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# New Polymer Syntheses. 77. Telechelic Oligo- and Poly(ether ketone)s

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ABSTRACT: Telechelic poly(ether ketone)s were prepared by bulk polycondensations of 4′-fluoro-4-(trimethylsiloxy)benzophenone and 4′-fluoro-2-methyl-4-(trimethylsiloxy)benzophenone and by cocondensation with 4′-fluoro-4-(trimethylsiloxy)diphenyl sulfone. These A−B type monomers were cocondensed with activated aromatic difluoro compounds or a silylated diphenol containing a relatively thermostable aliphatic group ($CH_2$ or $CH_3$). This synthetic approach has the following three advantages: first, the resulting telechelic poly(ether ketone)s possess two identical functional end groups. Second, the average degree of polymerization (DP) can be controlled by variation of the monomer/comonomer ratio. Third, the DPs of the isolated poly(ether ketone)s can be calculated from the $^1H$ NMR signals of the aliphatic and aromatic protons. The telechelic poly(ether ketone)s were also characterized by elemental analyses, inherent viscosities, DSC measurements, and (in individual cases) $^{13}C$ NMR spectroscopy.

## Introduction

Albeit rarely addressed in textbooks, monomers used for polycondensations and polyadditions should be subdivided into two classes: the A−B type and A−A/B−B type monomers. In this terminology A and B mean two different kinds of functional groups which can react with each other but not with themselves. Both groups of monomers differ largely in their usefulness for polymer syntheses. A−B type monomers possess a much higher potential for preparative purposes, which has not been explored yet in great depth and detail.

A−B type monomers have the characteristic advantage that cocondensations with A−A or B−B type monomers may yield oligomers or polymers with two identical end groups. If the comonomer is monofunctional under the given reaction conditions, the resulting telechelics will possess two different end groups. An additional advantage is the easy control of the molecular weight by variation of the monomer/comonomer (M/C) ratio. In a previous part of this series first results concerning the telechelic poly(ether sulfone)s were reported.[1] Telechelic poly(ether sulfone)s were also prepared from 4′-fluoro- or 4′-chloro-4-hydroxydiphenyl sulfone in solution by Attwood et al.,[2−4] but these telechelics were never isolated and characterized. The present work has the purpose to describe synthesis and characterization of telechelic poly(ether ketone)s. Silylated monomers were exclusively used in this study, because the polycondensation of silylated monomers may be conducted in bulk,[1,5−8] and thus, complications with liquid reaction media such as fractional crystallization or radical side reactions[9] are avoided.

## Experimental Section

**Materials.** 4′-Fluoro-4-hydroxybenzophenone, 4-fluorobenzene, and diphenylmethane were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. *m*-Cresol was a gift of Bayer AG (Leverkusen, Germany) and distilled. Bisphenol-P was purchased from Kennedy & Klim Inc. (Little Silver, NJ). 4′-Fluoro-4-(trimethylsiloxy)diphenyl sulfone ($n^{20}_D = 1.5466$) and 4′-fluoro-4-(trimethylsiloxy)benzophenone (mp 33−35 °C) were prepared as described previously.[1] Also 4,4′-bis(4-fluorobenzoyl)diphenyl ether (**5**) was synthesized as reported previously.[6] Hexamethyldisilazane was purchased from Dynamite Nobel (Troisdorf, Germany).

**Bis(trimethylsilyl)-Bisphenol-P (7).** Bisphenol-P (0.2 mol) and hexamethyldisilazane (0.25 mol) were refluxed in 250 mL of dry toluene until the evolution of $NH_3$ ceased. Afterward, the solvent and the excess of hexamethyldisilazane were evaporated in vacuo, and the product was distilled in a vacuum of $10^{-3}$ bar over a short-path apparatus. Yield 91%; mp 115−116 ° C. Anal. Calcd for $C_{30}H_{42}O_2Si_2$ (490.84): C, 73.41; H, 8.63. Found: C, 73.20; H, 8.71. $^1H$ NMR ($CDCl_3$/TMS): $\delta$ 0.25 (s, 18H), 6.67−7.12 (m, 12H).

**4′-Fluoro-2-methyl-4-hydroxybenzophenone.** 4-Fluorobenzoyl chloride (0.5 mol) was added dropwise under cooling with ice to a suspension of aluminum chloride (1.0 mol) in dry nitrobenzene (500 mL). Afterward, 3-cresol (0.5 mol) was added dropwise without cooling. The complete reaction mixture was stirred for 20 h at 60 °C and finally poured into 1 N hydrochloric acid containing crushed ice. The product was extracted with three 500 mL portions of diethyl ether. The combined extracts were dried over $Na_2SO_4$ and evaporated. The nitrobenzene was removed in vacuo, and the residual product was recrystallized from chloroform/ligroin. Yield 33%; mp 110−112 °C. Anal. Calcd for $C_{14}H_{11}FO_2$ (230.25): C, 73.00; H, 4.78. Found: C, 72.62; H, 4.97. $^1H$ NMR ($CDCl_3$/TMS): $\delta$ 2.78 (s, 3H), 6.66−7.75 (m, 7H).

**4′-Fluoro-2-methyl-4-(trimethylsiloxy)benzophenone (2).** 4′-Fluoro-2-methyl-4-hydroxybenzophenone (0.5 mol) and chlorotrimethylsilane (0.55 mol) were dissolved in hot, dry toluene (700 mL), and triethylamine (0.55 mol) was added dropwise with stirring. After 2 h of reflux the reaction mixture was cooled with ice, filtered under exclusion of moisture, and concentrated in vacuo. The residue was diluted with dry toluene (200 mL) and refluxed until all triethylamine hydrochloride had sublimed into the reflux condenser. Finally, the product was isolated by distillation over a short-path apparatus. Yield 93%. Anal. Calcd for $C_{17}H_{19}F_2Si$ (302.28): C, 66.68; H, 6.20. Found: C, 67.21; H, 6.37. $^1H$ NMR ($CDCl_3$/TMS): $\delta$ 0.29 (s, 9H), 2.33 (s, 3H), 6.63−7.86 (m, 7H).

Monomers **1** and **3** were prepared analogously.[1]

**4,4′-Bis((4-fluorophenyl)sulfonyl)diphenylmethane (6).** A solution of 4-fluorobenzenesulfonyl chloride (1.0 mol), diphenylmethane (0.5 mol), and $FeCl_3$ (0.01 mol) in dry nitrobenzene (70 mL) was stirred at 120 °C for 20 h. The nitrobenzene was evaporated in vacuo, and the residue was dissolved in chloroform and treated with charcoal. The product crystallized from chloroform was recrystallized from chloroform/ligroin. Yield 21%; mp 178−180 °C. Anal. Calcd for $C_{25}H_{18}F_2O_4S_2$ (484.44): C, 61.98; H, 3.74; S, 13.21. Found: C, 61.59; H, 3.91; S, 13.05. $^1H$ NMR ($CDCl_3$/TMS): $\delta$ 3.40 (s, 2H), 7.0−7.4 (m, 8H), 7.6−80 (m, 8H).

**Polycondensations.** A monomer and a comonomer (together 8−9 g) and CsF (20−50 mg) were weighed into a

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cylindrical round-bottomed glass reactor equipped with a stirrer and gas inlet and outlet tubes. The reaction vessel was placed into a metal bath preheated to 150 °C, and the temperature was rapidly raised to 220–240 °C where the polycondensation started. Depending on the reaction rate, the temperature was raised in steps of 20 °C up to the final temperature listed in Tables 1–4. The reaction mixture was kept at the maximum temperature for 30 min without vacuum and for an additional 30 min with vacuum. After cooling, the crude polymer was dissolved in a suitable solvent, precipitated into cold methanol, washed with methanol, and dried at 120 °C in vacuo.

The poly(ether ketone)s **8a–d** and **9a–d** were dissolved in concentrated $H_2SO_4$; all other poly(ether ketone)s were dissolved in mixtures of $CH_2Cl_2$ and trifluoroacetic acid (10–25 vol %).

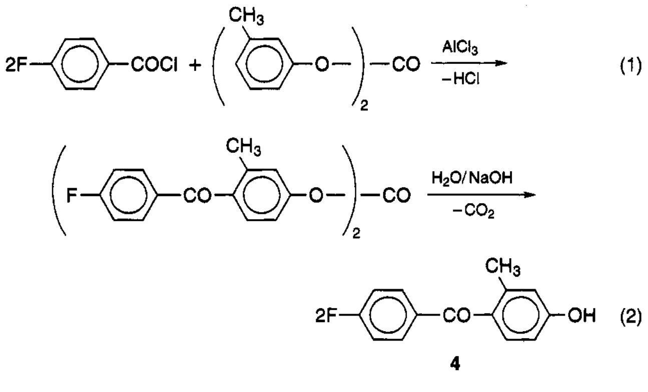
**Measurements.** The inherent viscosities were measured in an automated Ubbelohde viscometer thermostated at 25 °C.

The DSC measurements were conducted with a Perkin-Elmer DSC-4 at a heating rate of 20 °C/min in aluminum pans under nitrogen. Both the measurements of **8a–d** and the calibration were repeated to check their reproducibility.

The $^1H$ NMR spectra, were recorded with a Bruker AC-100 FT spectrometer in 5 mm o.d. sample tubes. All $^1H$ NMR spectra of oligo- and poly(ether ketone)s were measured in $CDCl_3$/TFA (4:1 by volume). The 90.5 MHz $^{13}C$ NMR spectra were recorded with a Bruker AM 360 FT spectrometer in 10 mm o.d. sample tubes. A pulse angle of approximately 30° was used with a pulse interval of 2 s.

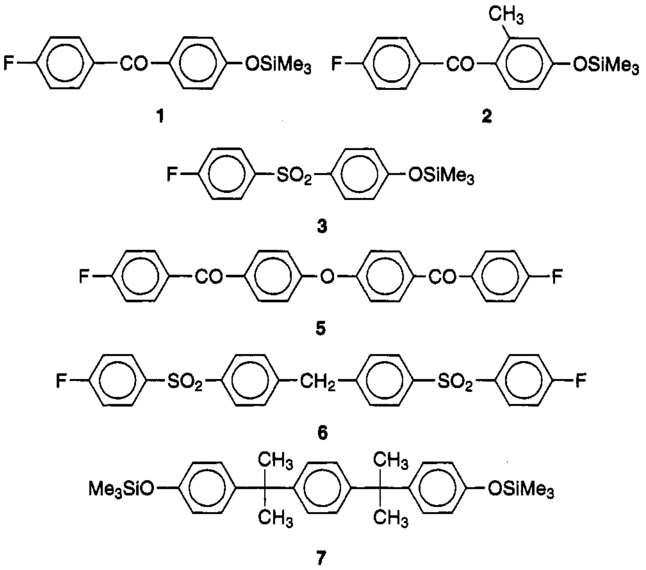
## Results and Discussion

**Syntheses of Monomers.** All polycondensations discussed in this work are based on the three monomers **1–3** (Chart 1). Monomer **1** was prepared from commercial 4′-fluoro-4-hydroxybenzophenone by silylation with hexamethyldisilazane as described previously.[1] In the case of **2**, the corresponding phenol (**4**) was synthesized from 4-fluorobenzoyl chloride and 3-cresol carbonate according to the literature[8] (eqs 1 and 2). The silylation of **4** and of 4′-fluoro-4-hydroxydiphenyl sulfone[9] were both achieved with chlorotrimethylsilane and triethylamine. All three monomers were purified by distillation.



In addition to monomers **1–3**, comonomers **5–7** were synthesized. Bisketone **5** was obtained by Friedel–Crafts acylation of diphenyl ether under standard conditions.[6] In an analogous way disulfone **6** was prepared by Friedel–Crafts type sulfonylation of diphenylmethane. The correct structure, i.e., the sulfonylation of both para positions, is proved by the $^1H$ NMR spectrum. Comonomer **7** resulted from silylation of commercial Bisphenol-P with hexamethyldisilazane in refluxing toluene.

**Chart 1**



**Crystalline Poly(ether ketone)s Based on Monomer 1.** A first series of polycondensations was conducted with monomer **1** and 4,4′-bis(4-fluorobenzoyl)diphenyl ether **5**. Preliminary polycondensations with this monomer combination (not listed in Table 1) have shown that reaction temperatures above 280 °C involve a risk of partial cross-linking. Therefore, the maximum reaction temperature for polycondensations of monomers **1** and **2** was limited to 280 °C. The results obtained with variation of the monomer **1**/comonomer **5** ratio are compiled in Table 1. In agreement with the expected cocondensation, the inherent viscosities of the poly(ether ketone)s **8a–d** increase with the monomer/comonomer ratio. Comonomer **5** has the advantage that the resulting polycondensates possess a perfect ether–ketone backbone, but because of this perfect structural agreement, there is no chance to detect the incorporation of **5** by spectroscopic methods.

The polycondensation of **1** with **6** yielded the poly(ether ketone)s **9a–d** with an opposite combination of properties. The monomeric unit of **6** represents an alien element in the ether–ketone backbone, but its incorporation is easily and quantitatively detectable by $^1H$ and $^{13}C$ NMR spectroscopy. A rapid incorporation of comonomer **6** is likely because a (fluorophenyl)sulfonyl group is more electrophilic than a fluorobenzophenone. In agreement with this consideration, the inherent viscosities increase with the monomer/comonomer ratio quite analogously to series **8a–d** (Table 1). The fact that the signal of the $CH_2$ group does not overlap with the signals of the aromatic protons allowed the calculation of average degrees of polymerization (DP's) by $^1H$ NMR spectroscopy. These NMR spectroscopic DP's are higher than those expected from the feed ratio, and the percentage of deviation decreases with increasing DP. This trend suggests that fractionation upon precipitation into methanol played a role. The small oligomer fraction isolated from the methanol after evaporation contained indeed a high fraction of comonomer **6**. This result is reasonable, because comonomer **6** improves the solubility of the oligo(ether ketone)s in organic solvents.

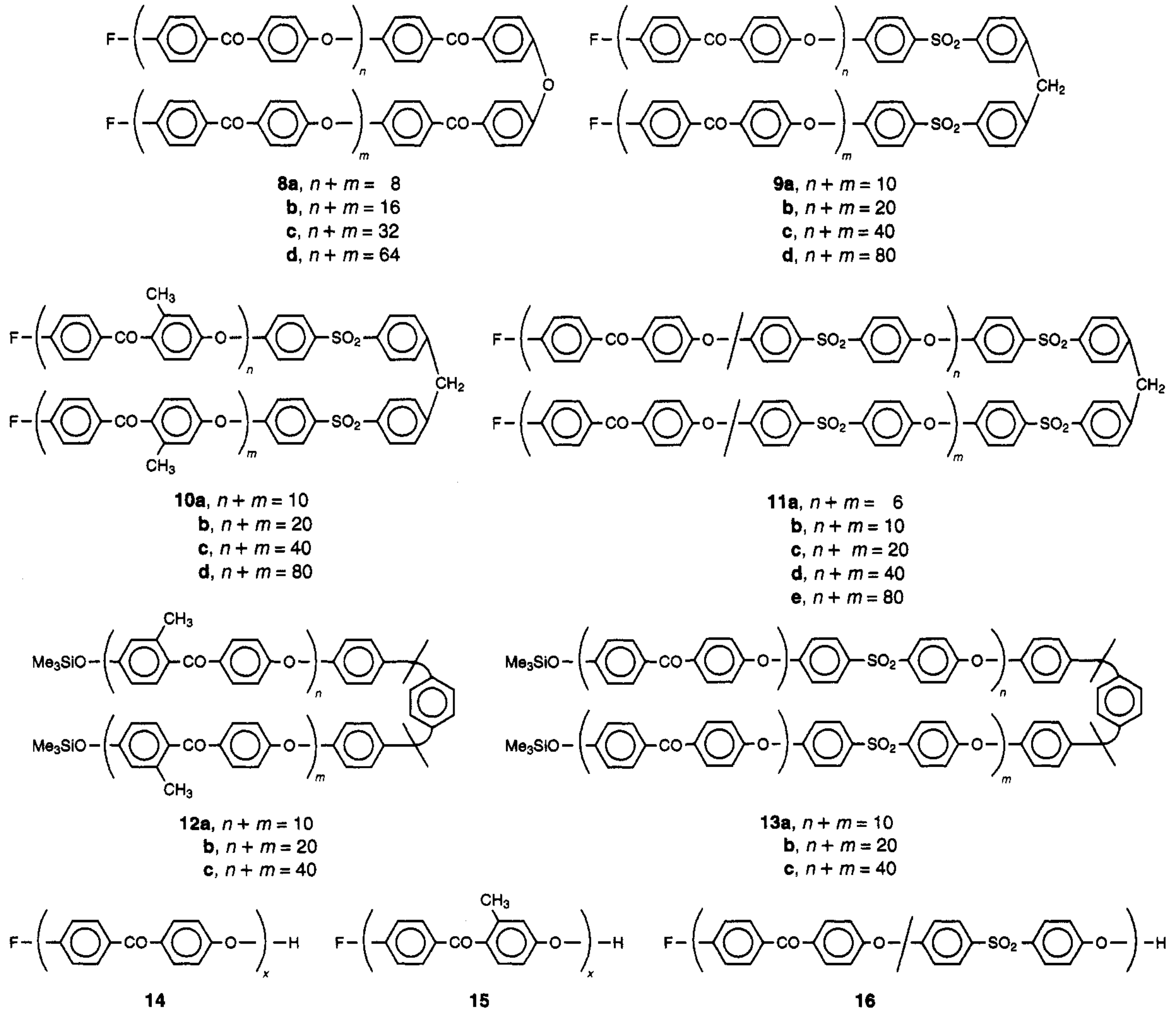
Somewhat unexpected are the thermal properties of both series of poly(ether ketone)s. It was predictable from the well-known properties of the homopolymer[10,11] that all telechelic oligomers and polymers are crystalline. It is obvious that both melting temperatures ($T_m$) and degree of crystallinity increase in series **9a–d** and approach the properties of the homopolymer, because

**Table 1. Polycondensations of 4'-Fluoro-4-(trimethylsiloxy)benzophenone (1) with 4,4'-Bis(4-fluorobenzoyl)diphenyl Ether (5) or 4,4'-Bis((4-fluorophenyl)sulfonyl)diphenylmethane (6)**

| polym formula | mon/comon[a] | temp[b] (°C) | yield (%) | $\eta_{inh}$[c] (dL/g) | DP[d] | $T_g$[e] (°C) | $T_m$[e] (°C) | elem anal. | % C | % H | % S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **8a** | 8/1 | 240–280 | 94 | 0.15 | | | 387 | calcd | 78.70 | 4.06 | |
| | | | | | | | | found | 77.83 | 4.11 | |
| **8b** | 16/1 | 240–280 | 91 | 0.19 | | | 386 | calcd | 79.09 | 4.08 | |
| | | | | | | | | found | 78.25 | 4.18 | |
| **8c** | 32/1 | 240–280 | 89 | 0.20 | | | 378 | calcd | 79.32 | 4.09 | |
| | | | | | | | | found | 78.30 | 4.21 | |
| **8d** | 64/1 | 240–280 | 87 | 0.27 | | | 374 | calcd | 79.45 | 4.10 | |
| | | | | | | | | found | 78.70 | 4.11 | |
| **9a** | 10/1 | 220–270 | 91 | 0.10 | 20 | 145 | 322 | calcd | 76.08 | 4.05 | 2.62 |
| | | | | | | | | found | 76.02 | 4.13 | 2.85 |
| **9b** | 20/1 | 220–270 | 87 | 0.15 | 28 | 146 | 355 | calcd | 77.64 | 4.08 | 1.45 |
| | | | | | | | | found | 77.44 | 4.11 | 1.52 |
| **9c** | 40/1 | 220–260 | 85 | 0.23 | 48 | 147 | 370 | calcd | 78.57 | 4.06 | 0.77 |
| | | | | | | | | found | 78.90 | 4.29 | 0.91 |
| **9d** | 80/1 | 220–260 | 92 | 0.28 | 88 | 148 | 371 | calcd | 79.06 | 4.07 | 0.40 |
| | | | | | | | | found | 78.51 | 4.10 | 0.55 |
| **14** | ∞ | 220–280 | 95 | 0.54 | | 150 | 375[f] | calcd | 79.58 | 4.11 | |
| | | | | | | | | found | 79.05 | 4.19 | |

[a] Molar feed ratio of monomer 1 and comonomer. [b] The reaction temperature was raised in steps of 20 °C. [c] Measured at 25 °C with $c$ = 2 g/L in concentrated $H_2SO_4$. [d] Average degree of polymerization as determined by $^1H$ NMR spectroscopy. [e] From DSC measurements with a heating rate of 20 °C/min. [f] $T_m$'s of 361[11] and 373 °C[12] have been reported in the literature.

**Chart 2**



**8a**, $n + m = 8$
**b**, $n + m = 16$
**c**, $n + m = 32$
**d**, $n + m = 64$

**9a**, $n + m = 10$
**b**, $n + m = 20$
**c**, $n + m = 40$
**d**, $n + m = 80$

**10a**, $n + m = 10$
**b**, $n + m = 20$
**c**, $n + m = 40$
**d**, $n + m = 80$

**11a**, $n + m = 6$
**b**, $n + m = 10$
**c**, $n + m = 20$
**d**, $n + m = 40$
**e**, $n + m = 80$

**12a**, $n + m = 10$
**b**, $n + m = 20$
**c**, $n + m = 40$

**13a**, $n + m = 10$
**b**, $n + m = 20$
**c**, $n + m = 40$

**14** **15** **16**

the comonomer is an alien element in the backbone. Yet surprising is the observation that the glass transition temperature ($T_g$) is almost independent of the DP (Table 1). Even more surprising are the properties of **8a–d** (Chart 2). The DSC curves (Figure 1) display sharp endotherms and an exotherm and no glass transition step. Both findings together clearly indicate a high degree of crystallinity. Furthermore, the $T_m$'s of oligomers **8a** and **8b** are 14–15 °C higher than that of the high molecular weight poly(ether ketone) **14**, when compared in the "as-polymerized" state which includes annealing at 280 °C. The $T_m$'s of **8c** and **8b** are in

**Table 2. Polycondensations of 4′-Fluoro-2-methyl-4-(trimethylsiloxy)benzophenone with 4,4′-Bis((4-fluorophenyl)sulfonyl)diphenylmethane in Bulk**

| polym formula | mon/comon[a] | temp[b] (°C) | yield (%) | $\eta_{inh}$[c] (dL/g) | DP[d] | $T_g$[e] (°C) | elem anal. | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | % C | % H | % S |
| **10a** | 10/1 | 220–280 | 88 | 0.07 | 11 | 141 | calcd | 76.60 | 4.61 | 2.48 |
| | | | | | | | found | 76.10 | 4.54 | 2.85 |
| **10b** | 20/1 | 220–270 | 81 | 0.25 | 25 | 143 | calcd | 78.11 | 4.69 | 1.37 |
| | | | | | | | found | 78.12 | 4.65 | 0.99 |
| **10c** | 40/1 | 220–270 | 77 | 0.48 | 65 | 147 | calcd | 79.02 | 4.71 | 0.43 |
| | | | | | | | found | 78.26 | 4.76 | 0.71 |
| **10d** | 80/1 | 220–270 | 86 | 0.54 | 110 | 149 | calcd | 79.50 | 4.73 | 0.37 |
| | | | | | | | found | 78.88 | 4.89 | 0.48 |
| **15** | ∞ | 220–280 | 89 | 0.62 | | 151 | calcd | 73.04 | 4.78 | |
| | | | | | | | found | 76.18 | 4.95 | |

[a] Molar monomer/comonomer ratio. [b] The reaction temperature was raised in steps of 20 °C. [c] Measured at 25 °C with $c$ = 2 g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [d] Average degree of polymerization as determined by $^1H$ NMR spectroscopy. [e] From DSC measurements with a heating rate of 20 °C/min.

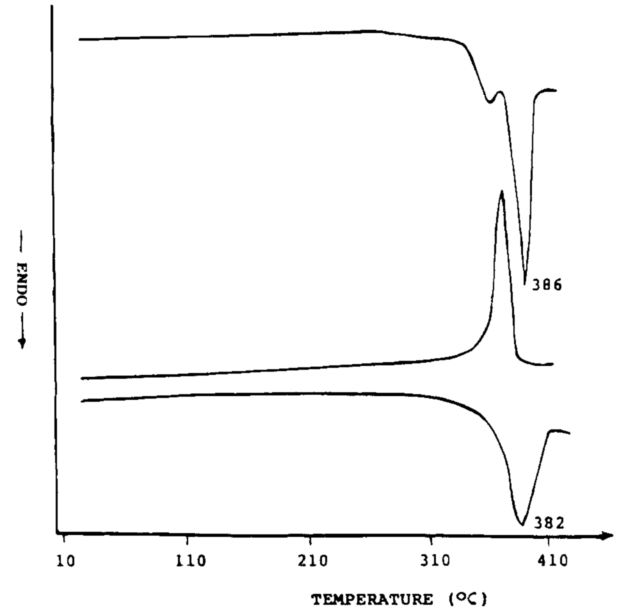


**Figure 1.** DSC measurements (heating/cooling rate 20 °C/min) of oligo(ether ketone) **8b**.

between those of **8a** and **8d**. In other words, the $T_m$'s decrease with increasing molecular weight, contrary to the properties of **9a–d**. The high $T_m$'s of **8a–d** may be explained either by a different crystal modification or by a greater size and perfection of the crystallites. The WAXD powder patterns presented in Figure 2 prove that the latter hypothesis is true. The reflections of **9a–d** and **14** show up in the same positions as those of **8a–d**. All oligo- and poly(ether ketone)s clearly adopt an orthorhombic crystal lattice almost identical with that described by Dawson and Blundell[13] for other poly(ether ketone)s.

However, WAXD measurements (e.g., Figure 2A) also demonstrate that the degree of crystallinity of **8a–d** is indeed significantly higher (60 ± 10%) than that of **9a–d** (5–20%) or that of polymer **14** (30 ± 5%). Furthermore, all reflections of **8a–d** are sharper than those of **9a–d** and **14** and clearly indicate a greater size and perfection of the crystallites. Possibly **8a** and **8b** form extended-chain crystals in contrast to **9a–d** and **14**. This speculative hypothesis needs, of course, more detailed X-ray and electron diffraction studies, which were beyond the scope of this work. In this connection it should be mentioned that a "double-melting" or "multiple-melting" behavior of poly(ether ether ketone) is well documented in the literature.[14–17] This means that the size and perfection of the crystallites of PEEK largely depend on their thermal history. The poly(ether ketone) **14** and its oligomers apparently possess similar properties.

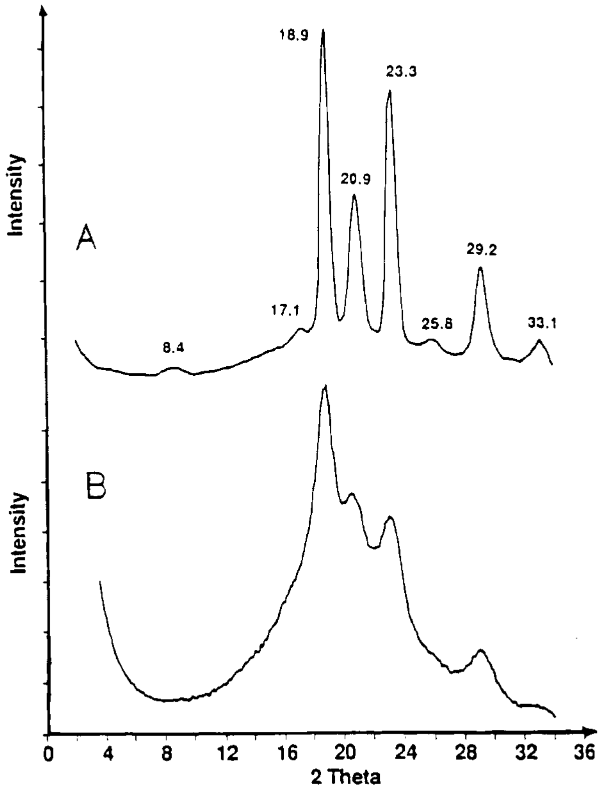


**Figure 2.** WAXD powder patterns of (A) oligo(ether ketone) **8b** as polymerized and (B) poly(ether ketone) **9c** as polymerized.

**Amorphous Poly(ether ketone)s Based on Monomers 2 and 3.** A series of cocondensations of monomer **2** with the "diphenylmethane" **6** was conducted in analogy to the synthesis of **9a–d**. Yields and properties of the resulting poly(ether ketone)s **10a–d** are summarized in Table 2 along with the data of the homopolymer **15** which was obtained by polycondensation of **2** without comonomer. Again the inherent viscosities increase with higher monomer/comonomer ratio. Even the $T_g$ increases slightly. The absence of a melting endotherm in the DSC traces and the WAXD pattern agree in that the poly(ether ketone)s **10a–d** and **15** are amorphous after precipitation. This property fits well in with the lack of crystallinity of other methyl-substituted poly(ether ketone)s.[18] However, annealing above $T_g$ yields a semicrystalline polymer **15** with a $T_m$

**Table 3. Polycondensations of 4′-Fluoro-4-(trimethylsiloxy)benzophenone[a] with 4′-Fluoro-4-(trimethylsiloxy)diphenylsulfone[a] and 4,4′-Bis((fluorophenyl)sulfonyl)diphenylmethane**

| polym formula | mon/comon[b] | temp[c] (°C) | yield (%) | $\eta_{inh}$[d] (dL/g) | DP[e] | $T_g$[f] (°C) | elem anal. |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | % C | % H | % S |
| **11a** | 6/1 | 200–290 | 86 | 0.11 | 10 | 135 | calcd | 67.85 | 3.77 | 9.08 |
|  |  |  |  |  |  |  | found | 66.69 | 3.67 | 9.36 |
| **11b** | 10/1 | 200–290 | 92 | 0.16 | 15 | 156 | calcd | 68.58 | 3.77 | 8.55 |
|  |  |  |  |  |  |  | found | 67.29 | 3.68 | 8.86 |
| **11c** | 20/1 | 200–290 | 94 | 0.23 | 25 | 168 | calcd | 69.30 | 3.74 | 8.06 |
|  |  |  |  |  |  |  | found | 67.84 | 3.90 | 8.36 |
| **11d** | 40/1 | 200–290 | 93 | 0.45 | 60 | 182 | calcd | 69.66 | 3.73 | 0.37 |
|  |  |  |  |  |  |  | found | 68.03 | 3.77 | 7.46 |
| **11e** | 80/1 | 200–290 | 87 | 0.62 | 100 | 191 | calcd | 69.87 | 3.74 | 7.63 |
|  |  |  |  |  |  |  | found | 68.76 | 3.87 | 7.46 |
| **16** | ∞ | 200–300 | 94 | 0.94 |  | 202 | see ref 1 |  |  |  |

[a] All polycondensations were conducted with an equimolar ratio of both monomers. [b] Molar monomer/comonomer ratio. [c] The reaction temperature was raised in steps of 20 °C. [d] Measured at 25 °C with $c = 2$ g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [e] Average degree of polymerization as determined by $^1H$ NMR spectroscopy. [f] From DSC measurements with a heating rate of 20 °C/min.

**Table 4. Polycondensations of Silylated Bisphenol-P (7) either with 4′-Fluoro-2-methyl-4-(trimethylsiloxy)benzophenone (2) or with an Equimolar Mixture of 4′-Fluoro-4-(trimethylsiloxy)benzophenone (1) and 4′-Fluoro-4-(trimethylsiloxy)diphenyl Sulfone (3)**

| polym formula | mon/comon[a] | temp[b] (°C) | yield (%) | $\eta_{inh}$[c] (dL/g) | DP[d] | $T_g$[e] (°C) | elem anal. |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | % C | % H | % S |
| **12a** | 10/1 | 220–270 | 82 | 0.14 | 12 | 133 | calcd | 80.46 | 5.15 |  |
|  |  |  |  |  |  |  | found | 78.10 | 5.01 |  |
| **12b** | 20/1 | 220–270 | 89 | 0.25 | 222 | 140 | calcd | 80.25 | 4.97 |  |
|  |  |  |  |  |  |  | found | 79.00 | 4.90 |  |
| **12c** | 40/1 | 220–270 | 93 | 0.35 | 44 | 144 | calcd | 80.13 | 4.87 |  |
|  |  |  |  |  |  |  | found | 79.00 | 4.92 |  |
| **13a** | 10/1 | 200–280 | 85 | 0.15 | 13 | 154 | calcd | 71.92 | 4.26 | 6.44 |
|  |  |  |  |  |  |  | found | 71.27 | 4.15 | 6.90 |
| **13b** | 20/1 | 220–270 | 91 | 0.24 | 22 | 171 | calcd | 71.08 | 4.01 | 6.93 |
|  |  |  |  |  |  |  | found | 68.48 | 3.92 | 6.97 |
| **13c** | 40/1 | 220–280 | 89 | 0.38 | 40 | 180 | calcd | 70.60 | 3.90 | 7.19 |
|  |  |  |  |  |  |  | found | 68.06 | 3.75 | 7.32 |

[a] Molar feed ratio of monomer and comonomer. [b] The reaction temperature was raised in stepwise manner from the minimum to the maximum value. [c] Measured at 25 °C with $c = 2$ g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [d] Average degree of polymerization as determined by $^1H$ NMR spectroscopy. [e] From DSC measurements with a heating rate of 20 °C/min.

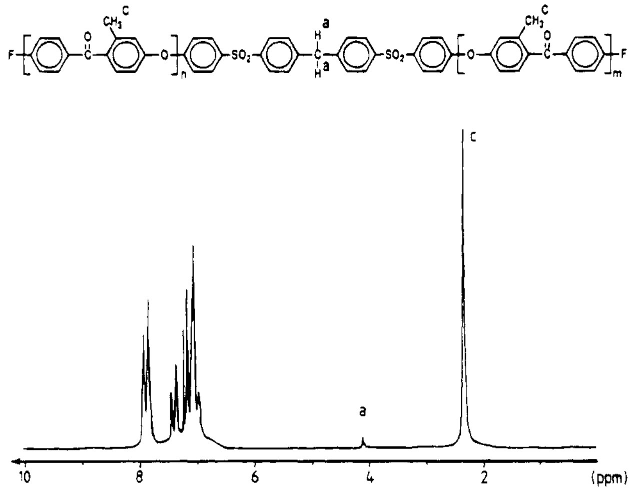


**Figure 3.** 100 MHz $^1H$ NMR spectrum of poly(ether ketone) **10b**.

of 305–310 °C. The $^1H$ NMR spectroscopic evaluation of the $CH_2$ group (Figure 3) provided DP's in satisfactory agreement with the feed ratio. The NMR spectroscopic DP's are all somewhat higher, in analogy to the results obtained with **9a–d**.

Finally, the cocondensations of monomers **1**, **3**, and **6** need to be discussed. Again the inherent viscosities and $^1H$ NMR spectroscopic DP's exhibit the expected trends (Table 3; the properties of a high molecular weight copoly(ether ketone sulfone) **16** prepared without cocondensation of an A–A type comonomer are included for comparison). Particularly remarkable is in this series the conspicuous increase of the $T_g$ with higher molecular weights. It contrasts sharply with the $T_g$'s of the poly(ether ketone)s **8a–d** or **9a–d**. In the latter case the crystallinity of these poly(ether ketone)s may be blamed for the constancy of the $T_g$'s. However, this argument does not hold for **10–d**, where the $T_g$'s show again a relatively weak influence of the molecular weight. Obviously, the $T_g/M_n$ relationship is different for poly(ether ketone)s and poly(ether sulfone)s, a hypothesis which is supported by the properties of **12a–c** and **13a–c** (Table 4).

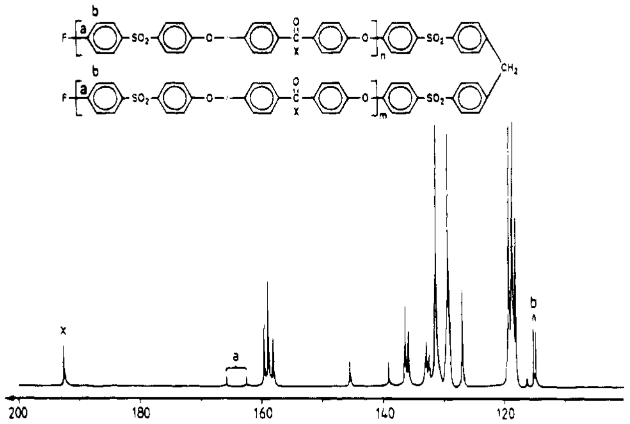


**Figure 4.** 90.4 MHz $^{13}C$ NMR spectrum of poly(ether ketone sulfone)s **11b**.

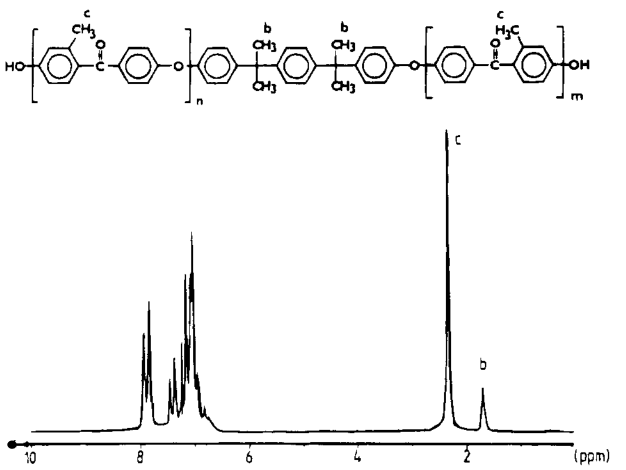
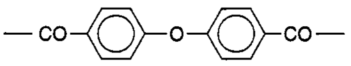
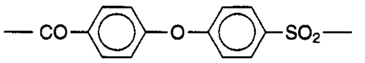


**Figure 5.** 100 MHz $^1$H NMR spectrum of poly(ether ketone) **12a**.

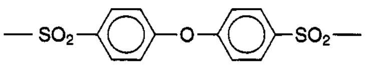
In the case of series **11a–d**, the $^{13}$C NMR spectra are particularly informative (Figure 4). They display like in the case of **8a–d**, **9a–d**, or **10a–d** the influence of the fluoro end groups on both chemical shift and coupling constants of the neighboring C atoms. Furthermore, a kind of triplet signal around 155 ppm is detectable, which reflects the sequence effects of CO and $SO_2$ groups on the ether carbons (formulas **17–19**). The symmetrical splitting along with the 1:2:1 intensity ratio clearly proves that the keto and sulfonyl units form a random sequence. This NMR spectroscopic information agrees in turn with the perfectly amorphous character of these samples, which contrasts sharply with the crystallinity of **8a–d** or **9a–d**.



**17**



**18**



**19**

Monomer **2** was polycondensed with the silylated Bisphenol-P (**7**) at three different feed ratios. Yields and properties of the resulting poly(ether ketone)s **12a–c** are listed in Table 4. The increase of both inherent viscosity and $T_g$ indicates the success of these polycondensations. Analogous results were obtained for three cocondensations of monomers **1**, **2**, and **7**. The viscosities of the copoly(ether ketone sulfone)s **13a–c** exhibit the same trend as **12a–c**, but the $T_g$'s vary over a broader range in analogy to **11a–d**. As illustrated by Figure 5, the 12 aliphatic protons of the Bisphenol-P unit allow an easy determination of the DP's. The results show an excellent fit with the feed ratios of both series (Table 4).

The complete incorporation of the Bisphenol-P in both classes of poly(ether ketone)s is not trivial for the following reason. The fluoride ions which catalyze the polycondensations generate phenoxide ions (eq 3), which in turn attack the activated fluoro groups (eq 4). The desilylation equilibrium (eq 3) is further shifted to the right side with increasing stability of the phenoxide anion. Obviously, the phenoxide ions of monomers **1**, **2**, and **3** are more stable than that of **7**, because the negative charges are partially stabilized by the electron-withdrawing CO and $SO_2$ groups in the para positions. However, the phenoxide ion of Bisphenol-P is more nucleophilic than the anions of the monomers. Possibly, the disadvantage of the lower concentration and the advantage of a higher nucleophilicity counterbalance each other to a large extent. Anyway, the results summarized in Tables 1–4 clearly demonstrate that (1) the polycondensations of monomers **1**, **2**, and **3** with suitable comonomers allow the synthesis of telechelic poly(ether ketone)s with either two fluoro or two hydroxy groups and (2) the cocondensations of comonomers **6** and **7** allow an easy $^1$H NMR spectroscopic evaluation of the DP's.

(3)

(4)

The usefulness of such telechelic, aromatic polyethers for the synthesis of block copolymers will be reported in a future part of this series.

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