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A New Class of Fluorinated Polymers by a Mild, Selective, and Quantitative Fluorination

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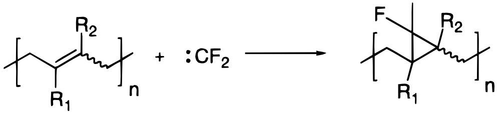
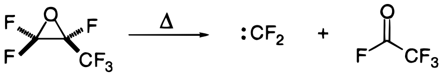
The incorporation of fluorine into synthetic[1] and biologically relevant[2] macromolecules leads to materials with unique properties such as low surface energies, low dielectric constants, high incompatibility with other polymers, solubility in supercritical CO_2,[3] and resistance to harsh chemical environments. Fluoropolymers are used commercially where the unique properties imparted by fluorine are necessary for the desired application (e.g., chemical resistant coatings, noncorrosive materials, antifouling coatings, interlayer dielectrics). Most fluorinated polymers are prepared by polymerization of the corresponding fluorinated monomers. Although selective modification of polymers can be an effective method for the preparation of new materials,[4] direct post-polymerization fluorination routes are chemically aggressive. Examples of synthetic polymer fluorinations include treatment with F_2,[5] SF_6 under electrical discharge,[6] $BF_3{\cdot}Et_2O$,[7] SF_4/HF,[8] fluorinated peroxides,[9] and HF electrochemically.[10] Fluorination yields are modest in these cases, and loss of pendant functionality, degradation of molecular weight, and cross-linking are undesirable side reactions.

Here we describe the preparation and characterization of a new class of fluoropolymers by a selective, mild, and quantitative fluorination of model polydienes with difluorocarbene ($:CF_2$) (eq 1).[11,12] The addition of halogenated carbenes to polymers



(1)

containing backbone unsaturation has been described in the literature,[13] however the use of $:CF_2$ for the fluorination of polymers has not been reported to the best of our knowledge. There are many ways to generate $:CF_2$,[12] and addition of $:CF_2$ to simple, alkyl-substituted alkenes gives modest yields of difluorocyclopropanes in most cases.[14] For the polymer analogous reaction a route that leads to quantitative conversion of the polydiene backbone double bonds is critical to the successful preparation of model fluorinated materials. We focused on the thermolysis of hexafluoropropylene oxide (HFPO) as a $:CF_2$ precursor (eq 2);[15] HFPO has been used for the fluorination of



(2)

electron-deficient olefins in modest to good yield.[12,16] As substrates we chose model polydienes prepared by anionic polymerization[17] with well-defined molecular weight, backbone regiochemistry,[18] and molecular weight distribution.

In a preliminary experiment (entry 1/Table 1) we heated a solution of cyclohexane containing 4.7 wt % of polyisoprene ($\overline{M}_n \approx 63$ kg/mol, PDI ≈ 1.12) and 3.5 equiv (relative to the backbone double bonds) of HFPO (bp $= -42$ °C) in a stainless steel high-pressure reactor to 185 °C for 18 h. The reactor was cooled and vented, and after isolation of the polymer it was determined by ^1H NMR spectroscopy that all of the backbone olefinic resonances were absent. Examination of the ^{19}F and ^{13}C NMR spectra corroborated the structure shown in eq 1 ($R_1 = H$, $R_2 = Me$). However, analysis of the fluorinated polyisoprene (FPI) by GPC showed a bimodal molecular weight distribution with $\overline{M}_n \approx 84$ kg/mol and PDI ≈ 1.91. Polyisoprene is particularly susceptible to cross-linking and chain degradation in the presence of free radicals, and the high reaction temperature is presumably responsible for the observed increase in the PDI. Although HFPO is a convenient $:CF_2$ source, the reaction conditions necessary for $:CF_2$ generation can lead to product rearrangements in small molecules.[19] To alleviate these side reactions we performed subsequent fluorinations in the presence of a radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (BHT).

The addition of BHT resulted in a remarkable finding: high-molecular-weight model polydienes were quantitatively fluorinated using HFPO while preserving the molecular parameters designed into the parent material (Table 1). Comparison of entries 1 and 2 in Table 1 shows that the addition of 5 wt % BHT preserves the PDI of the product without sacrifice in double bond conversion. The fluorination can be performed at temperatures as low as 170 °C (entry 3/Table 1), with a small excess of HFPO (entry 5/Table 1), and with low levels of BHT (entry 7/Table 1). In contrast to the high-molecular-weight case, low-molecular-weight polyisoprene can be successfully fluorinated in the absence of BHT (entry 8/Table 1).

The conversions in Table 1 were determined by integration of the ^1H NMR spectra of the fluorinated products.[20] Representative ^{13}C and ^{19}F NMR spectra are shown in Figure 1 for a sample of

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(18) The polydienes used in this study all have high 1,4 ($-CH_2-CR{=}CH-CH_2-$) microstructure but do contain a small fraction of 1,2 ($-CH_2-CH(CR{=}CH_2)-$) regioadditions (4,1 and 4,3 in the case of PI).

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Table 1. Reaction of HFPO with Model Polydienes[a]

entry	precursor polymer	precursor $\overline{M}_n$ (kg/mol)	precursor PDI	[C=C] (M)[b]	[HFPO]/[C=C]	BHT (wt %)	T (°C)	time (h)	isolated yield (%)	C=C[c] conv (%)	product $\overline{M}_n$ (kg/mol)	product PDI
1	PI	63	1.12	0.69	3.5	0	185	18	74	>99	84	1.91
2	PI	63	1.12	0.71	2.9	5	185	19	76	>99	70	1.16
3	PI	13	1.04	0.18	6.9	7	170	67		>99	14	1.08
4	PI	13	1.04	0.14	6.1	12	185	8	82	>99	17	1.03
5	PI	13	1.04	0.36	1.6	4	185	16	71	>99	15	1.06
6	PI	13	1.04	0.37	1.1	4	185	10		64	15	1.05
7	PI	13	1.04	1.26	2.5	1	185	21	87	>99	17	1.03
8	PI	13	1.04	0.18	5.8	0	185	18		>99	17	1.05
9	PDB	24	1.06	0.24	5.7	3.5	185	16	78	>99	21	1.16
10	PB	59	1.10	0.21	6.1	10	185	17	72	>99		
11	PI-*b*-PS	73	1.06	0.09	10.0	7	170	47	87	>99	79	1.10

[a] All GPC analysis was performed in $CHCl_3$, and $\overline{M}_n$ and PDI were calculated by using PS standards (the GPC solvent for entry 11 was THF). [b] Concentration of polydiene double bonds in cyclohexane solution. [c] From ^1H NMR.

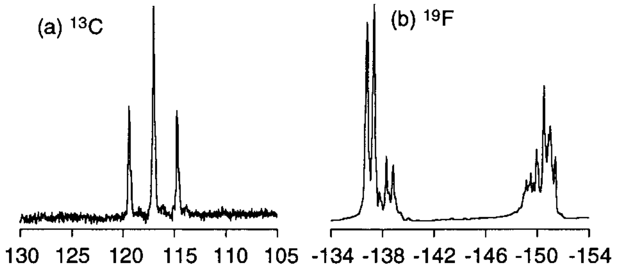

Figure 1. ^{13}C (a) and ^{19}F (b) NMR spectra of FPI (entry 3/Table 1). Scales are in ppm.

FPI (entry 3/Table 1). The doublet of doublets at 117.0 ppm (J_{CF} = 289 and 297 Hz) in the ^{13}C NMR spectrum is from the *gem*-difluoro-substituted carbon coupled to the two different fluorine atoms. The chemical shift and coupling constants are close to values reported for a similar trisubstituted difluorocyclopropane small molecule (116.5 ppm; J_{CF} = 280 and 306 Hz).[14] The ^{19}F NMR spectrum of this FPI was very similar to the spectrum of difluorotrimethylcyclopropane, which is an FPI repeat unit analogue.[14] However, the ^{19}F NMR spectrum of FPI is complicated by the presence of cis and trans backbone isomers and a small fraction of 4,3-regioisomer in the precursor. We further confirmed the structure of the fluorinated polymers by IR spectroscopy and elemental analysis.[21]

Fluorinated polydienes were prepared from polyisoprene, polydimethylbutadiene (PDB, $R_1 = R_2 = CH_3$), and polybutadiene (PB, $R_1 = R_2 = H$). From the ^1H, ^{13}C, and ^{19}F NMR spectra of the products it is evident that all of the olefinic sites have been selectively converted to the difluorocyclopropane species; no other $:CF_2$ insertion products were observed. Since both cis/trans 1,4 regioisomers and small amounts (≈5%) of 1,2 regioisomer are present in each of the starting polydienes,[18] the quantitative addition of $:CF_2$ to this set of polymers showed that fluorination of alkyl-substituted alkenes with every substitution pattern (mono; 1,1; 1,2(c/t), 1,1,2 (*E*/*Z*), and tetrasubstituted) proceeded smoothly under these reaction conditions. In a partially fluorinated PI (entry 6/Table 1) the ^1H NMR spectrum showed no change in the ratio of 4,3 to 4,1 regiochemistry, suggesting the trisubstituted and 1,1-disubstituted double bonds have similar reactivities under these conditions.

Preliminary physical characterization of the fluorinated polydienes was done by DSC and TGA (Table 2). The glass transition temperatures (T_g) of the fluorinated polymers increased by approximately 100 °C in all cases. This is presumably due to the dipole moment imparted by the CF_2 moiety in the polymer backbone leading to interchain dipole−dipole interactions. The thermal stability of the three-membered ring in the backbone of the polymer was investigated since the extrusion of $:CF_2$ from *gem*-difluorocyclopropanes has been observed in many systems.[22,23] From thermal gravimetric analysis (N_2 atmosphere, 10 °C/min), all of the polymers retained 95% of their original weight up above 300 °C. In addition, a sample of FPI (entry 5/Table 1) held at 200 °C under N_2 for 1 h retained 99.7% of its original weight, showed no significant change in molecular weight or PDI, had an identical ^1H NMR spectrum, and retained its solubility characteristics.

Table 2. Properties of Fluorinated Polydienes and Their Precursors

sample	T_g (°C)	T_d (°C)[a]	$\theta_a(H_2O)$[b]	$\theta_r(H_2O)$[b]
PB	−101[c]	404	91 ± 2	45 ± 2
FPB (entry 10)	−1	355	91 ± 1	85 ± 6
PI	−61[c]	344	98 ± 6	35 ± 7
FPI (entry 2)	43	309[d]	91 ± 1	81 ± 6
PDB	−5[e]	330	77 ± 1	75 ± 2
FPDB (entry 9)	89[e]	328	89 ± 1	81 ± 4

[a] Temperature at 5% weight loss. [b] Advancing and receding water contact angle. [c] Literature values. [d] Entry 5/Table 1. [e] These polymers showed melting endotherms (≈150 °C) in the DSC.

All of the fluorinated polydienes studied were insoluble in cyclohexane at room temperature (FPI was soluble in cyclohexane at ≈60 °C). Both FPI and FPDB were soluble in common organic solvents such as THF, chloroform, toluene, and methylene chloride at room temperature. FPB was not soluble in these solvents but only soluble in THF and trifluoromethylbenzene at elevated temperature. The solubility of these fluorinated polymers in polar solvents is further evidence for a polar repeat unit. Thin films prepared by spin casting were annealed (150 °C, vacuum, overnight) for contact angle measurements with deionized water (Table 2). Fluorination generally leads to a moderate increase in both the advancing and receding contact angle; however, the films we studied displayed large hysteresis, presumably due to surface roughness.[24]

We also demonstrated the fluorination of a model polyisoprene−polystyrene block copolymer (entry 11/Table 1). Under standard conditions only the polyisoprene was fluorinated and preservation of the molecular weight and PDI in the parent block copolymer was observed.

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(21) For entry 9 in Table 1: Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.64; F, 28.75. Found: C, 63.45; H, 7.54; F, 28.63. For entry 3 in Table 1: Anal. Calcd for $C_6H_8F_2$: C, 60.99; H, 6.84; F, 32.16. Found: C, 60.17; H, 6.68; F, 32.20. IR (NaCl plate) 1215, 1181, and 1118 cm^{-1} ($-CF_2-$ bending modes).

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