub>3</sub>/trifluoroacetic acid mixture (1:1 by volume) a solvent containing TMS as shift reference.

The IR spectra were recorded from KBr. Pellets on a Nicolet “Impact 410” FT IR spectrometer. The MALDI-TOF mass spectra were obtained on a Bruker “Biflex III” spectrometer equipped with a nitrogen laser ( $\lambda = 337$  nm) in the reflection mode. The irradiation targets were prepared from CHCl<sub>3</sub>/trifluoroacetic acid solutions (volume ratio 4:1). Dithranol served as matrix and K-trifluoroacetate as dopant.

## RESULTS AND DISCUSSION

### Polycondensations

In a previous publication<sup>[7]</sup> syntheses of functionalized poly(ether sulfone)s from silylated THPE and 4,4'-difluorodiphenyl sulfone have been reported. It was found that the polycondensation of silylated THPE in NMP yielded high molecular weight polymers, and it allowed one in situ alkylation of the pendant trimethylsiloxy groups with a broad variety of alkylating agents. Therefore, this approach was also used in the present work. However, the electrophilic reactivity of BFBB was known<sup>[9,10]</sup> to be much lower than that of 4,4'-difluorodiphenyl sulfone, and thus, the reaction conditions needed optimization with regard to time and temperatures. The results of these optimization experiments are summarized in Table 1. They demonstrate that the highest molecular weights were obtained with a 1.0:1.0 stoichiometry at 145°C. With a 10 mol% excess of DFBB crosslinking was observed in contrast to analogous polycondensations of silylated THPE with 4,4'-difluorodiphenyl sulfone. Therefore, all further polycondensations studied in this work were performed under the conditions of experiment No. 1, Table 1.

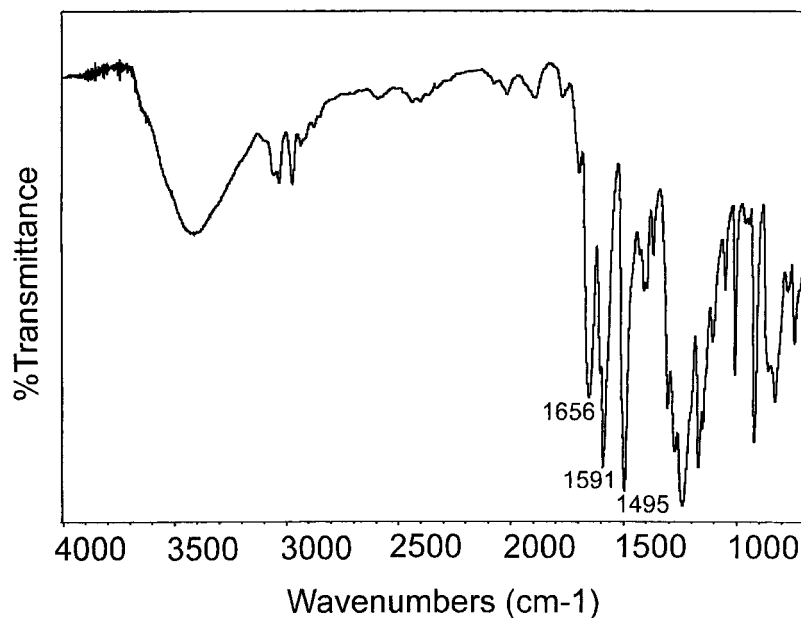
The poly(ether ketone)s isolated from the experiment Nos. 1–4 by precipitation into methanol had free OH-groups which displayed a broad band of its stretch vibration around 3400 cm<sup>-1</sup> in the IR spectra (Fig. 1). Furthermore, the stretch vibrations of the CO-groups were found in the typical position at 1659 cm<sup>-1</sup>. When these poly(ether ketone)s were examined by MALDI-TOF mass spectrometry, significant amounts of cycles were detected up to approximately 5,000 Da (Fig. 2). Whereas the classical Carothers-Flory theory of step-growth polymerization<sup>[11,12]</sup> did not foresee that cyclizations make a significant contribution to the total conversion, the recently published new concept of kinetically controlled polycondensations<sup>[13–15]</sup> predicts that cyclization can compete with propagation at any concentration

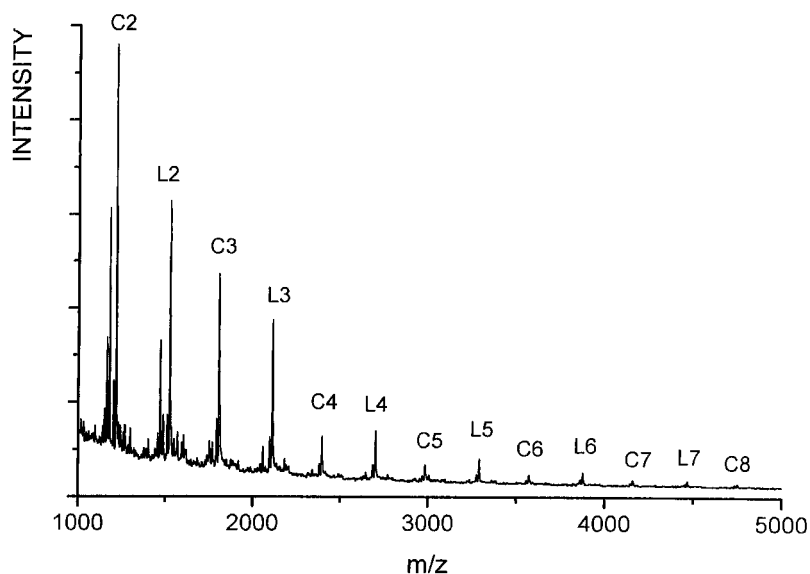
**Table 1.** Homopolycondensations of Silylated THPE and BFBB in Dry NMP with  $K_2CO_3$  as Catalyst

| Polyc. No. | $\frac{THPE^a}{BFBB}$ | Temp. ( $^{\circ}C$ ) | Time (h) | Yield (%) | $\eta_{inh}$ (dL/g) <sup>b</sup> |
|------------|-----------------------|-----------------------|----------|-----------|----------------------------------|
| 1          | 1.0/1.0               | 145                   | 24       | 89        | 0.59                             |
| 2          | 1.0/1.0               | 145                   | 48       | 94        | 0.57                             |
| 3          | 1.0/1.0               | 180                   | 24       | 90        | 0.21                             |
| 4          | 1.0/1.0               | 180                   | 48       | 87        | 0.18                             |
| 5          | 1.0/1.1               | 145                   | 24       |           | crosslinked                      |

<sup>a</sup>Molar feed ratio.<sup>b</sup>Measured at 20 $^{\circ}C$  with  $c = 2$  g/L in  $CH_2Cl_2/TFA$  (4:1 by volume).

stage of the polycondensation. On the basis of this new theory, the detection of cyclic poly(ether ketone)s in the products of this work is quite normal. These cyclizations have a dual effect, they limit the chain growth and they reduce the tendency of crosslinking even at conversions above 99% in contrast to the classical theory of Flory.<sup>[16]</sup> The formation of cycles does, of course, not prevent branching reactions, and the MALDI-TOF mass spectrometry cannot distinguish between a large cycle and a branched smaller cycle containing the same number of repeat units.

**Figure 1.** IR spectrum (KBr pellets) of the poly(ether ketone) 4.



**Figure 2.** MALDI-TOF mass spectrum of the poly(ether ketone) **4** No. 1, Table 1. (C10 means cyclic oligomer having a degree of polymerization of 10).

### Acylation and Akylation Reactions

Whereas the virgin PEK resulting from the polycondensation process contains a pendant trimethylsiloxy group (structure **3**) the polymer isolated after precipitation into water and reprecipitation into methanol had a free OH-group (structure **4**). Both versions of the PEK proved to be useful for further functionalization. When the PEK of structure **4** was treated with a

**Table 2.** Acylations of the Ppoly(Ether Ketone)**4**<sup>a</sup> Derived from THPE

| Exp. No. | Acylating Agent <sup>b</sup>     | Temp. (°C) | Time (h) | Yield (%) | $\eta_{inh}$ (dL/g) <sup>d</sup> | DS <sup>e</sup> |
|----------|----------------------------------|------------|----------|-----------|----------------------------------|-----------------|
| 1        | Acetic anhydride                 | 20, 40     | 4, 1     | 93        | 0.26                             | 96              |
| 2        | Methacrylic anh.                 | 20, 40     | 4, 1     | 82        | 0.41                             | 20              |
| 3        | Methacrylic anh.                 | 20, 40     | 20, 1    | 87        | 0.40                             | 22              |
| 4        | Methacrylic anh. <sup>c</sup>    | 20, 40     | 4, 1     | 79        | 0.44                             | 26              |
| 5        | Cinnamoyl chloride               | 20, 40     | 4, 1     | 88        | 0.20                             | 90              |
| 6        | Undecenoyl chloride              | 20, 40     | 4, 1     | 85        | 0.23                             | 34              |
| 7        | Undecenoyl chloride <sup>c</sup> | 20, 40     | 4, 1     | 80        | 0.46                             | 90              |

<sup>a</sup> $\eta_{inh} = 0.35$  dL/g in  $\text{CH}_2\text{Cl}_2/\text{TFA}$  (volume ratio 8:1).

<sup>b</sup>The molar feed ratio of acylating agent/THPE was 1.1:1.0.

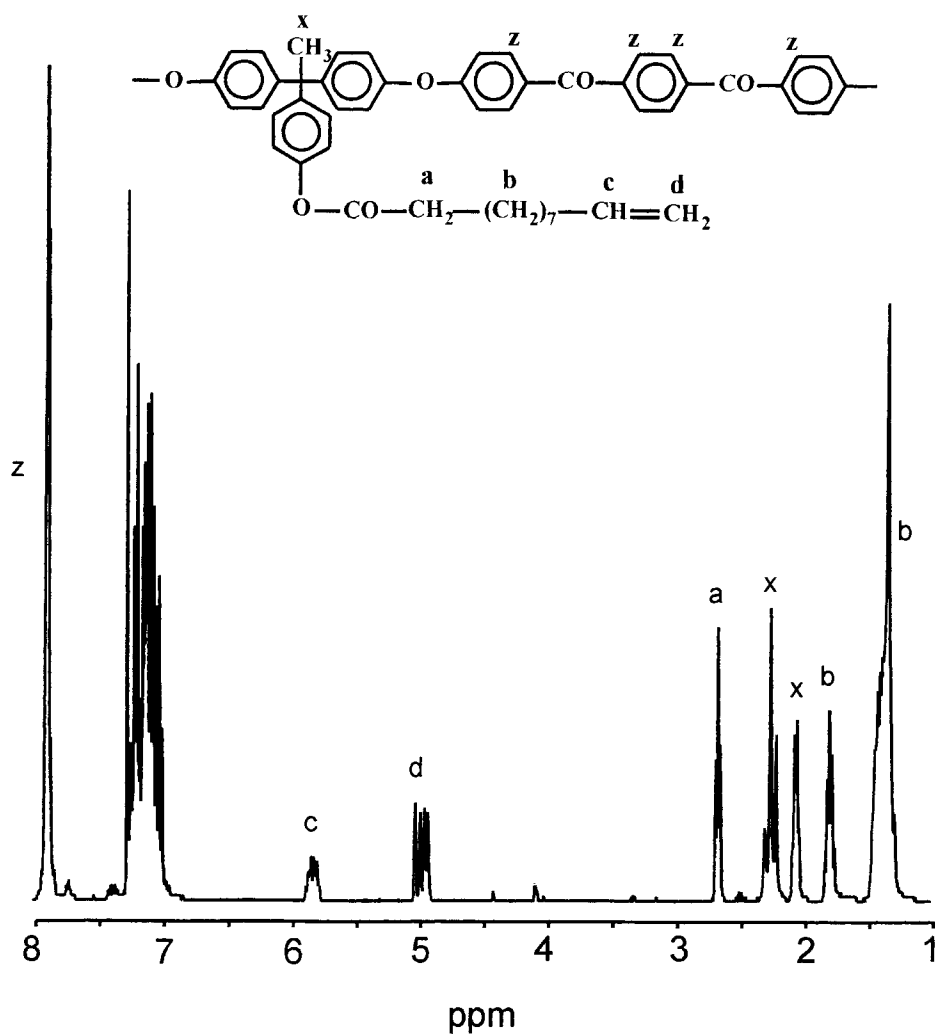
<sup>c</sup>The molar feed ratio of acylating agent/THPE was 1.5:1.0.

<sup>d</sup>Measured at 20°C with  $c = 2$  g/L in  $\text{CH}_2\text{Cl}_2$ .

<sup>e</sup>Degree of substitution determined by  $^1\text{H}$  NMR spectroscopy (margin of error  $\pm 2\%$ ).

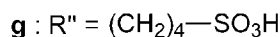
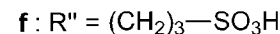
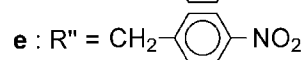
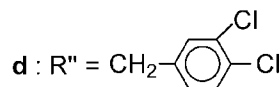
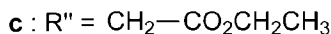
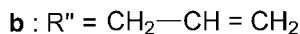
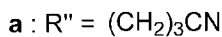
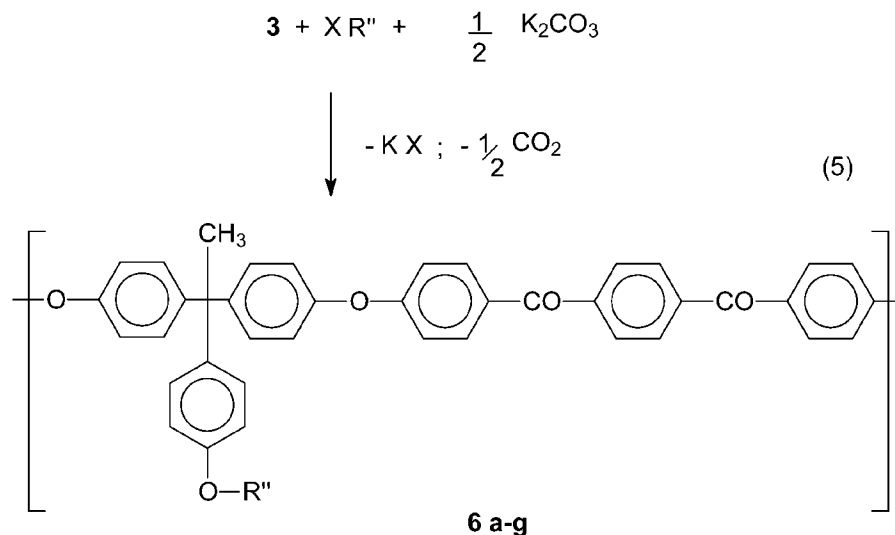


slight excess (10 mol%) of acetic anhydride in combination with pyridine a nearly complete acetylation of the OH-groups was achieved. The degrees of substitution (DS) listed in Table 2 were determined by means of  $^1\text{H}$  NMR spectroscopy. As illustrated exemplarily in Fig. 3, all acylating agents used in this work show at least one characteristic  $^1\text{H}$  NMR signal which does not overlap with the signals of the PEK chain. The intensity of this "acyl signal" (signal "a" in Fig. 3) was compared to that of the aromatic CH protons in ortho position to the CO-groups in the PEK backbone (signal "x" in Fig. 3).



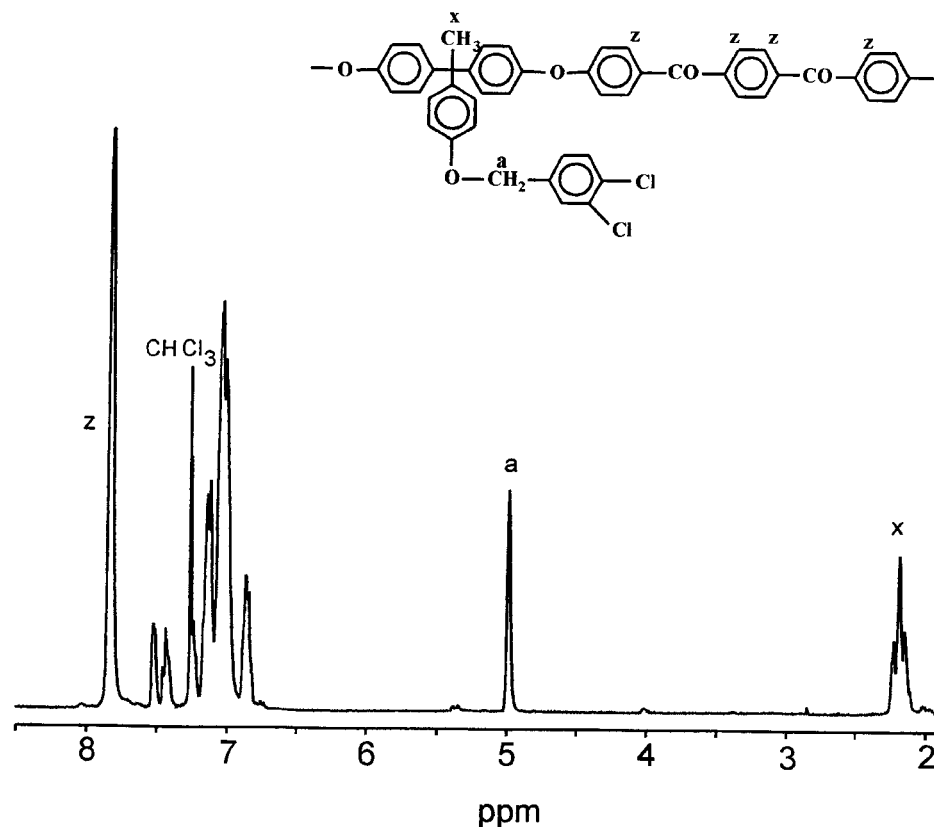
**Figure 3.** 400 MHz  $^1\text{H}$  NMR spectrum of the poly(ether ketone) **5d** containing undecenoyl groups.





When methacrylic anhydride was used for acylation of **4** under the conditions of the acetylation, a low DS of only 20% was found. It is well known that this anhydride is far less reactive than acetic anhydride because the conjugation of the  $\pi$ -electrons and CO-group reduce their electrophilicity. In a second experiment with methacrylic anhydride (No. 3, Table 2) the reaction time was increased from 4 to 20 h, but without any progress for the DS. In a third experiment (No. 4, Table 2) a larger excess of methacrylic anhydride was used, and again no significantly higher DS was found. A much higher DS resulted from acylation with cinnamoyl chloride, whereas an extremely low value was obtained with undecenoyl chloride (No. 6, Table 2). A larger excess of this acid chloride and a lower temperature for the drying of the precipitated polymer (to prevent methanolyses during the drying) significantly improved the DS (No. 7, Table 2, and Fig. 3).

It was found in our previous study of functionalized poly(ether sulfone)s derived from THPE<sup>[7]</sup> that alkylation of the pendant free OH-group was not successful in contrast to acylation. However, when the silylated OH-group of the virgin poly(ether sulfone) was alkylated in a "one-pot procedure" (combined with the synthesis of the poly(ether sulfone)) satisfactory results



**Figure 4.** 400 MHz  $^1\text{H}$  NMR spectrum for the poly(ether ketone) **6d** containing 3,4-dichlorobenzyl groups.

were obtained. Therefore, an analogous “one-pot procedure” was studied in the present work. With 3-chloropropionitrile, the least reactive alkylating agent of this work, the temperature was raised up to  $145^\circ\text{C}$ , but no significant alkylation was observed (No. 1, Table 3). All other alkylating agents gave DSs above 50 even at the relatively low temperature of  $60^\circ\text{C}$ , which was selected to avoid alkylation of aromatic rings and to avoid degradation (Table 3). With 3,4-dichlorobenzoyl chloride or with ethyl bromoacetate DS values above 90 were achieved (No. 4, Table 3). The  $^1\text{H}$  NMR spectrum PEK **6d** is presented in Fig. 4 as an example for an alkylated PEK. Particularly interesting are the PEKs alkylated with sultones because they possess pendant sulfonic acid groups. A reaction temperature of  $100^\circ\text{C}$  was required to obtain moderate DS values. The high inherent viscosities of these PEKs (**6f** and **6g**) obviously reflect a polyelectrolyte effect. A further optimization of the alkylation processes in direction of higher DS values is certainly feasible but was not intended in this work, since concrete applications of these

materials should not be studied. However, further studies of PEKs containing pendant sulfonic acid groups (**6f** and **6g**) are currently in progress.

### CONCLUSION

The polycondensation of silylated THPE with BFBB in NMP proved to be an useful method for the preparation of poly(ether ketone)s having pendant trimethylsiloxy or OH-groups (**3** or **4**). Due to cyclization crosslinking was avoided in all experiments despite high conversions. From the large fraction of cycles detected by MALDI-TOF mass spectroscopy it may also be concluded that the poly(ether ketone)s of this work mainly consist of cycles having linear and branched side chains. The use of silylated THPE as monomer had the additional advantage that in situ alkylation of the pendant siloxy group was feasible. In this way a broad variety of functional groups could be attached to the PEK backbone. Particular interesting is the introduction of sulfonic acid groups via alkylation with 1,3-propane sultone or 1,4-butane sultone. The membrane properties of these acidic PEKs are currently under investigation. Acylation of the PEK with pendant OH-groups was also feasible. Methacrylate and cinnamate substituents allow radical or photocrosslinking of these PEKs and thus open potential applications as insoluble, chemically stable coatings or membranes.

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Received March 19, 2002