A Unique Stepped Multifunctionality of Perfluorinated Aryl Compound and Its Versatile Use in Synthesizing Grafted Polymers with Controlled Structures and Topologies

ZHENHUA ZHAO, XIAOHUA MA, AIXIN ZHANG, NAIHENG SONG

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT: A unique stepped multifunctionality of perfluorinated aryl compound for the first time was studied by using model reactions between 2,5-dipentafluorophenyl-1,3,4-oxadiazole (FPOx) and mono functional *p*-cresol at different reaction conditions. Four distinctively different levels of reactivity were discovered for the para and ortho C—F of FPOx, which could be easily triggered by the reaction temperature in the range of r.t. to 160 °C. C—F of all levels of reactivity could react quantitatively with nucleophiles (such as phenoxide); and by controlling the reaction conditions, the low-level-reactivity C—F would not interfere with the reaction of C—F of higher reactivity. Application of this multistepped reactivity of FPOx in quantitative postpolymerization functionalization of polymer was successfully demonstrated. Stoichiometric amount of *p*-cresol, with the molar feed ratio of *p*-cresol in relative to the repeat unit of the polymer of FPOx and 6F-BPA in the range of 1–4, could be readily grafted onto the polymer by simply controlling the reaction temperature. FPOx-based, versatile one-pot synthesis of high molecular-weight grafted polymers with well-controlled structures and topologies were also demonstrated.
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KEYWORDS: controlled polymer synthesis; functionalization of polymers; perfluorinated aromatics; polyethers; quantitative functionalization; stepped multifunctionality; synthesis; topology

INTRODUCTION Postpolymerization functionalization represents an efficient approach for synthesizing functional polymers with desired properties.[1–4] One critical challenge, however, has been the quantitative control of functionalization and precise tailoring of materials properties. This is even true when multiple functional groups are to be incorporated into a polymer hierarchically, uniformly and densely. Although combination of different coupling chemistries could be employed to address this challenge,[3,4] it involves great difficulty with synthesizing specific reactive group-containing polymers and functional molecules. Thus, to enable quantitative hierarchical functionalization, simple solutions for realizing robust multifunctional polymers having high but non-crossing reactivity to readily accessible reactive groups (e.g., hydroxyl and amine) are desired.

Nucleophilic substitution reactions between aryl C—F and strong nucleophiles (e.g., phenoxide) have been well documented and extensively used for synthesizing high molecular weight (M_w) poly(aryl ether)s.[5–7] The reactivity of aryl C—F is due to the high electron negativity of fluorine and dictated to a great extent by the electronic property of the aryl structure. Typically, the presence of an electron-withdrawing group (EWG, e.g., ketone, sulfone, and cyanide) can effectively activate the para or ortho C—F bond(s), in relative to the EWG, for quantitative reactions with nucleophiles.[6,7] The para C—F can have a higher reactivity than the ortho C—F.[8,9] On the contrary, an electron-donating substituent (e.g., alkoxyl and aryloxy) will deactivate the C—F bond. Given these, a strong EWG-bearing perfluorinated aryl compound [e.g., 2,5-dipentafluorophenyl-1,3,4-oxadiazole (FPOx), Fig. 1] could be expected to exhibit an inherent multifunctionality with self-regulated stepped reactivity: (1) the para C—F_1 has the highest reactivity and will react predominantly with nucleophiles;[8,9] (2) once the para F_1 is substituted with an aryloxy, the reactivity of ortho C—F (i.e., C—F_2 and C—F_3) will decrease, yielding a distinctive difference (or "step") in reactivity between para and ortho C—F bonds. Due to the strong activation effect of oxadiazole and the neighboring fluorine atoms, the ortho C—F may still undergo quantitative condensation reaction with nucleophiles at improved reaction conditions; (3) substitution of one of the ortho F (e.g., F_2) with aryloxy will further depress the reactivity of the remaining ortho C—F_3, giving rise to the second reactivity step between C—F_2 and C—F_3 (Fig. 1). Similarly, C—F_3 may remain reactive to nucleophiles at appropriate conditions. Thus, by optimization and control of reaction conditions, these three levels of reactivity may be explored for quantitative hierarchical functionalization of polymers. Up to now,

Correspondence to: N. Song (E-mail: nsong@pku.edu.cn)

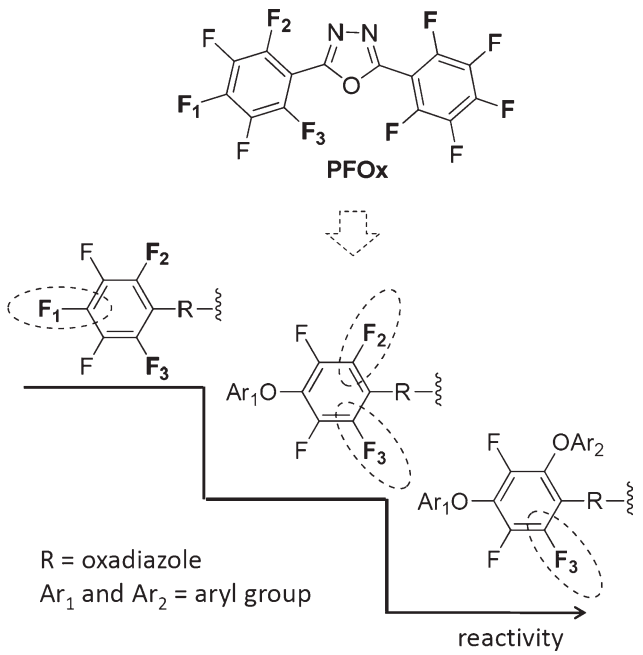


FIGURE 1 Illustration of structure of FPOx and the stepped reactivity of C—F bonds.

although high M_w polymers based on perfluorinated aromatic monomers are known,[8–10] the multifunctionality of stepped reactivity was not yet known. Indeed, the reaction of ortho C—F with nucleophiles has been purposely depressed to achieve linear noncrosslinking polymers. Herein, we report the discovery of the unique "stepped multifunctionality" of perfluorinated aryl compound and its versatile use in synthesizing grafted polymers with well-controlled structures and topologies.

RESULTS AND DISCUSSION

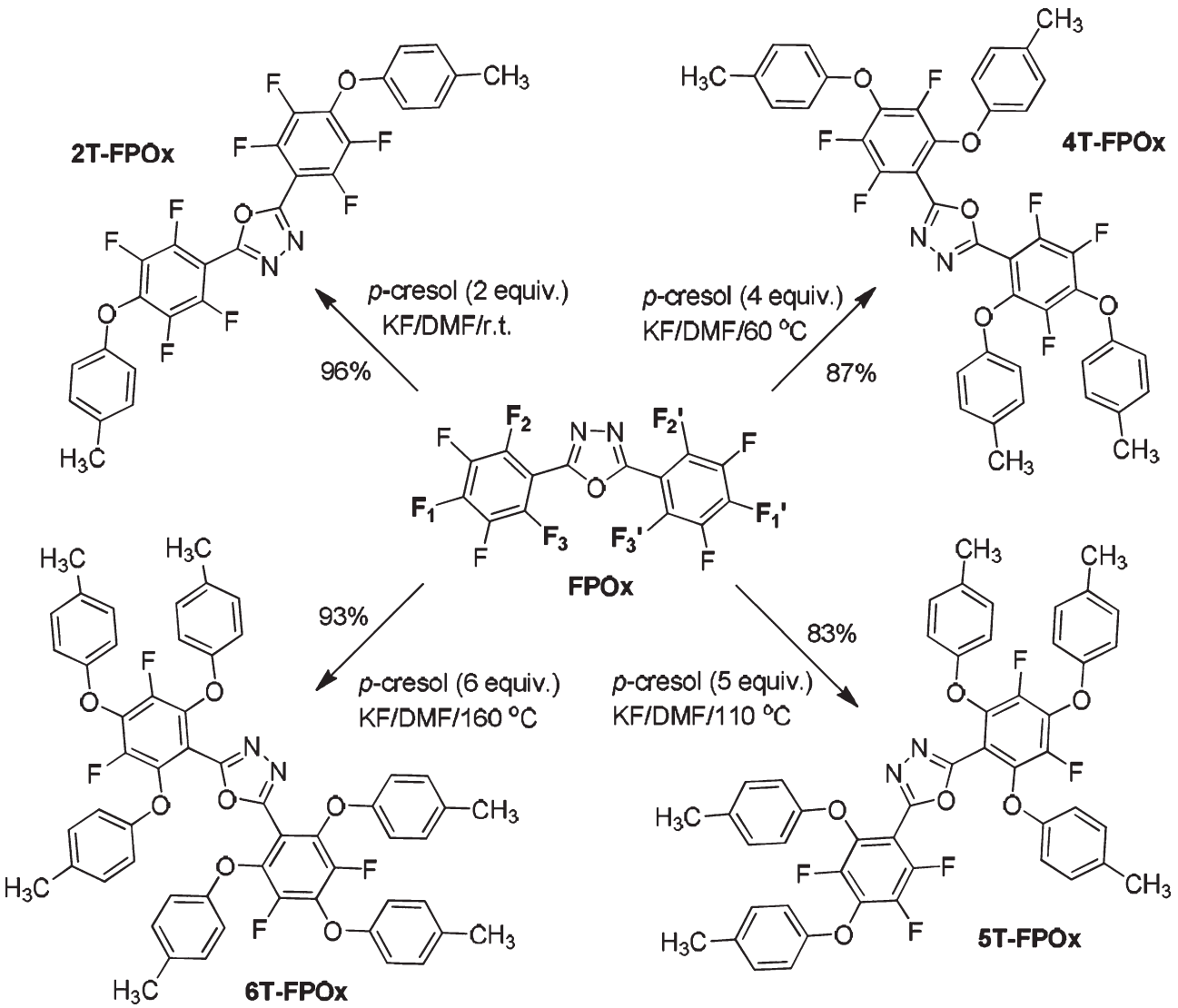
To understand the stepped reactivity of perfluorinated aromatics, FPOx was chosen as the compound of study because of the strong activation effect of oxadizaole (Ox),[11] which is known to be capable of facilitating reactions between para C—F and phenoxide at room temperature.[8] It is expected that Ox will also activate the ortho C—F to react efficiently with strong nucleophiles at appropriate reaction conditions, even with the presence of deactivating aryloxy substituent(s). The synthesis of FPOx has been reported by Ding and Day,[8(a)] where FPOx was polymerized with hexafluorobisphenol A (6F-BPA) to yield high M_w linear polymers.

Scheme 1 shows the model reactions of FPOx with *p*-cresol at different temperatures in anhydrous DMF using potassium fluoride as the base. It was found that when the reaction was carried out at room temperature (ca. 23 °C), FPOx could react quantitatively with two molar equivalent of *p*-cresol at the para positions (i.e., C—F_1 and C—F_1') to yield the double substituted 2T-FPOx. The reaction went to completion within 2 h. Extension of the reaction time (e.g., 3 h) yielded no discernible amount of further substituted products. Upon increasing the reaction temperature to about 60 °C, which activated the ortho C—F bonds, FPOx reacted efficiently with four equivalent of *p*-cresol to give the four substituted 4T-FPOx at a very high isolation yield of 87%. A reaction with a molar *p*-cresol/FPOx (*c*/*f*) ratio of about 3 was also carried out at 60 °C, which resulted in a mixture of double, tri- and four substituted products, suggesting the equivalence of ortho C—F_2 and C—F_2' in reactivity.

It is interesting to find that when the reaction temperature was increased to 110 °C, FPOx reacted with only five equivalent amount of *p*-cresol to give 5T-FPOx. Since the reactivity of C—F_3 and C—F_3' are not expected to be different, as evidenced by the well resolved ^{1}H NMR and ^{19}F NMR (Figs. 2 and 3) spectra of 4T-FPOx, this can be explained by the steric effect of 5T-FPOx, which limits the accessibility of *p*-cresol to the remaining ortho C—F bond. Further increase of reaction temperature to above 150 °C led to the fully substituted product 6T-PFOx at an isolation yield of 93%.

Figure 2 shows the expanded ^{1}H NMR spectra of the tolyloxylated FPOx, which agree very well with the expected structures. It can be seen that with the substitution of para and ortho C—F by tolyloxy, the aryl protons (e.g., protons 1 and 2) moved step by step to higher fields, indicating an increasing electron density of the fluorinated phenyl ring. It is noted that all the reactions between FPOx and *p*-cresol are nearly quantitative and lack of side reactions, which are highly desirable for synthesizing grafted functional polymers. The degree of reaction could be easily manipulated by controlling the reaction temperature and the molar *c*/*f* ratio. For example, 2T-FPOx can be first prepared by reacting FPOx with 2 mol equivalence of *p*-cresol at room temperature, followed by reacting additional 3 mol equivalence of *p*-cresol at 110 °C to yield 5T-FPOx. This makes hierarchical or multistep grafting of functional groups possible.

Application of the stepped reactivity of FPOx in quantitative functionalization of polymer was carried out by first polymerizing FPOx with 6F-BPA to give the linear polymer P1 (M_n = 21,000, GPC), followed by grafting with *p*-cresol in DMF with the presence of potassium fluoride as the base (Scheme 2). The feed molar ratio of *p*-cresol in relative to the repeat unit of P1 (*c*/*r* ratio) was controlled in the range of 1–4 and the grafting reaction temperature in the range of 60–160 °C depending on the *c*/*r* ratio. The syntheses and properties of the grafted polymers are summarized in Table 1. For all the cases, stoichiometric amount of *p*-cresol were grafted onto the polymer, as estimated from ^{1}H NMR spectra by comparing the integral of all aryl protons in relative to the integral of aryl protons of 6F-BPA residue (Fig. 4). As the grafting density increased, the glass transition temperature of the grafted polymer decreased (Fig. 5 and Table 1). One-pot, multistep synthesis of grafted polymers with well-defined structures is also possible. As shown by Scheme 3 (one-pot route 1), FPOx-based polymer P1 can be subjected to the stoichiometric grafting right after the polymerization, without the need of separation and purification of the polymer, by adding *p*-cresol and increasing the reaction temperature, as exemplified by the synthesis of P1-a′ and P1-b′.



SCHEME 1 Model reactions between FPOx and *p*-cresol.

By taking advantage of the high reactivity of the ortho C—F at elevated temperatures, polymerization of 4,4′-disubstituted FPOx (i.e., 2T-FPOx) with 6F-BPA was carried out at 60 °C in DMF in the presence of potassium fluoride as the base (Scheme 3 and Table 2). As expected, high M_w polymer P2 (M_n = 15,100, GPC) was obtained. In comparison with P1-b that has the same chemical composition, P2 has a different topology (Fig. 6). The grafted polymer P1-b has the grafted functional groups alternatively arranged along a linear chain, whereas P2 has the two side groups head-to-head linearly aligned along a somewhat zig-zag backbone. Depending on the side chain structures, this difference in topology may lead to different properties of the polymer, such as interchain interaction and thermal properties. Figure 7 shows the different ^{1}H NMR spectra of P1-b and P2. Similarly, P2 can also be prepared via a one-pot two-step synthesis (P2′, one-pot route 2 in Scheme 3).

One-pot one-step syntheses of random-topology P3 (i.e., P3-a and P3-b) were also carried out at an elevated temperature of 60 °C by polymerizing FPOx and 6F-BPA with the presence of a controlled amount (e.g., 1 or 2 molar equivalence) of mono functional *p*-cresol (Scheme 3). Since both para and ortho C—F bonds are highly reactive at 60 °C, an irregularly grafted polymer P3-a (M_n = 14,500, GPC) and P3-b (M_n = 16,500, GPC) were obtained. In comparison with P1-b and P2, the topologically different P3-b (Fig. 6) is expected to exhibit different materials properties. For example, P3-b (T_g = 124 °C) exhibited a much lower glass transition temperature than P1-b (T_g = 135 °C) and P2 (T_g = 132 °C) (Tables 1 and 2).

EXPERIMENTAL

Materials: Hexafluorobisphenol A (6F-BPA, Zhejiang Sanhe Pharmachem) and *p*-cresol were purified by recrystallization from toluene and ligroin, respectively. Anhydrous *N*,*N*-dimethylformamide (DMF) was distilled over phosphorus pentaoxide and stored over molecular sieves (3 Å). Anhydrous potassium fluoride was purchased from Beijing Chemical Reagent Company and treated at 200 °C over night.

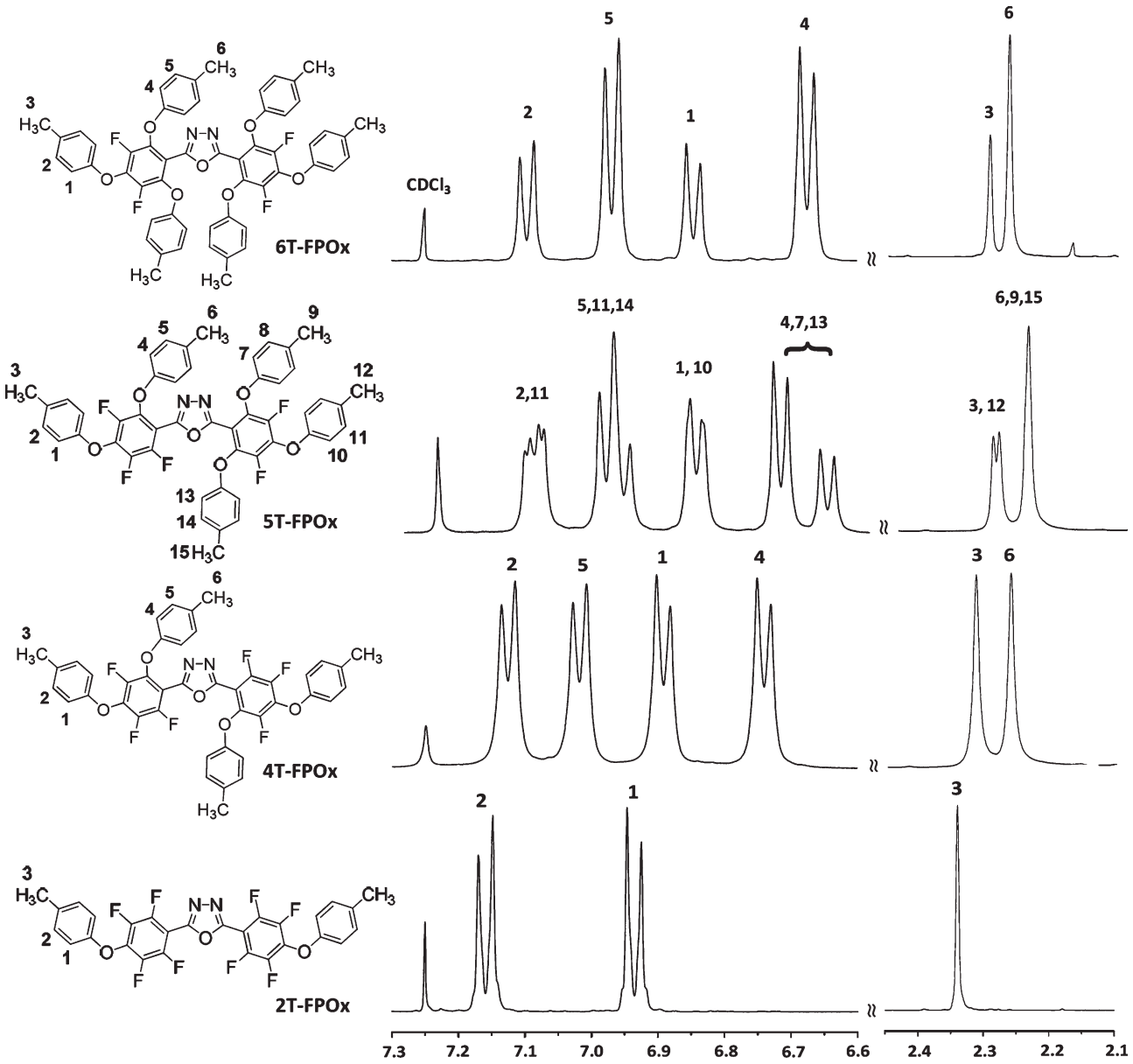


FIGURE 2 Expanded ^{1}H NMR (400 MHz, $CDCl_3$) spectra of *p*-tolyloxylated FPOx.

Pentafluorobenzoic acid was purchased from Yongtai Chemical and used as received. All other chemicals and reagents were purchased from Beijing Chemical Reagent Company and used as received.

Measurements: Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a Bruker ARX 400 MHz spectrometer (^{1}H NMR 400 MHz and ^{13}C NMR 100 MHz) or a Varian Mercury 300 MHz spectrometer (^{1}H NMR 300 MHz and ^{13}C NMR 75 MHz) using tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on a Varian 300 MHz (^{19}F NMR 282 MHz) using trifluoroacetic acid as an external standard. The chemical shifts are reported in the ppm scale. Gel permeation chromatographic (GPC) measurements were performed with a Waters 510 system at room temperature. Tetrahydrofuran was used as the eluent with a flow rate of 1.0 mL/min. All GPC data were calibrated with linear polystyrene standards. FTIR spectra were recorded on a Bruker Vector 22 Fourier transform infrared spectrometer. ESI-mass spectra were measured on a Bruker Daltonics apex IV FTMS mass spectrometer. Element analysis was conducted by an Elementar Vario EL instrument (Elementar Analysensysteme GmbH). Thermogravimetric analysis (TGA) was performed on a TA Q600 SDT instrument at a heating rate of 10 °C/min in nitrogen. Differential Scanning Calorimetry (DSC) was recorded with a TA Q100 thermal analyzer at a heating rate of 10 °C/min in nitrogen.

Synthesis of Model Compounds

2,5-Bis(pentafluorophenyl)-1,3,4-oxadiazole (FPOx)

FPOx was prepared according to the literature method (Ding and Day) and modified as follows: A mixture of

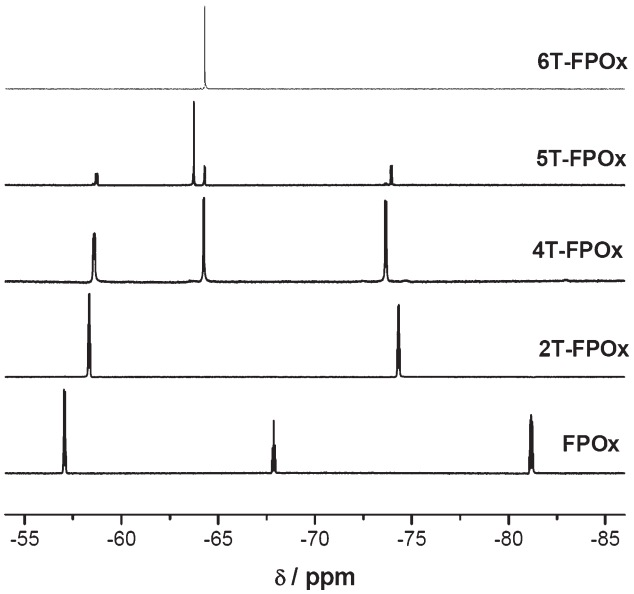
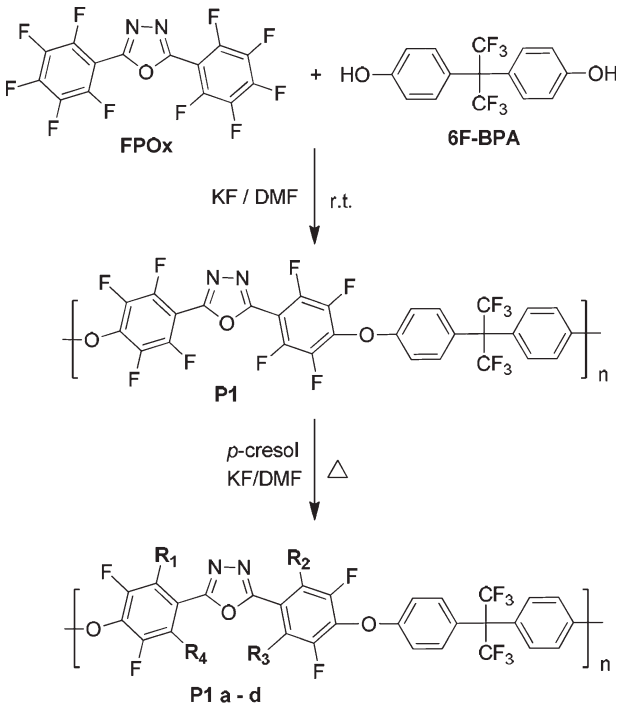


FIGURE 3 ^{19}F NMR (282 MHz, $CDCl_3$) spectra of *p*-tolyloxylated FPOx.

pentafluorobenzoic acid (5.1 g, 24.0 mmol), hydrazine sulfate (1.9 g, 14.6 mmol), and polyphosphoric acid (45 g) was stirred and heated in a 250 mL round-bottomed flask at 150 °C under argon for 2 h. The temperature was then slowly increased to 200 °C and the mixture was heated for another 2 h. After cooling down to about 50 °C, the reaction mixture was poured into vigorously stirring distilled water (200 mL). The resulting white powdered solid was collected by filtration and washed with hot water until neutral.

After drying, the crude product was recrystallized from toluene/methanol mixture (3/7, v/v) twice to give white needle-like crystals (3.5 g, 73% yield): mp. 155–156 °C; ^{13}C NMR (100 MHz, $CDCl_3$): δ: 156.2 (m), 145.2 (dm, $^1J_{F\text{-}C} = 260$ Hz), 143.6 (dm, $^1J_{F\text{-}C} = 261$ Hz), 138.0 (dm, $^1J_{F\text{-}C} = 252$ Hz), 99.8–100.2 (m); ^{19}F NMR (282 MHz, $CDCl_3$): δ −57.0 to −57.1 (m, 4F, Ar—F meta to Ox), −67.8 to −67.9, (m, 2F, Ar—F para to Ox), −81.1 to −81.2 (m, 4F, Ar—F ortho to Ox).



P1 a: R_1, R_2 = *p*-tolyloxy or H, $R_3 = R_4 = H$
P1 b: $R_1 = R_2$ = *p*-tolyloxy; $R_3 = R_4 = H$
P1 c: $R_1 = R_2 = R_3$ = *p*-tolyloxy; $R_4 = H$
P1 d: $R_1 = R_2 = R_3 = R_4$ = *p*-tolyloxy

SCHEME 2 Synthesis of FPOx-based linear and grafted polymers.

2,5-Bis(2,3,5,6-tetrafluoro-4-(p-tolyloxy)phenyl)-1,3,4-oxadiazole (2T-FPOx)

A mixture solution of FPOx (3.071 g, 7.637 mmol), *p*-cresol (1.801 g, 16.660 mmol) and anhydrous potassium fluoride (1.902 g, 32.736 mmol) in DMF (30 mL) was prepared and stirred under argon at room temperature for 2 h. The reaction solution was poured into a mixture solution of methanol and distilled water (200 mL, 1/1, v/v) and the resulting powder precipitates was collected by filtration and thoroughly washed with methanol and distilled water.

TABLE 1 Synthesis and Characterization of *p*-Cresol Grafted Polymers P1-a–P1-d

Polym.	Feed Ratio[a]	Temp. (°C)[b]	Yield (%)	Grafting Ratio (%)[c]	M_n ($\times 10^4$)[d]	PDI[d]	T_g (°C)[e]	T_d (°C)[f]
P1	–	23	90	–	2.1	2.4	175	478
P1-a	1:1	60	84	100	2.1	2.6	149	459
P1-b	2:1	60	91	100	2.2	2.9	135	436
P1-c	3:1	110	85	89	2.1	2.7	131	432
P1-d	4:1	160	88	100	1.6	2.6	128	416

[a] Molar feed ratio of *p*-cresol versus repeat unit of P1.
[b] Grafting reaction temperature.
[c] Determined from proton NMR analysis.
[d] Number-average molecular weight (M_n) and polydispersity (PDI) determined by GPC.
[e] Glass transition temperature measured by DSC in nitrogen at a heating rate of 10 °C/min.
[f] Onset temperature for 5% weight loss measured by TGA in nitrogen at a heating rate of 20 °C/min.

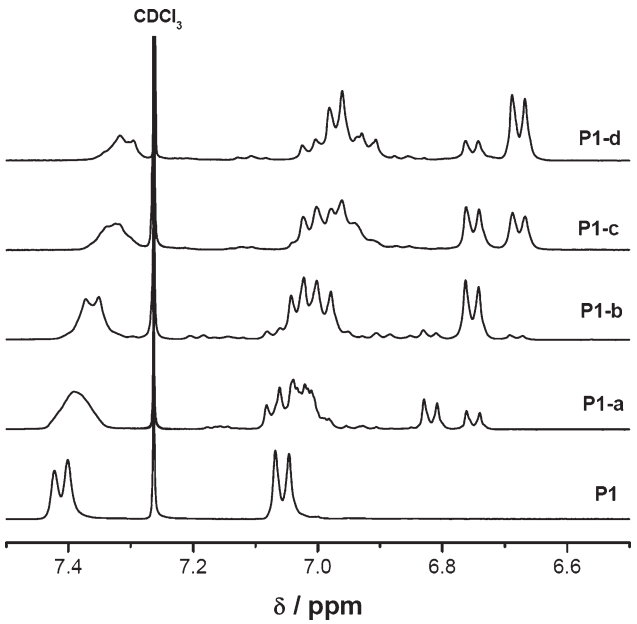


FIGURE 4 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of P1 and grafted polymers P1-a, P1-b, P1-c, and P1-d.

After drying at 60 °C in an oven over night, the crude product was recrystallized from toluene/methanol (3/7, v/v) to give white needle-like crystals (4.2 g, 96% yield): mp. 155–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, 4H, J = 8.4 Hz), 6.95 (d, 4H, J = 8.8 Hz), 2.35 (s, 6H); ^{13}C NMR (100 M, $CDCl_3$): δ 156.5 (s br), 154.7, 145.4 (dm, $^{1}J_{F\text{-}C}$ = 260 Hz), 141.7 (dm, $^{1}J_{F\text{-}C}$ = 252 Hz), 137.7–137.9 (m), 130.3, 115.9, 99.8–100.0 (m), 20.6; ^{19}F NMR (282 M, $CDCl_3$): δ −58.3 to −58.4 (m, 2F), −74.2 to −74.3 (m, 2F); FTIR (KBr, cm^{-1}): 1651, 1606, 1507 (br), 1215, 1103, 990, 818, 492; Anal. Calcd. for $C_{28}H_{14}F_8N_2O_3$: C, 58.14; H, 2.44; N, 4.84; Found: C, 58.17; H, 2.35; N, 4.83; ESI-MS (m/z): 578.0 $[M]^+$.

2,5-Bis(2,3,5-trifluoro-4,6-bis(p-tolyloxy)phenyl)-1,3,4-oxadiazole (4T-FPOx)

A mixture of FPOx (0.803 g, 1.997 mmol), *p*-cresol (1.070 g, 9.898 mmol) and anhydrous potassium fluoride (1.152 g, 19.827 mmol) in anhydrous DMF (20 mL) was prepared and stirred at 60 °C under argon for 8 h. After cooling to room temperature, the reaction solution was poured into a mixture of methanol and distilled water (200 mL, 1:1, v/v).

The resulting precipitates were collected by filtration, washed thoroughly with distilled water and methanol, and recrystallized from toluene/methanol (15/85, v/v) to give white needle-like crystals (1.3 g, 87% yield): mp. 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 4H, J = 8.4 Hz), 7.02 (d, 4H, J = 8.4 Hz), 6.89 (d, 4H, J = 8.8 Hz), 6.74 (d, 4H, J = 8.4 Hz), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1–157.2 (m), 155.3, 154.8, 146.0 (dm, $^{1}J_{F\text{-}C}$ = 260 Hz), 142.2 (dm, $^{1}J_{F\text{-}C}$ = 251 Hz), 138.9–139.1 (m), 137.2–137.5 (m), 133.7, 133.0, 130.2, 130.0, 115.6, 115.4, 105.2–105.4 (m) 20.6, 20.5; ^{19}F NMR (282 M, $CDCl_3$): δ −58.6 (dd, 2F, J = 21.4 Hz, J = 10.4 Hz), −64.2 (d, 2F, J = 10.4 Hz), −73.7 (d, 2F, J = 21.4 Hz); FTIR (KBr, cm^{-1}): 1639, 1604, 1494(br), 1410, 1205, 991, 848, 814, 490; Anal. Cacld. for $C_{42}H_{28}F_6N_2O_5$: C, 66.84; H, 3.74; N, 3.71; Found: C, 66.32; H, 3.80; N, 3.68; ESI-HRMS (m/z): 755.1978 $[M+H]^+$.

2-(3,5-Difluoro-2,4,6-tris(p-tolyloxy)phenyl)-5-(2,3,5-trifluoro-4,6-bis(p-tolyloxy)phenyl)-1,3,4-oxadiazole (5T-FPOx)

A mixture of FPOx (0.788 g, 1.96 mmol), *p*-cresol (1.397 g, 12.92 mmol) and anhydrous potassium fluoride (1.14 g, 19.6 mmol) in DMF (14 mL) was prepared and stirred at 110 °C under argon for 7 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was rotoevaporated to yield a liquid residue, to which was added methanol (4 mL) to develop a white crystalline product.

The product was collected by filtration, washed with distilled water and methanol, and recrystallized from toluene/methanol (15/85, v/v) to give white needle crystals (1.4 g, 85% yield): mp. 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, 4H, J = 8.4 Hz, J = 3.5 Hz), 6.97–7.02 (m, 6H), 6.87 (dd, 4H, J = 8.4 Hz, J = 2.1 Hz), 6.75 (d, 4H, J = 8.4 Hz), 6.68 (d, 2H, J = 8.4 Hz), 2.32 (s, 3H), 2.31 (s, 3H), 2.26 (s, 9H); ^{19}F NMR (282 M, $CDCl_3$): δ −58.7 (dd, 1F, J = 21.7 Hz, J = 10.4 Hz), −63.7 (s, 2F), −64.2 (d, 1F, J = 10.4Hz), −74.0 (d, 1F, J = 21.7Hz); FTIR (KBr, cm^{-1}): 3034, 2919, 1639, 1604, 1497, 1460, 1204, 990, 846, 815, 488; Anal. Calcd. for $C_{49}H_{35}F_5N_2O_6$: C, 69.83; H, 4.19; N, 3.32; Found: C, 69.40; H, 4.25; N, 3.27; ESI-HRMS (m/z): 843.2466 $[M+H]^+$.

5T-FPOx (an Altenative Two-Step Synthesis)

A mixture of 2T-FPOx (0.99 g, 2.46 mmol), *p*-cresol (0.93 g, 8.59 mmol) and anhydrous potassium fluoride (0.70 g, 12.0 mmol) in DMF (12 mL) was prepared and stirred at 110 °C under argon for 8 h. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble potassium fluoride. The filtrate was concentrated on a rota-evaporator to about 1 mL. To the residue was added methanol (4 mL) to yield a white crystalline product, which was collected by filtration, washed thoroughly with distilled water and

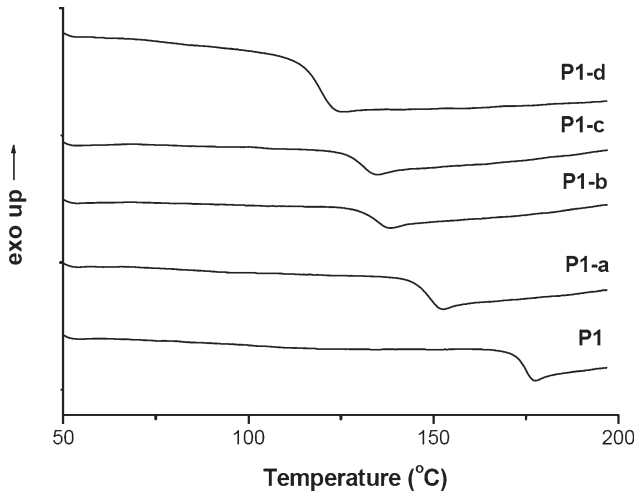
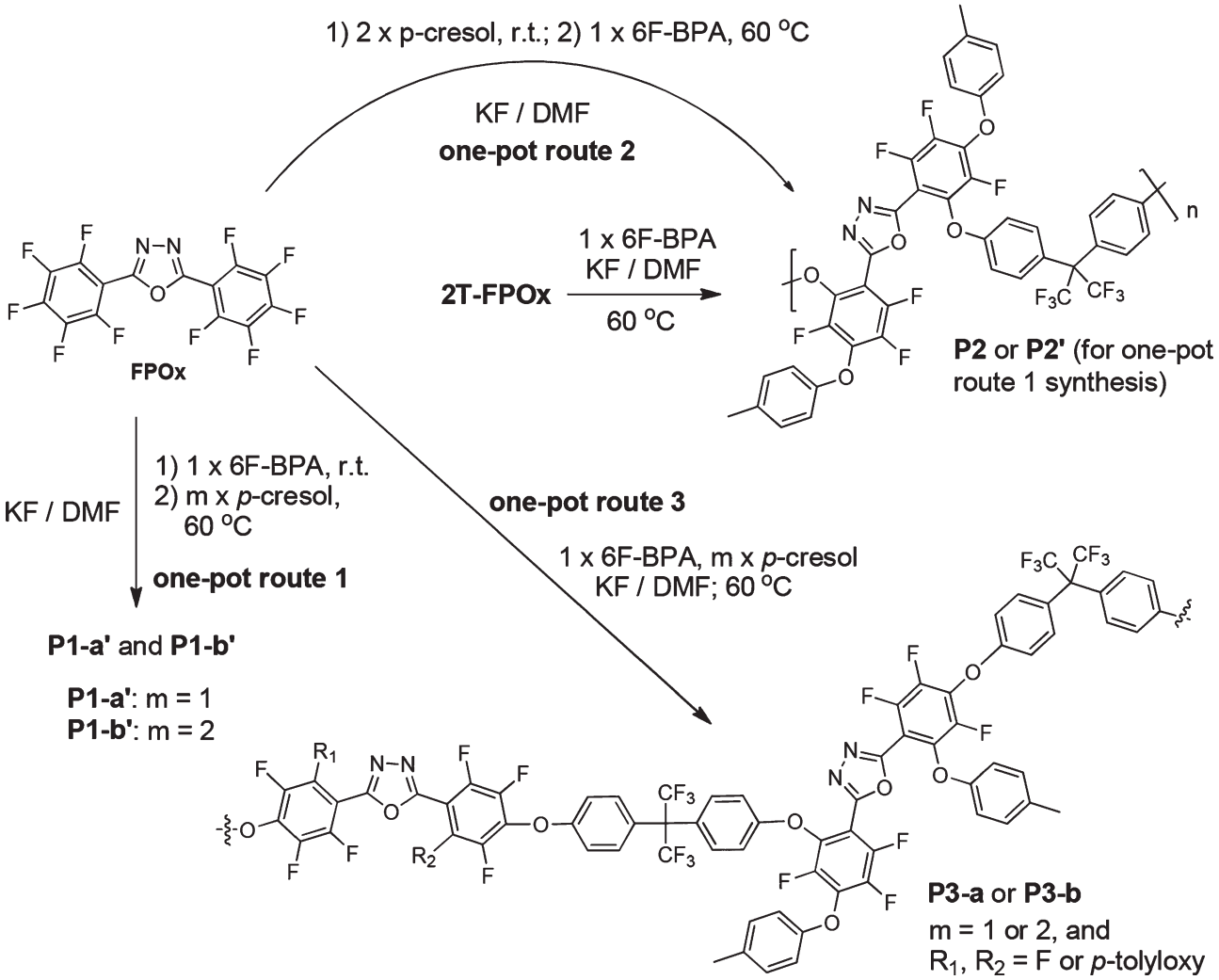


FIGURE 5 The second DSC heating curves of P1 and *p*-tolyloxylated polymers (P1-a–P1-d) in nitrogen with a heating rate of 10 °C/min.



SCHEME 3 Polymerization of 2T-FPOx and one-pot synthesis of grafted polymers with different topologies.

TABLE 2 Characterizations of Polymers Synthesized via One-Pot One-Step or Two-Step Method

Polym.	Monomer	Feed Ratio[a]	Yield (%)	M_n ($\times 10^4$)[b]	PDI[b]	T_g (°C)[c]	T_d (°C)[d]
P1-a′	(FPOx+6FBPA)+*p*-cresol[e]	1:1:1	90	4.9	2.6	158	428
P1-b′	(FPOx+6FBPA)+*p*-cresol[e]	1:1:2	88	6.2	2.4	143	431
P2	2T-FPOx+6FBPA	1:1	85	1.5	1.7	132	414
P2′	(FPOx+*p*-cresol)+6FBPA[e]	1:2:1	90	0.6	2.4	129	405
P3-a	FPOx+6FBPA+*p*-cresol[f]	1:1:1	94	1.5	5.9	151	457
P3-b	FPOx+6FBPA+*p*-cresol[f]	1:1:2	93	1.6	4.8	124	437

[a] Molar feed ratio of monomers.
[b] Number-average molecular weight (M_n) and polydispersity (PDI) determined by GPC.
[c] Glass transition temperature measured by DSC in nitrogen at a heating rate of 10 °C/min.
[d] Onset temperature for 5% weight loss measured by TGA in nitrogen at a heating rate of 20 °C/min.
[e] One-pot two-step polymerization.
[f] One-pot one-step polymerization.

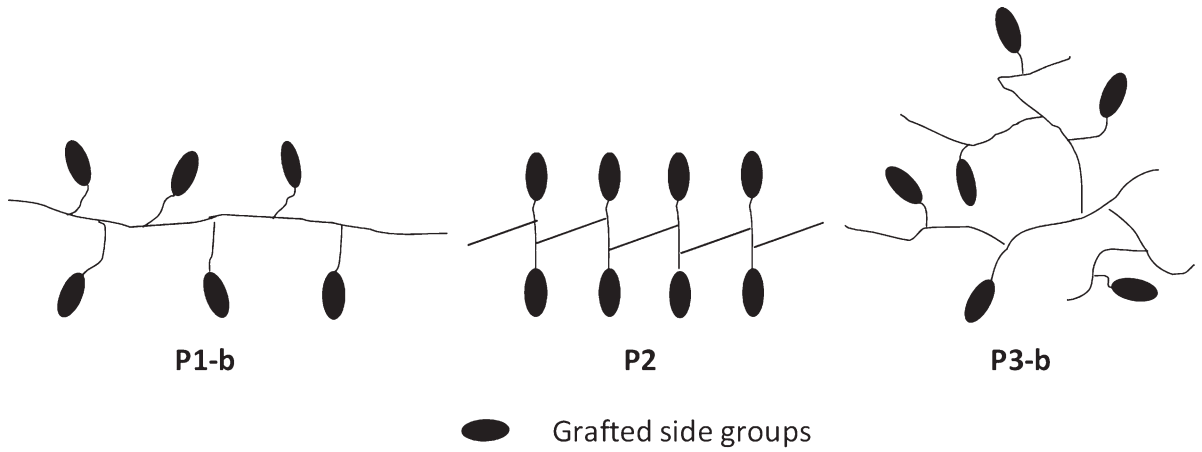


FIGURE 6 Illustration of different topologies of P1-b, P2, and P3-b.

methanol, and recrystallized from toluene/menthol (15/85, v/v) to give white needle crystals (1.2 g, 83% yield).

2,5-Bis(3,5-difluoro-2,4,6-tris(p-tolyloxy)phenyl)-1, 3,4-oxadiazole (6T-FPOx)

A mixture solution of FPOx (0.517 g, 1.285 mmol), *p*-cresol (1.130 g, 10.453 mmol) and anhydrous potassium fluoride (0.89 g, 15 mmol) in anhydrous DMF (12 mL) was prepared and stirred at 160 °C under argon for 8 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated on a rota-evaporator to about 1 mL.

To the residue was added methanol (4 mL) to precipitate the white crystalline product, which was collected by filtration, washed thoroughly with distilled water and methanol, and recrystallized from toluene/menthol (15/85, v/v) to give white needle crsytals (1.1 g, 93% yield): mp. 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 4H, J = 8.4 Hz), 6.96 (d, 8H, J = 8.4 Hz), 6.84 (d, 4H, J = 8.4 Hz), 6.67 (d, 4H, J = 8.4 Hz), 2.29 (s, 6H), 2.26 (s, 12H); ^{13}C NMR (100 M, $CDCl_3$): δ 157.9 (m), 155.5, 154.9, 146.5 (dd, $^{1}J_{F\text{-}C}$ = 252 Hz, $^{3}J_{F\text{-}C}$ = 3.5 Hz), 139.8 (dd, $^{2}J_{F\text{-}C}$ = 11.6 Hz, $^{4}J_{F\text{-}C}$ = 4.2 Hz), 136.9 (t, $^{2}J_{F\text{-}C}$ = 13.3 Hz), 133.3, 132.7, 130.1, 129.9, 115.7, 115.4, 111.3, 20.59, 20.57; ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.6 (s, 4F); FTIR (KBr, cm^{-1}): 3033, 2919, 1879, 1601, 1470, 1205, 988, 846, 811, 486; Anal. Calcd. for $C_{56}H_{42}F_4N_2O_7$: C, 72.25; H, 4.55; N, 3.01; Found: C, 71.90; H, 4.66; N, 2.95; ESI-MS (*m/z*): 931.1 $[M+H]^+$.

Synthesis of Polymers

P1: To a solution of FPOx (1.522 g, 3.784 mmol) and 6F-BPA (1.272 g, 3.784 mmol) in anhydrous DMF (22 mL) was added anhydrous potassium fluoride (0.922 g, 15.89 mmol). The resulting mixture was stirred at room temperature under argon for 90 min before additional FPOx (0.103 g, 0.25 mmol) was added to the solution to end-cap the polymer chains. The solution was stirred for another 2 h and then dropped into a methanol/distilled water mixture (300 mL, 1:1, v/v). The resulting polymer precipitates were

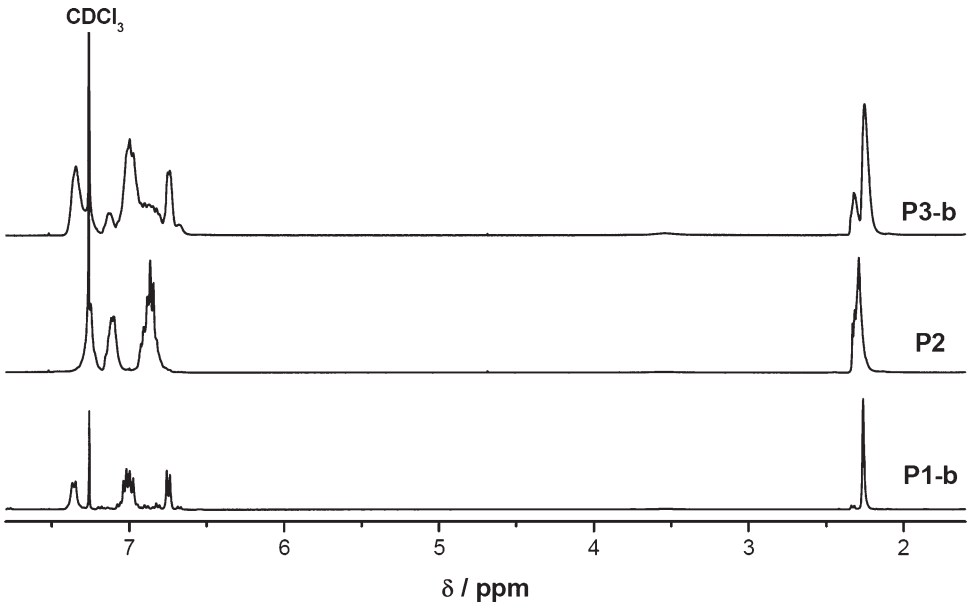


FIGURE 7 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of P1-b, P2 and P3-b.

collected by filtration and thoroughly washed with distilled water and methanol. To ensure a complete removal of any trapped impurities, the polymer was redissolved in tetrahydrofuran (9 mL) and reprecipitated in the methanol/water mixture (200 mL, 1:1, v/v), followed by Soxhlet extraction with methanol for 10 h.

The polymer was then dried at 60 °C in a vacuum oven (2.48 g, 90% yield): M_n = 21000, PDI = 2.4 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 4H, J = 8.1 Hz), 7.06 (d, 4H, J = 8.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.6 (s, 6F), −56.5 (m, 4F, Ar—F meta to Ox), −73.0 (m, 4F, Ar—F ortho to Ox); FTIR (KBr, cm^{-1}): 1653, 1607, 1510, 1482, 1219, 1173, 992, 931, 844; T_g = 175 °C (DSC); $T_{d,5\%}$ = 477 °C (TGA).

P1-a (Grafting of p-cresol, Feed Ratio of p-cresol/Repeat Unit = 1:1)

To a solution of P1 (0.223 g, 0.319 mmol of repeat unit), *p*-cresol (0.034 g, 0.314 mmol) in anhydrous DMF (4 mL) was added anhydrous potassium fluoride (0.074 g, 1.274 mmol). The mixture solution was heated under agron to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into a methanol/distilled water mixture (30 mL, 1:1, v/v) to precipitate the polymer.

The work-up procedure was the same as that for P1: 0.211 g, 84% yield; M_n = 20,600, PDI = 2.6 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s br), 6.98–7.08 (m), 6.82 (d, J = 8.4 Hz), 6.75 (d, J = 8.4 Hz), 2.26 (s); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.6 (s), −57.0 to −57.7 (m), −63.6 to −63.7 (m), −72.5 to −73.7 (m); T_g = 149 °C (DSC); $T_{d,5\%}$ = 458 °C (TGA).

P1-b (Grafting of p-cresol, Feed Ratio of p-cresol/Repeat Unit = 2:1)

To a solution of P1 (0.307 g, 0.439 mmol of repeat unit) and *p*-cresol (0.095 g, 0.878 mmol) in anhydrous DMF (5 mL) was added anhydrous potassium fluoride (0.102 g, 1.755 mmol). The mixture solution was heated under argon to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (30 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 0.352 g, 91% yield; M_n = 21,600, PDI = 2.9 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz), 7.05 (m), 6.75 (d, J = 8.4 Hz), 2.26 (s); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.6 (s), −56.0 to −57.9 (m), −63.6 to −63.7 (m), −72.9 to −73.7 (m); T_g = 135 °C (DSC); $T_{d,5\%}$ = 436 °C (TGA).

P1-c (Grafting of p-cresol, Feed Ratio of p-cresol/Repeat Unit = 3:1)

To a solution of P1 (0.250 g, 0.358 mmol of repeat unit) and *p*-cresol (0.116 g, 1.073 mmol) in anhydrous DMF (4 mL) was added anhydrous potassium fluoride (0.104 g, 1.790 mmol). The mixture solution was heated under argon to 110 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into a stirring methanol/distilled water mixture (30 mL, 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 0.260 g, 85% yield; M_n = 21000, PDI = 2.7 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz), 6.95–7.04 (m), 6.75 (d, J = 8.4 Hz), 6.68 (d, J = 8.4 Hz), 2.26 (s); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.6 (s), −57.9 (s br), −62.5 to −64.3 (m), −73.0 to −73.1 (m); T_g = 128 °C (DSC); $T_{d,5\%}$ = 417 °C (TGA).

P1-d (Grafting of p-cresol, Feed Ratio of p-cresol/Repeat Unit = 4:1)

To a solution of P1 (0.162 g, 0.232 mmol of repeat unit) and *p*-cresol (0.102 g, 0.943 mmol) in anhydrous DMF (3 mL) was added anhydrous potassium fluoride (0.080 g, 1.377 mmol). The mixture solution was heated under agron to 160 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (30 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 0.211 g, 88% yield; M_n = 16100, PDI = 2.6 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.34 (m), 6.96–7.02 (m), 6.75 (d, J = 8.4 Hz), 6.67 (d, J = 8.4 Hz), 2.25 (s); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.7 (s, 6F), −63.1 (s, 4F); T_g = 119 °C (DSC); $T_{d,5\%}$ = 410 °C (TGA).

P2 (Polymerization of 2T-FPOx with 6F-BPA)

To a solution of 2T-FPOx (2.278 g, 3.940 mmol) and 6F-BPA (1.324 g, 3.938 mmol) in anhydrous DMF (15 mL) was added anhydrous potassium fluoride (1.142 g, 19.655 mmol). The mixture solution was heated under agron to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into a methanol/distilled water mixture (200 mL, 1:1, v/v). The resulting polymer precipitates were collected by filtration and thoroughly washed with distilled water and methanol. To further purify the polymer, the solid product was redissolved in tetrahydrofuran (15 mL) and reprecipitated in the methanol/water mixture (200 mL, 1:1, v/v), followed by a Soxhlet extraction with methanol for 10 h.

The polymer was then dried at 60 °C in a vacuum oven (3.05 g, 85% yield): M_n = 15100, PDI = 1.7 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s br, 4H), 7.10 (m, 4H), 6.85 (m, 8H), 2.28 (s, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.5 (s), −58.2 (m), −63.7 (m), −72.3 (m); FTIR (KBr, cm^{-1}): 3043, 2929, 1608, 1550, 1179, 1088, 991, 842, 733, 595; T_g = 132 °C (DSC); $T_{d,5\%}$ = 414 °C (TGA).

P3-a (One-Step Synthesis of Random-Topology Polymer, FPOx/6F-BPA/p-cresol Feed Ratio = 1:1:1)

To a solution of FPOx (0.969 g, 2.409 mmol), 6F-BPA (0.810 g, 2.409 mmol) and *p*-cresol (0.262 g, 2.423 mmol) in anhydrous DMF (12 mL) was added anhydrous potassium fluoride (0.699 g, 12.031 mmol). The mixture solution was heated under agron to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture

(200 mL, 1:1, v/v) to precipitate the polymer, which was then collected by filtration, thoroughly washed with distilled water and methanol. To ensure the complete removal of any trapped impurities, the polymer was redissolved into tetrahydrofuran (10 mL) and reprecipitated into methanol/distilled water mixture (200 mL, 1:1, v/v), followed by Soxhlet extraction with methanol for 10 h.

The polymer was then dried at 60 °C in a vacuum oven (1.32 g, 94% yield): M_n = 14500, PDI = 5.9 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s br, 4H), 6.75–7.14 (m, 8H), 2.34 (s, ?H), 2.26 (s, ?H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.8 (s), −57.8 (m), −63.4 (m), −73.5 (m); FTIR (KBr, cm^{-1}): 2927, 1648, 1608, 1483(br), 1220, 1176, 1086, 994, 936, 845, 736; T_g = 151 °C (DSC); $T_{d,5\%}$ = 457 °C (TGA).

P3-b (One-Step Synthesis of Random-Topology Polymer, FPOx/6F-BPA/p-cresol Feed Ratio = 1:1:2)

To a solution of FPOx (0.933 g, 2.320 mmol), 6F-BPA (0.780 g, 32.320 mmol) and *p*-cresol (0.502 g, 4.643 mmol) in anhydrous DMF (16 mL) was added anhydrous potassium fluoride (0.808 g, 13.907 mmol). The mixture solution was heated under agron to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (200 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P3-a: 2.03 g, 93% yield; M_n =16500, PDI = 4.8 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s br, 4H), 6.74–7.13 (m, 12H), 2.32 (s, ?H), 2.25 (s, ?H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.5 (s), −58.1 (m), −63.8 (m), −74.1 (m); FTIR (KBr, cm^{-1}): 3044, 2929, 1642, 1607, 1501(br), 1215, 1176, 1083, 992, 936, 846, 736; T_g =124 °C (DSC); $T_{d,5\%}$ = 437 °C (TGA).

P1-a′ (One-Pot Two-Step Synthesis of Grafted Polymer P1-a, FPOx/6F-BPA/p-cresol Feed Ratio = 1:1:1)

To a solution of FPOx (0.569 g, 1.415 mmol) and 6F-BPA (0.476 g, 1.415 mmol) in anhydrous DMF (10 mL) was added anhydrous potassium fluoride (0.410 g, 7.056 mmol). The mixture solution was stirred at room temperature under nitrogen for 80 min before *p*-cresol (0.153 g, 1.415 mmol) was added. The reaction mixture was then heated to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (200 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 0.99 g, 90% yield; M_n = 49200, PDI = 2.6 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 4H), 7.01–7.03 (m, 6H), 6.81, 6.74 (m, 2H), 2.33, 2.26 (3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.7 (s), −57.4 (m), −63.5 (m), −73.4 (m); FTIR (KBr, cm^{-1}): 2927, 1652, 1608, 1488(br), 1225, 1178, 1086, 993, 934, 844, 738, 632, 526; T_g = 158 °C (DSC); $T_{d,5\%}$ = 428 °C (TGA).

P1-b′ (One-Pot Two-Step Synthesis of Grafted Polymer P1-b, FPOx/6F-BPA/p-cresol Feed Ratio = 1:1:2)

To a solution of FPOx (0.972 g, 2.417 mmol) and 6F-BPA (0.813 g, 2.418 mmol) in anhydrous DMF (12 mL) was added anhydrous potassium fluoride (0.561 g, 9.656 mmol). The mixture solution was stirred at room temperature under agron for 80 min before *p*-cresol (0.523 g, 4.838 mmol) was added. The reaction mixture was then heated to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (200 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 1.85 g, 88% yield; M_n = 61700, PDI = 2.4 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 4H), 7.07–7.00 (m, 8H), 6.81, 6.74 (m, 4H), 2.33, 2.26 (6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.7 (s), −57.4 (m), −63.4 (m), −73.4 (m); FTIR (KBr, cm^{-1}): 3049, 2928, 1649, 1607, 1480(br), 1219, 1175, 1085, 992, 936, 845, 737, 631, 519; T_g =143 °C (DSC); $T_{d,5\%}$ = 431 °C (TGA).

P2′ (One-Pot Two-Step Synthesis of Polymer P2 from FPOx)

To a solution of FPOx (0.925 g, 2.300 mmol) and *p*-cresol (0.498 g, 4.606 mmol) in anhydrous DMF (8 mL) was added anhydrous potassium fluoride (0.536 g, 9.2 mmol). The mixture solution was stirred at room temperature under agron for 120 min before 6F-BPA (0.773 g, 2.299 mmol) and anhydrous potassium fluoride (0.268 g, 4.6 mmol) were added. The reaction mixture was then heated to 60 °C and stirred at the temperature for 8 h. After cooling to room temperature, the mixture solution was dropped into methanol/distilled water mixture (200 mL 1:1, v/v) to precipitate the polymer.

The following work-up procedure was the same as that for P1: 1.69 g, 90% yield; M_n = 5500, PDI = 2.4 (GPC); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s br, 4H), 7.12 (m, 4H), 6.84–6.90 (m, 8H), 2.29 (s, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.6 (s), −58.4 (m), −63.7 (m), −72.3 (m); FTIR (KBr, cm^{-1}): 3042, 2928, 1641, 1607, 1503, 1412, 1174 (br), 1085, 990, 936, 846, 734, 630, 518; T_g =129 °C (DSC); $T_{d,5\%}$ = 405 °C (TGA).

CONCLUSIONS

In summary, we have successfully demonstrated the unique stepped multifunctionality of a perfluorinated compound, that is, FPOx. Four levels of reactivity have been identified for the para and ortho C—F of FPOx, which can be easily triggered by the reaction temperature to enable quantitative reactions with nucleophiles. The C—F at lower levels of reactivity did not interfere with reactions of the C—F at higher levels of reactivity, which makes it possible to realize clean and hierarchically controllable reactions. The successful applications of such a multistepped reactivity of FPOx in versatile synthesis of grafted polymers with well-controlled structures and topologies have been demonstrated.

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