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Synthesis and characterization of aromatic poly(ether sulfone)s with pendent benzoyl groups

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Summary

The new sulfone-activated difluoro monomers with benzoyl substituents, bis(2-benzoyl-4-fluorophenyl) sulfone and 2-benzoyl-4,4'-difluorophenyl sulfone, were synthesized and converted to the corresponding poly(aryl ether sulfone)s with bisphenol A. While homopolymerization of the two monomers gave low molecular weight polymers because of cleavage of sulfone induced by the pendent benzoyl group at ortho position, copolymerization with his(4-fluorophenyl) sulfone comonomer produced moderately high molecular weight polymers. The inherent viscosities of the synthesized polymers were 0.20-0.38 dL/g and the glass transition temperatures of the polymers were 173-195°C. Thermogravimetric analysis showed that thermal stability of the polymers decreased as the polymers contain more benzoyl substituents.

Introduction

Aromatic poly(ether sulfone)s (PES) are high performance engineering thermoplastics with many characteristic properties such as excellent thermooxidative stability, high glass transition temperature and mechanical strength. The preparation of the PES can be largely divided in two parts, nucleophilic and electrophilic synthetic methods (1). Because of deterioration of the physical properties of PES obtained by electrophilic method, most of the commercialized PES (e.g. Udel$^{\text{TM}}$) are prepared by nucleophilic synthetic method *via* caustic process (2) or carbonate process (3,4).

Much research effort has been made on structural variations and their effect on physical properties of PES, but structural variations were mostly focused on main chain not on substituents. Recently, Clark, J. H. *et al* reported the crystalline PES with trifluoromethyl groups at ortho position of the sulfone group though most of PES are amorphous (5). This result showed that how far pendent functional groups affect the polymer properties.

In this paper, we describe the synthesis and polymerization of the new sulfone-activated difluoro monomers that have one or two benzoyl substituents. The synthesized polymers have similar structure to Udel$^{\text{TM}}$ except pendent benzoyl groups. The effects of pendent substituents on polymerization and physical properties are also described.

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Experimental

Materials and general measurement

2-Chloro-5-nitrobenzophenone (Aldrich; 99%), 4-aminothiophenol (Aldrich; 90%) and N-methylpyrrolidinone (NMP; anhydrous 99.5%) were used as received. Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$; J.T.Baker) was recrystallized from H_2O, and then dried *in vacuo*. Bisphenol A (**BPA**) and bis(4-fluorophenyl) sulfone (**FPS**) were recrystallized from toluene, and sublimed under reduced pressure. Other commercially available chemicals were used without further purification.

NMR spectra of synthesized compounds were recorded on Brucker Fourier Transform AC 200 (200MHz) or AM 300 (300MHz) spectrometers. Splitting patterns designated as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), m (multiplet) and br (broad). FTIR spectra of the compounds were obtained with Bomem Michelson series FTIR spectrophotometer using KBr pellet. High-resolution mass spectra (HRMS) of the monomers were obtained on a Jeol JMS-SX-102. Inherent viscosity of the synthesized polymers was measured in DMAc by Canon-Ubbelohde type viscometer at 30°C. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system. Melting point (m.p.) was determined by DSC.

Monomer synthesis

Bis(2-benzoyl-4-nitrophenyl) sulfide (**1**) A round-bottomed flask was charged with 2-chloro-5-nitrobenzophenone (32.7g, 125mmol), $Na_2S{\cdot}9H_2O$ (12.0g, 50mmol) and 120mL of NMP. The solution was stirred under N_2 at 90°C for 5h, cooled to room temperature, and poured into an EtOH/H_2O mixture (v/v=1/5). The yellow precipitate was filtered, washed repeatedly with water and dried *in vacuo*. (20.0g, 41.3mmol, 82.6% yield): m.p. 197-199°C. ^1H NMR ($CDCl_3$, ppm) 8.25 (s, 2H), 8.23 (dd, 2H), 7.70-7.41 (m, 12H).

Bis(4-amino-2-benzoylphenyl) sulfide (**2**) A slurry of bis(2-benzoyl-4-nitrophenyl) sulfide (20.0g, 41.3mmol), stannous chloride ($SnCl_2$) (57g, 169mmol) and 150mL of anhydrous EtOH was stirred while 110mL of concentrated HCl was added slowly. After addition of HCl was over, the mixture was refluxed for 8h. Excess EtOH was evaporated and the remaining solution was poured into 150mL ice-water mixture. The solution was basified with 10% NaOH solution and the pale yellow precipitate was filtered off, washed repeatedly with hot water and dried *in vacuo*. (15.4g, 36.3mmol, 87.9% yield): FTIR (KBr, cm^{-1}) 3410, 3320 ($-NH_2$), 1658 (C=O), 1623, 1600 (aromatic C=C), 1326, 1247, ^1H NMR ($CDCl_3$, ppm) 7.65-7.50 (m, *ortho* benzoyl, 4H), 7.47-7.42 (m, *para* benzoyl, 2H), 7.34-7.26 (m, *meta* benzoyl, 4H), 7.12, 7.07 (d, 2H), 6.67, 6.66, 6.62, 6.61 (dd, 1H), 6.57, 6.56 (d, 1H), 3.62 (br, $-NH_2$, 4H).

Bis(2-benzoyl-4-fluorophenyl) sulfide (**3**) A reaction kettle equipped with mechanical stirrer and an addition funnel was charged with bis(4-amino-2-benzoylphenyl) sulfide (15.4g, 36.3mmol), 18mL of concentrated HCl and 18mL of H_2O. The reaction mixture was cooled below 0°C with ice-salt bath. Sodium nitrite ($NaNO_2$) solution (5.13g/10mL H_2O) was added slowly to the cold reaction mixture over 2h. Then sodium fluoroborate ($NaBF_4$) solution (10.6g/21mL H_2O) was added rapidly, then the reaction mixture was stirred at 0°C for 30min. The dark brown precipitate was filtered, and washed with cold water, methanol and diethyl ether. After sufficient drying *in vacuo*, the diazofluoroborate salt was decomposed at 150°C to produce the difluoro compound **3**. (7.05g, 16.4mmol, 45.2% yield): ^1H NMR ($CDCl_3$, ppm) 7.64 (m, *ortho* benzoyl, 4H), 7.51 (d, *para* benzoyl, 2H), 7.40 (m, *meta* benzoyl, 4H), 7.31-7.26 (m, 1H), 7.14-6.95 (m, 2H).

Bis(2-benzoyl-4-fluorophenyl) sulfone (**4**) A 100mL round-bottomed flask was charged with his(2-benzoyl-4-fluorophenyl) sulfide (2.54g, 5.90mmol), chromium (VI) oxide (CrO_3) (2.04g, 20.4mmol), concentrated H_2SO_4 (1mL), H_2O (1mL) and 40mL of glacial acetic acid. The solution was refluxed for 12h, and poured into an ice-water mixture to precipitate a white solid that was filtered. The difluoro monomer was recrystallized from dichloromethane/*n*-hexane. (2.54g, 5.49mmol, 93.12% yield): m.p. 218-220°C. $_1$H NMR ($CDCl_3$, ppm) 8.09 (dd, 1H), 7.54, 7.51, 6.63, 6.60 (dd, 4H), 6.21(s, 2H), 5.34 (s, 2H), 5.30 (s, 2H). ^{13}C NMR ($CDCl_3$, ppm) 194.31 (C=O), 164.72 (d, J=259.5Hz), 143.11 (d, J=7.8Hz), 136.04, 134.46 (d, J=9.6Hz), 134.06, 130.25, 128.58, 117.01 (d, J=22.0Hz), 115.26 (d, J=24.0 Hz). HRMS (m/e): calc. for $C_{26}H_{16}SO_4F_2$, 462.0737; found, 462.0773.

2-Benzoyl-4-nitrophenyl-4’-aminophenyl sulfide(**5**) A 250mL round-bottomed flask was charged with 2-chloro-5-nitrobenzophenone (10.82g, 41.4mmol), 4-aminothiophenol (7.20g, 57.5mmol), potassium carbonate (K_2CO_3) (31.0g) and 60mL NMP. The solution was stirred at 100°C for 6h, diluted with dichloromethane, and extracted with brine repeatedly. The solution was evaporated, and purified by column chromatography with dichloromethane as an eluent to give yellow solid. (12.0g, 34.2mmol, 82.7% yield): ^{1}H NMR ($CDCl_3$, ppm) 8.23 (d, 1H), 8.02 (dd, 1H), 7.02 (d, 1H), 7.80 (dd, *ortho* benzoyl, 2H), 7.64 (m, *para* benzoyl, 1H), 7.47 (dd, *meta* benzoyl, 2H), 7.28, 7.24, 6.85, 6.81 (dd, 4H), 3.81 (s, $-NH_2$, 2H).

2-Benzoyl-4,4’-diaminophenyl sulfide (**6**) The procedure used in preparation of **2** was repeated with the following quantities of reagent: 2-benzoyl-4-nitrophenyl-4’-aminophenyl sulfide (5.91g, 16.9mmol), $SnCl_2$ (30.0g), 75mL of EtOH and 50mL concentrated HCl. (4.65g, 14.5mmol, 85.8%): m.p. 138-140°C. ^{1}H NMR ($CDCl_3$, ppm) 7.79 (dd, *ortho* benzoyl, 2H), 7.50 (m, *para* benzoyl, 1H), 7.36 (d, *meta* benzoyl, 2H), 7.13 (d, 2H), 7.06, 7.02, 6.53, 6.49 (dd, 4H), 6.67 (d, 1H), 6.63 (s, 1H), 3.42 (br, $-NH_2$, 4H). ^{13}C NMR ($CDCl_3$, ppm) 197.00 (C=O), 146.05, 145.27, 141.77, 137.26, 133.98, 133.60, 132.93, 129.94, 128.23, 124.02, 123.70, 117.35, 115.50, 114.57.

2-Benzoyl-4,4’-difluorophenyl sulfide (**7**) The procedure used in preparation of **3** was repeated with the following quantities of reagent: 2-benzoyl-4,4’-diaminophenyl sulfide (4.65g, 14.5mmol), 20mL of concentrated HCl, 20mL of H_2O, $NaNO_2$ (4.27g/10mL of H_2O) and $NaBF_4$ (4.27g/10mL of H_2O). (1.98g, 6.07mmol, 41.9%): ^{1}H NMR ($CDCl_3$, ppm) 7.78-7.73 (m, *ortho* benzoyl, 2H), 7.56-7.54 (m, *para* benzoyl, 1H), 7.48-7.44 (dd, *meta* benzoyl, 2H), 7.30-7.19 (m, 3H), 7.12 (d, 1H), 7.09 (d, 1H), 7.04-6.92 (t, 2H).

2-Benzoyl-4,4’-difluorophenyl sulfone (**8**) The procedure used in preparation of **4** was repeated with the following quantities of reagent: 2-benzoyl-4,4’-difluorophenyl sulfide (1.40g, 4.29mmol), sodium perborate tetrahydrate ($NaBO_3.4H_2O$) (3.83g) and 50mL of glacial acetic acid. The difluoro monomer was recrystallized from toluene/*n*-hexane. (1.30g, 3.63mmol, 84.6%): m.p. 137-139°C. ^{1}H NMR ($CDCl_3$, ppm) 8.15 (dd, 1H), 7.94-7.87 (m, 2H), 7.76 (dd, *ortho* benzoyl, 2H), 7.58 (m, *para* benzoyl, 1H), 7.47 (d, *meta* benzoyl, 2H) 7.31 (dd, 1H), 7.15 (t, 2H), 6.99 (dd, 1H). ^{13}C NMR ($CDCl_3$, ppm) 193.96 (C=O), 165.41 (d, J=256.3Hz), 164.60 (d, J=258.8Hz), 142.52 (d, J=7.5Hz), 137.00, 135.87, 135.47, 133.98, 133.07 (d, J=9.5Hz), 130.87 (d, J=7.3Hz), 130.03, 128.49, 128.58, 117.25 (d, J =21.3Hz), 116.23 (d, J=19.9Hz), 115.43 (d, J=26.4Hz). HRMS (m/e): calc. for $C_{19}H_{12}SO_3F_2$, 358.0475; found, 358.0400.

Polymerization

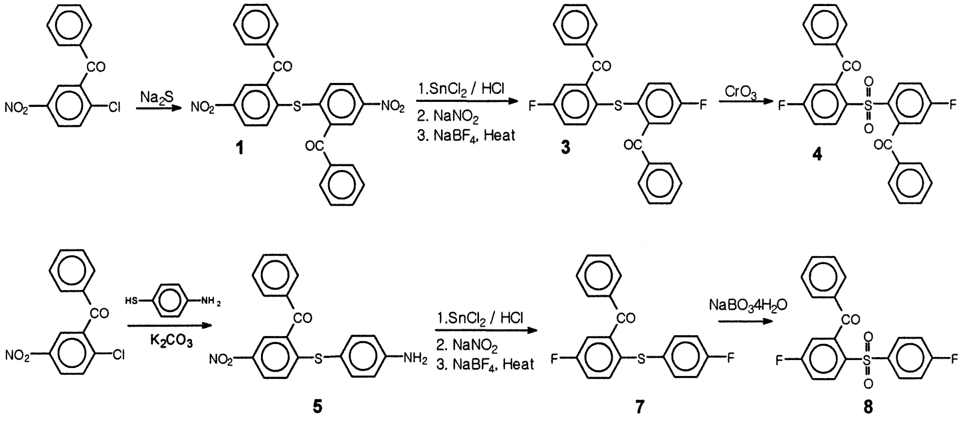
Difluoro monomers, **4** and **8**, as well as the mixture of **FPS** and **4** (or **8**) (mole ratio = 4:1) were polymerized with **BPA** to obtain four PES. All polymers were obtained with quantitative yield. A representative procedure is as follow (**PES1**): A three-neck flask equipped with a nitrogen inlet, mechanical stirrer and a Dean-Stark trap fitted with a condenser was charged with **4** (1.5114g, 3.2682mmol), **BPA** (0.7461g, 3.2682mmol), 3.57g (*ca* 4eq.) of K_2CO_3, and 8mL of NMP under N_2 flow. The reagents were carefully washed into the flask with 10mL of dry toluene. The mixture was heated to 140°C for 3h with periodical addition of dry toluene. The temperature was raised to 170'C, and the mixture was allowed to react for 24h. The polymer was precipitated into 300mL acetic acid/water (v/v=1/20), filtered, washed several times with water and methanol, and dried *in vacuo*. (2.1079g, 99.1% yield). The polymer was reprecipitated from DMAc/H_2O.

Results and discussion

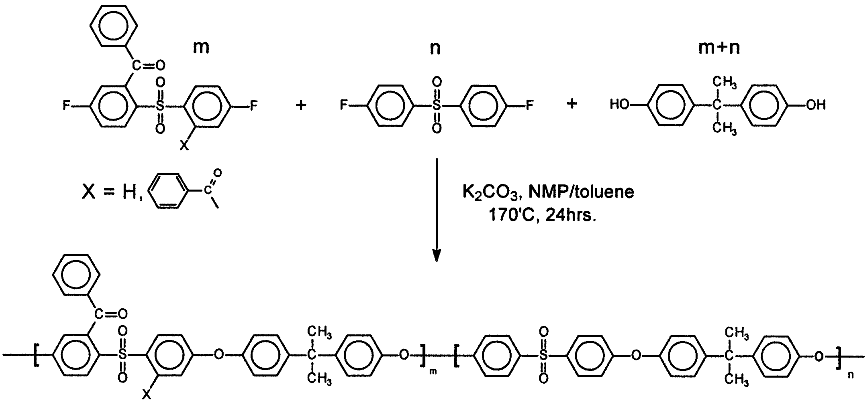
The sulfone-activated difluoro monomers with pendent benzoyl groups at *ortho* position of the sulfone group were prepared according to the reaction sequence of Scheme 1.

The difluoro monomer with two pendent benzoyl groups (**4**) was obtained from 2-chloro-5-nitrobenzophenone with several steps. 2-Chloro-5-nitrobenzophenone was reacted with sodium sulfide to provide **1** with high yield. The Cl group in 2-chloro-5-nitrobenzophenone was easily displaced to S^{2-} and PhS^- due to strong activation by benzoyl group at ortho position and nitro group at para position. Reduction of nitro groups produced the diamine compounds (**2**) which was converted to the difluoro compounds (**3**) through diazotation of the amine groups and subsequent decomposition of the salt. Finally, the difluoro monomer (**4**) was produced by oxidation of the sulfide groups. The sulfone-activated difluoro monomer with one benzoyl group (**8**) was also synthesized from 2-chloro-5-nitrobenzophenone and 4-aminothiophenol by using same synthetic sequence.

The synthesized monomers, **4** and **8**, were polymerized with **BPA** with K_2CO_3 as a base in NMP at 170°C for 24h to obtain **PES1** and **PES2**, respectively. Copolymerization with **FPS** was also conducted by using same method to obtain **PES1**$_{20}$ and **PES2**$_{20}$. The mole ratio of **FPS** and **4** (or **8**) was 4 to 1 (Scheme 2.). The synthesized polymers formed off-white precipitates on pouring of the reaction mixture into vigorously stirred water. In all cases, the polymers were obtained with almost quantitative yield.



Scheme 1.



Scheme 2.

The formation of PES was confirmed by spectroscopic data. FTIR spectra of the polymers showed characteristic absorption bands of ether linkage at 1230 cm^{-1}. ^{1}H NMR spectra showed broad peaks of the phenyl region and a peak of 1.6 ppm corresponding to six isopropylidene protons (Figure 1.). ^{1}H NMR spectra also showed that the copolymers have the composition according to the monomer ratio employed.

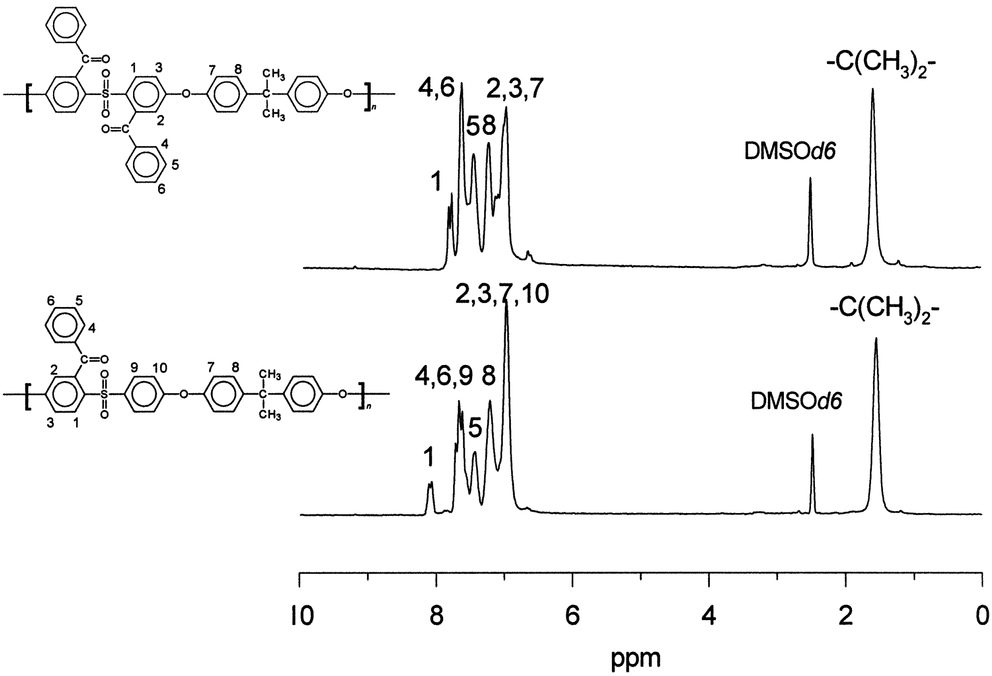


Figure 1. ^{1}H NMR Spectra of **PES1** (up) and **PES2** (bottom).

The homopolymers, **PES1** and **PES2**, having inherent viscosities of 0.20 and 0.21 dL/g, respectively, showed low degree of polymerization. It seems that small amount of sulfone groups activated by the ketone group of benzoyl substituent were displaced because sulfone group can act as a leaving group as well as a strong activating group in S_NAr reaction (6-8). Even if small amount of sulfone were cleaved, it is difficult to obtain a high molecular weight polymer in step-growth polymerization. The above explanation is further supported by copolymerization results. The copolymerization of the monomer **4** and **8** with **FPS** in which the number of pendent benzoyl substituents was less than that of the homopolymerization produced higher molecular weight polymers. The inherent viscosities of **PES1**$_{20}$ and **PES2**$_{20}$ are 0.28 and 0.38 dL/g, respectively.

All polymers are soluble in polar organic solvents (NMP, DMAc, DMF and DMSO) and THF at room temperature, but insoluble in acetone.

The thermal properties of the synthesized polymers were investigated with TGA and DSC. The TGA curves of the synthesized polymers are shown in Figure 2.5% weight loss temperatures of the polymers are 397-488°C in nitrogen. Apparently low molecular weight affected the thermal stability of the homopolymers. **PES1** has lower thermal stability than **PES2**, which may stem from steric hindrance and electron withdrawing effect of the two bulky benzoyl groups at ortho position of the sulfone groups resulting in weakening of the C-S-C bonds. However, the copolymers, **PES1**$_{20}$ and **PES2**$_{20}$, showed similar thermal stability to Udel™.

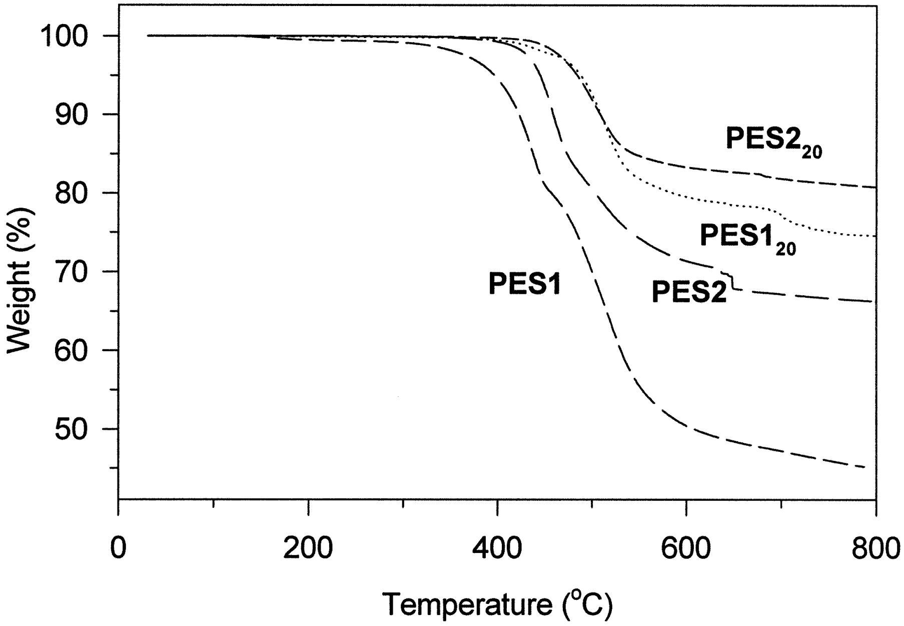


Figure 2. TGA curves of the synthesized PESs.

Table 1. Properties of the synthesized PES with benzoyl substituents

Polymer	**Composition**	η_{inh}[a] **(dL/g)**	T_g[b] **(°C)**	T_d[c] **in N_2 (°C)**
PES1	**4 + BPA**	0.20	173	397
PES2	**8 + BPA**	0.21	182	445
PES1$_{20}$	**4** (0.2) + **FPS** (0.8) + **BPA**	0.28	193	484
PES2$_{20}$	**8** (0.2) + **FPS** (0.8) + **BPA**	0.38	195	488

[a] Measured in DMAc at 30°C (0.5g/dL).
[b] Measured by DSC with a heating rate of 10°C/min under N_2 flow.
[c] 5% weight loss temp. measured by TGA with a heating rate of 10°C/min under N_2 flow.

The T_g values of the polymers are 173-195°C. Despite bulky benzoyl substituents, the homopolymers have lower T_g values than the copolymers that may be attributed to their low molecular weight. T_g values of the copolymers are similar to that of Udel™. The viscosity and thermal properties are summarized in Table 1.

In conclusion, aromatic poly(ether sulfone)s having similar structure to Udel™ except pendent benzoyl groups were synthesized from new difluoro monomers by using carbonate process. The number of pendent functional groups at *ortho* position of the sulfone groups was adversely effected polymerization of the monomers and thermal stability of the polymers.

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