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# Synthesis of polyfluorinated aromatic polyesters

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

#### Abstract

Perfluoroalkylation of phenolic compounds by  $R_FI/Na_2S_2O_4$  reagent system was used to synthesize fluorinated monomers useful in polycondensation reactions. A series of fluorinated aromatic polyesters was prepared from polyfluoroalkylated hydroquinone and terephthalic acid derivatives and some properties of these polymers were discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Fluorine-containing hydroquinone; Fluorinated aromatic polyester; Polycondensation

# 1. Introduction

In our systematic study on the application of  $R_FI/Na_2S_2O_4$  reagent system in organic synthesis [1], we were interested in the synthesis of fluoroalkylated phenolic compounds to be used as F-containing monomers in polycondensation reactions. It is well known that phenols can be readily perfluoroalkylated at *o*-and *p*-positions in good yields [2],



However, these *o*- and *p*-fluoroalkylated phenols are not stable under basic conditions. They lose  $\alpha$ -F atoms readily to form the corresponding  $\alpha$ -keto derivatives [3],



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In order to overcome these difficulties, we have devised the following structures:



In these ways we are able to protect the  $R_F$  group from the attack by base, i.e., by putting a short chain of several methylene groups between the phenolic OH or between the aromatic nucleus and the  $R_F$  group. For example, we perfluoroalkylated *p*-hydroxybenzoic acid ester under mild conditions to form the fluoroalkylated product, **1**, which was then treated with bromohydrin and NaH to form the corresponding *p*-( $\beta$ -hydroxyethoxy) derivatives, **2** [4],



As the subject of this paper, we also studied the synthesis of the F-containing phenols, in which a short chain of several methylene groups were placed between the aromatic nucleus and the  $R_F$  group.

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### 2. Results and discussion

We chose hydroquinone monomethyl ether as the starting material for the following sequence of reactions:



Then we studied the synthesis of polyesters from these fluoroalkylhydroquinones by reaction with terephthalic acid derivatives. First, we tried the method developed by Ogata et al. [5] because the reaction conditions are very mild, i.e., using hexachloroethane and PPh<sub>3</sub> in pyridine to effect the esterification.

While the reaction of benzoic acid and fluorinated monomethyl ether proceeded well, the results with terephthalic acid were not as good, especially in the polycondensation reaction between terephthalic acid and the hydroquinones.





Only low m.w. telomers were formed and in low yields as shown in the following equation:



Finally, by applying the classical Schotten–Baumann reaction, i.e., by reacting the hydroquinones with terephthaloyl chloride in the presence of pyridine, we succeeded in making a series of polycondensation products as well as copolycondensation products using a mixture of fluorinated and nonfluorinated hydroquinones. The polycondensation product of hydroquinone and terephthaloyl chloride was also prepared under similar condition for comparison in the preliminary study on the properties of these products.





These polycondensation reactions seems to give good yields of polymeric products with similar m.w. as shown by the intrinsic viscosity study of their solutions in conc.  $H_2SO_4$ .

Preliminary studies on the physicochemical properties of these F-containing polymers indicated that, in comparison with the F-free polyesters:

- 1. None of the F-containing polyesters showed a definite m.p. and all of them can be casted into films at about  $70 120^{\circ}$ C lower than that of the F-free polyester.
- 2. All of them showed better thermal stability.
- 3. The films of these F-containing polyesters showed improved water repellency.
- 4. The side chain of these F-containing polymers appeared to be a weak point during thermal decomposition.

Further studies on the properties of these polymers are in progress.

#### 3. Experimental

All melting points and boiling points were uncorrected. IR spectra were recorded with Schimadzu IR-440 Spectrometer, liquid film or KBr pellets for solids were used. <sup>1</sup>H NMR spectra were recorded on Varian EM-360A (60 MHz), FX-90Q (90 MHz) or Bruker AM 300 (300 MHz) spectrometers using TMS as internal standard. <sup>19</sup>F NMR spectra were recorded on Varian EM-360L (56.4 MHz) spectrometer and CF<sub>3</sub>CO<sub>2</sub>H was used as external standard,  $\delta_{CF_3CO_2H} = 0.00$ , positive toward high field. MS were measured on Finnegan GC-MS 4021 spectrometer. Silica gel H (size 10–40 µ) was used for TLC and column chromatography.

Solvents and reagents: CP or AR grade reagents were used. Pyridine was dried over CaH<sub>2</sub> and redistilled. Hydroquinone, hexachloroethane, triphenylphosphine and benzoic acid were purified by recrystallization from 95% ethanol. Terephthaloyl chloride was recrystallized from hot hexane. CHCl<sub>2</sub>CHCl<sub>2</sub> was treated with hot conc. H<sub>2</sub>SO<sub>4</sub> and then washed with conc. H<sub>2</sub>SO<sub>4</sub> and water successively, dried over anhydrous K<sub>2</sub>CO<sub>3</sub> overnight and redistilled, collecting the fraction boiling 145–146°C. *N*methylaniline was redistilled.

The conc.  $H_2SO_4$  solutions of these polymeric materials (250 mg/25 ml) were used for viscosity measurement employing an Ubbelohde viscometer in a thermostat at 30°C. Film casting was performed between two pieces of Al foil under a pressure of 40 KPa for 2 min at the temperature specified (200–300°C). The contact angles ( $\theta$ ) were

obtained using films thus obtained and a home-made contact angle gonimer.

# 3.1. Compound 3 and 4 [6]

Hydroquinone monomethyl monoallyl ether, **3**, was prepared from the reaction of hydroquinone monomethyl ether with allyl bromide in acetone in the presence of  $K_2CO_3$ under reflux in 96% yield. The Claisen rearrangement of the allyl ether to give 4-methoxy-2-allyl phenol (**4**) was carried out thermally (210°C) under a N<sub>2</sub> atmosphere. The crude product was distilled under reduced pressure to give **4** with an yield of 93%, b.p. 95°C/0.6 torr.

# 3.1.1. 2(3'-Perfluoroalkyl-2'-iodopropyl)-4-methoxyphenol (5a–5e)

*Typical procedure*: A mixture of 21 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (0.12 mol) and 11 g of NaHCO<sub>3</sub> (0.12 mol) was added to a solution of 15 ml of 4 (0.1 mol), 16 ml of  $Cl(CF_2)_2I$  in 80 ml of CH<sub>3</sub>CN and 32 ml of H<sub>2</sub>O with stirring. The whole mixture was stirred at room temperature and the progress of the reaction was monitored with <sup>19</sup>F NMR until the complete consumption of R<sub>F</sub>I. Then 200 ml of water was added and the whole mixture was extracted with ether (3 × 50 ml), the organic layer was washed with water and saturated NaCl solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight. The solid residue obtained after removal of solvent by distillation was crystallized from petroleum ether–ethyl acetate (15:1) to give 22 g of crystalline product, **5a**.

**5a**: Yield 63% m.p. 85.6–86.5°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}(\rm ppm)$ : 2.85(2H, d-d), 3.20(2H, m), 3.65(3H, s), 4.15(1H, s, OH), 4.63(1H, m, CHI), 6.60(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}(\rm ppm)$ : -6.20(2F, s, CF<sub>2</sub>Cl), 35.3(2F, t, CH<sub>2</sub>CF<sub>2</sub>); IR(cm<sup>-1</sup>): 3400(OH), 2920(CH), 1515(ArH), 1200(CF), 1100(CO); UV(nm): 298.0(0.230), 204(0.924); Anal.(%) C<sub>12</sub>H<sub>12</sub>CIF<sub>4</sub>IO<sub>2</sub>, Calc.: C, 33.79; H, 2.84; Cl, 8.31; F, 17.81; I, 29.75; Found: C, 33.92; H, 2.60; Cl, 8.37; F, 18.03; I, 29.97.

**5b**: Yield 70%. m.p. 83.0–83.5°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}(\rm ppm)$ : 2.80(2H, d-d), 3.28(2H, m), 3.79(3H, s), 3.93(1H, s, OH), 4.70(1H, m, CHI), 6.71(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}(\rm ppm)$ : -9.98(2F, t, CF<sub>2</sub>Cl), 35.8(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.6(2F, s), 45.6(2F, s); IR(cm<sup>-1</sup>): 3400(OH), 2920(CH), 1515(ArH), 1195(CF), 1100(CO); Anal.(%) C<sub>14</sub>H<sub>12</sub>CIF<sub>8</sub>IO<sub>2</sub>, Calc.: C, 31.87; H, 2.29; F, 28.81; Found: C, 31.41; H, 1.85; F, 28.90.

**5c**: Yield 75%. m.p. 82.0–83.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 2.81(2H, d-d), 3.06–3.20(2H, m), 3.80(3H, s), 4.70(1H, m, CHI), 6.72(3H, S); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): -9.60(2F, t, CF<sub>2</sub>Cl), 35.6(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.6(2F, s), 44.0(4F, s), 45.6(2F, s); IR(cm<sup>-1</sup>): 3400(OH), 2920(CH), 1515(ArH), 1200(CF), 1100(CO); Anal.(%) C<sub>16</sub>H<sub>12</sub>ClF<sub>12</sub>IO<sub>2</sub>, Calc.: C, 30.67; H, 1.93; Cl, 5.66; F, 36.38; Found: C, 30.73; H, 1.85; Cl, 5.41; F, 36.39.

**5d**: Yield 66%. m.p. 73.0–74.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 2.80(2H, d-d), 3.19–3.32(2H, m), 3.79(3H, s),

 $\begin{array}{l} 4.69(1H,\,m,\,CHI),\,6.72(3H,\,s);\,^{19}F\,\,NMR(CDCl_3),\,\delta_F(ppm):\\ 3.60(3F,\,s,\,CF_3),\,36.0(2F,\,t,\,CH_2CF_2),\,45.3(2F,\,s),\,46.0(4F,\,s),\\ s),\,\,49.0(2F,\,\,s);\,\,IR(cm^{-1}):\,\,3400(OH),\,\,2920(CH),\\ 1515(ArH),\,1200(CF),\,1100(CO);\,Anal.(\%)\,C_{16}H_{12}F_{13}IO_2,\\ Calc.:\,C,\,31.50;\,H,\,1.98;\,F,\,40.49;\,I,\,20.80;\,Found:\,C,\,31.55;\\ H,\,1.89;\,F,\,40.45;\,I,\,20.44. \end{array}$ 

**5e**: Crude yield: quantitative. m.p.  $81.0-82.5^{\circ}$ C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{H}$ (ppm): 2.82(2H, d-d), 3.15–3.41(2H, m), 3.81(3H, s), 4.70(1H, m, CHI), 6.73(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{F}$ (ppm): 3.20(3F, s, CF<sub>3</sub>), 35.7(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 44.2(10F, s), 48.8(2F, s); IR(cm<sup>-1</sup>): 3400(OH), 2920(CH), 1515(ArH), 1200(CF), 1100(CO); Anal.(%) C<sub>18</sub>H<sub>12</sub>F<sub>17</sub>IO<sub>2</sub>, Calc.: C, 30.44; H, 1.70; F, 45.49; I, 17.87; Found: C, 30.36; H, 1.51; F, 45.64; I, 15.66.

# 3.2. Compounds 6a-6e

There are two typical procedures:

*Method A*. A solution of 8.4 g **5a** (20 mmol) in 50 ml of ethanol was treated with 8 g (ca. 50 mmol) of activated zinc and a catalytic amount of acetic acid. The mixture was refluxed for 1.5 h. TLC monitoring indicated that the reaction was complete. The excess zinc was removed by filtration and the residue obtained after the removal of ethanol by distillation was treated with 50 ml of ether, the ethereal solution was washed with saturated NaCl solution until neutral and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight. The crude product was crystallized from petroleum ether–ethyl acetate (15:1) to give colorless platelets of **6a**, 4.2 g (yield 70%).

Method B. A mixture of 16.15 g zinc (ca. 0.22 mol) and 80 ml of 10% aqueous HCl was stirred for 2 min, the acidic solution was decanted and the residual zinc was washed successively with  $2 \times 80$  ml acetone, 80 ml ether and activated by boiling with a mixture 0.538 g AgOAc in 80 ml HOAc for 1 min. The recovered zinc was washed again with 40 ml HOAc,  $4 \times 80$  ml ether and 80 ml methanol successively. The activated zinc thus obtained was allowed to react with 19 g of 5a (44.5 mmol) in 40 ml methanol. The reaction was complete after stirring for 15 min at room temperature (TLC monitoring). The unreacted zinc was filtered off and the residue obtained after removal of solvent from the filtrate by distillation was dissolved in 250 ml ether. The ethereal solution was washed successively with 10% aqueous HCl solution, saturated NaCl solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was crystallized from petroleum ether-ethyl acetate (15:1) to give 11.5 g of **6a** as colorless platelets, yield 86%.

**6a**: m.p. 95.0–95.5°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.73–2.26(4H, m), 2.76(2H, t), 3.76(3H, s), 4.14–4.64(1H, broad, s), 6.68(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): -6.5(2F, s, CF<sub>2</sub>Cl), 36.3(2F, t, CH<sub>2</sub>CF<sub>2</sub>); IR(cm<sup>-1</sup>): 3320(OH), 2900(CH), 1500(ArH), 1200(CF), 1085(CO); Anal.(%) C<sub>12</sub>H<sub>13</sub>ClF<sub>4</sub>O<sub>2</sub>, Calc.: C, 47.94; H, 4.36; Cl, 11.29; F, 25.26; Found: C, 47.92; H, 4.35; Cl, 11.48; F, 25.53.

**6b**: Yield 68% (Method A), m.p. 71.5–72.5°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.92–2.06(4H, m), 2.68(2H, t), 3.77(3H, s), 4.30(1H, s), 6.66(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}(\rm ppm)$ : -9.5(2F, t, CF<sub>2</sub>Cl), 36.8(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.5(2F, 45.5(2F, s); IR(cm<sup>-1</sup>): 3350(OH), 2900(CH), s), 1510(ArH), 1200(CF), 1085(CO); Anal.(%) C<sub>14</sub>H<sub>13</sub>ClF<sub>8</sub>O<sub>2</sub>, Calc.: C, 41.97; H, 3.27; F, 37.93; Found: C, 41.81; H, 2.99; F, 38.32.6c: Yield 60% (Method A), m.p. 85.0-86.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.93–2.45(4H, m), 2.68(2H, t), 3.73(3H, s), 3.9(1H, s), 6.60(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}(\rm ppm)$ : -9.3(2F, t, CF<sub>2</sub>Cl), 36.3(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.6(2F, s), 44.1(4F, s), 46.0(2F, s); IR(cm<sup>-1</sup>): 3350(OH), 2900(CH), 1510(ArH), 1200(CF), 1085(CO); Anal.(%) C<sub>16</sub>H<sub>13</sub>ClF<sub>12</sub>O<sub>2</sub>, Calc.: C, 38.38; H, 2.62; F, 45.53; Found: C, 38.37; H, 2.38; F, 45.38.

**6d**: Yield 59% (Method A), m.p. 72.0–73.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 2.00(4H, m), 2.67(2H, t), 3.73(4H, s), 6.59(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): 3.6(3F, t, CF<sub>3</sub>), 36.9(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 44.7–46.0(6F, s), 49.0(2F, s); IR(cm<sup>-1</sup>): 3380(OH), 2900(CH), 1500(ArH), 1200(CF), 1075(CO); Anal.(%) C<sub>16</sub>H<sub>13</sub>F<sub>13</sub>O<sub>2</sub>, Calc.: C, 39.68; H, 2.71; F, 51.00; Found: C, 39.38; H, 2.56; F, 51.47. **6e**: Yield 85% (Method A), m.p. 85.0–86.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.88–2.21(4H, m), 2.66(2H, t), 3.77(3H, s), 3.89(1H, s), 6.67(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): 3.3(3F, s, CF<sub>3</sub>), 36.6(2F, s, CH<sub>2</sub>CF<sub>2</sub>), 45.3(10F, s), 48.5(2F, s); IR(cm<sup>-1</sup>): 3380(OH), 2900(CH), 1500(ArH), 1200(CF), 1040(CO); Anal.(%) C<sub>18</sub>H<sub>13</sub>F<sub>17</sub>O<sub>2</sub>, Calc.: C, 37.00; H, 2.24; F, 55.28; Found: C, 36.49; H, 1.95; F, 55.76.

#### 3.3. Monomer 7*a*-7*e*

Typical procedure: A solution of 30 ml BBr<sub>3</sub> in 20 ml of methylene chloride was added dropwise to a solution of 4.4 g 6a (14.6 mmol) in 30 ml of methylene chloride with stirring under N<sub>2</sub> atmosphere. The mixture was stirred for 3 h at room temperature. TLC monitoring indicated that the reaction was complete. Methanol (30 ml) was then added dropwise to the reaction mixture with stirring. 50 ml of water was added and the whole mixture was neutralized with Na<sub>2</sub>CO<sub>3</sub> solution, and then extracted with ether  $(2 \times 100 \text{ ml})$ . The organic layer was washed with saturated NaCl solution and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue obtained after removal of solvent was chromatographed and eluted with petroleum ether-ethyl acetate (12:1 to 4:1) to obtain 4.15 g of the product 7a (yield 98%) as white solid. m.p. 61.0–62.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.89-2.13(4H, m), 2.63(2H, t), 4.56(2H, OH), 6.60(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): -6.6(2F, s, CF<sub>2</sub>Cl), 36.3(2F, t, CH<sub>2</sub>CF<sub>2</sub>); IR(cm<sup>-1</sup>): 3300(OH), 2900(CH), 1500(ArH), 1200(CF); MS(m/z):  $286(M^+),$ 123; Anal.(%) C<sub>11</sub>H<sub>11</sub>ClF<sub>4</sub>O<sub>2</sub>, Calc.: C, 46.09; H, 3.87; Cl, 12.37; F, 26.51; Found: C, 46.04; H, 3.83; Cl, 12.35; F, 26.55.

**7b**: Yield 91%, m.p. 65.0–66.5°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.90–2.20(4H, m), 2.70(2H, m), 4.70(2H, OH), 6.63(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): -9.6(2F, s,

CF<sub>2</sub>Cl), 36.6(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.3(2F, s), 45.2(2F, s); IR(cm<sup>-1</sup>): 3350(OH), 2900(CH), 1450(ArH), 1200(CF); MS(m/z): 386(M<sup>+</sup>), 123; Anal.(%) C<sub>13</sub>H<sub>11</sub>ClF<sub>8</sub>O<sub>2</sub>, Calc.: C, 40.38; H, 2.87; F, 39.31; Found: C, 40.43; H, 2.84; F, 40.00.

**7c**: Yield 91%, m.p. 97.5–98.0°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.92–2.15(4H, m), 2.76(2H, m), 4.70(2H, OH), 6.62(3H, s); <sup>19</sup>F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): –9.9(2F, t, CF<sub>2</sub>Cl), 36.2(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 42.2–43.5(6F, m), 45.6(2F, s); IR(cm<sup>-1</sup>): 3280(OH), 2900(CH), 1460(ArH), 1200(CF); MS(m/z): 486(M<sup>+</sup>), 123; Anal.(%) C<sub>15</sub>H<sub>11</sub>ClF<sub>12</sub>O<sub>2</sub>, Calc.: C, 37.02; H, 2.28; F, 46.84; Found: C, 36.91; H, 1.95; F, 46.75.

**7d**: Yield 90%, m.p. 95.5–96.5°C. <sup>1</sup>H NMR[(CD<sub>3</sub>)<sub>2</sub>CO],  $\delta_{\rm H}$ (ppm): 1.52(4H, m), 2.15(2H, m), 2.82(2H, OH), 5.96– 6.26(3H, m); <sup>19</sup>F NMR[(CD<sub>3</sub>)<sub>2</sub>CO],  $\delta_{\rm F}$ (ppm): 4.6(3F, t, CF<sub>3</sub>), 37.5(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 45.5–46.5(6F, m), 49.6(2F, s); IR(cm<sup>-1</sup>): 3250(OH), 2900(CH), 1460(ArH), 1200(CF); MS(m/z): 440, 268, 123; Anal.(%) C<sub>15</sub>H<sub>11</sub>F<sub>13</sub>O<sub>2</sub>, Calc.: C, 38.31; H, 2.36; F, 52.52; Found: C, 38.20; H, 2.26; F, 52.98.

**7e**: Yield 85%, m.p. 117.5–118.0°C. <sup>1</sup>H NMR[(CD<sub>3</sub>)<sub>2</sub>CO], δ<sub>H</sub>(ppm): 1.54(4H, m), 2.16(2H, m), 2.76(2H, OH), 6.13(3H, m); <sup>19</sup>F NMR[(CD<sub>3</sub>)<sub>2</sub>CO], δ<sub>F</sub>(ppm): 4.8(3F, t, CF<sub>3</sub>), 37.8(2F, t, CH<sub>2</sub>CF<sub>2</sub>), 45.5 (10F, m), 49.8(2F, s); IR(cm<sup>-1</sup>): 3300(OH), 2900(CH), 1460(ArH), 1200(CF); Anal.(%) C<sub>17</sub>H<sub>11</sub>F<sub>17</sub>O<sub>2</sub>, Calc.: C, 35.81; H, 1.79; F, 56.64; Found: C, 35.65; H, 1.80; F, 56.82.

# 3.4. Polymerization study

#### 3.4.1. Compound 8

Hexachloroethane (750 mg, 3 mmol) was added to a solution of 122 mg of benzoic acid (1 mmol), 300 mg of **6a** (1 mmol) and 630 mg of triphenylphosphine (2.4 mmol) in 5 ml of pyridine at room temperature with stirring. An exothermic reaction started within 1 min and the whole mixture turned turbid gradually. The stirring was continued for 50 h, and the resulting mixture was treated with water and extracted with ether. The ethereal solution was washed with 1 N HCl, saturated NaCl solution successively, and dried over anhydrous Na2SO4. The crude product was chromatographed and eluted with petroleum ether-ethyl acetate (10:1) to give 280 mg of 8 as a colorless liquid (yield 77%). <sup>1</sup>H NMR(CDCl<sub>3</sub>),  $\delta_{\rm H}$ (ppm): 1.39–1.51(4H, m), 2.10(2H, t), 3.25(3H, s), 6.31(2H, m), 7.02(4H, m), 7.69(2H, d);  ${}^{19}$ F NMR(CDCl<sub>3</sub>),  $\delta_{\rm F}$ (ppm): -6.30(2F, s), 36.7(2F, t).

# 3.5. Polycondensation of terephthalic acid with hydroquinone

A solution of 220 mg of hydroquinone (2 mmol) and 1.5 g of  $C_2Cl_6$  in 5 ml of pyridine was added dropwise to a solution of 330 mg of terephthalic acid (2 mmol) and 1.26 g of triphenylphosphine (4.8 mmol) in 5 ml pyridine at

room temperature with stirring. The mixture soon turned turbid and the stirring was continued for 5 h. The resulting mixture was poured into 200 ml methanol and the precipitate was filtered and washed with several portions of methanol and water successively, and then dried to give 144 mg of crude solid product. GPC analysis indicated that the part soluble in THF was a mixture of oligomers, **9**, with an average m.w. of 600.

## 3.6. Polymers 10a-10e

Typical procedure: A mixture of 670 mg of terephthaloyl chloride (3.3 mmol), 860 mg 7a (3 mmol) and 15 ml CHCl<sub>2</sub>CHCl<sub>2</sub> was stirred under a N<sub>2</sub> atmosphere in a three necked round bottom bottle to give a clear solution. To the solution 2 ml of pyridine was added dropwise and the stirring was continued for 24 h, and then diluted with 15 ml of CHCl<sub>2</sub>CHCl<sub>2</sub>. The whole mixture was added to 300 ml of methanol with stirring. The precipitate was collected by filtration and washed twice with methanol. The crude product was triturated with aqueous methanol 2-3 times, filtered and the solid was washed with methanol twice. The product was dried to constant weight under reduced pressure to give white polymeric product 10a, 1.16 g (93% yield). Anal.(%), (C<sub>19</sub>H<sub>13</sub>ClF<sub>4</sub>O<sub>4</sub>)<sub>n</sub>, Calc.: C, 54.76; H, 3.14; F, 18.23; Found: C, 54.88; H, 2.86; F, 17.94.  $\eta$ (dl/g), 0.3601;  $\theta$ (°), 39.83.

**10b**: Yield 97%. Anal.(%),  $(C_{21}H_{13}ClF_8O_4)_n$ , Calc.: C, 48.81; H, 2.54; F, 29.41; Found: C, 49.36; H, 2.27; F, 29.47.  $\eta(dl/g)$ , 0.4696;  $\theta(^{\circ})$ , 43.13.

**10c**: Yield 84%. Anal.(%),  $(C_{23}H_{13}ClF_{12}O_4)_n$ , Calc.: C, 44.79; H, 2.12; F, 36.96; Found: C, 45.04; H, 1.93; F, 34.70.  $\eta(dl/g)$ , 0.4632;  $\theta(^{\circ})$ , 50.99.

**10d**: Yield 88%. Anal.(%),  $(C_{23}H_{13}F_{13}O_4)_n$ , Calc.: C, 46.02; H, 2.18; F, 41.14; Found: C, 45.93; H, 1.88; F, 40.56.  $\eta$ (dl/g), 0.3909;  $\theta$ (°), 56.86.

**10e**: Yield 76%. Anal.(%),  $(C_{25}H_{13}F_{17}O_4)_n$ , Calc.: C, 42.88; H, 1.87; F, 46.12; Found: C, 42.86; H, 1.78; F, 45.97.  $\eta$ (dl/g), 0.3735;  $\theta$ (°), 60.57.

#### 3.7. Copolycondensation

*Typical Procedure*: Copolymer **11a** was prepared from a warm solution of 670 mg of terephthaloyl chloride (3.3 mmol), 430 mg of **7a** (1.5 mmol) and 165 mg of hydro-

quinone (1.5 mmol) in 15 ml of CHCl<sub>2</sub>CHCl<sub>2</sub> by treating with 2 ml of pyridine and stirring the resulting mixture for 24 h at room temperature. Workup in the usual way gave copolymer **11a**, 1.03 g (yield 80%). Anal.(%),  $(C_{33}H_{21}ClF_4O_8)_n$ , Calc.: C, 60.33; H, 3.22; F, 11.57; Found: C, 60.03; H, 2.91; F, 9.55.  $\eta$ (dl/g), 0.4631;  $\theta$ (°), 41.88.

**11b**: Yield 90%. Anal.(%),  $(C_{35}H_{21}ClF_8O_8)_n$ , Calc.: C, 55.53; H, 2.80; F, 20.08; Found: C, 53.94; H, 2.62; F, 20.14.  $\eta(dl/g)$ , 0.4820;  $\theta(^{\circ})$ , 54.41.

**11c**: Yield 87%. Anal.(%),  $(C_{37}H_{21}ClF_{12}O_8)_n$ , Calc.: C, 51.86; H, 2.47; F, 26.60; Found: C, 52.52; H, 2.43; F, 23.48.  $\eta(dl/g)$ , 0.4632;  $\theta(^{\circ})$ , 51.42.

**11d**: Yield 76%. Anal.(%),  $(C_{37}H_{21}F_{13}O_8)_n$ , Calc.: C, 52.87; H, 2.52; F, 29.38; Found: C, 52.55; H, 2.58; F, 29.17.  $\eta$ (dl/g), 0.3909;  $\theta$ (°), 53.34.

**11e**: Yield 75%. Anal.(%),  $(C_{39}H_{21}F_{17}O_8)_n$ , Calc.: F, 34.34; Found: F, 33.91.  $\eta$ (dl/g), 0.3735;  $\theta$ (°), 54.22.

**12a**: Yield 78%. Anal.(%),  $(C_{47}H_{29}ClF_4O_{12})_n$ , Calc.: F, 8.47; Found: F, 7.99.  $\eta$ (dl/g), 0.4583;  $\theta$ (°), 32.15.

**12c**: Yield 95%. Anal.(%),  $(C_{51}H_{29}ClF_{12}O_{12})_n$ , Calc.: F, 20.78; Found: F, 19.84.  $\eta(dl/g)$ , 0.4581;  $\theta(^{\circ})$ , 43.12.**12d**: Yield 93%. Anal.(%),  $(C_{51}H_{29}F_{13}O_{12})_n$ , Calc.: F, 22.85; Found: F, 21.44.  $\eta(dl/g)$ , 0.3836;  $\theta(^{\circ})$ , 54.66.**12e**: Yield 92%. Anal.(%),  $(C_{53}H_{29}F_{17}O_{12})_n$ , Calc.: F, 27.35; Found: F, 27.10.  $\eta(dl/g)$ , 0.3663;  $\theta(^{\circ})$ , 51.30.

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#### References

- F.-H. Wu, W.-Y. Huang, Chin. J. Org. Chem. (Youji Huaxue) 17 (1997) 106.
- [2] W.-Y. Huang, W.-P. Ma, W. Wang, Chin. J. Chem. (1990) 175.
- [3] W.-Y. Huang, W.-P. Ma, J.-H. Chen, B. Zhan, Chin. J. Org. Chem. (Youji Huaxue) 10 (1990) 214.
- [4] H.-B. Yu, R.-Q. Li, W.-Y. Huang, Chin. J. Chem. 5 (1997) 475.
- [5] N. Ogata, K. Sanin, H. Tanaka, S. Yasuda, Polym. J. 13 (1981) 989.
- [6] W.N. White, D. Gwynn, R. Schlitt, C. Girard, W. Fife, J. Am. Chem. Soc. 80 (1958) 3271.