New Base-Doped Polyfluorene Derivatives

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ABSTRACT: A series of new well-defined acidic poly(2,7-fluorene) derivatives have been synthesized by palladium-catalyzed Suzuki couplings. Upon deprotonation (i.e., *base doping*), these conjugated polymers generate stable polymeric anions counterbalanced by alkali metal cations. The resulting polymeric salts exhibit interesting conducting properties. For instance, *base-doped* poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] exhibits an electrical conductivity of $10^{-2}-10^{-3}$ S/cm in air, at room temperature. In all these polymeric systems, a strong polarization of the electrical conduction is observed which seems to indicate a significant ionic transport. These electrical properties confirm the good potential of these novel acidic fluorene-based π-conjugated polymers for the development of various electrical and electrochemical solid-state devices.

Introduction

The wide-ranging applications of electroactive and photoactive conjugated polymers have attracted great interest in the development of functionalized polyacetylenes, polypyrroles, polythiophenes, polyanilines, polyfluorenes, etc.[1] For instance, these processable polymers (and related oligomers) have been utilized in the fabrication of light-emitting devices (LEDs and LECs),[2] electrochromic display devices,[3] laser dyes,[4] and organic transistors.[5] These materials combine then the excellent electrical and optical properties of metals or inorganic materials with the advantages of organic materials such as low density, easy processability, and synthetic tunability. The exceptional physical properties of conjugated polymers are mainly related to their π-conjugated backbone which leads to a strong absorption in the UV−vis range and allows the generation of stable and mobile charge carriers (radical cations, dications, or their negative analogues) upon partial oxidation or reduction.[1,3] The electronic structure of these conjugated polymers is modified by these reversible redox reactions (also called *doping reactions*), leading also to new electronic states within the band gap and associated electrochromic properties.[3,6] Another important way to generate mobile charge carriers in conjugated polymers is performed through an *acid doping* of amine-containing π-conjugated polymers. The best examples of this class of materials are polyaniline derivatives which exhibit an insulating-to-conducting transition through a simple protonation of the imine moieties, without any external redox process.[7] These acid-dopable polymers produce stable p-type conducting materials used for hole-injecting electrode in batteries and electrooptical devices.[8] Conversely, the preparation of novel acidic conjugated polymers could be interesting to develop n-type doped polymers through a *base-doping* process. Indeed, the extraction of the acidic protons could, in principle, generate delocalized anions in the π-conjugated system serving as negative charge carriers for electrical conduction. This novel approach could then be employed for the preparation of electron-injecting electrodes in light-emitting or electrochemical devices. On the other hand, it is possible to imagine that these polyanions (generated through base doping) could also serve as counterions to alkali metal cations (also generated through base doping) to produce an ionic (presumably, purely cationic) conducting polymer, useful for the development of polymer electrolytes in solid-state electrochemical cells.[9]

Along these lines, our research group has recently reported, for the first time, the synthesis of well-defined polymers possessing acidic fluorene derivatives for this new type of doping, called *base doping*.[10] These alternating polymers have been obtained from palladium-catalyzed couplings between acidic dibromoaryl compounds and diborolanylaryl compounds following a method previously developed for the synthesis of poly(paraphenylene)s.[11] In the past decade, oxidative polymerization methods[12] were used to generate various polyfluorenes, but these nonspecific polymerization reactions have led to partially cross-linked materials. A nickel-catalyzed reductive polymerization reaction, utilized by Yamamoto et al.,[13] Pei and Yang,[14] Zotti et al.,[15] and Miller et al.,[16] can lead to 2,7-linked polyfluorenes, but until now, this method does not seem appropriate for the preparation of acidic 9-monosubstituted polyfluorenes. First results obtained on poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-(ethylfluorene-9-carboxylate)] have revealed an electrical conductivity of $10^{6}-10^{-5}$ S/cm after base doping, but it was impossible to distinguish between ionic or electronic conduction.[10] After previous studies,[17] 9-monosubstituted fluorene derivatives bearing a stronger electron-withdrawing substituent than an ester group should exhibit a pK_a clearly lower than the pK_a of water, affording air-stable, base-doped materials. For these reasons, it could be interesting to introduce ketone or benzoyl group at the 9-position of 2,7-dibromofluorenes. However, in addition to the formation of stable charge carriers, some structural aspects are also required to optimize the electrical properties of the polymeric materials. For instance, it is believed that a good stacking of the polymeric chains is necessary to allow an efficient intermolecular electronic charge transport. The recent determination of the crystalline structure of 9,9-substituted fluorenes[18] has revealed

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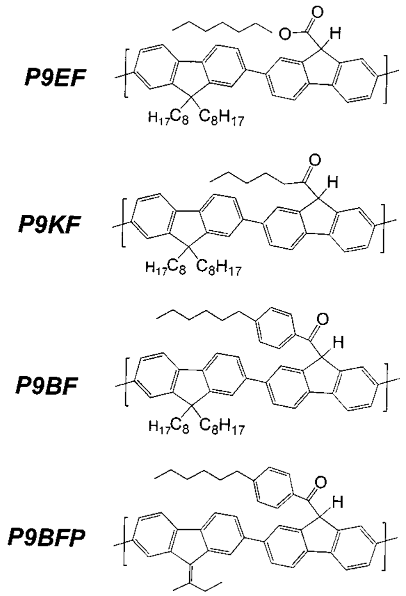
Chart 1



that such a good stacking could be difficult in poly(9,9-dialkylfluorene) derivatives, and it would be then interesting to include a sp^2 hybridization at the 9-position to get the substituents parallel to the conjugated backbone in the base-doped form.

Therefore, following the above-mentioned structural requirements, we report here the synthesis and characterization of a new series of acidic polyfluorenes, poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-(hexylfluorene-9-carboxylate)] (**P9EF**), poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(pentylfluorene-9-carbonyl)] (**P9KF**), poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (**P9BF**), and poly[2,7-(9-isobutylidenefluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (**P9BFP**) (see Chart 1). It is expected that these polymers could be used as air-stable conducting materials (through base doping) for various electrical and electrochemical solid-state devices.

Experimental Section

Material. Fluorene, hexanoic anhydride, and 4-hexylbenzoyl chloride were obtained from Aldrich Co. and used without purification. Hexyl chloroformate (Aldrich) was distilled over a $CaCl_2$ and K_2CO_3 mixture. Tetrakis(triphenylphosphine)-palladium(0) was synthesized following the procedure reported in the literature[19] and stored in a drybox in inert (and light-free) conditions to prevent the oxidation of palladium(0).[20] THF (Aldrich) was dried over sodium and benzophenone as drying indicator.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 and AMX400 in deuterated chloroform ($CDCl_3$) solutions whereas 2D analyses were carried out using a Bruker AMX600 in deuterated benzene (C_6H_6-d_6) solutions, at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with a HPLC Waters 510 Pump using a Waters 410 differential refractometer. The calibration curve was made with a series of monodispersed polystyrene standards in tetrahydrofuran (HPLC grade, Aldrich) at 308 K. UV−vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A).

The base doping was done by the treatment of polymers by potassium or lithium *tert*-butoxide in warm anhydrous THF. Precipitated polymers were filtered on nylon filters (0.45 μm) under vacuum and washed with cooled THF to remove unreacted potassium or lithium *tert*-butoxide. Before electrical measurements on pressed pellets, all base-doped polymers were put under reduced pressure (25 °C/0.1 mmHg) for few hours. Electrical conductivities were evaluated by the four-probe technique[21] on pressed pellets, in air, at room temperature.

The impedance measurements were performed, under ambient conditions, with a Hewlett-Packard impedance/admittance analyzer HP4192a instrument over a frequency range of 1−13 000 kHz. Each sample was prepared as a pressed pellet of an average thickness of 0.015 cm and an average area of 0.75 cm^2. The impedance cell was made of two stainless electrodes with a surface area of 1.32 cm^2. The sinusoïdal (ac) voltage used was 5, 10, or 15 mV.

Synthesis. 9,9-Dioctylfluorene (**1**), 2,7-dibromo-9,9-dioctylfluorene (**2**), 2,7-dibromofluorene (**3**), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) were prepared following already published procedures.[3a,10,22]

Hexyl 2,7-Dibromofluorene-9-carboxylate (5). To a solution of diisopropylamine (3.08 g, 30.4 mmol, Aldrich) in anhydrous THF (5 mL) at −78 °C was added dropwise 11.6 mL (28.95 mmol) of *n*-butyllithium (2.5 M in hexane, Aldrich). The mixture was stirred at −78 °C for 20 min and at 0 °C for 15 min and cooled again at −78 °C. 2,7-Dibromofluorene (**3**, 4.689 g, 14.48 mmol) in anhydrous THF (70 mL) was added dropwise to the lithium diisopropylamide (LDA) solution and stirred for 30 min at this temperature. Hexyl chloroformate (2.359 g, 14.33 mmol, Aldrich), previously distilled over $CaCl_2$, was added to the mixture. The solution was warmed to room temperature and was stirred for 3 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 3% ethyl acetate in hexane, Rf 0.49) to provide 5.70 g (87%) of the title product as a yellow solid. Mp 85−87 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 142.10; 139.25; 131.35; 129.05; 121.32; 121.16; 65.93; 52.97; 31.25; 28.39; 25.50; 22.43; 13.87.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.82 (s, 2H); 7.54 (m, 4H); 4.82 (s, 1H); 4.18 (q, 2H, J = 6.6 Hz); 1.66 (m, 2H); 1.32 (m, 6H); 0.90 (t, 3H, J = 6.3 Hz).

HRMS. Calcd for $C_{20}H_{20}O_{2}79Br_{2}$: 449.9830. Found: 449.9822.

Pentyl 2,7-Dibromofluorene-9-carbonyl (6). To a solution of diisopropylamine (3.94 g, 38.9 mmol, Aldrich) in anhydrous THF (5 mL) was added dropwise 7.41 mL (18.52 mmol) of *n*-butyllithium (2.5 M in hexane, Aldrich), at −78 °C. The mixture was stirred at this temperature (−78 °C) for 20 min and at 0 °C for 15 min and cooled again at −78 °C. 2,7-Dibromofluorene (**3**, 3.00 g, 9.26 mmol) in anhydrous THF (70 mL) was added dropwise to the lithium diisopropylamide (LDA) solution and stirred for 30 min at this temperature. Hexanoic anhydride (1.964 g, 9.17 mmol, Aldrich) was added to the mixture. The solution was allowed to warm to room temperature and stirred for 5 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 4% ethyl acetate in hexane, Rf 0.47) to provide 3.20 g (82%) of the title product as a yellow solid. Mp 136−138 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 206.43; 142.35; 139.69; 131.39; 128.10; 121.49; 121.45; 62.30; 38.03; 30.66; 22.94; 22.02; 13.63.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.65 (s, 1H); 7.63 (m, 3H); 7.58 (dd, 2H, J = 1.9 and 6.2 Hz); 4.78 (s, 1H); 1.92 (t, 2H, J = 7.2 Hz); 1.38 (m, 2H); 1.11 (m, 2H), 1.04 (m, 2H); 0.77 (t, 3H, J = 7.0 Hz).

HRMS. Calcd for $C_{19}H_{18}O^{79}Br_2$: 420.982. Found: 420.980.

4-Hexylbenzoic Acid (7). To a mixture of 2 M NaOH aqueous solution (25 mL) and THF (25 mL) was added 4-hexylbenzoyl chloride (2.247 g, 10 mmol, Aldrich). This solution was stirred and refluxed for 3 h. The mixture was then poured in 1 M NaOH aqueous solution (60 mL) and extracted with $CHCl_3$. 4-Hexylbenzoyl chloride was left in organic phase, and the acidic compound was recovered in the aqueous phase. The aqueous extracts were acidified to pH 1 and extracted again with $CHCl_3$ where 4-hexylbenzoic acid was recovered in the neutral form. The organic extracts were dried over magnesium sulfate. The solvent was removed to give 2.00 g (97%) of the title compound. White crystal. Mp 97−98 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 172.69; 149.57; 130,-26; 128.51; 126.76; 36.07; 31.63; 31.04; 28.91; 22.55; 14.03.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): >10 (1H acid); 8.04 (dd, 2H, $J = 1.8$ and 4.9 Hz); 7.30 (d, 2H, $J = 8.5$ Hz); 2.69 (t, 2H, $J = 7.8$ Hz); 1.65 (m,2H); 1.33 (m, 6H); 0.90 (t, 3H, $J = 7.2$ Hz).

Phenyl 4-Hexylbenzoate (8).[23] To a solution of 4-hexylbenzoic acid (3.02 g, 14.79 mmol, Aldrich) in diethyl ether (65 mL) was added 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.181 g, 1.48 mmol, Aldrich), phenol (1.531 g, 16.27 mmol, Aldrich), and dicyclohexylcarbodiimide (DCC) (3.354 g, 16.27 mmol, Aldrich). The one-pot reaction was stirred for 4 h at room temperature. The white precipitate (dicyclohexylurea) was filtrated on a Büchner funnel, and the residue was extracted with distilled water (60 mL), 5% acetic acid aqueous solution (40 mL), and water again (50 mL). The extracts were dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 5% ethyl acetate in hexane, Rf 0.6) to provide 4.06 g (97%) of the title product as a colorless oil.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 165.17; 151.00; 149.28; 130.18; 129.38; 128.58; 126.95; 125.70; 121.71; 36,02; 31.61; 31.05; 28.86; 22.53; 14.02.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 8.15 (dd, 2H, $J = 4.9$ and 1.7 Hz); 7.45 (m, 2H); 7.34 (d, 2H, $J = 8.5$ Hz); 7.27 (m, 3H); 2.72 (t, 3H, $J = 7.5$ Hz); 1.68 (q, 2H, $J = 7.6$ Hz); 1.35 (m, 6H); 0.93 (t, 3H, 6.8 Hz).

HRMS. Calcd for $C_{19}H_{23}O_2$: 283.170. Found: 283.170.

4-Hexylphenyl (2,7-Dibromofluorene-9-carbonyl) (9). To a solution of diisopropylamine (3.94 g, 38.9 mmol, Aldrich) in anhydrous THF (5 mL) at −78 °C was added dropwise 7.41 mL (18.52 mmol) of *n*-butyllithium (2.5 M in hexane, Aldrich). The mixture was stirred at −78 °C for 20 min and at 0 °C for 15 min and cooled again at −78 °C. 2,7-Dibromofluorene (**3**, 3.00 g, 9.26 mmol) in anhydrous THF (70 mL) was added dropwise to the lithium diisopropylamide (LDA) solution and stirred for 30 min at this temperature. Phenyl 4-hexylbenzoate (**8**, 2.60 g, 9.17 mmol) was added to the mixture. The solution was allowed to warm to room temperature and was stirred for 6 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 7% ethyl acetate in hexane, Rf 0.53) to provide 3.17 g (67%) of the title product as a yellow solid. Recrystallization in 2-propanol can replace column chromatography. Mp 139−141 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 195.48; 149.73; 144.00; 139.50; 133.64; 131.20; 129.18; 128.88; 128.24; 121.54; 121.42; 57.19; 35.90; 31.50; 30.75; 28.81; 22.43; 13.96.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.77 (d, 2H, $J = 8.1$ Hz); 7.62 (d, 2H, 8.1 Hz); 7.55 (d, 2H, $J = 8.5$ Hz); 7.49 (s, 2H,); 7.27 (d, 2H, $J = 8.0$ Hz); 5.61 (s, 1H); 2.68 (t, 2H, $J = 7.5$ Hz); 1.64 (q, 7.3 Hz); 1.33 (m, 6H); 0.90 (t, 3H, $J = 6.1$ Hz).

HRMS. Calcd for $C_{26}H_{25}O^{79}Br_2$: 511.0251. Found: 511.0243.

2,7-Dibromofluoren-9-one (10).[24] CrO_3 (2.4 g, 24 mmol) was added to a suspension of 2,7-dibromofluorene (**3**, 3.19 g, 9.86 mmol) in acetic anhydride (45 mL) under stirring at room temperature. The reaction mixture was stirred for 5 h. The solid was then added and put in suspension into a 2% HCl solution (100 mL). The suspension was filtered off and washed with cold water. The product was recrystallized in 2-propanol or purified by column chromatography (silica gel, 8% ethyl acetate in hexane, Rf 0.3) to provide 3.13 g (94%) of the title product as a yellow solid. Mp 202−204 °C; mp (lit.) 203−205 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 142.15; 137.36; 135.16; 127.73; 123.21; 121.74.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.76 (d, 2H, $J = 1.9$ Hz); 7.63 (q, 2H, $J = 1.3$ and 0.5 Hz); 7.61 (dd, 2H, $J = 0.6$ and 1.5 Hz); 7.37 (d, 2H, $J = 7.9$ Hz).

HRMS. Calcd for $C_{13}H_6O^{79}Br_2$: 336.887. Found: 336.886.

2,7-Dibromo-9-(1-methylpropyl)-9-hydroxyfluorene (11). To a solution of 2,7-dibromofluoren-9-one (**10**, 1.555 g, 4.60 mmol) in anhydrous THF (35 mL) was added *sec*-butylmagnesium chloride (2.53 mL, 2.0 M, Aldrich) at −78 °C. The color of the mixture changed to deep red. After 2 h at −78 °C, the solution was quenched at −40 °C with methanol and was warmed to room temperature gradually. The organic phase was extracted with a 2% HCl aqueous solution (60 mL) and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 10% ethyl acetate in hexane, Rf 0.38) to provide 978 mg (54%) of the title product (**11**) as a viscous brown oil.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 150.22; 149.83; 137.91; 137.66; 131.83; 131.81; 127.41; 127.24; 121.82; 121.77; 120.99; 120.94; 84.81; 43.88; 23.33; 13.11; 12.21.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.55 (dd, 2H, $J = 11.4$ and 1.4 Hz); 7.46 (dd, 2H, $J = 6.8$ and 1.3 Hz); 7.39 (d, 2H, $J = 8.0$ Hz); 2,41 (s, 1H); 2.02 (m, 1H);1.55 (m, 1H); 0.83 (m, 4H); 0.73 (d, 3H, $J = 6.8$ Hz).

HRMS. Calcd for $C_{17}H_{16}\,O^{79}Br_2$: 393.9568. Found: 393.9578.

2,7-Dibromo-9-isobutylidenefluorene (12).[25] Compound **11** (800 mg, 2.37 mmol) and *p*-TsOH (25 mg) in benzene (8 mL) were heated to reflux for 5 h, and generated water was removed by using a Dean−Stark apparatus. The mixture was cooled to room temperature and then extracted with a K_2CO_3 2% solution (2 × 30 mL). The organic phase was dried, filtered, and evaporated to give, in a quantitative yield, the title compound as a pale-yellow solid. Mp 104−105 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 150.51; 140.54; 139.68; 137.33; 137.23; 129.95; 129.31; 129.26; 128.02; 127.45; 120.99; 120.84; 120.43; 120.33; 31.64; 24.03; 11.69.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.89 (d, 2H, $J = 18.2$ Hz); 7.53 (dd, 2H, $J = 6.4$ and 1.7); 7.42 (dd, 2H, $J = 6.9$ and 1.1 Hz); 2.79 (q, 2H, $J = 7.5$ Hz); 2.47 (s, 3H); 1.32 (t, 3H, $J = 7.6$ Hz).

HRMS. Calcd for $C_{17}H_{14}{}^{79}Br_2$: 375.9479. Found: 375.9462.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-isobutylidenefluorene (13). To a solution of 2,7-dibromo-9-isobutylidenefluorene (**12**, 660 mg, 1.75 mmol) in THF (18 mL) at −78 °C was added, with a syringe, 1.41 mL (35.3 mmol) of *n*-butyllithium (2.5 M in hexane, Aldrich). The mixture was stirred at −78 °C, warmed to 0 °C for 15 min, and cooled again at −78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.798 g, 4.28 mmol, Aldrich) was added rapidly to the solution, warmed to room temperature, and stirred for 24 h. The mixture was poured into water and extracted with diethyl ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, 8% ethyl acetate in hexane, Rf 0.15) to provide 529 mg (64%) of the title product as a pale-yellow solid. Mp 218−220 °C.

^{13}C NMR (75 MHz, $CDCl_3$). δ (ppm): 147.61; 141.95; 139.10; 138.23; 132.92; 132.86; 131.27; 131.10; 130.79; 130.77; 127.8 (2C linked to boron,[26] broad peak); 119.03; 118.95; 83.52; 31.66; 24.76; 24.13; 11.94.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 8.27 (d, 2H, $J = 7.9$ Hz); 7.76 (m, 4H); 2.90 (q, 2H, $J = 7.6$ Hz); 2.56 (s, 3H); 1.31 (m, 27H).

HRMS. Calcd for $C_{29}H_{38}O_4{}^{11}B_2$: 472.2956. Found: 472.2970.

General Procedure of Polymerization. Carefully purified 2,7-dibromofluorene derivative (1.00 equiv), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-substitued fluorene (1.00 equiv), and $(PPh_3)_4Pd(0)$ (0.5−2.0 mol %) were dissolved in a mixture of THF ([monomer] = 0.4 M) and aqueous 2 M K_2CO_3 (1:1.5 THF). Solvents were purged with dry argon for 3 h under reflux. The solution was first put under argon atmosphere and was heated at 80 °C with vigorous stirring for 48 h. The whole mixture was then poured into methanol (150 mL). The precipitated material was recovered by filtration through a Büchner funnel and washed with a dilute aqueous HCl solution. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF and $CHCl_3$. Yields: ∼60−75%.

Poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-(hexylfluorene-9-carboxylate)] (P9EF). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) and hexyl 2,7-dibromofluorene-9-carboxylate (**5**) were used in this polymerization.

^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 170.84; 151.62; 141.62; 140.83; 140.07; 140.03; 139.88; 128.65; 127.33; 127.06; 126.04; 124.28; 121.31; 120.22; 119.95; 65.53; 55.25; 53.58; 40.47; 31.65; 31.26; 29.97; 29.57; 29.14; 28.53; 25.48; 23.74; 22.47; 22.39; 13.93; 13.86.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 8.02 (m, 2H); 7.88 (m, 2H); 7.81 (m, 4H); 7.65 (m, 4H); 5.07 (s, 1H); 4.27 (m, 2H); 2.13 (m, 4H); 1.74 (m, 4H), 1.54 (m, 6H); 1.40 (m, 4H); 1.12 (m, 20H); 0.81 (m, 9H).

UV−vis. λ_{max} ($CHCl_3$): 368 nm.

Poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(pentylfluorene-9-carbonyl)] (P9KF). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) and pentyl 2,7-dibromofluorene-9-carbonyl (**6**) were used in this polymerization.

^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 209.39; 152.32; 142.52; 141.61; 141.31; 140.69; 140.11; 128.02; 126.56; 124.10; 121.77; 121.12; 120.60; 64.01; 55.88; 40.85; 37.91; 32.16; 31.36; 30.45; 30.11; 29.65; 29.62; 23.86; 22.99; 22.62; 14.45; 14.24.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.96 (m, 2H); 7.84 (m, 6H); 7.74 (m, 6H); 5.04 (s, 1H); 2.10 (m, 6H); 1.46 (m, 2H); 1.11 (m, H); 0.81 (m, 3H); 0.74 (t, 3H, J = 7.5 Hz).

UV−vis. λ_{max} ($CHCl_3$): 373 nm.

Poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)-fluorene-9-carbonyl)] (P9BF). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) and 4-hexylphenyl (2,7-dibromofluorene-9-carbonyl) (**9**) were used in this polymerization.

^{13}C NMR (100 MHz, $CDCl_3$). δ (ppm): 197.45; 151.64; 143.49; 140.91; 140.25; 140.03; 139.67; 134. 11; 129.38; 128.64; 127.21; 125.95; 123.71; 122.99; 121.25; 120.64; 119.89; 58.92; 55.24; 40.36; 35.95; 31.64; 31.53; 30.85; 30.54; 29.91; 29.09; 28.90; 28.81; 24.84; 23.73; 22.47; 13.94.

^{1}H NMR (300 MHz, $CDCl_3$). δ (ppm): 7.98 (m, 2H); 7.77 (m, 8H); 7.56 (m, 2H); 5.80 (s, 1H); 2.66 (m, 2H); 2.04 (m, 4H), 1.63 (m, 2H); 1.30 (m, 2H); 1.10 (m, 26H); 0.90 (m, 3H); 0.80 (m, 6H); 0.72 (m, 2H).

UV−vis. λ_{max} ($CHCl_3$): 377 nm.

Poly[2,7-(9-isobutylidenefluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (P9BFP). 4-Hexylphenyl (2,7-dibromofluorene-9-carbonyl) (**9**) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-isobutylidenefluorene (**13**) were used in this polymerization. No NMR analysis was performed because this polymer is not sufficiently soluble. The insoluble high weight fraction was used for the electrical measurements.

UV−vis. λ_{max} ($CHCl_3$): 386 nm.

Results and Discussion

Polymerization. Following a synthetic procedure similar to that described in Scheme 1, all required monomers, as well as poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-(hexylfluorene-9-carboxylate)] (**P9EF**), poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(pentylfluorene-9-carbonyl)]-(**P9KF**), poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (**P9BF**), and poly[2,7-(9-isobutylidenefluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (**P9BFP**), have been prepared in good yields. In particular, the synthesis of compound **12** gives an interesting method to develop 9-(dialkylmethylene)-fluorene derivatives from the required alkylmagnesium bromide. The utilization of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-substituted fluorenes simplified their purification by column chromatography combined with the advantage of the presence of a protecting group (1,1,2,2-tetramethylethylene glycol) on the boronic acid moieties. These protecting groups did not affect the yield of couplings, since, as reported for ethylene glycol,[26] a deprotection reaction is induced by potassium carbonate during the polymerization reaction. Tetrahydrofuran (THF) has been used instead of toluene[10] to increase the solubility of the growing chains and, consequently, to obtain higher molecular weights. The resulting alternating P9EF, P9KF, and P9BF are completely soluble in $CHCl_3$ and THF and slightly in CH_2Cl_2. On the basis of size-exclusion chromatography (performed in THF with a calibration curve using monodispersed polystyrene standards), the number-average molecular weight of these polymers is around 12 000 with a polydispersity index of about 2, consistent with a polycondensation reaction (see Table 1). Only P9BFP is poorly soluble in these solvents, and it is believed that the soluble fraction is related to low molecular weight polymer chains. This poor solubility could be explained by the presence of short side chains, relatively long and flexible side chains being required to enhance the solubility of these stiff macromolecules.[10]

Scheme 1

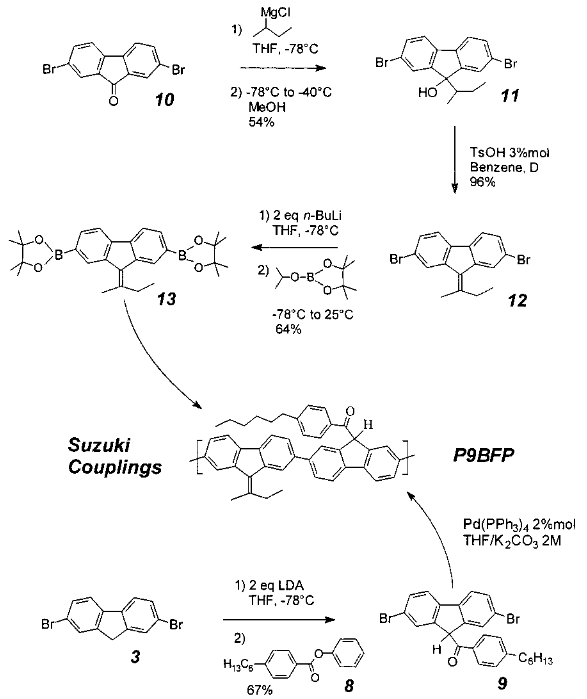


Table 1. Number-Average (M_n) and Weight-Average (M_w) Molecular Weights of the Polyfluorene Derivatives

polymer	M_n	M_w	M_w/M_n
P9EF	12 600	23 700	1.9
P9KF	11 200	31 500	2.8
P9BF	10 900	20 500	1.9
P9BFP[a]	4 400	7 000	1.6

[a] Low molecular weight, soluble fraction (<10%).

^{1}H NMR Analysis. In Figure 1, it is easy to find the characteristic peaks of each monomer in the ^{1}H NMR spectrum of the polymer P9BF. The first methylene of alkyl chains of monomer **4** around 2.0 ppm and the first methylene of the alkyl chain of compound **9** about 2.6 ppm are clearly visible in the spectrum of the corresponding alternating copolymer. As mentioned in the Introduction, different electron-withdrawing groups have been introduced at the 9-position of fluorene to develop highly acidic (base-dopable) conjugated polymers. Along these lines, it is worth noting that alkyl

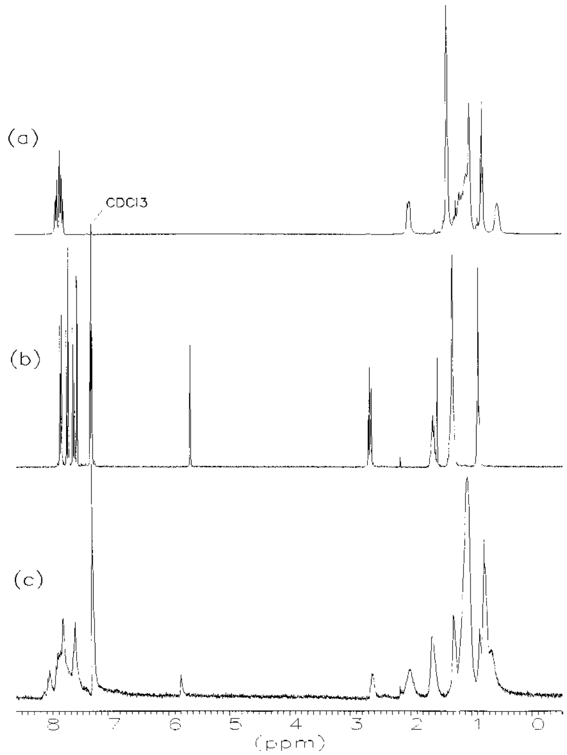


Figure 1. ^{1}H NMR spectrum of (a) 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**), (b) 4-hexylphenyl (2,7-dibromofluorene-9-carbonyl) (**9**), and (c) poly[2,7-(9,9-dioctylfluorene)-*alt*-2,7-((4-hexylphenyl)fluorene-9-carbonyl)] (**P9BF)** in $CDCl_3$ solution, at 298 K.

fluorene-9-carboxylate shows a pK_a about 14 in water while 9-cyanofluorene has a pK_a of 12 in the same solvent.[17b,c] Considering that the benzoyl group is an electron-withdrawing agent as strong as a cyano group,[17d,e] it can then be assumed that a benzoyl moiety at the 9-position of fluorene should give a pK_a comparable to that one observed for 9-cyanofluorene. Therefore, it can be expected that the present acidic polyfluorenes should have a pK_a below the pK_a of water, leading to air-stable base-doped polymers. The acidic strength of the proton at the 9-position of these fluorene derivatives can be also derived from its chemical shift in their respective ^{1}H NMR spectrum. Interestingly, polymers show a peak for the acidic proton at slightly higher values than those obtained for their corresponding monomers (see Experimental Section) which could be explained by the better stability of the anions in the delocalized polymeric systems. For example in Figure 1, the acidic proton of P9BF (at the 9-position) is observed at 5.80 ppm, a 0.19 ppm shift compared to the corresponding acidic monomer. Moreover, P9BF shows the highest chemical shift or the acidic proton in the present series of copolymers which could be explained by the stronger electron-withdrawing effect of the benzoyl group. The presence of an ester group at the 9-position in P9EF leads to a chemical shift at 5.07 ppm for the acidic proton while P9BK exhibits an acidic proton at 5.04 ppm.

Base-Doping and Electrical Properties. Upon deprotonation with potassium *tert*-butoxide in THF (see Scheme 2), all these acidic polyfluorenes exhibit a color change from yellow (maximum of absorption around 368−386 nm) to dark orange (a new band around 415−445 nm). As reported in a previous study,[10] this phenomenon is reversible, and upon reprotonation, the polymers recover their initial color. However, upon deprotonation, all polymeric salts become pratically insoluble in THF. Four-probe electrical measurements on dried pellets of base-doped polymers revealed good electrical conductivities (see Table 2). For comparison purposes, first measurements have been performed on base-doped P9EF. As previously reported for a similar polymer,[10] an electrical conductivity of 10^{-6}−10^{-5} S/cm was measured. More precisely, a conductivity of 10^{-5} S/cm is first measured, which stabilizes around 10^{-6} S/cm after few hours of electrolysis. Due to their peculiar chemical structure, these polymeric salts could be electronic and/or ionic conductors. The electronic contribution would be related to the intrachain and interchain transport of negative charge carriers whereas it can be also assumed that the potassium ions could contribute to a purely cationic conductivity. However, at this relatively low conductivity level, it is difficult to distinguish between both processes. A similar behavior was also observed with P9KF. This base-doped polymer with potassium as the counterion shows an initial conductivity of 5×10^{-3} S/cm, which stabilizes around 10^{-4} S/cm. However, a strong polarization has been observed in this case, the conductivity level being stable only if the polarity of the electrodes is reversed periodically after a certain period time (e.g., few hours) of electrolysis. These results point out a possible significant contribution of an ionic mechanism in the conduction processes. To enhance the air stability of the generated anion, a benzoyl group was introduced at the 9-position of fluorene (P9BF). This base-doped polymer should be clearly stable in the presence of water. This base-doped polymer gives a conductivity up to 5×10^{-2}

Scheme 2

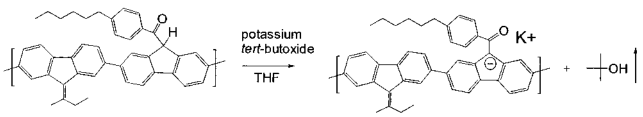


Table 2. Electrical Conductivity of Acidic Polyfluorene Derivatives in Their Deprotonated (Base-Doped) Form at 298 K, in Air

		dc analysis[a]	ac analysis
polymer	cation	σ (S/cm)[b]	σ (S/cm)[c]
P9EF	K^+	1×10^{-6}	
P9KF	K^+	2×10^{-4}	2×10^{-3}
P9BF	K^+	8×10^{-4}	4×10^{-3}
P9BF	Li^+	6×10^{-3}	8×10^{-2}
P9BFP	K^+	1×10^{-3}	

[a] Four-probe technique. [b] "Stable" conductivity. [c] Conductivities evaluated by impedance measurements.

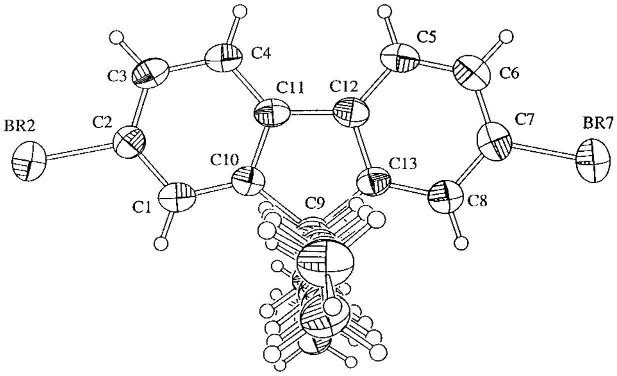


Figure 2. Solid-state structure of 2,7-dibromo-9,9-dioctylfluorene, at 210 K.

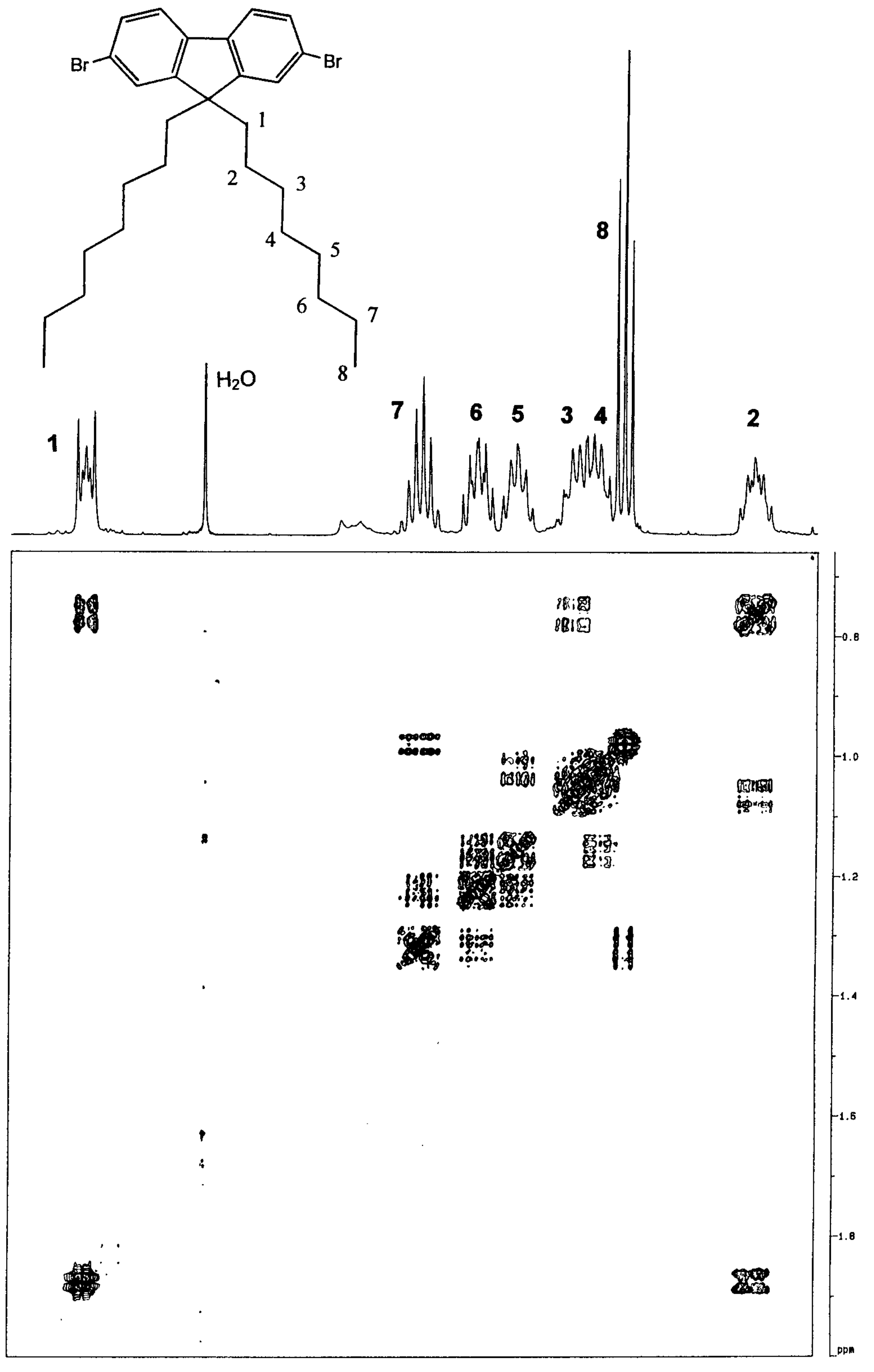


Figure 3. The 600 MHz ^{1}H NMR 2D-COSY spectrum of 2,7-dibromo-9,9-dioctylfluorene in deuterated benzene (C_6H_6-d_6), at 298 K.

S/cm with a stable value around 10^{-3} S/cm. Once again, a strong polarization of the electrical conductivity has been observed. By changing potassium as the counterion to lithium, the resulting base-doped P9BF (lithium salt) gives a slightly higher conductivity which could be related to a smaller ionic radius of the lithium, allowing a better cationic migration in the polymeric materials. Some crystallographic analyses on deprotonated monomers showed that the lithium ion interacts with all carbon atoms of the cyclopentadienyl ring due to the delocalization of the generated anion.[28] From these results, it is possible to believe that lithium ions are inserted within the main chains, and their high mobility could then be explained by a more delocalized interaction with the π-conjugated polyanions. Interestingly, these base-doped polyfluorenes show higher electrical

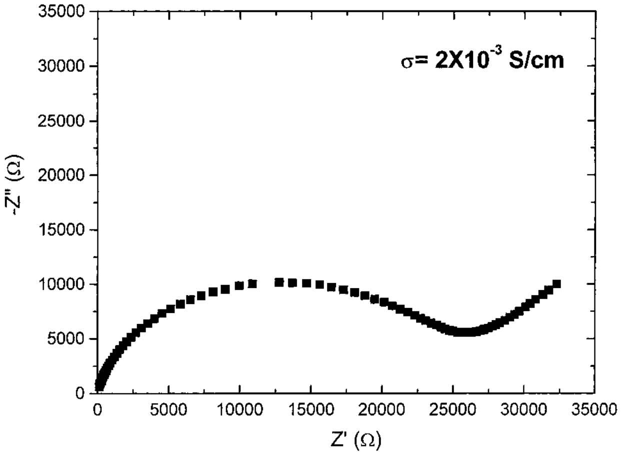


Figure 4. Impedance spectrum of base-doped **P9KF**, with potassium as counterion. The analysis was done on a pressed pellet with a thickness of 0.015 cm and section area of 0.79 cm^2. The frequency range was (1−5) × 10^5 Hz, and the sinusoidal voltage was 10 mV.

conductivities than those reported for similar oxidized polyfluorenes[12c,29] (electronic conductivity of around 10^{-4} S/cm), which could give another indication of a different conduction mechanism.

The stability of the base-doped form is an obvious requirement to obtain useful conducting materials, but for electronically conducting polymers, an efficient intrachain and interchain transport is also very important. Recently, from X-ray analyses on model compounds,[18] it has been shown that the alkyl side chains in 9,9-dioctylfluorene are orthogonal to the fluorene unit (Figure 2), which should hinder the interchain electrical transport. A similar conformation is also found in solution since, as shown in Figure 3, the protons attached to the second and fourth carbon atoms of the octyl side chains are more shielded than those attached to the first and third carbon atoms, respectively. This fact is explained by the position of protons in the anisotropic cone induced by the aromatic ring, confirming that alkyl chains are also orthogonal to the fluorene moieties in solution. To enhance such an interchain electrical transport, P9BFP was then synthesized. Indeed, in its base-doped form, it can be anticipated that all substituents of P9BFP (including possibly an enolate form of the deprotonated unit) are placed within the same axis as the fluorene backbone. A better stacking of the polymer chains could also improve the mobility of the ionic species. Interestingly, this base-doped polymer shows an electrical conductivity near 10^{-1} S/cm, which stabilizes at 10^{-3} S cm^{-1} after several hours of electrolysis in air. This conductivity level is then stable for days, assuming a regular switching of the polarity of the electrodes. Clearly, the stable conductivity levels of all these polymers include an important ionic contribution, but the nature of the initial conductivity is intriguing. Indeed, the initial dc conductivity levels are unstable, which could mean that the charge carriers are not stable or become trapped. The possible presence of an enolate form in these materials could explain this behavior, and it would be therefore interesting to incorporate cyano groups instead of benzoyl moieties in such acidic polyfluorenes.

Impedance spectroscopy is also a good technique to evaluate electrical conductivities and to investigate the nature of the conduction mechanism. For instance, in Figure 4, impedance measurements on base-doped P9KF revealed the presence of one semicircle at high frequencies, which could suggest the presence of only one major type of conduction.[30] By the extrapolation of this semicircle on the X axis, the absolute resistance obtained for each copolymer gives conductivities in the same range as the values obtained by the four-probe technique (see Table 2). Although the determination of the exact nature of the electrical transport is obviously a subject of further investigation, the strong polarization phenomena observed in the dc measurements seem to indicate a signification contribution of an ionic transport in the electrical conduction.[31] These actual air-stable electrical conductivities obtained with this novel base-doping approach are then certainly promising enough to justify their evaluation in various electrical devices.

Conclusion

A new type of doping process (i.e., base doping) has been demonstrated with well-defined acidic poly(2,7-fluorene) derivatives. Electrical conductivities up to 10^{-2}−10^{-3} S/cm have been observed with base-doped polyfluorenes. The determination of the nature of the charge carriers and of the transport mechanisms in these base-doped polymers is still a subject of investigation, but the strong polarization observed in dc measurements in these materials suggests a significant contribution of an ionic (cationic) mechanism. Therefore, acidic polyfluorene derivatives could possibly be useful as polymeric (and purely cationic) electrolytes for the development of solid-state electrochemical devices as well as n-type electrically conducting polymers.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **P9EF**, **P9KF**, and **P9BF** as well as UV−vis spectra of **P9EF**, **P9KF**, **P9BF**, and **P9BFP** in CHCl$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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