# Functionalized Poly(ether ether ketones) from 4,4-Bis(4-hydroxyphenyl)pentanoic Acid, 2,2′-Isopropylidenediphenol, and 4,4′-Difluorobenzophenone: Synthesis, Behavior, and Polymer Analogous Amidation of the Carboxylic Groups

**Thomas Koch and Helmut Ritter***

*Bergische Universität Wuppertal, FB 9, Macromolecular Chemistry, Gaussstrasse 20, D-42097 Wuppertal, Germany*

*Received October 5, 1994; Revised Manuscript Received March 27, 1995*®

ABSTRACT: A new type of aromatic poly(ether ether ketones) (**4a**–**4c**) were prepared by polycondensation of different amounts of 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**) and 2,2′-isopropylidenediphenol (**2**), respectively, with 4,4′-difluorobenzophenone (**3**). The homocondensate (**4a**) from **1** and **3** shows a high $T_g$ (190 °C) and a loss in weight of 6.8% at 350 °C. The amorphous polycondensates **4a**–**4c** were cast from NMP or DMAc solutions to produce homogeneous, self-standing films that were clear and colorless. In the case of the membrane from **4a** a preferred permeability of $O_2$ from a $O_2/N_2$ gas mixture was found (α = 2). Additionally, the carboxylic group has been condensed with several amines via acid chlorides. A strong influence of the side chain length on the glass transition temperature was detected.

## Introduction

In the last decades, several aromatic poly(ether ether ketones) (PEEKs) have been developed and commercially used mainly for constructive elements (e.g. in aerospace industries[1]), for electrical isolating components,[2,3] and in the medical sector as material for implants.[3] Typical characteristics of PEEKs are good mechanical and hydrolytical stabilities and resistance to radioactive radiation, fire, hydrolysis and several organic liquids such as alcohols, ethers, or esters.[4]

Maier et al.[5] have synthesized indan based PEEKs that show a good solubility, thermal stability, and the ability to form clear films. Ohno et al.[6] have reported on a naphthalene-based PEEK with similar characteristics. An influence of the polycondensation time on the molecular weight of the products is described. Furthermore, we have synthesized 1,5-naphthylene-based PEEKs with long alkoxy side chains. An enhanced solubility of these products and the possibility of producing free-standing films were observed.[7]

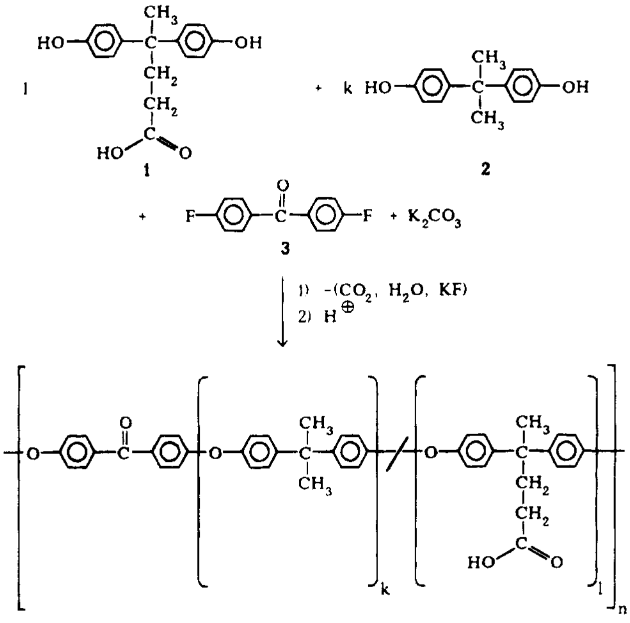
Recently, polysulfones containing 4,4-diphenylpentanoic acid units were synthesized and modified by several polymer analogous reactions.[8,9] In connection with this, we observed a good thermal stability of these polysulfones condensed with several amines.[9,10]

Up to now, no information was available on the synthesis and chemical modification of a reactive PEEK containing 4,4-bis(4-hydroxyphenyl)pentanoic acid as a bis(phenol) component.

Thus, the present paper deals with the synthesis, modification, and some characteristics of PEEKs containing carboxylic groups at the end of the side chains.

## Results and Discussion

**Scheme 1**



**4a - 4c**

| PEEK | 4a | 4b | 4c |
|---|---|---|---|
| k/l | 0 | 1 | 9 |

Poly(ether ether ketones) **4a**–**4c** were obtained by condensation of various amounts of the bis(phenols) 4,4-bis(4-hydroxyphenyl)pentanoic acid (**1**) and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A, **2**) with 4,4′-difluorobenzophenone (**3**) via nucleophilic aromatic displacement (see Experimental Section).

The chemical structures of the poly(ether ether ketones) were proved by $^1$H- and $^{13}$C-NMR spectroscopy. As typical examples, the spectra of **4a** are illustrated in Figures 1 and 2.

The DSC diagrams of **4a**–**4c** indicate an amorphous structure of the materials. Obviously, the glass transition temperature ($T_g$) increases with the content of 4,4-diphenylpentanoic acid units in the main chain (Table 1).

---

* To whom all correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* June 1, 1995.

0024-9297/95/2228-4806$09.00/0

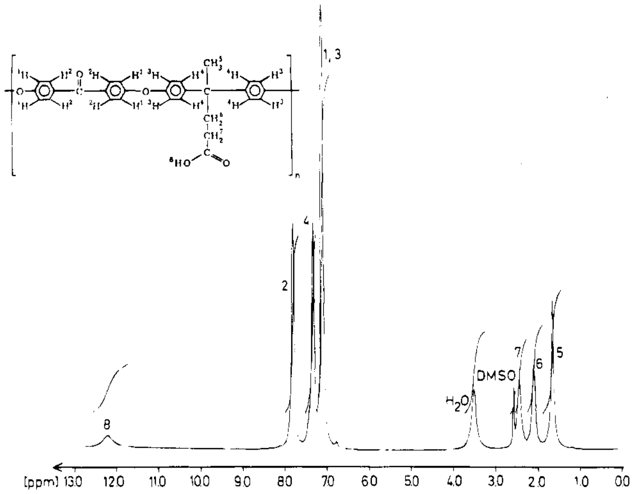


**Figure 1.** $^1$H-NMR spectra of **4a** (solvent: DMSO-$d_6$).

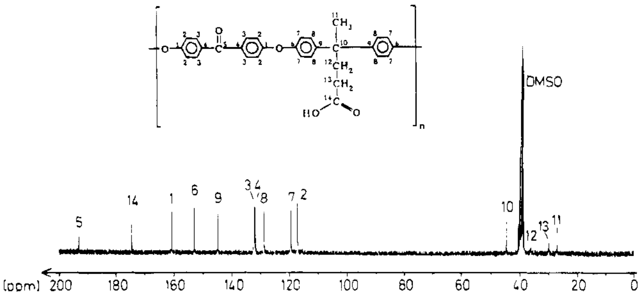
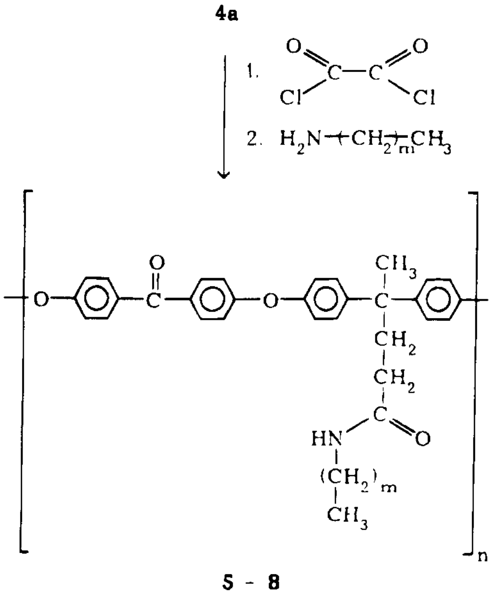


**Figure 2.** $^{13}$C-NMR spectra of **4a** (solvent: DMSO-$d_6$).

**Table 1. DSC Data for the Polycondensates 4a–4c (Heating Rate: 20 °C/min)**

| polycondensate | $T_g$ (°C) |
|---|---|
| **4a** | 187.6 |
| **4b** | 166.2 |
| **4c** | 158.4 |

**Scheme 2**



| m | 3 | 5 | 9 | 15 |
|---|---|---|---|---|
| PEEK | **5** | **6** | **7** | **8** |

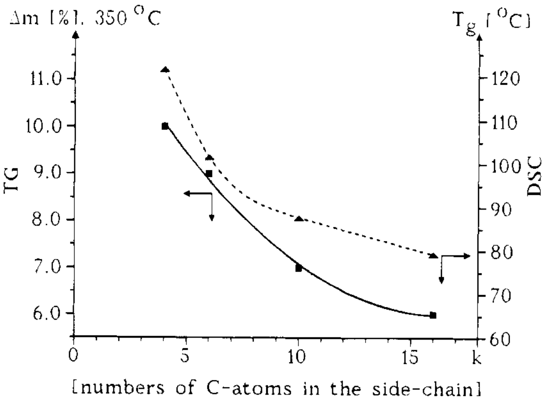


**Figure 3.** Relation between $\Delta m$ and $T_g$ of the polycondensates **5–8** and the number of C atoms ($k$) in the amine compound.

**Table 2. Thermogravimetrical Estimation of the Degradation of the Polycondensates at 350 °C in Air (Heating Rate: 10 °C/min)**

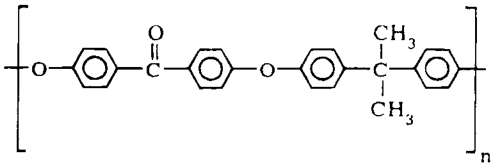
| polycondensate | deg of degrad (%) | polycondensate | deg of degrad (%) |
|---|---|---|---|
| **4a** | 6.8 | **8** | 5.8 |
| **4b** | 5.1 | **9a** | 3.1 |
| **4c** | 1.6 | **9b** | 2.5 |
| **5** | 10.0 | **9c** | 1.4 |
| **6** | 8.9 | **10** | 2.2 |
| **7** | 6.7 | | |

The unmodified PEEK **4a** was applied for the preparation of symmetric membranes from solution (Experimental Section) and from the melt. It was shown that in the case of an $O_2/N_2$ mixture as permeate a slightly higher permeability of oxygen occurs with a separation factor ($\alpha$)[9] of about 2.0.

The free carboxylic group of homocondensate **4a** was activated with oxalyl chloride, yielding the corresponding acid chlorides and then condensed with different *n*-alkylamines to produce the corresponding poly(ether ether ketones) containing alkylamides as side chains (**5–8**).

The influence of the side chain length of the amides **4–8** on their $T_g$ is illustrated in Figure 3, showing a decrease of $T_g$ with increasing side chain length. A similar relationship between side chain length and $T_g$ values has recently been observed with poly(ether sulfones).[9]

Thermogravimetric investigations of **4a–4c**, the corresponding sodium salts **9a–9c** (Experimental Section), the amides **5–8**, and a commercially available PEEK (AMPEK 494, **10**) indicate a high thermal stability of the materials. In Table 2 the degrees of degradation at 350 °C are summarized.



**10**

An increasing thermal stability of the PEEKs **4** with decreasing fraction of 4,4-diphenylpentanoic acid units is indicated in Table 2. As expected, the unmodified PEEK (**10**) shows a similar thermal stability compared with the slightly modified PEEK **4c**. The incorporation of ionic units seems to stabilize the polymeric material. Thus the polymers **9a–9c** (Experimental Section) containing sodium salts show a lower degree of degradation

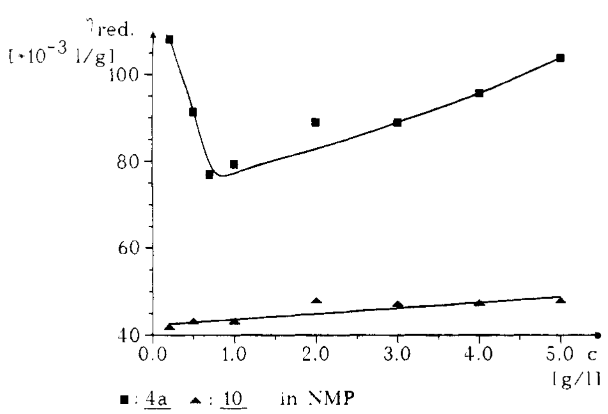


**Figure 4.** Viscosity measurements of **4a** (■) and **10** (▲) in NMP.

**Table 3. GPC Data for the Polycondensates 4a–4c and 10 in THF (Polystyrene as Standard[13])**

| polycondensate | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| **4a** | 47 000 | 10 000 | 4.7 |
| **4b** | 33 000 | 7 500 | 4.4 |
| **4c** | 73 000 | 10 000 | 7.3 |
| **10** | 42 000 | 13 000 | 3.2 |

compared with the corresponding acidic polymers **4a–4c** (Table 2). Under the same conditions, the alkylamides **5–8** tend to degrade nearly inversely proportional to the length of the alkyl side chains.

The viscosities of the polycondensates **4a** and **10** in NMP as solvent were measured, showing a linear increase of viscosity with increasing concentration in the case of **10** and, in contrast, a strong increase of viscosities of **4a** at lower concentrations (Figure 4) as a typical behavior of polymers containing carboxylic groups.

GPC measurements (Experimental Section) with polystyrene standards indicate a high molecular weight of the polycondensates **4a–4c** and **10** (Table 3).

It can be concluded that modified poly(ether ether ketones) containing 4,4-diphenylpentanoic acid units may be useful for, e.g., the preparation of thermally stable films or membranes. Additionally, the free carboxylic group can be condensed with alkylamines to modify the solubility and glass transition temperature of the materials in a wide range.

## Experimental Section

**Synthesis of 4–8. Materials.** 4,4-Bis(4-hydroxyphenyl)-pentanoic acid (**1**) has been prepared according to the literature.[11,12] The other materials were obtained from Fluka GmbH, Neu Ulm, Germany. AMPEK 494 was obtained from the Hoechst AG, Frankfurt, Germany. Dimethyl sulfoxide (DMSO) was dried with $CaH_2$ and distilled. Toluene was dried by azeotropic distillation.

**Synthesis of the Poly(ether ether ketones) 4a–4c.** 4,4-Bis(4-hydroxyphenyl)pentanoic acid (**1**) and 2,2-bis(4-hydroxyphenyl)propane (**2**) were dissolved in a mixture of dry DMSO and toluene. Then $K_2CO_3$ was added to the solution (Table 4). The mixture was stirred and heated at 170 °C to remove water and toluene by azeotropic distillation for about 2 h. Then, 4,4′-difluorobenzophenone (**3**) was added to the dispersion. After 10 h, the solution became viscous. During cooling, a phase separation was observed. The upper phase was removed, and the remaining viscous solution was diluted with 200 mL of a THF/concentrated HCl mixture (3/1). The crude polycondensate was obtained by pouring the solution into 3000 mL of water. After stirring for about 20 h, PEEK was filtered off, washed with water, dissolved in 80 mL of THF, and precipitated again in 1200 mL of EtOH. The pure product was dried for 3 days at 90 °C under reduced pressure. The analytical data are summarized in Table 5.

IR (film, 12 μm) of **4a**: $\tilde{\nu}$ = 3300 ($-COOH_{dimer}$), 3060–3040 ($C-H_{aromatic}$), 2970–2940 ($-CH_3$), 1730–1710 ($-COOH$), 1650 ($C=O_{ketone}$), 1610–1590, 1500–1490 ($C-H_{aromatic}$), 1415 ($CH_2$, $CH_3$ deform.), 1250 ($-O-_{arylic}$), 930 ($-COOH_{dimer}$), 840 $cm^{-1}$ (1,4-disubst aromat). The same IR signals have been obtained from **4b** and **4c**.

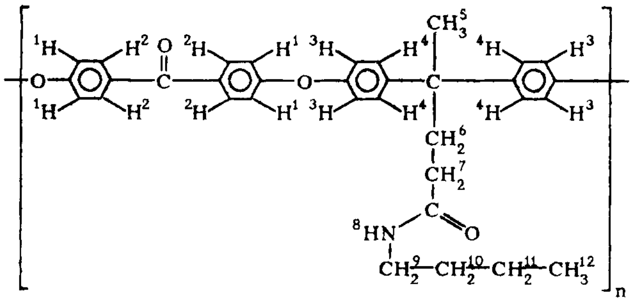
$^1H$-NMR (250 MHz, 100 mg of **4a** in 0.5 mL of DMSO-$d_6$ at 25 °C) (assignment of the protons: see Figure 1), δ: 1, 7.11; 2, 7.79 (d, 6.2 Hz); 3, 7.11; 4, 7.31; 5, 1.65; 6, 2.10; 7, 2.44; 8, 12.20.

$^{13}C$-NMR (62.9 MHz, 100 mg of **4a** in 0.5 mL of DMSO-$d_6$ at 25 °C) (assignment of the carbon atoms: see Figure 2), δ: 1, 160.75; 2, 117.17; 3, 132.16; 4, 131.76; 5, 193.08; 6, 153.02; 7, 119.53; 8, 128.85; 9, 144.88; 10, 44.75; 11, 26.98; 12, 36.32; 13, 29.90; 14, 174.52.

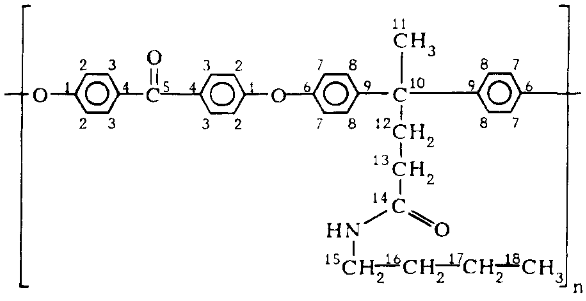
**Synthesis of the Amides 5–8. 4a** was dissolved in 15 mL of dry THF. After oxalyl chloride was added (Table 6), the solutions were stirred for 4 days at room temperature. Then THF and the excess of oxalyl chloride were removed by reduced pressure at ambient temperature (3 days). After the residue was dissolved in 15 mL of dry $CH_2Cl_2$, the amine was added and the solution was stirred for 1 day at room temperature. The crude product was obtained by precipitating the solution in 300 mL of EtOH. After the polycondensate was dissolved in THF, it was reprecipitated in 250 mL of $Et_2O$ and finally dried for 3 days at 90 °C under reduced pressure. The analytical data are summarized in Table 7.

IR (film, 12 μm) of **5**: $\tilde{\nu}$ = 3400–3300 (N–H), 3080–3040 ($C-H_{aromatic}$), 2980–2940 ($-CH_3$, $CH_2$), 1670 ($C=O_{amide}$), 1650 ($C=O_{ketone}$), 1610–1590, 1510–1490 ($C-H_{aromatic}$), 1530 (N–H), 1415 ($CH_2$, $CH_{3deform.}$), 1250 ($-O-_{arylic}$), 840 $cm^{-1}$ (1,4-disubst aromat). The IR signals of **6–8** are identical with those from **5**.

$^1H$-NMR (400 MHz, 100 mg of **5** in 0.5 mL of $CDCl_3$ at 25 °C), δ: 1, 7.01 (d, 6.5 Hz); 2, 7.77 (d, 6.5 Hz); 3, 6.98; 4, 7.24 (d, 6.8 Hz); 5, 1.65; 6, 2.01; 7, 2.49; 8, 5.79; 9, 3.19; 10, 1.43 (d, 6.8 Hz); 11, 1.32 (t, 6.8 Hz); 12, 0.89 (t, 6.5 Hz).



$^{13}C$-NMR (100.62 MHz, 100 mg of **5** in 0.5 mL of $CDCl_3$ at 25 °C), δ: 1, 161.67; 2, 117.67; 3, 132.60; 4, 130.79; 5, 194.37; 6, 153.65; 7, 119.95; 8, 126.62; 9, 145.31; 10, 44.81; 11, 28.19; 12, 30.66; 13, 32.05; 14, 173.21; 15, 39.74; 16, 32.78; 17, 20.46; 18, 13.88.



**Preparation of Membranes.** A 0.1 g sample of the polycondensate **4a–4c** and **5–8** were dissolved in 10 mL of THF, cast on a glass plate (diameter: 9 cm), and dried for 2 h at 40 °C. The colorless homogeneous membranes were removed from the glass by pouring in water and finally dried in vacuum at 80 °C for 20 h. The membranes were used for IR

**Table 4. Weight Instructions for the Synthesis of the Polycondensates**

| | amt of **1** | | amt of **2** | | amt of **3** | | | |
|---|---|---|---|---|---|---|---|---|
| PEEK | g | mol | g | mol | g | mol | amt of $K_2CO_3$ (g) | DMSO/toluene (mL) |
| **4a** | 7.1575 | 0.025 | | | 5.4550 | 0.025 | 7.0 | 60/30 |
| **4b** | 3.5787 | 0.0125 | 2.8536 | 0.0125 | 5.4550 | 0.025 | 7.0 | 60/30 |
| **4c** | 0.7158 | 0.0025 | 5.1365 | 0.0225 | 5.4550 | 0.025 | 7.0 | 60/30 |

**Table 5. Analytical Data for the Polycondensates 4**

| | elemental analysis | | | | | |
|---|---|---|---|---|---|---|
| | C | | H | | yield (g) | |
| PEEK | cal | found | cal | found | cal | found (%) |
| **4a** | 77.57 | 77.66 | 5.21 | 5.50 | 11.61 | 10.9 (94) |
| **4b** | 79.98 | 79.81 | 5.32 | 5.32 | 10.89 | 10.5 (96) |
| **4c** | 82.15 | 82.15 | 5.43 | 5.49 | 10.31 | 10.1 (98) |

**Table 6. Weight Instructions for the Reaction of the Amines with 4a**

| PEEK with amide groups | amt of polycondensate | | amt of oxalyl chloride | | $H_2N-(-CH_2-)-_mCH_3$ | |
|---|---|---|---|---|---|---|
| | g | mol | mL | mol | *m* | |
| **5** | 1.84 | 0.004 | 1.0 | 0.012 | 3 | 2.4 mL |
| **6** | 1.84 | 0.004 | 1.0 | 0.012 | 5 | 3.2 mL |
| **7** | 1.84 | 0.004 | 1.0 | 0.012 | 9 | 4.8 mL |
| **8** | 1.84 | 0.004 | 1.0 | 0.012 | 15 | 5.80 g |

**Table 7. Analytical Data for the Polycondensates 5–8**

| | elemental analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | | H | | N | | yield (g) | |
| PEEK | cal | found | cal | found | cal | found | cal | found |
| **5** | 78.58 | 76.32 | 6.40 | 6.50 | 2.92 | 2.81 | 2.07 | 2.04 |
| **6** | 78.94 | 77.26 | 6.81 | 6.93 | 2.57 | 2.32 | 2.19 | 2.17 |
| **7** | 79.57 | 78.27 | 7.51 | 7.51 | 2.33 | 2.15 | 2.41 | 2.38 |
| **8** | 80.31 | 78.71 | 8.35 | 8.31 | 2.05 | 1.92 | 2.75 | 2.71 |

spectroscopy and in the case of **4a** for the gas separation experiments.

**Synthesis of the Sodium Salts of 4a–4c.** **9a**–**9c** were obtained by treating the corresponding polycondensates **4a**–**4c** with a NaOH solution (15% by weight) for 1 day at 80 °C. The residues were washed with water and finally dried for 3 days at 80 °C.

**GPC Measurements.** For gel permeation chromatography a column combination of $10^5$, $10^4$, $10^3$, 500, and 100 Å (Ultrastyragel column, Millipore, column temperature: 35 °C, flow rate: 1 mL/min) was used and combined with a refractive index detector. The injection volume was 60 $\mu$L with an injection concentration of 0.5 wt % in THF as solvent. Polystyrene standards with a molar masses from 600 to $1.75 \times 10^6$ g/mol were used for calibration. Before injection the samples were carefully filtered through a membrane filter of 0.45 $\mu$m.

**Acknowledgment.** Financial support from DFG and measurements of permeability by the Hoechst AG, Frankfurt, Germany, are gratefully acknowledged.

## References and Notes

(1) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.
(2) Lücke, A. *Kunststoffe* **1990**, *80*, 10, 1154.
(3) Münstedt, H.; Zeiner, H. *Kunststoffe* **1989**, *79*, 10, 993.
(4) *Römpps Chemie Lexikon*, 9th ed.; Falbe, J., Pegitz, M., Eds.; Verlag Thieme: Stuttgart, 1992; Vol. 5, p 3530.
(5) Maier, G.; Yang, D.; Nuyken, O. *Makromol. Chem.* **1993**, *194*, 1901.
(6) Ohno, M.; Takata, T.; Endo, T. *Macromolecules*, manuscript in preparation.
(7) Ritter, H.; Thorwirth, R. *Makromol. Chem.* **1993**, *194*, 1469.
(8) Esser, I. C. H. M.; Parsons, I. W. *Polymer* **1993**, *34*, 13, 2836.
(9) Koch, T.; Ritter, H. *Makromol. Chem. Phys.* **1994**, *195*, 1709.
(10) Born, M.; Koch, T.; Ritter, H. *Acta Polym.* **1994**, *45*, 68.
(11) Bader, A. R.; Kontowicz, A. D. *J. Am. Chem. Soc.* **1954**, *76*, 4465.
(12) Mikroyannidis, J. A. *Eur. Polym. J.* **1985**, *21*, 1031.

MA9462971