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Synthesis of Soluble High Molecular Weight Poly(aryl ether ketones) Containing Bulky Substituents[†]

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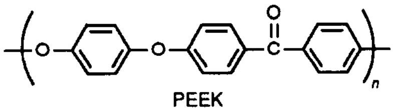
ABSTRACT: *tert*-Butyl- and phenyl-substituted poly(aryl ether ketones) were prepared by a nucleophilic substitution reaction from the corresponding substituted hydroquinones and 4,4′-difluorobenzophenone. Reaction temperatures of 170 °C were sufficient to give high molecular weight poly(oxy-(2-*tert*-butyl-1,4-phenylene)oxy-1,4-phenylenecarbonyl-1,4-phenylene). This polymer was found to be amorphous, T_g = 175 °C, and highly soluble in common organic solvents, such as chloroform, THF, and toluene. The *tert*-butyl substituent was cleaved with trifluoromethanesulfonic acid in a reversed Friedel–Crafts alkylation reaction to produce PEEK (poly(aryl ether ether ketone)). This reaction proceeded to high conversions in the presence of a *tert*-butyl group acceptor such as toluene.

Introduction

Aromatic poly(ether ketones) are currently receiving considerable commercial interest as high-performance engineering thermoplastics. They are polymers with high chemical resistance and excellent mechanical and insulating properties that are retained at high temperatures. These polymers can be fabricated by conventional techniques such as extrusion and compression molding and can be applied as matrix resins for high-performance reinforced composites. There are two different synthetic routes for the preparation of poly(aryl ether ketones): aromatic electrophilic substitution (Friedel–Crafts acylation) and aromatic nucleophilic substitution.

The first preparation of a low molecular weight (η_{inh} = 0.18 dL/g) poly(aryl ether ketone) was reported by Bonner[1] in 1962. He reacted diphenyl ether and isophthalic acid dichloride by Friedel–Crafts polycondensation using aluminum chloride as the catalyst and nitrobenzene as solvent. When Goodman et al.[2] used dichloromethane as solvent, slightly enhanced molecular weights were obtained. The resulting poly(ether ketone) precipitated in both reaction media, nitrobenzene and dichloromethane. Marks[3] achieved a substantial increase in molecular weight (η_{inh} = 1.0–2.8 dL/g) by using the system HF/BF_3, as liquid hydrogen fluoride proved to be a good solvent for poly(aryl ether ketones). He obtained polymers with good dimensional stability derived from terephthalic and isophthalic acid dichloride. Dahl[4] successfully applied the same solvent/catalyst system to different monomers, such as 4-phenoxybenzoic acid.

The second route to aromatic poly(ether ketones) is the nucleophilic aromatic substitution reaction of aromatic diols and 4,4′-difluorobenzophenone in the presence of a base. Johnson et al.[5] obtained a brittle, low molecular weight polymer when they used hydroquinone as dihydric phenol. Rose et al.[6,7] achieved the synthesis of a tough thermoplastic poly(aryl ether ether ketone) (PEEK) from the same monomers by using diphenyl sulfone as solvent. This inert, high boiling point solvent permits the application of reaction temperatures approaching the melting temperature of the polymer (280–340 °C). At lower reaction temperatures, premature crystallization occurs, thereby limiting the molecular weight.



PEEK

In the present paper, we report a different approach to the synthesis of high molecular weight poly(aryl ether ketones) that involves synthesis of a soluble amorphous prepolymer by introduction of removable bulky substituents, followed by removal of the substituents to give the final crystalline polymer.

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Table I
Substituted Poly(aryl ether ketones) Prepared by Nucleophilic Aromatic Substitution

no.	polymer	polym method[a]	T, °C[b]	η_{inh}, dL/g	solvent
1	**1a**	A	170	1.50	$CHCl_3$
				2.25	CH_3SO_3H
				2.70	H_2SO_4
2	**1a**	A	170	1.10	$CHCl_3$
				1.62	CH_3SO_3H
3	**1a**	A	175	1.19	$CHCl_3$
				1.74	CH_3SO_3H
4	**1a**	A	170	1.32	$CHCl_3$
				1.88	CH_3SO_3H
5	**1a**	B	170	0.16	$CHCl_3$
6	**1a**	B	185	0.77	$CHCl_3$
7	**1b**	A	170	0.18	CH_3SO_3H
8	**1b**	A	250	0.54	CH_3SO_3H
9	**1c**	A	185	0.47	$CHCl_3$
10	**1c**	A	240	0.73	$CHCl_3$

[a] Polymerization method: (A) water formed during the reaction was removed as an azeotrope with toluene; (B) removal of water by using a 4-fold molar excess of anhydrous K_2CO_3. [b] Reaction temperature; DMSO and sulfolane as solvents for reaction temperatures below and above 190 °C, respectively.

The introduction of bulky substituents can suppress crystallization of a polymer, thereby improving its solubility substantially. Thus, the incorporation of removable substituents provides a strategy for preparing high molecular weight polymers that otherwise are not easily accessible.

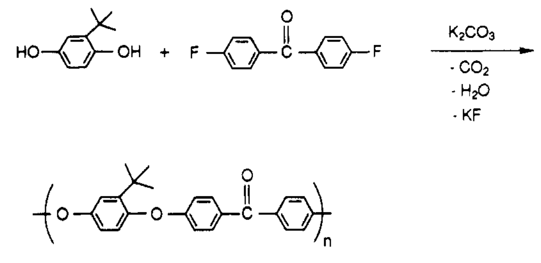
Friedel–Crafts alkylation[8] is a reversible reaction. The ease for removal[9] of an alkyl group from the aromatic ring depends on the nature of other substituents on the aromatic ring and on the thermodynamic stability of the corresponding alkyl cation. After our work was completed and patent filing was in progress, McGrath et al.[10] reported a similar approach to PEEK synthesis. They reported the synthesis of a poly(ether ketone) copolymer with *tert*-butyl substituents and the subsequent reaction with $AlCl_3$. The cleavage of *tert*-butyl substituents by the reaction with $AlCl_3$ amounted to approximately 50% due to the insolubility of the product in the solvent used.

The present work studied the effectiveness of Lewis acids and trifluoromethanesulfonic acid for removal of *tert*-butyl groups from substituted poly(ether ketones). No residual *tert*-butyl substituents could be detected when trifluoromethanesulfonic acid was used. Furthermore, the synthesis and characterization of *tert*-butyl- and phenyl-substituted poly(ether ketones) are presented.

Results and Discussion

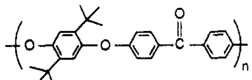
Substituted Poly(ether ketones). Aromatic poly(ether ketones) **1a–d** were prepared by the reaction of aromatic diols and 4,4′-difluorobenzophenone in the presence of anhydrous potassium carbonate as base (eq 1). *tert*-Butylhydroquinone, 2,5-di-*tert*-butylhydroquinone, phenylhydroquinone, and mixtures of *tert*-butylhydroquinone and hydroquinone were used as aromatic diols with DMSO or sulfolane as solvent (Table I).

Under comparably mild conditions (reaction temperatures of 170 °C were sufficient), *tert*-butylhydroquinone was converted to a high molecular weight polymer of structure **1a**. The water formed during the reaction was most effectively removed as an azeotrope with toluene (method A, Table I). Polymers with inherent viscosities up to 1.50 dL/g (in chloroform) were obtained. An excess of anhydrous potassium carbonate could also be used to bind the water (method B, Table I). However, in such cases, reaction temperatures of at least 185 °C were needed to obtain reasonably high molecular weights, as indicated in Table I by polymer 6 (η_{inh} = 0.77 dL/g) and polymer 5 (η_{inh} = 0.16) obtained at 185 and 170 °C, respectively.

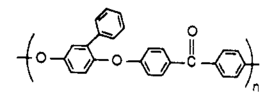


(1)

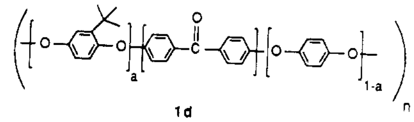
1a



1b



1c

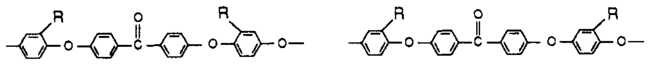


1d

Phenylhydroquinone required higher reaction temperatures than *tert*-butylhydroquinone to give a polymer with sufficient molecular weight for moldings with good dimensional stability. A reaction temperature of 240 °C resulted in the corresponding poly(ether ketone) **1c** with η_{inh} = 0.733 dL/g (polymer 10 of Table I).

One bulky substituent, such as *tert*-butyl or phenyl, on the hydroquinone unit of the poly(ether ketone) repeat unit results in a solubility behavior which stands in sharp contrast to that of the unsubstituted polymer PEEK. PEEK[7,11] is described as insoluble in all common organic solvents at room temperature, except for strong proton-donating acids, such as concentrated sulfuric acid, hydrofluoric acid, methanesulfonic acid, and trifluoromethanesulfonic acid. In addition, A. J. Lovinger[12] found solubility in benzophenone above 220 °C and in α-chloronaphthalene above 230 °C.

The bulkiness of the *tert*-butyl and phenyl substituents as well as a random distribution of structures A and B in **1a** and **1c** inhibits close packing of the polymer chains, thus suppressing crystallization. The solubility is considerably improved and permits the synthesis of high molecular weight polymers **1a** and **1c** below 250 °C (in case of the *tert*-butyl-substituted polymer as low as 170 °C). Polymer **1a** has unlimited solubility in dichloromethane, chloroform, THF, toluene, and NMP at room temperature. Polymer **1c** is soluble in these solvents up to 5–10% (w/v).



A **B**

R = t-butyl, phenyl

The 2,5-di-*tert*-butylhydroquinone unit in **1b** is too symmetrical to result in solubility greatly superior to that of PEEK. Low solubility results in low molecular weight polymer 7 (Table I) at 170 °C reaction temperature. A product of moderate molecular weight, η_{inh} = 0.54 dL/g (in methanesulfonic acid), was obtained at 250 °C (polymer 8 of Table I).

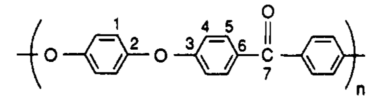
Random copolymers of structure **1d** were prepared from mixtures of *tert*-butylhydroquinone and hydroquinone. The

Table II
Random Copoly(ether ketones) from *tert*-Butylhydroquinone and Hydroquinone

no.	a(theory)[a]	a(exptl)[a]	η_{inh}, dL/g	solvent
11	0.50	0.53	0.64	TCE[b]
12	0.30	0.28	0.73	CH_3SO_3H

[a] a(theory) and a(exptl): theoretical and experimental number (by ^1H NMR spectroscopy) of *tert*-butyl groups per repeat unit, respectively; 3 h of reaction time at 190 °C. [b] 1,1,2,2-Tetrachloroethane.

Table III
Assignment of ^{13}C NMR Signals of PEEK

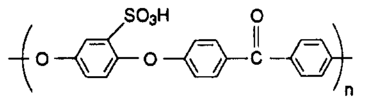


no.	δ(calcd)[a]	δ(CP/MAS)[b]	δ(solution/H⁺)[c]
C_1	120.1	120.4	122.7
C_2	149.7	151.5	151.2
C_3	161.0	160.7	169.5
C_4	118.7	120.4	117.9
C_5	131.4	132.9	138.9
C_6	130.2	132.9	123.0
C_7		193.2	198.1

[a] In ppm, calculated from increments.[14] [b] In ppm, cross-polarized/magic angle spinning spectrum. [c] In ppm, solution spectrum in CF_3SO_3H.

ratio of incorporated diol units was found to be essentially the same as the molar ratio of diols in the reaction mixture (Table II). A polymer with 0.53 *tert*-butyl groups per repeat unit is only partially soluble in $CHCl_3$, CH_2Cl_2, THF, and toluene. A good solvent is tetrachloroethane. Polymer 12 (Table II), a product with 0.28 *tert*-butyl groups per repeat unit, already requires strong acids for complete dissolution.

Due to its very low solubility in organic solvents, characterization of PEEK[12b,c] in solution by viscosimetry has mostly been done by using concentrated sulfuric acid as a solvent. Chemical modification of the polymer by sulfonation,[13] resulting in polymer structure 2, had to be taken into account in these studies.



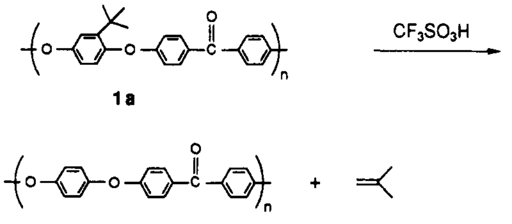
2

The good solubility of *tert*-butyl-substituted PEEK allows solution viscosimetry in an organic solvent such as chloroform, thereby avoiding any structural changes. In addition, the inherent viscosity of 1a was determined in methanesulfonic acid and concentrated sulfuric acid (polymer 1 of Table I). Protonation by methanesulfonic acid results in η_{inh} = 2.25 dL/g compared to η_{inh} = 1.50 dL/g (in chloroform) indicating enhanced molecular rigidity due to electrostatic interactions. Sulfonation in addition to protonation causes a further increase of η_{inh} to a value of 2.70 dL/g (in H_2SO_4).

Further indication for protonation of the carbonyl group of poly(aryl ether ketones) by Brønsted acids comes from ^{13}C NMR spectroscopy. Table III lists chemical shifts of the solid-state and the solution (trifluoromethanesulfonic acid) ^{13}C NMR spectra of PEEK. The signals for the carbonyl group and the adjacent aromatic ring are shifted toward a lower field in the solution spectrum. The chemical shift assignments in the CP/MAS (cross-polarized/magic angle spinning) spectrum are generally in accordance with a recent study.[15] The signals at 160.7 and 151.5 ppm, however, have to be reassigned to C_3 and C_2, in agreement with calculated chemical shifts for PEEK and experimental chemical shifts of model compounds. Further proof comes from the solution NMR spectrum, as C_3 is expected to be shifted to a low field upon protonation of the carbonyl group. No significant change in chemical shift is anticipated for C_2, as this carbon atom is not part of an aromatic ring adjacent to a carbonyl group.

Tough, transparent films of poly(ether ketone) derived from *tert*-butylhydroquinone, **1a**, were either pressed at 300 °C or cast from solution (solvent toluene). The mechanical properties of solvent-cast films of **1a** are comparable to the properties of melt-processed PEEK:[16] tensile modulus of **1a** = 2.2×10^9 N m^{-2}, tensile strength = 6.1×10^7 N m^{-2}, and elongation at break = 180%. A uniaxially oriented sample (stretched to 150% elongation) had a tensile modulus of 3.1×10^9 N m^{-2} and a tensile strength of 1.73×10^8 N m^{-2}.

Cleavage of the *tert*-Butyl Substituent from *tert*-Butyl-Substituted Poly(ether ketones). Friedel–Crafts alkylation is a reversible reaction. In the present study, trifluoromethanesulfonic acid was used as a catalyst for removing *tert*-butyl substituents from the corresponding poly(ether ketones). Two variations of a reversed Friedel–Crafts alkylation reaction were applied: (a) de-*tert*-butylation in neat trifluoromethanesulfonic acid (eq 2) and (b) trans-*tert*-butylation in the presence of a *tert*-butyl group acceptor, such as toluene (eq 3).



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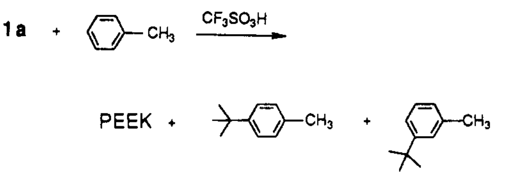


(3)

De-*tert*-butylation (eq 2) occurs upon dissolution of polymers **1a** and **1b** in trifluoromethanesulfonic acid. This acid acts as catalyst for de-*tert*-butylation and as solvent for the resulting polymer simultaneously. Isobutylene gas evolves during the reaction. The reaction is usually run at ambient temperature for 24 h. High conversions are obtained. The ^{13}C CP/MAS spectra of de-*tert*-butylated product and a PEEK reference sample are identical. No signals for remaining aliphatic carbons can be identified. ^1H NMR spectroscopy reveals several signals of very weak intensity in the range 0.9–1.6 ppm indicating the presence of residual aliphatic protons. Total aliphatics amount to 10% or less. Uncommon solvents, such as CF_3SO_3H and CH_3SO_3H (undeuterated), did not allow a more accurate quantification by proton NMR spectroscopy. IR spectra show weak signals of aliphatic C–H at 2960 and 2870 cm^{-1}. The signals at 1505, 1370, 1080, and 870 cm^{-1} disappear after cleavage of the *tert*-butyl groups.

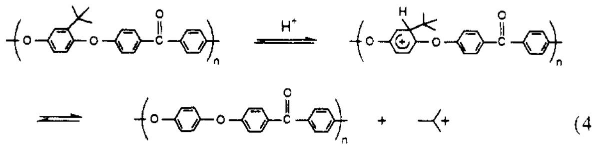
Cationic oligomerization[17] of dissolved isobutene and electrophilic substitution of the corresponding oligomeric cations on the aromatic ring of the hydroquinone unit can be considered as side reactions besides de-*tert*-

Table IV
De-*tert*-butylation and Trans-*tert*-butylation Reactions with Trifluoromethanesulfonic Acid and Lewis Acids[a]

no.[b]	conversion method[c]	catalyst	conversion,[d] %
13	de	CF_3SO_3H	90[e]
14	de	CF_3SO_3H	90[e]
17	trans	CF_3SO_3H	100
18	trans	$AlCl_3$ (1.1 equiv)	16
19	trans	$AlCl_3$ (4.1 equiv)	65
20	trans	$BF_3{\cdot}O(C_2H_5)_2$ (4.0 equiv)	0
21	trans	$ZnBr_2$ (4.0 equiv)	8

[a] Conversion determined by proton NMR spectroscopy. [b] Polymer 14 was obtained from the reaction of **1b**; the other polymers resulted from **1a**. [c] de = de-*tert*-butylation, trans = trans-*tert*-butylation. [d] Proton NMR spectroscopy in CH_3SO_3H and CF_3SO_3H. [e] Total aliphatics amount to approximately 10%.

butylation (eqs 4 and 5). A lower volatility (than isobutene) causes isobutene oligomers **3** to remain in the reaction mixture.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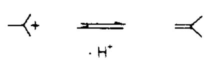
(5)

Considerably cleaner than de-*tert*-butylation is trans-*tert*-butylation with trifluoromethanesulfonic acid in the presence of toluene. This aromatic coreagent acts as an effective trap for *tert*-butyl cation formed according to eq 4. No isobutene gas formation according to eq 5 was observed. Toluene was applied in 10–20-fold molar excess. The toluene layer was analyzed by GC/MS. One peak (besides toluene) with $M^+ = 148$ corresponding to *tert*-butyltoluene was observed. ^1H NMR and IR spectroscopy reveal the presence of two isomers: *p*-*tert*-butyltoluene and *m*-*tert*-butyltoluene in a molar ratio of approximately 40/60. The amount of *tert*-butyltoluene formed after 20 h of reaction time is essentially quantitative. No residual alkyl groups can be detected in the resulting poly(ether ketone) by IR and NMR spectroscopy.

The Lewis acids $AlCl_3$, $ZnCl_2$, and boron trifluoride etherate were found to be markedly less effective for trans-*tert*-butylation of **1a** than trifluoromethanesulfonic acid (Table IV). Toluene was used as the *tert*-butyl group acceptor but proved to be a very poor solvent for the resulting polymer, as precipitation occurred within a few minutes. $AlCl_3$ resulted in 65% of *tert*-butyl loss when 4.1 equiv was applied. The conversion was determined from the intensity of the *tert*-butyl ^1H NMR signal at 1.1 ppm. $ZnCl_2$, boron trifluoride etherate, and smaller amounts of $AlCl_3$ (1.1 equiv) gave less than 20% trans-*tert*-butylation (Table IV).

Table V
Thermal Transitions and Decomposition Temperatures of Poly(aryl ether ketones) Determined by DSC and TGA

polymer	T_g, °C[a]	T_m, °C[a]	T_{dec}, °C[b]
PEEK	151[18]	338[19]	500
1a	175		450
1b	206	*c*	400
1c	154		*d*

[a] T_g, T_m = glass and melt transition temperatures by DSC, determined after cooling from 350 °C at a rate of 10 °C/min; heating rate = 10 °C/min. [b] Temperature for 2 wt % weight loss by TGA. [c] Weak endotherm at 305 °C in first heat run; no transition in second heat run. [d] Not determined.

Table VI
Thermal Properties of Poly(ether ketones), Copolymers 1d, and Polymers Obtained after De-*tert*-butylation and Trans-*tert*-butylation

no.[a]	polymer	method[b]	reaction time, h	T_g, °C[c]	T_m, °C[c]
00	PEEK	ha		151	338
11	**1d** (*a* = 0.53)	ha		162	192
11a	**1d** (a = 0.53)	de	24	155	306
12	**1d** (a = 0.28)	ha		154	284
13	**1a**	de	24	158	293
14	**1b**	de	24	154	308
15	**1a**	trans	1.5	165	
16	**1a**	trans	5	153	313
17	**1a**	trans	20	154	329

[a] Polymer 00 = PEEK reference sample; *a* = number of *tert*-butyl groups per repeat unit of the corresponding random copolymer **1a**. [b] de = polymer after de-*tert*-butylation; trans = polymer after trans-*tert*-butylation; ha = no dealkylation reaction applied. [c] T_g, T_m = glass transition and melt transition temperature, respectively, determined by DSC at a heating rate of 10 °C/min; T_g of highly crystalline polymers was determined in a heat run after cooling from melt at −10 °C/min.

Thermal Analyses. The influence of the number and nature of the substituents on melt and glass transition temperatures of the corresponding poly(ether ketone) was investigated by DSC (differential scanning calorimetry) studies (Table V). One *tert*-butyl substituent on the hydroquinone unit results in an increase of T_g by 24 °C from T_g = 151 °C (PEEK)[18] to T_g = 175 °C (**1a**), whereas a phenyl substituent causes only a minor increase in the glass transition temperature (T_g = 154 °C for **1c**). The glass transition of the poly(ether ketone) derived from 2,5-di-*tert*-butylhydroquinone (T_g = 206 °C for **1b**) is 55 °C higher than the T_g of PEEK. None of the substituted polymers of Table V shows a melt transition by DSC in the second heat cycle.

Changes in the melt transition provide a sensitive probe for structural defects of PEEK, such as residual amounts of alkyl groups. The peak temperature of the melt transition[19] is markedly reduced by substituents on the chain. Table VI lists melt and glass transition temperatures of random copolymers and dealkylated polymers. The melt temperature of polymer 13 of Table VI, a poly(ether ketone) obtained after de-*tert*-butylation of **1a**, is 293 °C, 35 °C lower than T_m of a commercial PEEK sample. No melt transition could be observed after cooling from the melt. The melt temperatures of dealkylated polymers derived from **1b** and **1d** (*a* = 0.53) (polymers 14 and 11a of Table VI) are 308 and 306 °C, respectively. In comparison, T_m = 192 and 284 °C for **1d** with *a* = 0.53 and 0.28 (polymers 11 and 12 of Table VI). The glass transition temperatures of the corresponding copolymers and dealkylated polymers are slightly higher than T_g of PEEK.

Polymers 15–17 of Table VI are samples of poly(ether ketones) prepared by trans-*tert*-butylation. These samples were obtained after reaction times of 1.5–20 h. With increasing reaction time, the melt transition temperature approaches the T_m of PEEK. The melt temperature of a polymer obtained after 20 h of reaction time is 329 °C (polymer 17 of Table VI).

Conclusions

The incorporation of *tert*-butyl and phenyl substituents results in soluble, amorphous poly(aryl ether ketones). In contrast to the synthesis of PEEK, reaction temperatures of 170 °C are sufficient to produce high molecular weight polymers derived from *tert*-butylhydroquinone. The suppressed crystallinity and the good solubility in organic solvents allow processing from the melt and from solution. The *tert*-butyl group is easily cleaved in a retro Friedel–Crafts alkylation reaction to produce semicrystalline PEEK. High conversions are achieved by trans-*tert*-butylation with trifluoromethanesulfonic acid in the presence of toluene as a *tert*-butyl group acceptor.

Experimental Section

Materials. *tert*-Butylhydroquinone and 2,5-di-*tert*-butylhydroquinone were recrystallized from toluene. Phenylhydroquinone was recrystallized from a 50/50 (v/v) mixture of toluene and *n*-hexane and 4,4′-difluorobenzophenone from a 70/30 (v/v) mixture of *n*-hexane and ethanol. Toluene was purified by distillation from calcium hydride. DMSO and sulfolane were distilled under reduced pressure. Trifluoromethanesulfonic acid, aluminum chloride, zinc chloride, and boron trifluoride etherate were used as obtained from the vendor (Aldrich).

Equipment. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were made on Du Pont 1090 and Du Pont 9900 thermal analyzers. ^{13}C CP/MAS spectra were recorded on a General Electric S-100 spectrometer (25.2 MHz), and solution NMR spectra were obtained on Nicolet NT-300 WB, General Electric QE 300, and IBM NR/80 spectrometers. GC/MS measurements were made with a Varian 3700 GC with a V.G. Micromass 16-F mass spectrometer. Thin-film mechanical properties were determined on 0.001-in. films at 25 °C by the use of an Instron Model TTD universal testing instrument. Inherent viscosities of polymer solutions were determined with an Übbelohde viscosimeter at concentrations of 0.3 g/dL at 25 °C.

Synthesis of Poly(oxy-(2-*tert*-butyl-1,4-phenylene)oxy-1,4-phenylenecarbonyl-1,4-phenylene) (1a). A three-necked 500-mL flask equipped with a mechanical stirrer, a Dean Stark trap, a condenser, and two adapters for Ar inlet and outlet was flushed with argon for 10 min and then charged with 4.98 g (30 mmol) of *tert*-butylhydroquinone, 6.54 g (30 mmol) of 4,4′-difluorobenzophenone, 150 mL of DMSO, and 30 mL of toluene. After 15 min of stirring at room temperature, 12.42 g (90 mmol) of anhydrous potassium carbonate was added, causing the reaction mixture to turn slightly yellow. The reaction mixture was stirred at 170 °C (oil bath), whereupon it turned brown. Adjusting the argon flow caused a toluene/water azeotrope to distill off at a rate of approximately 0.2 mL/min. After 3 h at 170 °C, the mixture was allowed to cool for 10 min. The reaction mixture (still hot) was poured into 700 mL of methanol to precipitate the white polymer. The polymer was washed with water (2 × 200 mL) and methanol (200 mL) and dried. The crude product was redissolved in 200 mL of chloroform, filtered to remove residual amounts of inorganic salts, reprecipitated with 700 mL of methanol, filtered, and dried at 0.2 Torr and 50 °C for 24 h: yield 9.39 g (91%); η_{inh} (viscosity) 1.50 dL/g (polymer 1 of Table I).

The other polymers of structure **1a–d** of Tables I and II were prepared under similar conditions. Reaction temperatures were applied as reported in the tables (50–98% yield).

Removal of the *tert*-Butyl Substituent by De-*tert*-butylation. Under argon, 0.5 g of *tert*-butyl-substituted polymer **1a** was dissolved in 10 mL of trifluoromethanesulfonic acid. The formation of isobutene gas could be observed. The dark solution was stirred at room temperature for 24 h. The mixture was poured into 100 mL of water to precipitate the white polymer. The polymer was filtered, washed successively with water and methanol, and dried under vacuum: yield 405 mg (97%) of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (polymer 13 of Table VI). The same procedure was applied for de-*tert*-butylation of the other polymers of Table VI.

Trans-*tert*-butylation by Lewis Acids. Under argon, 794 mg (5.9 mmol) of aluminum chloride was added to a solution of 0.5 g of poly(ether ketone) **1a** in 20 mL of toluene. A dark-yellow gummy precipitate formed within a few minutes. The mixture was stirred for 24 h at room temperature and finally poured into 100 mL of methanol. The polymer was filtered, washed with water and methanol, and dried under reduced pressure: yield 0.43 g of polymer 19 (Table IV).

The other reactions of **1a** with Lewis acids were performed in a similar fashion (Table IV).

Trans-*tert*-butylation by Trifluoromethanesulfonic Acid. Under argon, 8 mL of trifluoromethanesulfonic acid was added to a solution of 0.5 g of polymer **1a** in 20 mL of toluene. The mixture was stirred at room temperature. Two phases formed, and part of the polymer precipitated temporarily. Samples of 1 mL of the trifluoromethanesulfonic acid layer were precipitated with water after 1.5 and 5 h. The remaining mixture was poured into water after 20 h of reaction time. The polymer samples were washed with water and methanol, dried, and characterized by DSC (polymers 15–17 of Table 6).

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Registry No. **1a** (copolymer), 119799-53-0; **1a** (SRU), 119822-48-9; **1b** (copolymer), 119799-54-1; **1b** (SRU), 119824-53-2; **1c** (copolymer), 125431-09-6; **1c** (SRU), 118546-87-5; **1d** (copolymer), 103901-96-8; CF_3SO_3H, 1493-13-6; $AlCl_3$, 7446-70-0; BF_3, 7637-07-2; $O(C_2H_5)_2$, 60-29-7; $ZnCl_2$, 7646-85-7.