Synthesis, Characterization, and Langmuir–Blodgett Films of Fluorinated Polythiophenes

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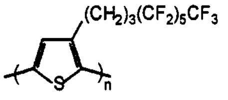
ABSTRACT: Fluorinated poly(alkylthiophenes) and poly(alkoxythiophenes) have been chemically and electrochemically synthesized. Poly[3-(tridecafluorononyl)thiophene] has been found to be soluble in octafluorotoluene and has been characterized by ^{1}H NMR spectroscopy, while poly[3-[(pentadecafluorooctyl)-oxy]-4-methylthiophene] and poly(3′-perfluorohexylterthiophene) are insoluble in common or fluorinated organic solvents. Electrical, electrochemical, and optical properties of the fluorinated polythiophenes are compared with those of their respective alkyl analogues. Langmuir–Blodgett films have been obtained from pure poly[3-(tridecafluorononyl)thiophene]. Monolayers of this polymer have shown thermochromic properties similar to those of spin-coated films, indicating that the interchain interactions are not the dominant factor in this thermally induced conformational transition.

Introduction

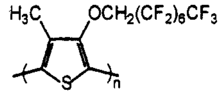
Polythiophenes have recently received much attention because of their interesting and unusual electrical, electrochemical, and optical properties. For instance, it has been reported that some poly(3-alkylthiophenes) and poly(3-alkoxy-4-methylthiophenes) exhibit interesting thermochromic properties.[1-8] Different studies[1-6] have revealed that these optical effects are related to an increase of disorder in the side chains upon heating, which then forces the polymer backbone to adopt a twisted conformation. Moreover, it has been recently shown that the thermochromic properties observed in some polythiophene derivatives are not directly associated with the melting or glass transition of the materials.[9] However, it is still unclear whether this conformational transition is a property of the material (bulk property) or of the polymer chain (molecular property).

Although the preparation of an isolated polymer chain is practically impossible, the preparation of a monolayer of these polymers by the Langmuir–Blodgett technique could allow the study of a bidimensional material and should therefore give a better understanding of the influence of the interchain interactions (packing) on this conformational transition. However, it is well-known that pure poly(3-alkylthiophenes) do not form stable monolayers onto the water subphase, but aggregate into islands of polymer.[10,11] Surface pressure is observed only at very small molecular areas when the aggregates of polymer are forced together. On the other hand, many studies have shown that it is possible to fabricate high-quality Langmuir–Blodgett films from alkyl-substituted polythiophenes by dispersing them in stearic or arachidic acid[10-19] or other polymers.[20] However, the presence of such a matrix changes the interactions and the free volume between the polymer chains and, consequently, the observed thermochromic behavior is not that of the pure polymer but that of the blend.

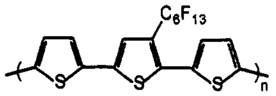
Because of the high hydrophobicity of fluorinated molecules, the replacement of the alkyl side chain by fluorinated analogues could lead to the formation of molecules with an amphiphilic nature and, therefore, could allow the formation of stable monolayers of pure polythiophene derivatives at an air–water interface. For this purpose, we report here the synthesis and characterization of poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)-thiophene] (PFALKYL) and poly[3-[(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentadecafluorooctyl)oxy]-4-methylthiophene] (PFALKOXY). We also want to report, for the first time, the synthesis of a polythiophene derivative with a perfluorinated group (longer than a methyl group)[21] immediately attached to the thiophene ring, poly(3′-perfluorohexylterthiophene) (PFTRIMER). The electrical, electrochemical, and optical properties of all these fluorinated polymers are analyzed and compared to those of their respective alkyl analogues. The preparation and thermochromic properties of monolayers of PFALKYL are also described.



PFALKYL



PFALKOXY



PFTRIMER

Results and Discussion

Polymer Characterization. All polymers were synthesized by chemical and electrochemical oxidation. The oxidation potentials of the monomers and their corresponding polymers are given in Table 1. Values for poly(3-decylthiophene),[22,23] poly[3-(octyloxy)-4-methylthiophene],[24] and poly(3′-heptyltertiophene)[25] are also included for comparison purposes. As already reported by Büchner et al.,[26] three methylene groups between the thiophene ring and the fluorinated part were needed to obtain fluorinated poly(3-alkylthiophene)s with electrochemical and electrical properties similar to those of their alkyl analogues. This effect can be attributed to the high electronegativity of the fluorinated group, which increases the oxidation potential of the monomers and makes difficult the subsequent formation of well-defined polymers. For instance, 3-perfluorohexylthiophene exhibits an oxidation potential higher than 3 V vs SCE and does not lead to any polymeric products by chemical or

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Table 1. Summary of Properties of the Electrochemically Prepared Fluorinated and Alkylated Polythiophenes

polymer	E_{ox}[a] (V vs SCE)	E_{ox}[b] (V vs SCE)	λ_{max} (nm) in the solid state[c]	λ_{max} (nm) in $CHCl_3$ solution[c]	σ (S/cm)	T_g (°C)
PFALKYL	2.07	1.37[d] 1.18	488[d] 496	424[d]	0.5	61[d]
PFALKOXY	1.73	1.23	534 514 (sh) 576 (sh)		0.5	59[d]
PFTRIMER	1.44	1.31	448			56[d]
PT10[d,e,22,23]	1.84	0.95	505	440	10–20	−5
POMT[d,e,24]	1.59	0.64	545 505 (sh) 590 (sh)	420	1	12
PHT[e,25]	0.90	0.58	540			
POT[d,e,31]			510	468	10	

[a] Oxidation potential of the monomer. [b] Oxidation potential of the polymer. [c] At 25 °C. [d] Chemically prepared polymers. [e] PT10, poly(3-decylthiophene); POMT, poly[3-(octyloxy)-4-methylthiophene]; POT, poly(3′-octylterthiophene); PHT, poly(3′-heptylterthiophene).

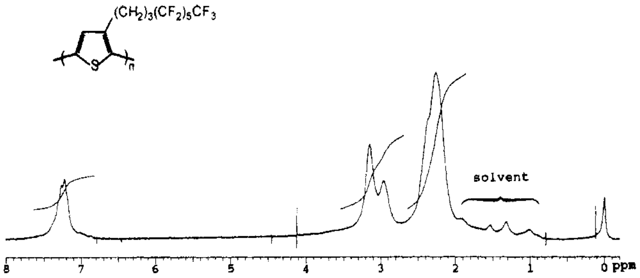

Figure 1. ^1H NMR spectrum of chemically prepared poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)thiophene] in octafluorotoluene solution.

electrochemical oxidation.[27] On the other hand, as found in 3-[(pentadecafluorooctyl)oxy]-4-methylthiophene and its corresponding polymer (PFALKOXY), the number of methylene spacers can be decreased by the introduction of an electron-donating alkoxy group. In this particular case, the strong electro-attracting effect of the fluorinated methylene groups is counterbalanced by the fact that they are included in an alkoxy substituent. Finally, the use of a trimer (terthiophene) as starting material allowed the preparation of a polythiophene copolymer with a perfluorinated alkyl side chain. On the basis of this example, development can be now considered of novel electroactive polymers with strong electron-withdrawing substituents by attaching them to low oxidation potential moieties.

PFALKYL has been found to be soluble in octafluorotoluene, while PFALKOXY and PFTRIMER are insoluble in common or fluorinated organic solvents. The optical and electrical properties of these polymers have also been characterized and are summarized in Table 1. PFALKYL exhibits an absorption maximum at a smaller wavelength and a lower electrical conductivity than poly(3-alkylthiophene)s do.[22] These results could be explained by the electron-withdrawing effect of the fluorinated substituent and/or by a less regular chemical structure for PFALKYL compared to that of the alkyl analogues. Indeed, it has been determined by ^1H NMR spectroscopy that poly(3-alkylthiophene)s have a head-to-tail content of approximately 80%.[22] These results were related to the presence of a splitting of the signal for the methylene group directly attached to the thiophene ring. The low-field peak was assigned to head-to-tail couplings and the high-field peak to head-to-head linkages. A similar characterization of PFALKYL was carried out, and its ^1H NMR spectrum is presented in Figure 1. A splitting of the signal of the first methylene group attached to the thiophene ring is also observed. In analogy to the results obtained with poly(3-alkylthiophene)s,[22] the peak at 3.14 ppm can be assigned to head-to-tail couplings and the peak at 2.95 ppm to head-to-head couplings. A head-to-tail content of 70% is then calculated for PFALKYL. A splitting of the signal of the aromatic signal around 7 ppm is also observed. This splitting was associated with the formation of four different triads along the polymer backbone.[28] The lack of resolution, in our case, does not allow the observation of distinct peaks and therefore the calculation of head-to-tail content with this signal. This lower content of head-to-tail couplings can cause additional rotational defects along the polymer backbone[22,29–31] and can contribute to the absorption maximum at a smaller wavelength, the lower conductivity, and the higher oxidation potential observed for PFALKYL compared to those of its alkyl analogues.

PFALKOXY exhibits an absorption maximum (λ_{max}) in the UV–visible range at 534 nm with two other well-resolved absorption (vibronic) peaks at 514 and 576 nm (Table 1). This absorption spectrum is comparable to that of its alkyl analogue, poly[3-(octyloxy)-4-methylthiophene] (POMT, Table 1), and could be related to a well-defined structure which is consistent with a high content of head-to-tail couplings in both materials.[24] A conductivity of 0.5 S/cm was observed for the electrochemically synthesized PFALKOXY, which is also comparable to the conductivity of POMT.[24] PFTRIMER exhibits an absorption maximum in the UV–visible range at a smaller wavelength than that of other alkyl-substituted polythiophenes (Table 1), and this behavior as well as its higher oxidation potential can be explained by the strong electron-withdrawing effect of the substituent.

DSC measurements have revealed a rather amorphous structure for the three fluorinated polymers with glass transitions around 60 °C. Moreover, it should be noted that it was impossible to measure the conductivities of the chemically prepared polymers. Indeed, due to the high hydrophobicity and lipophobicity of the polymers, it was impossible to oxidize them by the usual method (soaking in a $FeCl_3$/nitromethane solution), and due to their high oxidation potentials, it was also impossible to oxidize them with iodine vapor.

Thermochromic Properties. Temperature-dependent UV–visible absorption measurements were carried out on a spin-coated film of chemically prepared PFALKYL and on electropolymerized thin films of PFALKOXY and PFTRIMER. As shown in Figure 2, the maximum of absorption of PFALKYL is shifted from 488 to 396 nm upon heating. The presence of an isosbestic

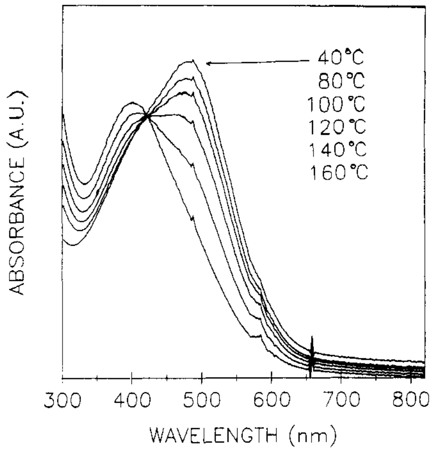

Figure 2. Temperature-dependent UV–visible absorption spectra of a poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)thiophene] (chemically prepared) spin-coated film (heating scan).

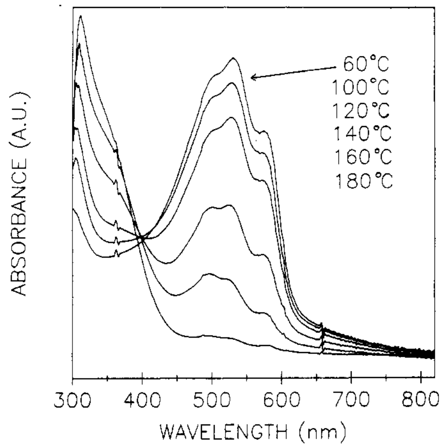

Figure 3. Temperature-dependent UV–visible absorption spectra of a poly[3-[(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentadecafluorooctyl)oxy]-4-methylthiophene] electropolymerized film (heating scan).

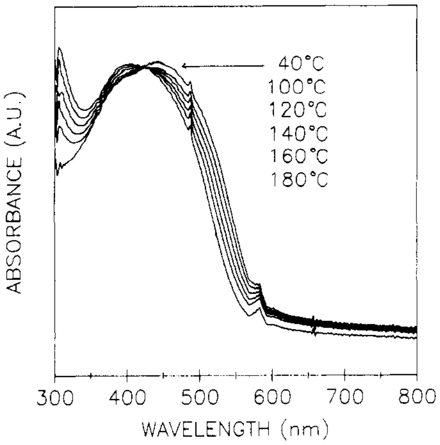

Figure 4. Temperature-dependent UV–visible absorption spectra of a poly(3′-perfluorohexylterthiophene) electropolymerized film (heating scan).

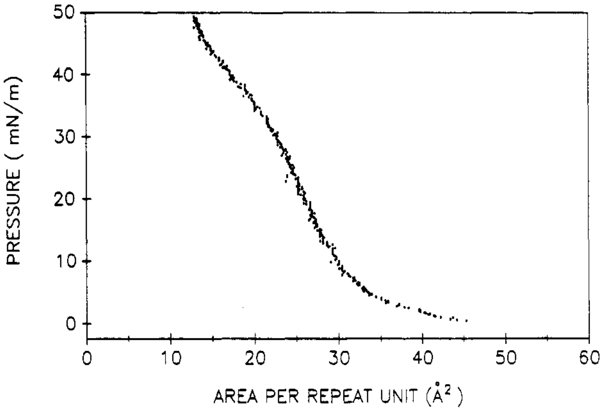

Figure 5. Pressure–area isotherm for a monolayer of poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)thiophene] (chemically prepared) at 10 °C.

point during the transition indicates the coexistence of two distinct forms in the polymer, the observed transition being a variation of the ratio of these two phases. These optical effects have been attributed to a conformational transition of the main polymer chain from a coplanar structure at low temperatures to a nonplanar form at high temperatures.[1-6]

PFALKOXY exhibits a temperature dependence similar to that of its alkyl analogue.[1,2] Poly[3-(octyloxy)-4-methylthiophene] (POMT) shows a significant blue shift of its absorption maximum (from 545 to 386 nm) upon heating. PFALKOXY exhibits a comparable blue shift from 534 to 360 nm upon heating between 25 and 180 °C (Figure 3). In both cases, a clear isosbestic point is observed during the transition. However, the transition in PFALKOXY seems to occur at higher temperatures than does that in POMT. This observation is consistent with the higher rigidity of the fluorinated alkyl chain.

Figure 4 presents the thermochromic behavior of PFTRIMER. This polymer also exhibits a blue shift (from 448 to 398 nm) upon heating. In contrast to poly(3′-octylterthiophene), an isosbestic point is observed during the optical transition. Indeed, a continuous shift of the absorption maximum was observed when poly(3′-octylterthiophene) was heated from 24 to 240 °C.[32] It then appears that the presence of the fluorine atoms (greater size and/or rigidity) has a strong influence on the thermochromic properties of these polymeric materials.

Langmuir–Blodgett Films. PFALKYL was the only soluble polymer and, therefore, the only polymer available for Langmuir–Blodgett experiments. Figure 5 shows a pressure–area isotherm for PFALKYL on water at 10 °C. This isotherm was recorded after several compression–expansion cycles; pressures between 0 and 25 mN/m gave reproducible traces. Figure 5 clearly demonstrates that stable monolayers can be formed from PFALKYL. The stability of the monolayer of PFALKYL compared to poly(3-alkylthiophene)s is explained by the higher hydrophobicity and rigidity of $-CF_2-$ groups compared to $-CH_2-$ groups, which can lead to a packing of the side chains oriented perpendicularly to the water surface. In agreement with this assumption, the area per repeat unit found by extrapolation of the linear section of the pressure–area curve to zero pressure is 34 Å², which is consistent with previous data on close packing of fatty fluorinated acids.[33] This isotherm shows also a region of partial collapse above 30 mN/m, indicating that a reorganization is taking place in the film. This may be due to some folding over of the monolayer to form a bilayer structure.[33,34]

With the pressure held constant at 10, 14, or 18 mN/m, negligible changes in film area and pressure were observed over a period of more than 30 min. Under these conditions, transfers were carried out on silanized glass slides. However, only monolayers were obtained with transfer ratios of about 0.6 for the upstroke. It seems that, due to the highly hydrophobic nature of this material, the polymer leaves the substrate upon immersion (downstroke) to go to the water surface.

Temperature-dependent UV–visible absorption measurements of one of these monolayers (transferred at 18 mN/m) are shown in Figure 6. It must be first noted that the monolayer exhibits at 40 °C an absorption maximum

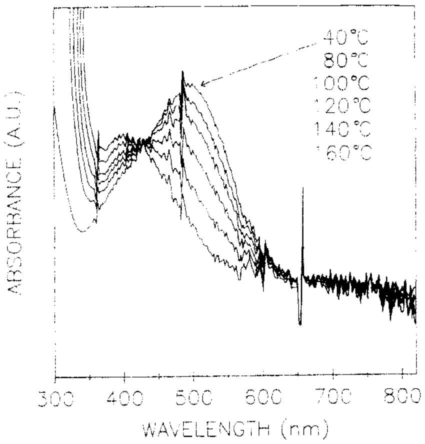

Figure 6. Temperature-dependent UV–visible absorption spectra of a poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)thiophene] (chemically prepared) monolayer (heating scan).

at 498 nm, which is slightly higher than that observed in the bulk material. It seems that the polymer chains in the monolayer have a more planar structure (related to the slightly higher conjugation length) than that adopted by the chains in the bulk material. On the other hand, it can be seen that the monolayer exhibits the same temperature dependence as the bulk material. From these results, it therefore seems that the thermally induced conformational transition in polythiophenes is mainly driven by a delicate balance between energy of conjugation and repulsive intramolecular interactions and not by interchain interactions. However, it is still unclear if the initial planar conformation of this substituted polythiophene is made possible by some interactions between the substrate and the monolayer. Some theoretical calculations and physical measurements on oligomers in the gas phase are currently being carried out to clarify this point.

Conclusion

Fluorinated alkyl- and alkoxy-substituted polythiophenes have been chemically and electrochemically synthesized. Poly[3-(1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorononyl)-thiophene] (PFALKYL) was found to be soluble in octafluorotoluene. ^{1}H NMR spectroscopy has revealed that PFALKYL has a head-to-tail content of about 70%, which could explain the absorption maximum at a smaller wavelength and the lower conductivity of PFALKYL compared to that of poly(3-alkylthiophene)s. Poly[3-[(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-pentadecafluorooctyl)oxy]-4-methylthiophene] (PFALKOXY) exhibits electrical and optical properties similar to those of its alkyl analogue. For the first time, a polythiophene derivative with a perfluorinated side chain has been synthesized, poly[3′-perfluorohexylterthiophene] (PFTRIMER). It has been demonstrated that the use of trimers as starting materials decreases the oxidation potential of the thiophene moieties substituted by strong electron-withdrawing groups and allows the subsequent formation of polymeric materials.

Temperature-dependent UV–visible absorption measurements on these fluorinated polythiophenes have shown a blue shift of their absorption maximum upon heating with the presence of an isosbestic point in each case. These thermochromic properties are related to a conformational transition of the polymer backbone from a relatively planar structure at low temperatures to a more twisted form at high temperatures. Langmuir–Blodgett experiments have allowed the preparation and transfer of monolayers of PFALKYL. The presence of highly hydrophobic fluorinated substituents has improved the stability of the monolayers compared to the poly(3-alkylthiophene)s. Monolayers of PFALKYL have shown thermochromic properties similar to those of spin-coated films, which seems to indicate that the driving force of this conformational transition is related to a single chain phenomenon.

Experimental Section

3-Thiophenecarboxaldehyde, 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol, and perfluorohexyl iodide were obtained from Aldrich Chemical Co. and were used without further purification. Diethyl ester and ethylene glycol dimethyl ether were distilled over sodium before use.

3-(1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorononyl)thiophene was synthesized following the procedure described by Büchner et al.[26] The monomer was purified by distillation under reduced pressure (bp 94–96 °C/0.55 mmHg): yield 27%; IR (cm^{-1}) 3050, 2960, 1460, 1360–1000, 900, 835, 800, 770, 720, 690, 630; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.30 (1H, dd, J = 3.0 and 4.85 Hz), 6.97 (2H, m), 2.76 (2H, t, J = 7.2 Hz), 2.2–1.9 (4H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) 140.84, 127.70, 125.75, 120.59, 30.23, 29.33, 21.03; ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) −82.50 (3F, CF_3), −115.81 (2F, CF_2), −123.60 (2F, CF_2), −124.55 (2F, CF_2), −125.15 (2F, CF_2), −127.84 (2F, CF_2).

3-[(1,1,1,2,2,3,3,4,4,5,5,6,6,7,7-Pentadecafluorooctyl)oxy]-4-methylthiophene was obtained by a coupling reaction between 3-bromo-4-methylthiophene[35] and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol according to a procedure similar to that described by El Kassmi et al.[36] Sodium hydride (0.433 g, 18 mmol) was added under argon to a solution of 6.070 g (15 mmol) of pentadecafluorooctanol in 12 mL of ethylene glycol dimethyl ether (DME). The mixture was stirred at room temperature for 30 min, and then 5.313 g (30 mmol) of 3-bromo-4-methylthiophene and 1.405 g of copper iodide were successively introduced. The reaction mixture was refluxed for 15 h, then cooled, and filtered. The residue was taken up in diethyl ester, washed with dilute hydrochloric acid and distilled water, dried over magnesium sulfate, and concentrated. The monomer was purified by distillation under reduced pressure (bp 84–88 °C/0.30 mmHg): yield 18%; IR (cm^{-1}) 3120, 2950, 1575, 1465, 1400–1000, 955, 875, 845, 820, 765, 735, 700, 640; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 6.88 (1H, m), 6.27 (1H, d, J = 3.1 Hz), 4.44 (2H, t, J = 11.2 Hz), 2.11 (3H, s); ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) 154.21, 129.12, 120.74, 97.94, 66.77, 12.01; ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) −82.34 (3F, CF_3), −120.97 (2F, CF_2), −123.60 (4F, $2CF_2$), −124.31 (2F, CF_2), −124.68 (2F, CF_2), −127.69 (2F, CF_2).

3′-Perfluorohexylterthiophene was obtained by a cross-coupling reaction between 3′-bromoterthiophene[37] and perfluorohexyl iodide following the procedure described by Chen and Tamborski.[38] In a 100-mL three-neck flask under inert atmosphere, 2.031 g (32 mmol) of copper bronze and 10 mL of DMSO were heated to 125 °C. Perfluorohexyl iodide (6.738 g, 15 mmol) was added dropwise at such a rate that the reaction temperature did not rise over 135 °C. The reaction mixture was stirred for 1.5 h, and a solution of 3′-bromoterthiophene (1 g, 3 mmol) in 11 mL of DMSO was added at the reaction temperature. The mixture was stirred overnight at 125 °C and then cooled at room temperature. Distilled water was added to the reaction flask placed in an ice–water bath at 0 °C. The mixture was filtered on a Büchner funnel. The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with dilute hydrochloric acid and distilled water. The ether solution was dried over magnesium sulfate, and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexanes as eluent (mp 55–57 °C): yield 11%; IR (cm^{-1}) 3050, 1510, 1380–1000, 830, 775, 725, 700, 650; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.44–7.04 (7H, m); ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) 137.96, 137.73, 135.08, 131.60, 129.35, 127.96, 127.86, 127.29, 125.67, 124.81, 123.41 (2 carbon atoms); ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) −82.29 (3F, CF_3), −104.40 (2F, CF_2), −122.22 (2F, CF_2), −123.21 (2F, CF_2), −124.29 (2F, CF_2), −127.64 (2F, CF_2).

Chemical Polymerization. Polymers were prepared by chemical oxidation of the monomers using iron trichloride according to a procedure similar to that of Sugimoto et al.[39] In a 50-mL three-neck flask, 1.078 g (6.4 mmol) of iron trichloride was dissolved in 16 mL of chloroform under argon and 0.800 g (1.6 mmol) of the monomer in 11 mL of chloroform was added dropwise. The mixture was stirred for 24 h at room temperature. Then, the mixture was poured in methanol (900 mL). The precipitate was collected on a Büchner funnel and washed with methanol. The polymer was then washed by Soxhlet extraction using methanol and dried under reduced pressure at room temperature.

Electrochemical Polymerization. Polymer films were prepared in a nitrobenzene solution containing monomer (0.1 mol/L) and tetrabutylammonium hexafluorophosphate (0.02 mol/L) as an electrolyte. The oxygen in the solution was swept out with argon prior to the electrolysis. The polymerizations were performed at room temperature by applying a constant current density of 1 mA/cm^2 on platinum electrodes. Polymerization time varied from 2 min to 1 h, and the polymers were obtained as a film covering the anode of the electrolysis cell. The neutral polymers were obtained by reversing the polarity of the electrodes.

Characterization. Infrared spectra were obtained by a Perkin-Elmer spectrometer (Model 783) using NaCl windows. NMR spectra were obtained in deuterated chloroform solution on a 300-MHz Varian instrument. ^{19}F NMR spectra were recorded with trifluorotoluene as internal standard. Melting temperatures were measured using a Gallenkamp melting point apparatus. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments thermal analyst (Model 2910) calibrated with an ultrapure indium sample. UV-visible spectra were performed on a Hewlett-Packard diode array spectrophotometer (Model 8452A). A temperature control unit was installed to allow measurements over a range from 25 to 200 °C. The sample temperature was measured by a thermocouple with a maximum error of ± 2.0 °C. UV-visible absorption measurements were taken from neutral polymers dissolved in octafluorotoluene, from neutral polymer films cast on quartz plates, or from neutral polymers electropolymerized on an indium tin oxide coated glass electrode. Cyclic voltammetry was carried out in a one-compartment cell using an EG&G PAR (Model 273) potensiostat/galvanostat. These measurements were performed in dry acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 mol/L) as supporting electrolyte. The oxidation potentials were determined at a scan rate of 100 mV/s vs a saturated calomel electrode (SCE). Conductivity measurements were performed at room temperature in air by the four-probe method on polymer films. Spin-coated films of PFALKYL were prepared by spinning an octafluorotoluene solution of the polymer onto glass microscope slides. The procedure has been reported in a previous paper.[40]

Langmuir-Blodgett Film Preparation. All films were prepared using a Joyce-Loebl Model 4 constant-perimeter Langmuir trough situated under a laminar flow unit. The surface pressure was continuously monitored using the Wilhelmy plate method. Monolayers of PFALKYL were obtained from octafluorotoluene solutions (2 mg/mL). Films were deposited onto hydrophobic substrates (glass microscope slides treated with hexamethyldisilane) using vertical dippings. Film preparation has been previously described in detail.[34]

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