New Polymer Syntheses. 33. Poly(ether ketone)s with Alternating Sequences of Aliphatic Spacers and Aromatic Ether–Ketone Blocks

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ABSTRACT: "Minisegmented" poly(ether ketone)s were obtained by thermal condensation of silylated alkylenebis(phenol)s with 6, 10, or 14 methylene groups and aromatic difluoro ketones. The difluoro ketones possess two, four, five, six, or eight para-linked aromatic rings. The poly(ether ketone)s were characterized by elemental analyses, inherent viscosities, DSC measurements, WAXS measurements, microscopic observation under polarized light, and thermomechanical and thermogravimetric analyses. All poly(ether ketone)s are crystalline materials which reach, after short annealing, 45–55% crystallinity as determined by broad-line ^{1}H NMR measurements. Despite two melting endotherms in the DSC traces, and despite a layered supermolecular structure in the crystalline state, these minisegmented poly(ether ketone)s do not form a mesophase. Low molecular weight model compounds confirm the absence of mesophases but show solid–solid transitions. The poly(ether ketone)s possess unusually high heat-distortion temperatures, which are directly related to their melting points and not to their glass transitions. Due to a favorable morphology the crystallites seemingly form the coherent matrix. The minisegmented poly(ether ketone)s also possess relatively high thermostabilities in air with 5% loss of weight in the temperature range 390–420 °C.

Introduction

In the past five years ICI began to commercialize aromatic poly(ether ketone)s[1,3] in particular PEEK 1, and this step also enhanced the scientific interest in this class of thermoplastic engineering plastics. Poly(ether ketone)s possess a combination of useful properties, such as high chemical and thermal stabilities, an exceptional stability against radioactive irradiation, and good mechanical properties. The temperature dependence of mechanical properties, such as the heat distortion temperature, mainly depends on the degree of crystallinity and on the melting point (T_m). In addition to the crystallizing poly(ether ketone)s, so-called amorphous poly(ether ketone)s are known, which are reluctant to crystallize under normal reaction conditions or upon annealing.[4,5] Regardless of the tendency to crystallize, all poly(ether ketone)s reported so far possess fully aromatic backbones. Thus, it was the purpose of the present work to synthesize and characterize poly(ether ketone)s with a regular sequence of aliphatic spacers in the main chain (**2a–d**, **3a–d**, **4a–d**, and **5a–b**). Two aspects of these "minisegmented" poly(ether ketone)s are of particular interest. First, their ability to form a liquid-crystalline melt. Second, the influence of the aliphatic spacer on rate of crystallization and degree of crystallinity.

Experimental Section

Materials. Diphenyl ether, phenol, and adipic and sebacic acids were gifts of Bayer AG (D-4150 Krefeld, FRG) and were used without further purification. Hydroquinone diphenyl ether was a gift of Hoechst AG (Hoechst, FRG). Tetradecane diacid and 4-fluorobenzoic acid were purchased from Aldrich Co. (St. Louis, MO). All acid chlorides were prepared by heating the carboxylic acids in a large excess of freshly distilled thionyl chloride. All acid chlorides were distilled in vacuo prior to use.

Diphenyl Tetradecanedicarboxylate. A solution of tetradecanedicarboxylic chloride (0.8 mol) in 500 mL of dry dichloromethane was added dropwise to a cooled solution of phenol (1.7 mol) in 500 mL of dry pyridine, so that the temperature did not rise above 10 °C. The reaction mixture was stirred for 12 h at ca. 20 °C, diluted with 1 L of dichloromethane, and washed with the following solutions: 1 L of 4 N hydrochloric acid (twice), 1 L of 2 N hydrochloric acid (once), 500 mL of 10% sodium hydrogen carbonate (once), and 500 mL of water (once). The organic solution was then dried over calcium chloride and concentrated in vacuo. Crystallization was completed by portionwise addition of ligroin. The crude product was recrystallized from acetone; yield, 71%; mp 78–80 °C. Anal. Calcd for $C_{26}H_{34}O_4$ (410.60): C, 76.04; H, 8.36. Found: C, 76.32; H, 8.43.

The diphenyl esters of adipic acid[6] (mp 109 °C) and sebacic acid[7] (mp 62–64 °C) were prepared analogously.

1,14-Bis(4-hydroxyphenyl)-1,14-dioxotetradecane (9c). Diphenyl tetradecanedicarboxylate (100 mmol) was dissolved in a mixture of perfluorobutanesulfonic acid (40 mmol) and methanesulfonic acid (360 mmol). The reaction mixture was stirred for 1 h at 80 °C and then poured into 600 mL of a water/acetone mixture (10:1 by volume). The crystallized product was isolated by filtration, washed with sodium hydrogen carbonate solution (10% by weight) and water, and dried at 60 °C (12 mbar). The crude product was then dissolved in hot ethanol treated with charcoal and crystallized by dropwise addition of water. The resulting product was dissolved in a mixture of hot toluene and tetrahydrofuran (10:1 by volume) and crystallized under cooling by portionwise addition of carbon tetrachloride. Yields and properties of all diacyl bisphenols **9a–c** are summarized in Table I.

1,14-Bis(4-hydroxyphenyl)tetradecane (10c). 1,12-Bis((4-hydroxyphenyl)carbonyl)dodecane (40 mmol), hydrazine hydrate (25 mmol), and potassium hydroxide (320 mmol) were refluxed for 1 h in triethylene glycol under stirring. Excess hydrazine and water were then slowly removed by distillation until the temperature reached 195 °C. This temperature was maintained until the evolution of N_2 ceased (approximately 5 h). After it was cooled the reaction mixture was diluted with water (100 mL), acidified with concentrated hydrochloric acid, and four times extracted with 150-mL portions of ethyl acetate. The combined extracts were washed with sodium hydrogen carbonate and water and dried over sodium sulfate. The crude product isolated after removal of ethyl acetate was recrystallized from hot toluene by portionwise addition of carbon tetrachloride. For yields and properties, see Table I. The structures of all three bisphenols **10a–c** were checked by ^{1}H NMR spectroscopy. Correct ratios of aliphatic and aromatic protons were obtained in all cases.

1,14-Bis(4-(trimethylsiloxy)phenyl)tetradecane (6c). 1,14-Bis(4-hydroxyphenyl)tetradecane (100 mmol) and hexamethyldisilazane (250 mmol) were refluxed in 150 mL of dry xylene for 8 h. The cold reaction mixture was filtered without moisture. The filtrate was concentrated in vacuo, 100 mL of dry xylene was added to the residue, and the concentration was repeated to remove residual hexamethyldisilazane. Finally, all volatile contaminants were removed at 100 °C (0.1 mbar). The remaining crude product was used for polycondensation, because distillation led to partial decomposition. Both over silylated bis(phenol)s (**6b,c**) were purified by distillation in a vacuum of 10^{-3} mbar at a bath temperature of 220–250 °C. For yields and properties, see Table I.

Bis(4-(4-phenoxybenzoyl)phenyl) Ether. Potassium *tert*-butoxide (0.8 mol) was added to a solution of phenol (0.8 mol) in 1.3 L of dry dimethylformamide. The reaction mixture was

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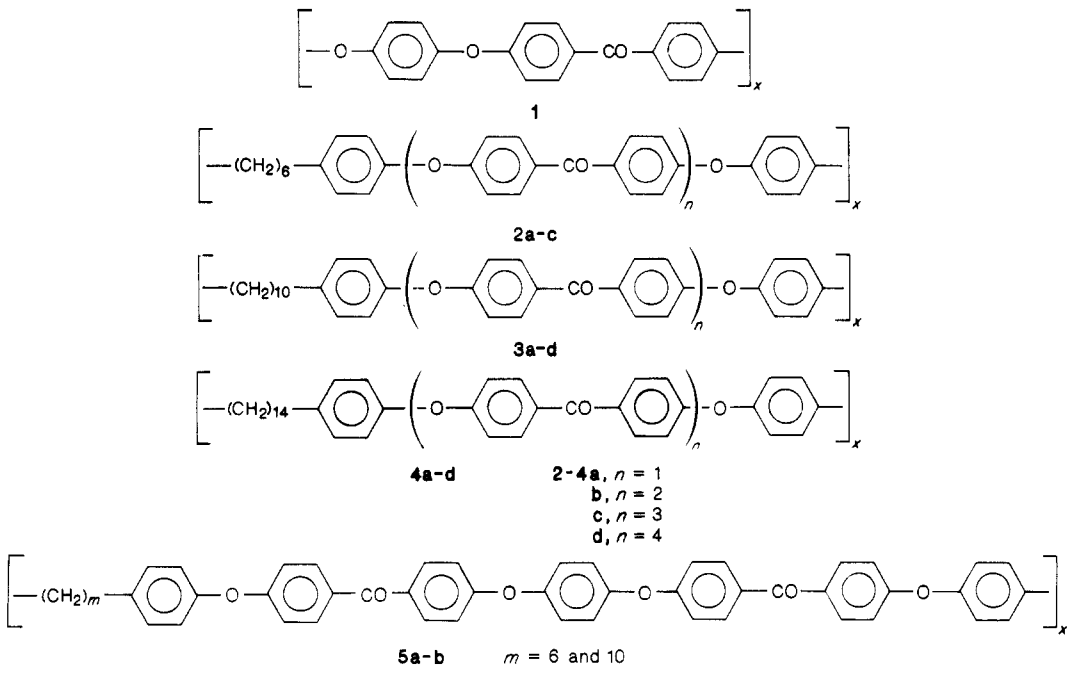


Table I
Yields and Properties of α,ω-Bis(4-(trimethylsiloxy)phenyl)alkanes and Their Precursors

compound	yield, %	mp, °C	elem formula (mol wt)	elem anal.	C	H
1,6-bis(4-hydroxyphenyl)-1,6-dioxohexane (**9a**)	60	232–238 (dec)	$C_{18}H_{18}O_4$ (298.36)	calcd	72.45	6.09
				found		
1,10-bis(4-hydroxyphenyl)-1,10-dioxodecane (**9b**)	49	200–240	$C_{22}H_{26}O_4$ (354.48)	calcd	74.54	7.41
				found	74.15	7.44
1,14-bis(4-hydroxyphenyl)-1,14-dioxotetradecane (**9c**)	75	156–159	$C_{26}H_{34}O_4$ (410.60)	calcd	76.04	8.36
				found	76.10	8.35
1,6-bis(4-hydroxyphenyl)hexane (**10c**)	85	143–144	$C_{18}H_{22}O_2$ (270.40)	calcd	79.95	8.22
				found		
1,10-bis(4-hydroxyphenyl)decane (**10b**)	57	132–134	$C_{22}H_{30}O_2$ (326.52)	calcd	80.92	9.28
				found	80.25	9.21
1,14-bis(4-hydroxyphenyl)tetradecane (**10c**)	75	125–128	$C_{26}H_{38}O_2$ (382.64)	calcd	81.60	10.03
				found	80.62	10.00
1,6-bis(4-(trimethylsiloxy)phenyl)hexane (**6a**)	94	36–38	$C_{24}H_{32}O_5Si_2$ (408.67)	calcd	70.54	7.89
				found	70.52	7.88
1,10-bis(4-(trimethylsiloxy)phenyl)decane (**6b**)	80	28–30	$C_{28}H_{46}O_2Si_2$ (470.91)	calcd	71.41	9.87
				found	72.29	10.07
1,14-bis(4-(trimethylsiloxy)phenyl)tetradecane (**6c**)[a]	95	37–39	$C_{32}H_{54}O_2Si_2$ (527.04)	calcd	72.92	10.35
				found	74.21	9.77

[a] Crude product; contains xylene.

heated with stirring to 140 °C and most *tert*-butyl alcohol was removed with a moderate stream of nitrogen. After the mixture was cooled to 100 °C, bis(4-(4-fluorobenzoyl)phenyl) ether (0.4 mol) was portionwise added and heating to 140 °C was continued for an additional 2.5 h. After it was cooled to approximately 100 °C, where the product began to crystallize, the reaction mixture was poured into 3 L of cold water. The crystalline product was isolated by filtration, washed with water and ethanol, and dried at 120 °C (12 mbar). The crude product was then dissolved in a refluxing mixture of dichloromethane and trifluoroacetic acid (6:1 by volume), and after filtration crystallization was induced by concentration and cooling. The recrystallized product was dried at 60 °C (12 mbar) over sodium hydroxide; yield, 71%; mp 230–232 °C. Anal. Calcd for $C_{38}H_{26}O_5$ (562.64): C, 81.11; H, 4.67. Found: C, 81.03; H, 4.65.

Difluoro Ketone 7d. 4-Fluorobenzoyl chloride (0.6 mol) was added to a suspension of aluminum chloride (1.3 mol) and 100 mg of ferric chloride in 3 L of dry dichloromethane cooled with ice. Bis(4-(4-phenoxybenzoyl)phenyl)ether (0.28 mol) was added portionwise under stirring and cooling. After complete addition, stirring was continued for 12 h without cooling the reaction mixture was then refluxed for 1 h and finally poured into 4 L of methanol containing 400 mL of 2 N HCl. The crystallized product was isolated by filtration; successively washed with 1 N HCl, sodium hydrogen carbonate solution (10% by weight), and water; and finally dried at 120 °C (12 mbar). The crude product was dissolved in 4 L of boiling *N*-methylpyrrolidone and a mixture of dioxane and water (10:1 by volume) was added dropwise until crystallization began, which was completed by cooling. The product was filtered off, refluxed with ethanol, and dried at 120 °C (12 mbar); yield, 92%; mp 307–309 °C (optically) or 311 °C (DSC endotherm). Anal. Calcd for $C_{52}H_{32}F_2O_7$: C, 81.12; H, 4.20. Found: C, 80.89; H, 4.13. ^{13}C NMR measured in $CDCl_3$ + TFA (4:1 by volume) with internal TMS: 199.58 and 199.61 ppm (carbonyl groups), 166.57 and 165.16 ppm (quartary C, split due to coupling with ^{19}F); intensity ratio 2.1:2.1:1.0:1.0 measured with 6-s relaxation delay and pulse width of 45°.

Hydroquinone bis(*p*-(4-fluorobenzoyl)phenyl ether (8) was prepared analogously and purified by recrystallization from a mixture of dichloromethane and trifluoroacetic acid (9:1 by volume); yield, 57%; mp 223–225 °C. Anal. Calcd for $C_{32}H_{20}F_2O_4$: C, 75.90; H, 4.20. Found: C, 76.10; H, 3.93.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscosimeter thermostated at 20 °C. Solutions of 100 mg of polymer in 50 mL of a 1:4 (by volume) mixture of trifluoroacetic acid and dichloromethane were used in all cases.

The DSC traces were measured with a Perkin-Elmer DSC-4

in aluminum pans at a heating rate of 20 °C/min.

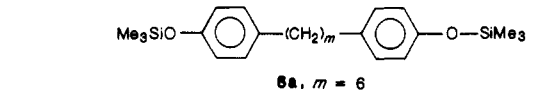
The thermomechanical analyses were conducted with a Perkin-Elmer TMS-2 at a heating rate of 5 °C/min. The films with a thickness of ca. 0.5 mm were pressed at 320–340 °C.

The thermogravimetric analyses were obtained on a Perkin-Elmer TGS-2 at a heating rate 10 °C/min in air.

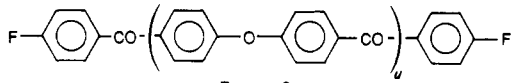
The wide-angle X-ray scattering (WAXS) curves were measured at 25 °C with a powder diffractometer "Siemens D-500" by means of Ni-filtered Cu Kα radiation. The time-resolved WAXS measurements at elevated temperatures were performed on a synchrotron radiation beam line (λ = 1.50 Å) at HASYLAB, DESY, Hamburg, by means of a vacuum furnace and a one-dimensional position-sensitive detector. The heating rate was 20 °C/min, and the accumulation time for one pattern was 10 s.

Results and Discussion

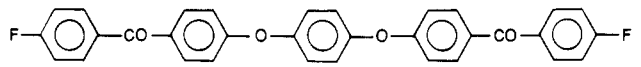
Syntheses of Monomers and Polymers. The poly(ether ketone)s 1–4 were all synthesized via the so called silyl method, which has proven to be a convenient procedure on the laboratory scale.[4,5] Its characteristic advantages are 2-fold. First, in contrast to the classical procedure no high-boiling inert reaction medium is required and the poly(ether ketone)s do not need to be purified from such a reaction medium. Second, the highly volatile fluorotrimethylsilane is the only byproduct. The application of the silyl method in the present work required the preparation of the silylated bis(phenol)s **6a–c** and of the difluoro ketones **7a–d** and 8.



6a, m = 6
b, m = 10
c, m = 14



7a, u = 0
b, u = 1
c, u = 2
d, u = 3



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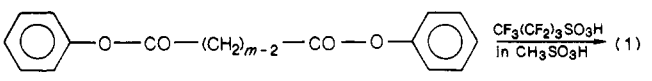
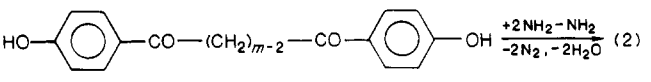
The synthesis of the alkylenebis(phenol)s **10a,b** was first described by Wagner in a recent patent.[8] In the present work a modified version of the original procedure was used for the synthesis of the precursors **9a–c** (eq 1, 2). Whereas, the free bis(phenol)s **10a–c** were easily purified by re-

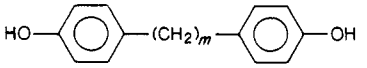


(1)



(2)

9a-c



10a-c

a, m = 6; **b**, m = 10; **c**, m = 14

crystallization, the silylated monomers **5a,b** were distilled under high vacuum. Yet in the case of **5c** beginning decomposition prevented purification by distillation and this monomer was used as crude crystalline material. In the case of the difluoro ketones, the benzophenone **7a** is commercially available and the synthesis of **7b,c** was described in a previous part of this series.[5] **7d** was prepared from **7b** in a similar way according to eq 3 and 4. Monomer 8 was prepared by Friedel–Crafts acylation of hydroquinone diphenyl ether with 4-fluorobenzoyl chloride by analogy with eq 4. The polycondensations of **6a–c** with **7a–d** and 8 were conducted in the melt at temperatures up to 320 °C and in the presence of cesium fluoride as previously described for other poly(ether ketone)s.[4,5]

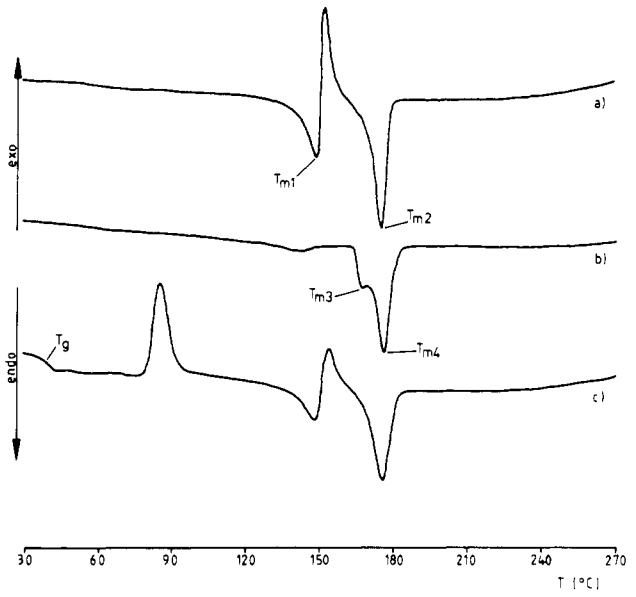
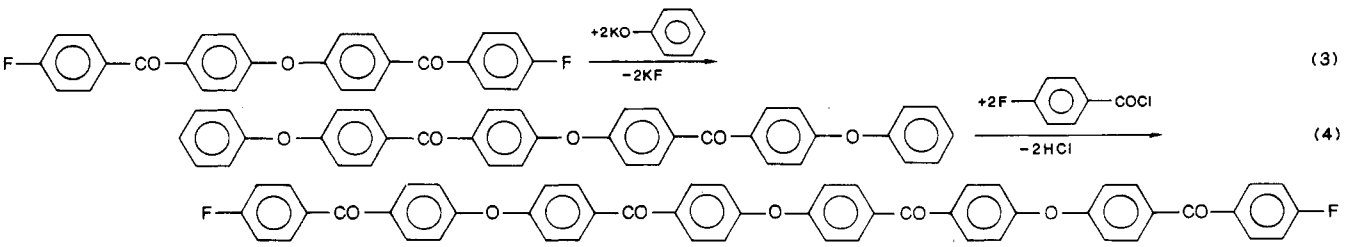


Figure 1. DSC traces of poly(ether ketone) **3a** measured at a heating rate of 20 °C/min: (a) first heating; (b) second heating after annealing at 160 °C for 30 min; (c) third heating after quenching from the melt.

DSC Measurements and Microscopy. All poly(ether ketone)s were subjected to DSC measurements with a heating rate of 20 °C/min: When the samples precipitated from cold methanol were dried at a temperature above or close to the glass transition temperature (T_g) the first heating trace only displayed a weak T_g step and never a crystallization exotherm. However, in most cases two melting endotherms were detectable, and the first endotherm was immediately followed by a more or less significant crystallization exotherm (Figure 1, curve a). When the samples were annealed at a temperature between both endotherms, the low-temperature endotherm (T_{m_1}) gradually disappeared, whereas T_{m_2} remained unchanged (Figure 1, curve b). This finding clearly demonstrates that the first endotherm represents the melting process of smaller and less perfect crystallites or of a different crystal modification. After rapid cooling from the melt (cooling rate ca. −200 °C/min), the third heating curve (c in Figure 1) displays a distinct glass transition step, a first recrys-



(3)

(4)

Table II
Yields and Properties of Poly(ethyl ketone)s Prepared from Silylated Hexamethylenebis(phenol) (6a) and Various Difluoro Ketones

polymer	ketone	yield, %	η_{inh}, dL/g	elem formula (mol wt)	elem anal.	C	H	T_g, °C	T_{m_1}, °C	T_{m_2}, °C
2a	**7a**	95	0.57[a]	$C_{31}H_{28}O_3$ (448.62)	calcd	83.00	6.30	66	168	207
					found	82.77	5.81			
2b	**7b**	95	0.46[a]	$C_{44}H_{36}O_5$ (644.84)	calcd	81.96	5.64	88	264	282
					found	81.99	5.76			
2c	**7c**	87	1.38[b]	$C_{57}H_{44}O_7$ (841.01)	calcd	81.40	5.28	109	256	300
					found	80.77	5.30			
2d	**7d**	91	0.29[a]	$C_{70}H_{52}O_9$ (1037.22)	calcd	81.05	5.06	102	266	279
					found	81.10	5.33			
5a	**8**	88	0.69[b]	$C_{50}H_{40}O_6$ (736.90)	calcd	81.49	5.48	88	204	274
					found	79.59	5.58			

[a] Measured with c = 2 g/L at 20 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [b] Measured with c = 2 g/L at 20 °C in dichloromethane/methanesulfonic acid (4:1 by volume).

Table III
Yields and Properties of Poly(ether ketone)s Prepared from Silylated Decamethylenebis(phenol) (6b) and Various Difluoro Ketones

polymer	ketone	yield, %	η_{inh}, dL/g	elem formula (mol wt)	elem anal.	C	H	T_g, °C	T_{m_1}, °C	T_{m_2}, °C
3a	**7a**	79	1.61[a]	$C_{35}H_{36}O_3$ (504.71)	calcd	83.29	7.20	41	150	176
					found	83.14	7.22			
3b	**7b**	94	1.00[a]	$C_{48}H_{44}O_5$ (700.92))	calcd	82.25	6.34	72	191	241
					found	82.27	6.35			
3c	**7c**	95	1.55[b]	$C_{61}H_{52}O_7$ (897.13)	calcd	81.66	5.85	89		253
					found	79.76	5.82			
3d	**7d**	94	0.38[a]	$C_{74}H_{60}O_9$ (1093.34)	calcd	81.29	5.54	87		266
					found	80.81	5.85			
5b	**8**	88	0.58[b]	$C_{54}H_{48}O_6$ (793.02)	calcd	81.78	6.11	70	206	247
					found	79.65	5.93			

[a] Measured with c = 2 g/L at 20 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [b] Measured with c = 2 g/L at 20 °C in dichloromethane/methanesulfonic acid (4:1 by volume).

Table IV
Yields and Properties of Poly(ether ketone)s Prepared from Silylated Tetradecamethylenebis(phenol) (6c) and Various Difluoro Ketones

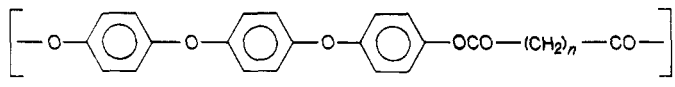
polymer	ketone	yield, %	η_{inh}, dL/g	elem formula (mol wt)	elem anal.	C	H	T_g, °C	T_{m_1}, °C	T_{m_2}, °C
4a	**7a**	79	0.58[a]	$C_{39}H_{44}O_3$ (560.83)	calcd	83.52	7.92	22		130
					found	82.79	8.09			
4b	**7b**	72	0.13[a]	$C_{52}H_{52}O_5$ (757.04)	calcd	82.49	6.97	(26)	166	192
					found	81.07	6.88			
4c	**7c**	90	0.48[b]	$C_{65}H_{60}O_7$ (953.25)	calcd	81.79	6.36	70	(244)	250
					found	80.28	6.30			
4d	**7d**	79	0.71[b]	$C_{78}H_{60}O_9$ (1149.46)	calcd	81.50	5.27	91		284
					found	79.88	5.80			

[a] Measured with c = 2 g/L at 20 °C in dichloromethane/trifluoroacetic acid (4:1 by volume). [b] Measured with c = 2 g/L at 20 °C in dichloromethane/methanesulfonic acid (4:1 by volume).

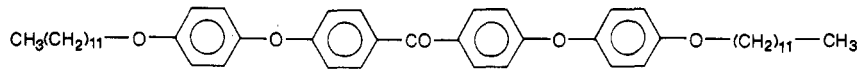
tallization exotherm, a first melting process (T_{m_1}), followed again by a weaker recrystallization exotherm, and the final melting at T_{m_2}. The DSC traces shown in Figure 1 are also characteristic for other "minisegmented" poly(ether ketone)s; yet in some cases only one endotherm is detectable in the first or second heating curve (**3c,d**, Table II, and **4a,d**, Table IV).

These DSC results clearly indicate that the two endotherms represent the melting process of two sorts of crystallites. Yet, it could not be elucidated whether the low-melting sort is another modification or a smaller and less perfect version of the higher melting crystallites. Anyway, the exotherm between both endotherms and the success of annealing clearly vote against the existence of a mesophase between both endotherms. This conclusion needs to be emphasized for two reasons. First, the microscopic observation under polarized light gives ambiguous results, because birefringent particles dispersed in a seemingly isotropic mobile phase are observable. The birefringent particles might be a smectic phase or a dispersion of the high-melting crystallites in the melt of amorphous phase and less stable crystallites. The second reason, is from a recent paper[9] claiming that the poly(ether ester) **11** forms a mesophase. Unfortunately the characterization of **11** is mainly based on DSC measurements, so that the observation of two endotherms might have deceived the authors. The reason why neither the triphenyl ether blocks of **11** nor the ether ketone blocks of **2–5** are suitable as mesogens, is their permanent deviation from planarity. The protons in the ortho position to ether or keto groups partially overlap in a coplanar conformation of the aromatic rings. Convincing experimental evidence for the noncoplanarity of aromatic polyethers and ether ketone **1** was reported by several authors on the basis of X-ray measurements.[3,10]

In order to obtain additional evidence in favor of or against the mesogenic character of aromatic ether ketone blocks, the model compound **12–14** were synthesized. Their synthesis was achieved from hydroquinone dodecyl



11



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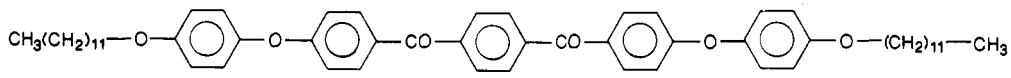

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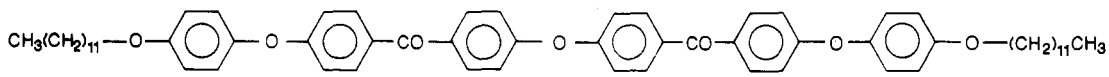

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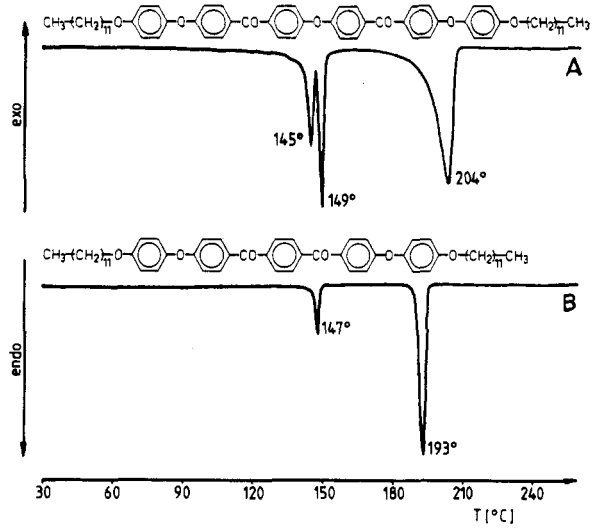
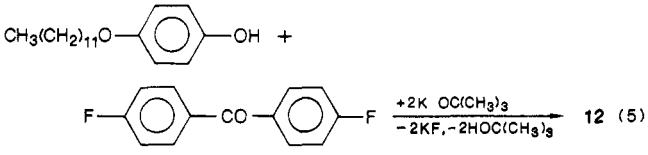


Figure 2. DSC measurements (first heating traces) conducted at a heating rate of 20 °C/min: (A) model compound 14; (B) model compound 13.

ether and various difluoro ketones according to the example outlined on eq 5. The DSC traces of these model



12 (5)

compounds display two endotherms (Figure 2). Yet, observation under polarized light clearly shows that the first endotherm represents a solid → solid transition. Furthermore, model 14 was subjected to WAXS measurements with synchrotron radiation at variable temperature. The powder patterns displayed in Figure 3 show that the sharp reflections persist above T_{m_1}, although with reduced intensity. This result indicates a change of the modification but not the formation of a mesophase. Thus it may be concluded that neither aromatic ether ketone sequences nor pure ether blocks are suited as mesogens.

Finally it should be noted that in three cases, **2a** and **3a,b**, enthalpy changes observed from the heating curves at a rate of 20 °C/min were quantified. For the sum of both exotherms values in the range of 45–50 J/g were found, and for both endotherms values were in the range of 55–60 J/g.

Wide-Angle X-ray Measurements (WAXS). In order to obtain some basic information on the supermolecular structure of the poly(ether ketone)s **2–4** and on their degree of crystallinity, WAXS measurements were conducted.

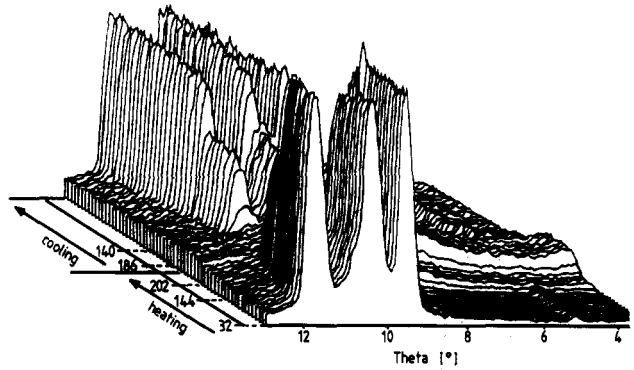


Figure 3. WAXS powder pattern of model compound 14 measured with synchrotron radiation at a heating rate of 20 °C/min.

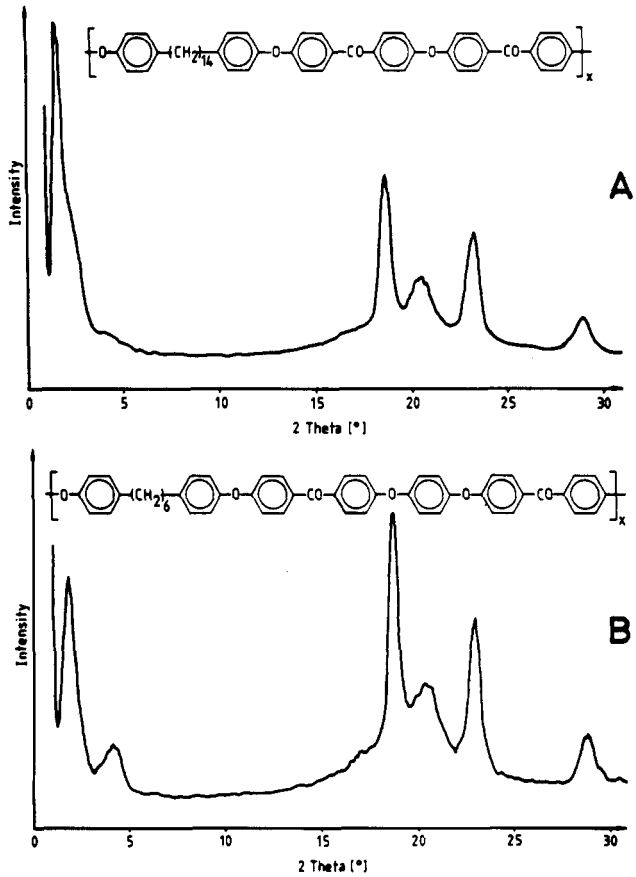


Figure 4. WAXS powder patterns measured with Cu Kα radiation at 25 °C: (A) poly(ether ketone) **4b**; (B) poly(ether ketone) **5a**.

The powder patterns obtained at room temperature display in a few cases three and in most cases four distinct

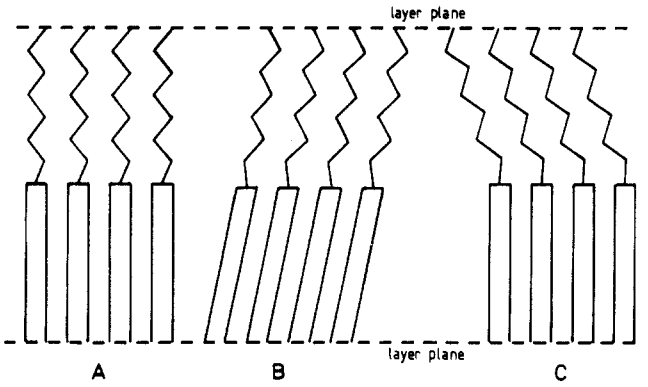


Figure 5. Schematic models of the layered supermolecular structure of minisegmented poly(ether ketone)s.

reflections in the range ϑ = 8–15° (Figures 4 and 5). Those poly(ether ketone)s with relatively long aromatic blocks **2–4c,d** exhibit four reflections with scattering angles and intensity ratios that perfectly agree with the X-ray pattern reported for PEEK and similar fully aromatic poly(ether ketone)s.[3,9] Hence, it may be concluded that the aromatic blocks of the minisegmented poly(ether ketone)s adopt the same orthorhombic crystal lattice described for PEEK. The lattice of poly(ether ketone)s with short blocks **2–4a,b** slightly deviate from the standard lattice, yet the nature of this deviation was not studied in detail.

In contrast to PEEK and other fully aromatic poly(ether ketone)s the minisegmented poly(ester imide)s exhibit a strong reflection at small angles (1–1.8°, see Figures 4 and 5). In two cases, namely, **5a,b**, also a weaker reflection of second order was observed (Figure 5). A reliable and accurate determination of these small-angle reflection by means of WAXS techniques was only feasible for the poly(ether ketone)s with the shortest repeating units (**2a**, **3a**, **4a**). In all other cases small-angle X-ray measurements (SAXS) are necessary, or at least desirable; a work in this area is currently in progress. The ϑ-values obtained from WAXS measurements of **2a**, **3a**, and **4a** roughly agree with the lengths of the repeating units derived from Dreiding models. This result and the finding that the aromatic blocks adopt the same orthorhombic elementary cell as PEEK suggest that the minisegmented poly(ether ketone)s form a layered supermolecular structure. Such layered structures are known from several thermotropic polyesters with an alternating sequence of aliphatic spacers and aromatic mesogens.[11-14] Such layered structures have in common that they represent a phase separation of aromatic and aliphatic building blocks on the molecular level. In the case of the minisegmented poly(ether ketone)s, the repeating units may be perpendicular to the layer planes (Figure 5A) or slightly tilted (Figure 5B), or the aromatic blocks are perpendicular and the aliphatic spacers tilted (Figure 5C). A detailed SAXS investigation which will presumably elucidate the exact structure of the chain packing is in progress and will be published separately.

For the interpretation of the thermomechanical measurements discussed below, at least a crude estimation of the degree of crystallinity seemed to be useful. From X-ray and density measurements of PEEK, it is know that annealed samples reach a degree of crystallinity of around 45%.[3] When the WAXS patterns of the minisegmented poly(ether ketone)s were compared with that of annealed PEEK at identical coordinates it became evident that annealed samples of minisegmented poly(ether ketone)s may reach a degree of crystallinity between 45 and 55%. The intensity distribution between sharp reflections and

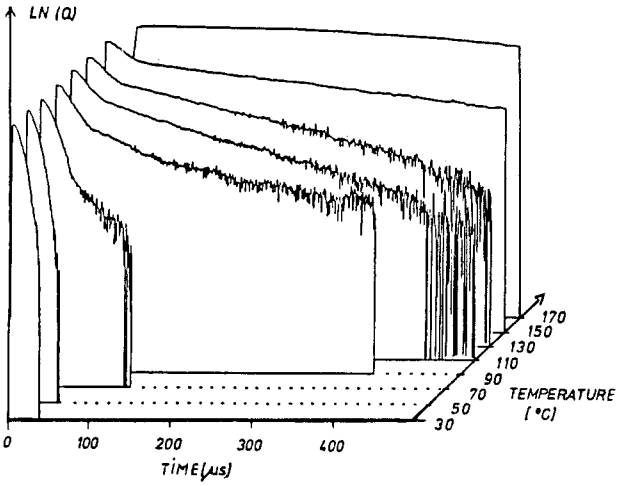


Figure 6. ^{1}H NMR broad-line measurements of the transversal relaxation time T_2: plot of the natural logarithm of transversal magnetization [(ln (Q)] versus time and temperature.

the amorphous halo was almost independent of the chemical structure.

Broad-Line ^{1}H NMR Measurements. In order to determine the degree of crystallinity by a second method independently of X-ray measurements, annealed samples of three minisegmented poly(ether ketone)s, **2a**, **3a**, and **4a**, were subjected to broad-line ^{1}H NMR measurements. This ^{1}H NMR technique was designed to measure the line width of a broad ^{1}H NMR line $\Delta\upsilon$ in hertz containing all signals of aliphatic and aromatic protons at variable temperatures. The line width depends on the transversal relaxation time, T_2 (eq 6), which, in turn, is related to

$$\Delta\delta = 1/2\pi T_2 \quad (6)$$

segmental mobility of the polymer chain as described for instance in ref 15. A detailed report of these measurements will be published separately.[16]

The three samples **2a**, **3a**, and **4a** were selected with regard to the following two parameters: (A) low melting point, because for technical reasons T_m's above 160 °C could not be measured; (B) broad variation of the molar fraction of aliphatic protons.

The second point was important because the measurements of **2a**, **3a**, and **4a** enabled a discrimination between the following two models: (I) The fraction of mobile proton in the temperature range between T_g and T_m is identical with the molar fraction of aliphatic protons. In other words, only the spacers are mobile. (II) The mobile protons belong to an amorphous fraction consisting of entire chains or long chain segments including both aliphatic and aromatic protons.

As demonstrated in Figure 6 only one fast relaxation process exists below T_g and only one very slow relaxation above T_m, whereas between T_g and T_m a rapid and a slow relaxation process are coexistant. By means of a suitable computer program, the molar fractions of mobile and immobile protons were calculated at a temperature halfway between T_g and T_m. For all three poly(ether ketone)s, a fraction of 50–55% of immobile protons was found, a result which perfectly agrees with model B. Since the fraction of immobile protons may be higher but never lower than the fraction of crystalline material, the ^{1}H NMR measurements show a good agreement with the degree of crystallinity (45–55%) estimated from the WAXS patterns.

Thermomechanical Measurements. Two thermal properties, which are of basic interest for the usefulness of a thermoplastic material, were determined in this work, heat distortion temperatures (HDTs) and thermostabili-

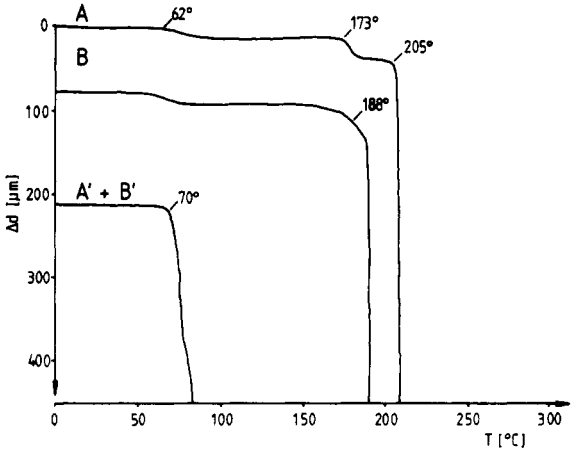


Figure 7. Thermomechanical analyses (penetration method) of poly(ether ketone) **2a** conducted at a heating rate of 5 °C/min: (A) annealed sample, load 0.05 kg/mm^2; (B) annealed sample, load 1.0 kg/mm^2; (A′) quenched sample, load 0.05 kg/mm^2; (B′) quenched sample, load 1.0 kg/mm^2.

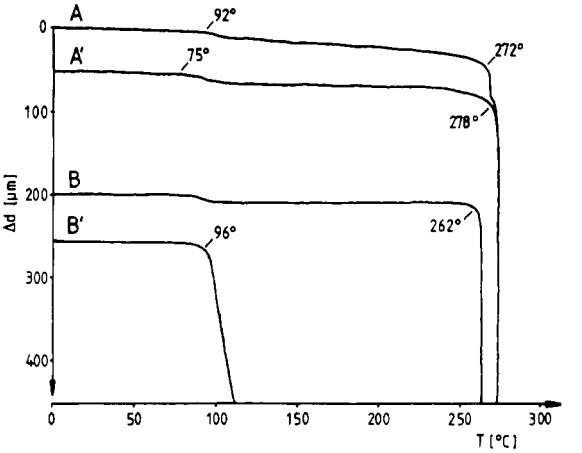


Figure 8. Thermogravimetric analyses (penetration method) of poly(ether ketone) **2c** conducted with a heating rate of 5 °C/min: (A) annealed sample, load 0.05 kg/mm^2; (B) annealed sample, load 1.0 kg/mm^2; (A′) quenched sample, load 0.05 kg/mm^2; (B′) quenched sample, load 1.0 kg/mm^2.

ties. The HDTs were measured by means of the penetration method at a heating rate of 5 °C/min under a load of 0.5 MPa (ca. 0.05 kg/mm^2) or 10 MPa (ca. 1.0 kg/mm^2). The samples used for these thermomechanical analyses were prepared in two ways. The products were molten in a metal frame and pressed to thick films between heated metal blocks. The hot metal blocks were then replaced by cooled metal blocks and the samples rapidly cooled to room temperature. Finally the films were cut into two parts and one part was annealed for 5 min at approximately 30 °C below the highest melting point.

The combination of DSC measurements and thermomechanical analyses revealed the existence of two extreme cases. Either the quenched samples were amorphous or they were highly crystalline. However, most samples possessed after quenching a low degree of crystallinity which significantly increased upon annealing. As demonstrated by curves A′ + B′ of Figure 7, the quenched sample of a slowly crystallizing poly(ether ketone), e.g., **2a**, shows a HDT identical with T_g regardless of the applied load. The same sample annealed for 5 min at 150 °C exhibits HDTs correlated with the melting process (curves A and B in Figure 7). In contrast the quenched and annealed samples of a rapidly crystallizing poly(ether ketone), e.g., **2c**, yield nearly identical thermomechanical analyses, when measured under low load (curves A and A′ in Figure 8). However, a differentiation is detectable under high load (curves B and B′ in Figure 8). The quenched sample shows then a HDT almost identical with T_g, whereas the HDT of the annealed sample is still correlated with the melting process. The thermomechanical analysis **2b** was similar to that of **2c**, whereas the thermomechanical properties of **3a,b** and **4a,b** resembled those of **2a**.

A comprehensive mechanical study of all minisegmented poly(ether ketone)s is beyond the scope of this work. Yet, a few preliminary measurements revealed two interesting results. First, long aliphatic spacers enhance the rate of crystallization, if the aromatic block is relatively long (more than six aromatic rings). Yet long spacers are not advantageous, if the aromatic blocks are short (less than six aromatic rings). Second, when the minisegmented poly(ether ketone)s reach their maximum degree of crystallinity (50 ± 5%), they show HDTs correlated with T_m and not with T_g. Similar thermomechanical properties were also found for several thermotropic poly(ester imide)s with a regular sequence of aliphatic spacer and aromatic mesogen. Yet these LC polyesters possess an unusually high degree

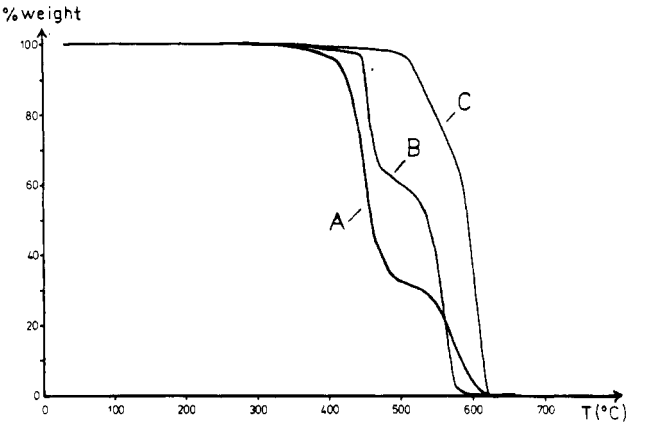


Figure 9. Thermogravimetrical analyses conducted at a heating rate of 10 °C/min in air: (A) poly(ether ketone) **3a**; (B) poly(ether ketone) **3b**; (C) poly(ether ketone) prepared from **7a** and phenylhydroquinone.

crystallinity (probably >80%) in contrast to the minisegmented poly(ether ketone)s. Thus, the thermomechanical analyses of the poly(ether ketone)s demonstrate that despite the long aliphatic spacers, unusual high degrees of crystallinity are not a necessary requirement for high HDTs. Obviously, the morphology plays also an important role, and in this regard to alternative models are imaginable. Either the polymers form a network of extented-chain crystals, or the folded-chain crystallites are interconnected with numerous tie molecules. A discrimination between these models requires detailed X-ray and electron microscopy studies.

Thermogravimetric Analyses. The thermostabilities were determined at a heating rate of 10 °C/min in air. The presence of oxygen has the expected consequence that poly(ester ketone)s with long spacers degrade more rapidly than those with short spacers, or in other words, a low fraction of aliphatic protons reduces the thermostability. Nonetheless, 5% loss of weight requires temperatures of 390–420 °C and rapid degradation only occurs above 450 °C (Figure 9). This is the highest thermostability the authors ever observed for polymers with aliphatic chain segments in the backbone. Obviously the direct attachment of the aliphatic spacers to the aromatic rings reduces their sensitivity to oxidation compared to polymers with XCH_2 groups (X = O, N, S). A comparison of curves A and B with curve C, which was obtained from a poly(ether ketone) prepared from 4,4′-difluorobenzophenone (**7a**) and

phenylhydroquinone, illustrates the difference between minisegmented and fully aromatic poly(ether ketone)s. Of course, the thermogravimetric analyses presented in Table IV and Figure 9 only give information on the short-time thermostability which defines the upper limit for any thermal processing. The long-term stability of minisegmented poly(ester ketone)s will certainly be significantly lower than that of fully aromatic polymers.

Acknowledgment. We thank Dr. G. Scholtyssek and Prof. Dr. H. G. Zachmann (University of Hamburg) for the ^{1}H NMR broad-line measurements.

Registry No. **2a** (copolymer), 116701-89-4; **2a** (SRU), 116701-72-5; **2b** (copolymer), 116701-90-7; **2b** (SRU), 116701-73-6; **2c** (copolymer), 116701-91-8; **2c** (SRU), 116701-74-7; **2d** (copolymer), 116701-93-0; **2d** (SRU), 116701-75-8; **3a** (copolymer), 116701-96-3; **3a** (SRU), 116701-77-0; **3b** (copolymer), 116724-89-1; **3b** (SRU), 116701-78-1; **3c** (copolymer), 116701-97-4; **3c** (SRU), 116701-79-2; **3d** (copolymer), 116701-98-5; **3d** (SRU), 116701-80-5; **4a** (copolymer), 116702-01-3; **4a** (SRU), 116724-88-0; **4b** (copolymer), 116702-02-4; **4b** (SRU), 116701-82-7; **4c** (copolymer), 116702-03-5; **4c** (SRU), 116701-83-8; **4d** (copolymer), 116702-04-6; **4d** (SRU), 116701-84-9; **5a** (copolymer), 116701-94-1; **5a** (SRU), 116701-76-9; **5b** (copolymer), 116701-99-6; **5b** (SRU), 116701-81-6; **6c**, 116702-00-2; **7b**, 95042-14-1; **7d**, 116701-92-9; **9c**, 116724-85-7; **10c**, 115914-44-8; **13**, 116724-87-9; **14**, 116724-86-8; diphenyl tetradecanedicarboxylate, 116724-84-6; tetradecanedicarboxyl chloride, 21646-49-1; hexamethyldisilazane, 999-97-3; phenol, 108-95-2; bis(4-(4-phenoxybenzoyl)phenyl) ether, 63347-89-7; 4-fluorobenzoyl chloride, 403-43-0.

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Liquid Crystalline Polyethers Based on Conformational Isomerism. 2. Thermotropic Polyethers and Copolyethers Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and Flexible Spacers Containing an Odd Number of Methylene Units

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ABSTRACT: The synthesis and characterization of the first examples of thermotropic main-chain liquid crystalline polyethers and copolyethers based on flexible rodlike mesogenic units or rodlike mesogenic units based on conformational isomerism and flexible spacers are described. The particular examples presented in this paper refer to polyethers (MBPE-5, MBPE-7, MBPE-9, and MBPE-11) and copolyethers (MBPE-X/Y; X, Y = 5, 7, 9, 11) based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane (MBPE) and flexible spacers containing 5, 7, 9, and 11 methylene units. Both MBPE-5 and MBPE-9 exhibit a nematic and a smectic monotropic mesophase and MBPE-7 is crystalline, while MBPE-11 displays a monotropic nematic mesophase. Copolymers with various compositions close to a 50/50 molar ratio of the two spacers exhibit both nematic and smectic enantiotropic mesophases. Both liquid crystalline transition temperatures and the corresponding enthalpies of the copolymers are weight-averaged values of the similar parameters of the parent homopolymers. Extrapolation of mesomorphic transition temperatures and of enthalpy changes has demonstrated that all homopolymers exhibit virtual nematic and smectic mesophases. The thermal transition temperatures and the enthalpy changes associated with the virtual nematic and smectic mesomorphic transitions of the homopolymers were determined from several sets of copolymers with very good agreement.

Introduction

Traditional *rigid rodlike* mesogenic units are constituted of linearly substituted aromatic or cycloaliphatic rings connected by rigid interconnecting groups which provide a linear and eventually planar conformation to the resulting compound. Although there is free rotation about certain carbon–carbon single bonds of these compounds, it is essential that rotation about these single bonds does not perturb the elongated or extended conformation of the mesogenic group. Therefore, in *rigid rodlike* mesogenic units, the extended conformation of the molecule is accomplished and maintained through the rigidity and linearity of its constituents, i.e., its rigid rodlike character (Scheme I).

The transplant of this concept from low molar mass liquid crystals to macromolecular liquid crystals led to the presently accepted pathway used in the synthesis of both main-chain and side-chain liquid crystalline polymers.

An alternative solution to the creation of an extended conformation of a molecule can be considered when the rigid interconnecting groups from the *rigid rodlike mesogens* are replaced with *flexible* interconnecting units, as, for example, ethylene or methyleneoxy. Although ethylene and methyleneoxy units can adopt an extended confor-

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