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Modification of polystyrene via aromatic per(poly)fluoroalkylation by per(poly)fluorodiacyl peroxides

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Abstract

Facile electron-transfer reactions between polystyrene and per(poly)fluorodiacyl peroxides at ~20 °C in dichloromethane produced high yields of ring-peer(poly)fluoroalkylated polystyrenes with excellent water- and oil-repellency, chemical resistance and much lowered refractive indices.

Keywords: Polystyrene modification; Aromatic per(poly)fluoroalkylation; Per(poly)fluorodiacyl peroxides; NMR spectroscopy; IR spectroscopy; Contact angle measurements; Refractive indices

1. Introduction

To obtain the valuable properties of water- and oil-repellency, chemical resistance and much lowered refractive indices for some of the most widely used polymers by introducing per(poly)-fluoroalkyl groups has long been an aim in organic chemistry and polymer sciences [1].

Since the improved synthesis and kinetic studies of the thermal decomposition of per(poly)-fluorodiacyl peroxides (FAPs) were carried out in 1982 [2], and the reactions of FAPs as per(poly)fluoroalkylating agents with arenes by Zhao and coworkers succeeded in 1983 [3], FAP have been established as clean and highly effective per(poly)-fluoroalkylating and per(poly)fluoroacyloxylating agents for arenes [4], aromatic heterocycles [5], olefins [6], fullerenes [7] and many other substrates with a wide variety of structures. Consequently, the chemistry of FAP plays a role of increasing importance in the synthesis of organo-fluoro functional materials.

For polymeric substrates, Sawada and coworkers [8] reported the high efficiency of the heterogeneous perfluoroalkylation of powdered polystyrene by FAPs in F113 ($CCl_2F{-}CClF_2$) at 40 °C. However, our efforts to reproduce Sawada's results failed and we could only obtain very low yields ($<1\%$) of ring-perfluoroalkylation in heterogeneous systems.

In the present work, we have carefully designed the reaction systems, characterized the products and proposed a mechanism for the reactions of polystyrene (PS) with FAPs. Also, we have measured the contact angles of water and paraffin oil (before and after treatment with aqueous solutions of NaOH and H_2SO_4) and the refractive indices of the resultant fluoropolymer film coated on glass slides or quartz plates.

2. Results and discussion

2.1. Homogeneous reactions of PS with FAPs at ~20 °C

Under deoxygenated conditions with gentle stirring, FAPs [$R_f = H(CF_2)_4$, n-C_3F_7 and n-C_7F_{15}] solutions (~0.2 M) in F113 were slowly dropped into a polystyrene (PS) solution (0.5 M) in dichloromethane. The molar ratios FAP/S (styrene) were fixed at 0.05, 0.10, 0.15, 0.20, 0.30 and 0.40, respectively. The reactions were usually complete within 1 h, and additional stirring of 2–3 h was usually carried out.

2.2. Products

From the reactions of representative FAPs [$R_f = H(CF_2)_4$, n-C_3F_7 and n-C_7F_{15}] with PS at different molar ratios, the ring-per(poly)fluoroalkylated polystyrene (R_f–PS) formed was isolated and characterized by IR and ^{19}F NMR spectroscopy as the sole polymerized solid. Because of steric hindrance at the *ortho* positions, the *para*-substituted R_f–PS was formed preferentially. In all the runs studied, quantitative

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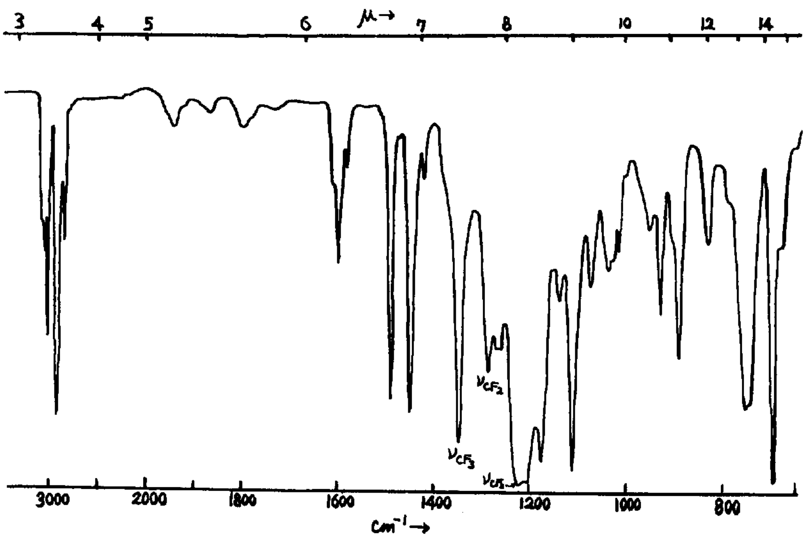


Fig. 1. IR spectrum of a representative R_f–PS, n-C_3F_7–PS (FAP/PS = 0.30).

conversion of FAPs was ensured. The yields of R_f–PS based on the amount of FAPs added were calculated from ^{19}F NMR integrations. Yields for the reactions of $[H(CF_2)_4CO_2]_2$ as well as (n-$C_3F_7CO_2)_2$ were fairly high (70%–90%) while that from (n-$C_7F_{15}CO_2)_2$ was appreciably lower (50%–70%). This is probably because the long fluorocarbon chain (n-C_7F_{15}) might lead to lipophilic aggregation in the medium and thus give the opportunity for radical coupling, i.e. 2 n-$C_7F_{15}\cdot \rightarrow$ n-$C_{14}F_{30}$.

Along with R_f–PS, the corresponding carboxylic acids R_fCO_2H were always detected. The yields of R_fCO_2H (determined by acid–base titration) were approximately equivalent to that of R_f–PS.

The IR spectrum of a representative R_f–PS (R_f = n-C_3F_7) is shown in Fig. 1. The characteristic absorption bands for $\nu(CF_3)$ at 1350 cm^{-1}, and $\nu(CF_2)$ at 1280 and 1220 cm^{-1}, indicate the presence of n-C_3F_7 groups on the phenyl rings. The IR pattern at 1800–2000 cm^{-1}, characteristic of a *para*-disubstituted phenyl ring, provides strong evidence for *p*-perfluoropropylation of PS. The lack of carbonyl absorption at ca. 1700 cm^{-1} shows the absence of ring-perfluoroacyloxylation. The simple ^{19}F NMR spectra of R_f–PS clearly shows that only ring-per(poly)fluoroalkylated PS was formed as the isolated polymers.

The yields, IR and ^{19}F NMR characterization of the products R_f–PS formed in the reactions at ~20 °C at different FAP/S molar ratios are summarized in Table 1.

2.3. Mechanism

The unimolecular decomposition of FAPs in dilute F113 solutions (0.02 M) has been studied carefully [2]. At 20±0.05 °C, the rate constants of FAPs employed in this work were: 3.29×10^{-5} s^{-1} [$R_f = H(CF_2)_4$], 2.19×10^{-5} s^{-1} (R_f = n-CF_3F_7) and 3.01×10^{-5} s^{-1} (R_f = n-C_7F_{15}). The corresponding half-life times were 5.83, 8.78 and 6.40 h, respectively.

In the presence of PS, the disappearance of FAPs was significantly accelerated via its bimolecular interaction. The alkylated phenyl rings of PS are reactive enough to transfer an electron to the highly effective one-electron oxidant FAP as reported previously [3,4]. The concentration of R_fCO_2H formed, which was roughly equivalent to that of R_f–PS, is a clear indication of the electron-transfer nature of the reactions as depicted in Scheme 1.

2.4. Determination of contact angles (θ) of R_f–PS (see Table 2)

Tests of water-repellency

The parent polymer PS and the R_f–PS products were coated uniformly on glass slides (7.5×2.5 cm). Contact angles (θ) of water on the coated polymers were obtained using the maximum height method. Plots of θ_{H_2O} versus the various R_f ratios are shown in Figs. 2–4.

Tests of oil-repellency

The contact angles of dodecane on the coated polymers were directly read on a contact angle meter as shown in Fig. 5.

Tests of chemical resistance

Glass slides coated with PS and R_f–PS were immersed at room temperature for 7 d in sealed glass tanks containing 27% H_2SO_4 and 10% NaOH solutions. After this time the samples were carefully washed and dried, and the contact angles θ_{H_2O} measured (see Table 2).

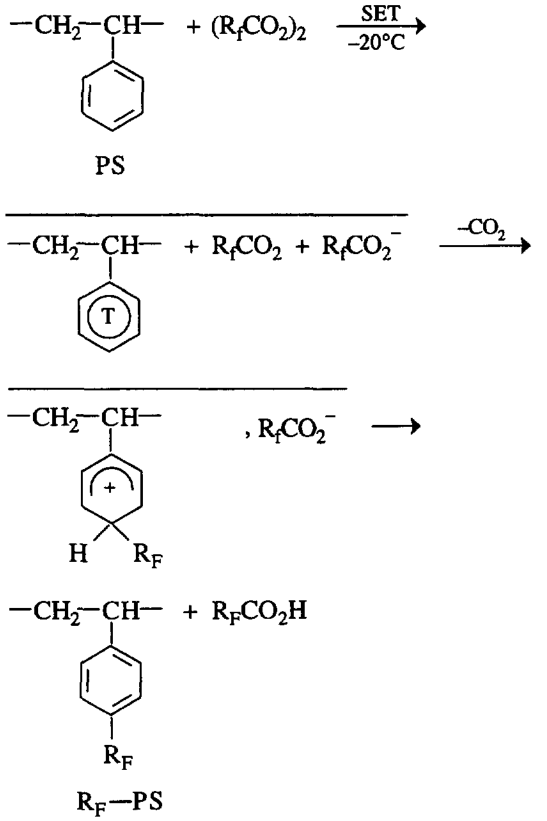
From Table 2 and Figs. 2–5, the following trends may be discerned:

1. For all the ring-per(poly)fluoroalkylated polystyrenes, both θ_{H_2O} and θ_{oil} increase with an increase in the FAP/PS molar ratio.
2. However, for all the R_f–PS coatings, sharp increases of θ_{H_2O} are found at %R_f up to 5%. When %R_f is above 10%,

Table 1
Reactions of $(R_fCO_2)_2$ (FAP) with PS in dichloromethane at ~20 °C

R_f	$(R_fCO_2)_2/S$ [a]	R_f-ratios [b] (%)	R_f-group yields [c] (%)	IR (cm^{-1})	^{19}F NMR (ppm)
$H(CF_2)_4$	0.05:1	4	80		
	0.1:1	9	90	1310	−65.2
	0.15:1	11.5	77	1260 (CF_2)	(2F, $J_{HF}=52.2$ Hz)
	0.2:1	15	76	1170	−57.7 (2F)
	0.3:1	22	73		−51.9 (2F)
	0.4:1	29	73		−38.5 (2F)
$n-C_3F_7$	0.05:1	2	40	1350 (CF_3)	−8.0 (3F)
	0.1:1	7	70		−39.5 (2F)
	0.15:1	11	73	1280, 1120, (CF_2)	−54.0 (2F)
	0.2:1	18	90		
	0.3:1	23	78		
	0.4:1	35	88		
$n-C_7F_{15}$	0.05:1	2	40	1365 (CF_2)	−3.3 (3F)
	0.1:1	7	70	1240, 1205 (CF_2)	−48.7 (2F)
	0.2:1	10	50		−44.4 (8F)
	0.3:1	15	50		−33.0 (2F)
	0.4:1	21	52		

[a] Molar ratios.
[b] R_f-ratios of phenyl ring in PS.
[c] Based on $(R_fCO_2)_2$.



Scheme 1.

θ_{H_2O} reaches 100° and above. This trend provides a very definite indicator of the change in surface composition brought about by the quite dramatic extent of surface segregation of the R_g groups [9,10].

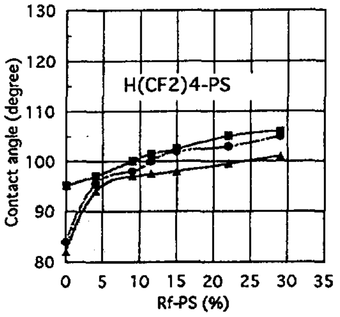


Fig. 2. Plots of θ_{H_2O} vs R_f% for $H(CF_2)_4$–PS films: without treatment (■); treatment with 27% H_2SO_4 for 7 days (●); treated with 10% NaOH for 7 days (▲).

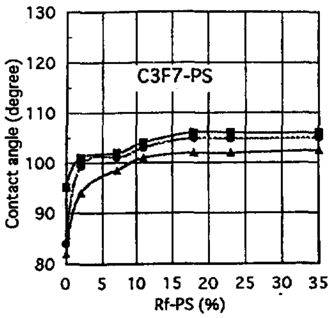


Fig. 3. Plots of θ_{H_2O} vs R_f% for $n-C_3F_7$–PS films: without treatment (■); treatment with 27% H_2SO_4 for 7 days (●); treated with 10% NaOH for 7 days (▲).

3. At a fixed $\%R_f$, when the θ_{H_2O} values of R_f–PS bearing different R_f groups are compared, θ_{H_2O} increases in the order $H(CF_2)_4 < n-C_3F_7 < n-C_7F_{15}$. The introduction of quite long perfluorocarbon chains such as $n-C_7F_{15}$ into PS significantly reduces the $\%R_f$, ensuring the saturation of

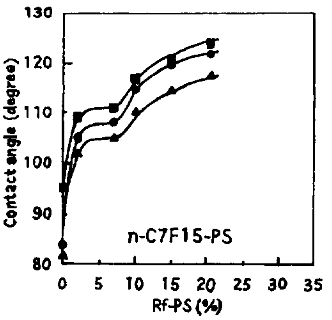


Fig. 4. Plots of θ_{H_2O} vs R_f% for n-C_7F_{15}–PS films: without treatment (■); treatment with 27% H_2SO_4 for 7 days (●); treated with 10% NaOH for 7 days (▲).

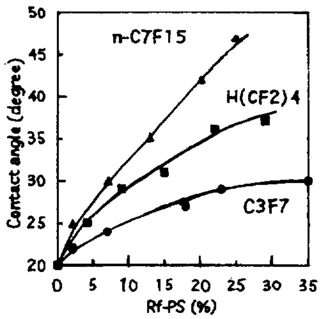


Fig. 5. Plots of $\theta_{n\text{-}C_{12}H_{26}}$ vs R_f% for R_f–PS films. [Rf = $H(CF_2)_4$ (■), n-C_3F_7 (●) and n = C_7F_{15} (▲)].

the surface segregation of R_f groups [θ_{H_2O} much greater than 100° and close to that of PTFE (θ_{H_2O} = 129°)]. For $H(CF_2)_4$–PS, on the other hand, because of the polarization of the C–H bond, the ω-hydrogen atom is slightly acidic and thus the hydrophobicity of the polymer is decreased, while the lipophobicity is increased as shown in Fig. 5.

4. After treatment with 27% H_2SO_4 or 10% NaOH solutions for 7 d, a small decrease in θ_{H_2O} (Figs. 2–4) and θ_{oil} (Fig. 5) was found for all the coated films. Slight corrosion occurred however, although R_f–PS with $\%R_f \geqslant 5\%$ showed excellent chemical resistance of applicable significance.

2.5. *Optical properties of R_f–PS via refractive indices (n_D) determination*

Seeking for polymers with much lowered refractive indices in an important theme in modern materials science.

We found that R_f–PS polymers have a very much lower n_D compared to the parent polymer PS (n_D = 1.5813) as shown in Table 3. In the $\%R_f$ range from 0% to ~20%, each curve shows an n_D maximum at increasing $\%R_f$ ratio in the order $H(CF_2)_4$ (11.5%) < n-C_3F_7 (18.0%) < n-C_7F_{15} (20%). Interestingly, $H(CF_2)_4$–PS has a minimum n_D of 1.5424 at $\%R_f = 9\%$; n-C_3F_7–PS exhibits two minima at 1.5083 at 7% and 1.5093 at 23%; n-C_7F_{15}–PS has the lowest minimum n_D of 1.4888 at 13%. From our present knowledge, it is difficult to explain the relationships between such changes in n_D and the R_f chain length in the R_f polymers. Nevertheless, we have successfully made R_f–PS with different R_f contents. Their refractive indices are low enough to meet the essential condition ($\sqrt{n_D(1) - n_D(2)} \geqslant 0.5$) for any polymer to be a coating material on a plastic optical fiber.

3. Experimental details

3.1. *Materials*

Solvent F113 (CCl_2F–$CClF_2$) was carefully washed in turn with concentrated H_2SO_4, 5% $NaHCO_3$ and distilled

Table 2
Contact angles of PS and R_f–PS before and after treatment with 27% H_2SO_4, 10% NaOH at ~20 °C for 7 days

R_f in FAP	R_f-ratios (%)	θ_{oil} (dodecane, 5 °C)	θ_{H_2O} (20 °C)		
			Before treatment	H_2SO_4 (27%)	NaOH (10%)
$H(CF_2)_4$	4	25	97	95.5	94
	9	29	100	98	97
	11.5		101.5	100	97.5
	15	31	102.5	102	98
	22	36	105	103	99.5
	29	37	106	105	101
n-C_3F_7	2	22	101	99.4	94
	7	24	102	101.1	98.5
	11		104	103	101
	18	27	106	104.9	102
	23	29	106	104.8	102
	35	30	106	105	102.5
n-C_7F_{15}	2	25	109	105	102
	7	30	111	108	105
	10	35	117	115	110
	15	42	121	120	115
	21	47	124	122	118
PS	0	20	95.1	84	82

Table 3
Refractive indices (n_D) of R_f–PS

R_f–PS	R_f-ratios (%)	n_D
$H(CF_2)_4$	4.0	1.5758
	9.0	1.5424
	11.5	1.5638
	15.0	1.5429
	22.0	1.5375
	29.0	1.5167
n-C_3F_7	2.0	1.5363
	7.0	1.5083
	11.0	1.5280
	18.0	1.5300
	23.0	1.5093
	35.0	1.5255
n-C_7F_{15}	2.0	1.5658
	7.0	1.5327
	13.0	1.4888
	20.0	1.5108
	25.0	1.4945
PS	0	1.5813

water, dried over anhydrous $MgSO_4$ and then distilled, b.p. 47.5–48 °C.

FAPs were prepared from the corresponding acid chlorides R_fCOCl, H_2O_2 (30%) and aqueous NaOH (10%) at −8 °C to −10 °C according to the reported procedure [2] and kept in a deep freeze before use. Their concentrations were determined by standard iodimetry.

3.2. Instruments

Hitachi IR-408 and IR-435 spectrometers, and a Bruker FT-AC80 NMR spectrometer, were used for the characterization of the products. Trifluoroacetic acid was used as an external standard and *m*-trifluoromethylaniline was used as an internal standard in the quantitative analysis of products by ^{19}F NMR spectroscopy. A JY-82 contact angle meter was used for the contact angle measurements. A TP-77 ellipsometer (Beijing) was used for determination of the refractive indices.

3.3. Reactions of FAPs with PS

In a typical experiment at room temperature (~20 °C), 2.1 g (20 mmol) of PS was dissolved in 40 ml of halocarbon solvent with gentle stirring in a reactor with a flat bottom. After flushing with nitrogen, 2.0 mmol of FAP dissolved in F113 (usually at a concentration of ~0.2 M) was dropped into the PS solution over 1 h. Stirring was continued for an additional 2 h. A few millilitres of the reaction mixture were removed for the determination of the yield of R_fCO_2H by acid–base titration. The reaction mixture (usually without precipitate) was washed in turn with 5% $NaHCO_3$, several times with distilled water and then dried over anhydrous Na_2SO_4. After removing a large part of the solvent by distillation, a large volume of methanol was added, the system filtered and the polymeric precipitate dried at 80 °C under vacuum for 24 h. After weighing the product, the R_f–PS samples were dissolved in $CDCl_3$ for quantitative analysis by ^{19}F NMR spectroscopy and to allow the characteristic IR absorption of R_f–PS to be checked.

3.4. Determination of refractive indices (n_D)

Films of R_f–PS were deposited on thin quartz plates (5×3 mm) which were then dried under vacuum. The reflecting angles were detected by an ellipsometer equipped with a He–Ne laser ($\lambda = 6328$ Å, incident angle = 70°). Refractive indices were derived from the reflecting angles by data treatment with a computer.

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