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Direct aromatic fluoroalkylations of poly(*p*-phenylene) with fluoroalkanoyl peroxides: an approach to highly soluble fluorinated conducting polymers

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Abstract

Direct aromatic fluoroalkylations of poly(*p*-phenylene) (PPP) using fluoroalkanoyl peroxides were found to give excellent to moderate fluoroalkylated ratios even in heterogeneous systems. The fluoroalkylated products (PPP-R_F) were shown to possess dramatically higher solubilities than parent PPP, and the improvement in the solubility enabled measurements of the molecular weights of PPP-R_F to be made by gel permeation chromatography analyses. Perfluoropropylated PPP formed a monomolecular film at the air–water interface. This deposited film was found to conduct electricity, and its electric conductivity was comparable with the conductivities of similar films formed from other compounds of potential interest in this field. © 1997 Elsevier Science S.A. All rights reserved.

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1. Introduction

The increasing importance of organic conducting polymers in applications for electronic devices, such as capacitors, batteries and transistors, has led to considerable interest in the synthesis of soluble and fusible conducting polymers. The usual conducting polymers known hitherto are insoluble in common organic solvents because of the stiffness of the main chains consisting of conjugated double bonds [1]. Polyphenylene, with a high heat resistance and a good electric conductivity, has been regarded as a good electrolytic material for solid electrolyte capacitors [2]. From the synthetic and practical point of view, the development of soluble polyphenylenes is of particular interest. We have been actively studying the reactivities of a series of fluoroalkanoyl peroxides ($(R_FCOO)_2$; R_F = perfluoroalkyl and perfluorooxaalkyl groups), which are useful reagents for the introduction of the corresponding fluoroalkyl groups into arenes and olefins [3]. Furthermore, it has been demonstrated that direct aromatic fluoroalkylations of polymers, such as polystyrene, polyimides and polyamic acids, can be achieved using fluoroalkanoyl peroxides [4]. In this paper, we report the direct fluoroalkylation of poly(*p*-phenylene) (PPP) with fluoroalkanoyl peroxides and the application to new fluorinated conducting polymers.

2. Results and discussion

The reactions of a series of fluoroalkanoyl peroxides with PPP were carried out at 45 °C for 5 h under nitrogen in a 1:1 mixed solvent (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane. The direct fluoroalkylations of PPP were found to proceed smoothly to give excellent to moderate fluoroalkylated ratios (R_F ratios), although the reactions were carried out in heterogeneous systems as shown in Scheme 1. The fluoroalkylations of PPP with the peroxides can be explained as single electron transfer reactions from the substrate to the antibonding ($2p\sigma^*$) O–O bond of the peroxides, as proposed

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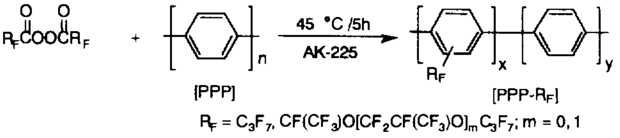
Table 1
Reactions of fluoroalkanoyl peroxides with poly(p-phenylene) in AK-225

R_F in peroxide (mmol)	PPP (mmol) [c]	Product (PPP-R_F)	
		R_F ratio [a]	$\overline{M_n}$ ($\overline{M_w}/\overline{M_n}$) [b]
C_3F_7			
10.0	13.2	7	1150 (1.85)
7.5	6.6	50	1160 (1.74)
$CF(CF_3)OC_3F_7$			
8.6	6.6	4	830 (1.57)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
8.6	6.6	3	920 (1.50)
13.2	6.6	23	660 (1.71)

[a] R_F ratio indicates the value of $[x/(x+y)] \times 100$ (%). It was determined by ^{19}F NMR by comparison of the peak area of the CF_3 groups of the polymer with benzotrifluoride as the internal standard.

[b] Calculated value is based on the PPP monomer unit.

[c] Molecular weight of PPP-R_F was determined by GPC analysis.



Scheme 1.

for the aromatic fluoroalkylation of polystyrene with fluoroalkanoyl peroxides [3,4]. The results are listed in Table 1.

As shown in Table 1, in the aromatic fluoroalkylations of PPP, it was found that the perfluoropropylated ratios are generally higher than the perfluorooxaalkylated ratios. This result arises since the unoccupied $2p\sigma^*$ (O–O) orbital level of perfluorobutyryl peroxide is lower than that of the perfluorooxaalkanoyl peroxides [5], and the lower unoccupied molecular orbital can accept a π electron more easily from PPP.

Interestingly, the series of PPP-R_F compounds thus obtained were shown to possess good solubilities in common organic solvents, such as chloroform, carbon tetrachloride, dichloromethane, tetrahydrofuran and benzene. In contrast, PPP is poorly soluble in organic solvents. Hitherto, the molecular weights of PPP could not be measured owing to the insolubility in various solvents. It is very interesting that such a drastic improvement in the solubility has enabled measurements of the molecular weights of PPP-R_F to be made easily by gel permeation chromatography (GPC) analyses.

The melting of the synthesized perfluoropropylated PPP (PPP-C_3F_7; with an R_F ratio of 7%) was investigated by thermogravimetric analysis (TGA). As shown in Fig. 1, no weight loss for parent PPP was observed below approximately 300 °C; however, a significant weight loss for PPP-C_3F_7 was observed above about 150 °C.

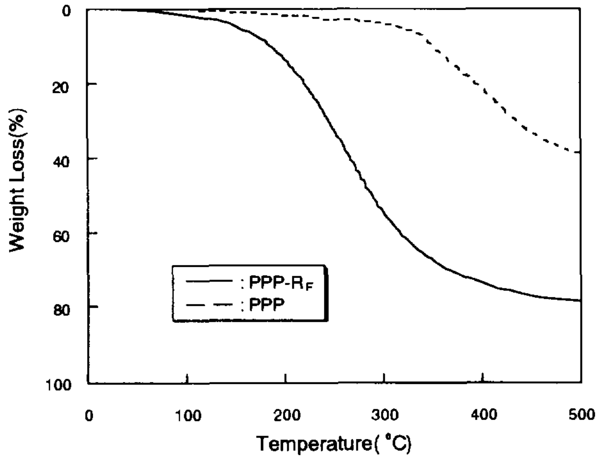


Fig. 1. Thermogravimetric analysis of PPP-R_F and PPP ($R_F = C_3F_7$; R_F ratio, 7%).

An improvement in solubility and a significant weight loss for PPP-R_F can be understood in terms of the weakening of the relative strengths of the π–π and other intermolecular interactions of PPP by the fluoroalkyl substituents. In particular, the good solubility of PPP-C_3F_7 is partly attributable to the relatively weak interchain interaction due to the space factor effect of the perfluoropropyl group.

In order to clarify the effects imparted by fluorine, we tried to prepare a Langmuir–Blodgett (LB) film of PPP-C_3F_7. The preparation of the PPP-C_3F_7 LB film was achieved by spreading the polymer solution on water and allowing the solvent to evaporate. A chloroform solution of PPP-C_3F_7 was spread on the water surface, and the surface pressure–surface area (π–A) isotherm was measured. The π–A isotherm on pure water is shown in Fig. 2.

As shown in Fig. 2, PPP-C_3F_7 forms a monomolecular film at the air–water interface. This polymer forms an expanded film in the lower surface pressure region, which indicates that the perfluoropropyl groups are parallel with the water surface. A condensed film, which indicates that the perfluoropropyl groups are perpendicular to the water surface, is found in the higher surface pressure region. The transition point between the two states for this polymer is in the vicinity of 25 mN m^{-1}. The limiting area of PPP-C_3F_7 at zero pressure (π_0) was around 1000 Å^2. The π_0 value of PPP-C_3F_7, which is structurally reasonable, suggests that the perfluoropropyl

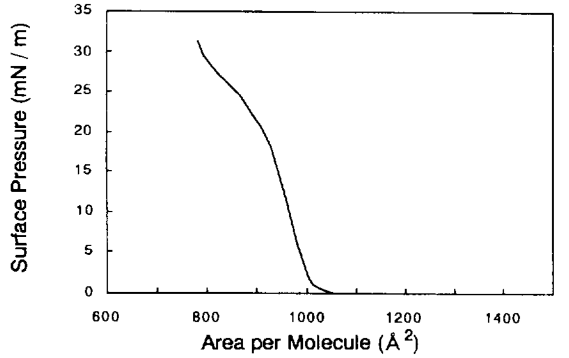
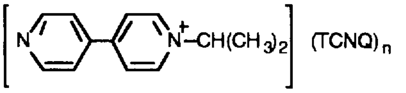


Fig. 2. π–A isotherm of PPP-R_F on water subphase ($R_F = C_3F_7$; $\overline{M_n}$ ($\overline{M_w}/\overline{M_n}$) = 1150 (1.85); R_F ratio, 7%).

groups are perpendicular to the water surface and closely packed to each other.

We were interested in testing this LB film as a conducting polymer, because it formed well-ordered structures. The polymer films were deposited on glass as Y-type films under a surface pressure of 25 mN m^{-1}. The electrical conductivity in the plane of the film was measured by a d.c. two-probe or four-probe method, and the results are shown in Fig. 3. The figure also shows, for comparison, the conductivities of LB films, produced in a similar manner, of poly(3-perfluoropropylthiophene) (Thi-C_3F_7) and of Thi-C_3F_7 after irradiation with a helium ion beam in an attempt to improve successfully the quality of the film as a conductor. The electrical conductivity of 7,7,8,8-tetracyanoquinodimethane (TCNQ)–1-isopropyl-4,4′-bipyridinium complex (TCNQ complex)



was also measured under the same conditions for comparison.

Poly(3-perfluoropropylthiophene) was prepared by the nickel-catalysed, magnesium-promoted polycondensation (the Yamamoto method [5]) of 2,5-dibromo-3-perfluoropropylthiophene, which was obtained by the reaction of 2,5-dibromothiophene with perfluorobutyryl peroxide as shown in Scheme 2. (Firstly, we tried to prepare perfluoropropylated poly(thiophene) by the direct aromatic perfluoropropylation of poly(thiophene) with perfluorobutyryl peroxide. However, the expected soluble polymer could not be obtained.)

As shown in Fig. 3, PPP-C_3F_7 has a conductivity of approximately 6×10^{-6} S cm^{-1}, although this value is smaller than that (approximately 3×10^{-5} S cm^{-1}) of the TCNQ complex, which is one of the most popular organic conducting materials so far. However, it was found that the conductivity of the PPP-C_3F_7 film is higher than that of the Thi-C_3F_7 film (approximately 3.3×10^{-6} S cm^{-1}) (the electrical conductivity of the undoped poly(3-hexylthiophene) film, which was obtained by casting, was reported to be around 10^{-10} S cm^{-1} [6]) after irradiation with a helium ion beam. This may be because PPP-C_3F_7 favours the hopping of electrons between the molecules compared with Thi-C_3F_7, since fewer perfluoropropyl segments were introduced into PPP. An increase in the electric conductivity of the Thi-C_3F_7 film on irradiation with helium may be due to the formation of ordered structures.

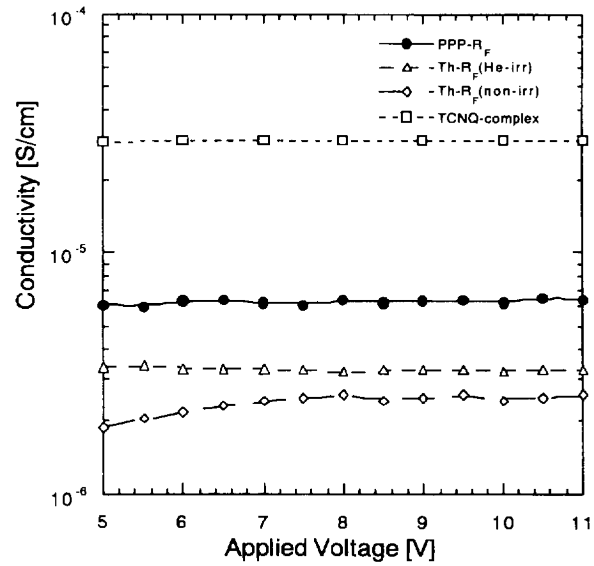
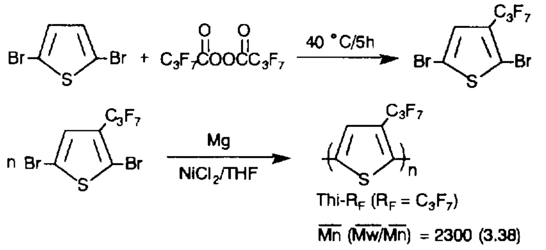


Fig. 3. Conductivities of PPP-R_F, Thi-R_F and TCNQ complex (PPP-R_F: $R_F \equiv C_3F_7$, R_F ratio = 7%; Thi-R_F: $R_F \equiv C_3F_7$).



Scheme 2.

Thus our new fluoroalkylated PPPs are promising fluorinated organic conducting materials for which there are no convenient direct syntheses.

3. Experimental details

3.1. Measurements

Nuclear magnetic resonance (NMR) spectra were measured with a Varian Unity-plus 500 (500 MHz) spectrometer. IR spectra were recorded on a Horiba FT-300 FT-IR spectrophotometer. The molecular weights of a series of fluoroalkylated PPPs were measured using a JASCO 830-RI gel permeation chromatograph calibrated with standard polystyrene using tetrahydrofuran as eluent. Thermal analyses were recorded on a SEIKO DSC-200 differential thermobalance. Surface pressure–molecular area isotherms were measured by the moving-wall method using a Nippon Laser & Electronics Lab. NL-LB240S-MWA apparatus. A Kaufman-type ion source was prepared for irradiation of LB films. During the irradiation of LB films, the ion source was driven with an ion beam energy of 100 eV and an ion beam current of 80 μA cm^{-2}.

3.2. Materials

A series of fluoroalkanoyl peroxides was prepared from the corresponding acyl halides and hydrogen peroxide in aqueous sodium hydroxide according to the previously reported method [4,7]. PPP was prepared by the method described in the literature [8].

3.3. General procedure for the synthesis of fluoroalkylated PPPs

Perfluorobutyryl peroxide (10.0 mmol) in a 1 : 1 mixed solvent (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (40 g) was added to a mixture of PPP (1.00 g (13.2 mmol calculated from PPP monomer unit)) and AK-225 (70 g) which was stirred vigorously at 45 °C for 5 h under nitrogen. After removal of the solvent, chloroform (200 ml) was added to the reaction mixture and the solution was stirred for 10 min; the chloroform layer was then separated. The chloroform layer was washed with water (200 ml) and dried over molecular sieves. After removal of the solvent, the product was dried at 50 °C under reduced pressure to give 0.65 g of the expected perfluoropropylated PPP (PPP-C_3F_7). This polymer showed the following spectral data: IR ν (cm^{-1}): 1344 (CF_3), 1226 (CF_2); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ: -4.56 (3F), -38.08 (2F), -57.41 (2F) (R_F ratio, 7%). Average molar mass $\overline{M_n} = 1150$ ($\overline{M_w}/\overline{M_n} = 1.85$).

The following spectral data were obtained for the other fluoroalkylated PPPs (PPP-R_F) studied.

PPP-C_3F_7 (R_F ratio, 50%). IR ν (cm^{-1}): 1346 (CF_3), 1228 (CF_2); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ: -4.68 (3F), -38.26 (2F), -51.81 (2F). Average molar mass $\overline{M_n} = 1160$ ($\overline{M_w}/\overline{M_n} = 1.74$).

PPP-$CF(CF_3)OC_3F_7$ (R_F ratio, 4%). IR ν (cm^{-1}): 1340 (CF_3), 1241 (CF_2); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ: -4.53–-8.37 (8F), -57.36 (3F). Average molar mass $\overline{M_n} = 830$ ($\overline{M_w}/\overline{M_n} = 1.57$).

PPP-$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (R_F ratio, 3%). IR ν (cm^{-1}): 1392 (CF_3), 1243 (CF_2); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ: -4.54–-9.58 (13F), -57.28 (3F), -73.82 (1F). Average molar mass $\overline{M_n} = 920$ ($M_w * \$/\overline{M_n} = 1.50$).

PPP-$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (R_F ratio, 23%). IR ν (cm^{-1}): 1370 (CF_3), 1244 (CF_2); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ: -4.33–-9.25 (13F), -57.33 (3F), -73.87 (1F). Average molar mass $\overline{M_n} = 660$ ($\overline{M_w}/\overline{M_n} = 1.71$).

3.4. Synthesis of poly(3-perfluoropropylthiophene)

Poly(3-perfluoropropylthiophene) was prepared by the nickel-catalysed, magnesium-promoted condensation according to the literature [5] of 2,5-dibromo-3-perfluoropropylthiophene, which was obtained by the reaction of perfluorobutyryl peroxide with 2,5-dibromothiophene reported by Yoshida et al. [9]. The perfluoropropylated polymer obtained was soluble in chloroform, tetrahydrofuran, ethyl acetate, benzene, toluene, *N,N*-dimethylformamide and dimethyl sulphoxide, and the molecular weight of this polymer was similarly measured by GPC analysis. The average molar mass and IR spectrum of this polymer were as follows: $\overline{M_n} = 2300$ ($\overline{M_w}/\overline{M_n} = 3.38$); IR ν (cm^{-1}): 1340 (CF_3), 1228 (CF_2).

Acknowledgements

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