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CHEMISTRY

Conjugated Poly(fluoroalkyl 3-thienylacetate)s Synthesized in Supercritical Carbon Dioxide

M. L. Keshtov[a], A. M. Lopatin[a], D. V. Marochkin[a], Fang-Chung Chen[b], and Academician A. R. Khokhlov[a]

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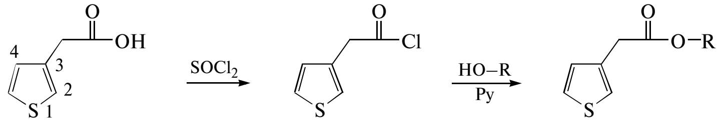
Conjugated polymers and supercritical carbon dioxide (sc-CO_2) in recent time have attracted a considerable attention of researchers not only from scientific but also from practical viewpoint on account of their use in different areas of science and technology. These polymers are intensely used as electroactive materials for light-emitting diodes, field-effect transistors, electrochromic devices, chemosensors, and solar photoelectric cells [1–7], whereas sc-CO_2 behaves as an environmentally-friendly "green" solvent that becomes a real alternative to organic solvents for different chemical processes, including fine organic synthesis and polymer preparation [8, 9]. However, the practical application of sc-CO_2 for the synthesis of polymers is confined on account of poor solubility of the majority of polymers except for amorphous fluorine-containing polymers and silicones [10].

At present, fluoropolymers are widely studied due to their low surface energy, chemical and thermal stability, hydrophobicity, and the ability of fluoroalkyl chain to self-organization [11]. The combination of unique characteristics of fluorine and electronic characteristics of conjugated polymers can lead to the development of novel materials that are of great interest from the viewpoint of both basic and applied research. Among numerous conjugated polymers under study, polythiophenes and their derivatives attract enhanced attention due to a unique combination of electronic properties such as electrochemical stability, photo- and electrical conductivity, electrochromism, facile structural modification, etc. However, these polymers are insoluble in sc-CO_2. A number of authors showed that poly(fluoroalkylthiophene)s, on the contrary, are soluble in sc-CO_2 [12, 13].

Taking into account the fluorophilicity of sc-CO_2 [10] and strong interaction between sc-CO_2 and carbonyl groups [14], we have modified the polythiophene chain with fluoroalkyl ester groups to obtain polymers well soluble in sc-CO_2. In this work, we obtained a series of novel conjugated polythiophenes containing fluoroalkyl ester groups in the side chain using sc-CO_2 as a solvent.

RESULTS AND DISCUSSION

To obtain novel conjugated poly(fluoroalkyl 3-thienylacetate)s, we developed monomers, fluoroalkyl 3-thienylacetates **1**–**5**. The synthesis of compounds **1**–**5** was carried out according to scheme that implies the conversion of 3-thienylacetic acid into corresponding acid chloride followed by its reaction with fluoroalkyl alcohols to form fluoroalkyl 3-thienylacetates **1**–**5**.



1–**5**

[R = $CH_2(CF_2)_4CF_3$ (**1**); $CH_2(CF_2)_5CF_3$ (**2**); $(CH_2)_3(CF_2)_5CF_3$ (**3**); $CH_2(CF_2)_7CF_3$ (**4**); $(CH_2)_2(CF_2)_7CF_3$ (**5**)].

Scheme 1.

The composition and structure of target compounds **1**–**5** were confirmed by elemental analysis data, IR spectroscopy, and ^1H and ^{19}F NMR (Table 1).

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[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

[b] *National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan*

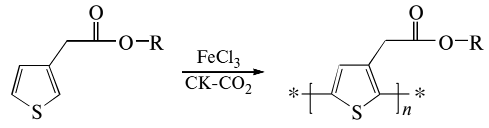
Table 1. Spectral characteristics of thiophene monomers **1–5**

Monomer	T_m, °C	^{1}H NMR, δ, ppm	^{19}F NMR, δ, ppm	Elemental analysis, found/calculated, %			
				C	H	F	S
1	115 [a]	7.34 (dd, *J* 5.0, 3.0 Hz, 1H), 7.22 (dd, *J* 2.0, 1.0 Hz, 1H), 7.09 (dd, *J* 5.0, 1.2 Hz, 1H), 4.67 (t, *J* 13.7 Hz, 2H), 3.80 (s, 2H)	−126.65 (2F), −123.86 (2F), −123.28 (2F), −119.89 (2F), −81.39 (CF_3)	$\frac{34.00}{33.97}$	$\frac{1.61}{1.66}$	$\frac{49.00}{49.26}$	$\frac{7.66}{7.56}$
2	120 [a]	7.30 (dd, *J* 4.9, 3.0 Hz, 1H), 7.19 (m, 1H), 7.06 (dd, *J* 4.9, 1.1 Hz, 1H), 4.63 (t, *J* 13.6 Hz, 2H), 3.77 (s, 2H)	−126.67(2F), −123.75 (2F), −123.26 (2F), −122.53 (2F), −119.94 (2F), − 81.50 (CF_3)	$\frac{33.16}{32.92}$	$\frac{1.32}{1.49}$	$\frac{52.03}{32.08}$	$\frac{7.15}{6.76}$
3	38	7.30 (dd, *J* 5.0, 3.0 Hz, 1H), 7.17 (dd, *J* 1.9, 0.8 Hz, 1H), 7.07 (dd, *J* 5.0, 1.1 Hz, 1H), 4.20 (t, *J* 6.3 Hz, 2H), 3.69 (s, 2H), 2.21–2.09 (m, 2H), 1.97 (dt, *J* 16.6, 6.2 Hz, 2H)	−126.63 (2F), −123.86 (2F), −123.28 (2F), −122.28 (2F), −114.86 (2F), −81.49 (CF_3)	$\frac{35.91}{35.87}$	$\frac{2.22}{2.21}$	$\frac{49.27}{49.17}$	$\frac{6.43}{6.38}$
4	45	7.33 (dd, *J* 5.0, 3.0 Hz, 1H), 7.21 (m, 1H), 7.07 (dd, *J* 5.0, 1.0 Hz, 1H), 4.64 (t, *J* 13.6 Hz, 2H), 3.79 (s, 2H)	−126.40 (2F), −123.49 (2F), −122.93 (2F), −122.13 (6F), −119.71(2F), −81.11 (CF_3)	$\frac{31.30}{31.37}$	$\frac{1.07}{1.22}$	$\frac{56.30}{56.25}$	$\frac{5.67}{5.58}$
5	40	7.32 (dd, *J* 4.9, 3.0 Hz, 1H), 7.19 (m, 1H), 7.07 (dd, *J* 5.0, 1.1 Hz, 1H), 4.44 (t, *J* 6.6 Hz, 2H), 3.71 (s, 2H), 2.56–2.44 (m, 1H)	−126.64 (2F), −123.91 (2F), −123.14 (2F), −122.30 (6F), −122.04 (2F), −81.39 (CF_3)	$\frac{33.57}{32.55}$	$\frac{1.53}{1.54}$	$\frac{53.96}{54.90}$	$\frac{6.07}{5.45}$

[a] Bp at 2 mmHg.

In particular, the IR spectra of all monomers **1–5** show a strong absorption band typical of carbonyl group in the region 1738–1762 cm^{-1}. The ^{1}H NMR spectra of compounds **1–5** in the region δ = 7.40–7.00 ppm show two doublets of doublets and one doublet arising from the different protons of the thiophene fragment (Table 1). In the aliphatic region, the spectrum shows a singlet at δ = 3.7 ppm related to the protons of the methylene group directly bound to the thiophene ring. Moreover, the integrated intensity ratio of the aliphatic to aromatic fragments agrees well with the suggested structures. The ^{19}F NMR spectra of compounds **1–5** in the region of δ = 80 ppm show signals typical of CF_3 group. The number of signals in the ^{19}F NMR spectra of all monomers **1–5** corresponds to the number of fluorine atoms in the molecules of these compounds.

The synthesis of poly(fluoroalkyl 3-thienylacetate)s (PFT) **I–V** was accomplished under conditions of the Sugimoto reaction [15] according to the scheme:



1–5 **I–V**

Scheme 2.

Poly(fluoroalkyl 3-thienylacetate)s were obtained by the oxidative polymerization of fluoroalkyl 3-thienylacetates in supercritical carbon dioxide and chloroform in the presence of $FeCl_3$ as a catalyst. The polymers were prepared in chloroform at ambient temperature, while polymerization in sc-CO_2 was conducted at 35–40°C to achieve supercritical state. The oxidative polymerization of fluoroalkyl 3-thienylacetates in both solvents proceeded successfully with rather high yields: 80–91 and 70–79%. However, the conversion in sc-CO_2 was slightly lower, probably because of poor solubility of $FeCl_3$ in sc-CO_2. All polymers **I–V** are soluble in common and fluorinated organic solvents. Nonetheless, partially soluble polymers were obtained on prolonged polymerization (longer than 2 h). The different solubility may be associated with crosslinking of PFT at the 4-position of the thiophene ring.

The structure of the polymers was confirmed by the IR and ^{1}H and ^{19}F NMR spectra (Fig. 1, Table 2). In particular, the IR spectra of all polymers **I–V** exhibit bands typical of carbonyl group in the region 1737–1762 cm^{-1}. The ^{1}H NMR spectra of the polymers display signals in the range 6.91–7.65 ppm arising from the aromatic protons of the thiophene ring. The signals in the range 4.42–2.50 ppm refer to aliphatic protons. The ratio of integrated intensity of the signals of the aliphatic to aromatic portions agrees well with the suggested structures for all polymers. Poly(fluoroalkyl 3-thienylacetate)s obtained in sc-CO_2 and chloroform have similar structures.

We also used ^{1}H NMR spectra to study the PFT microstructure. Indeed, the signal at δ = 3.7 ppm from the methylene group directly bound to the thiophene

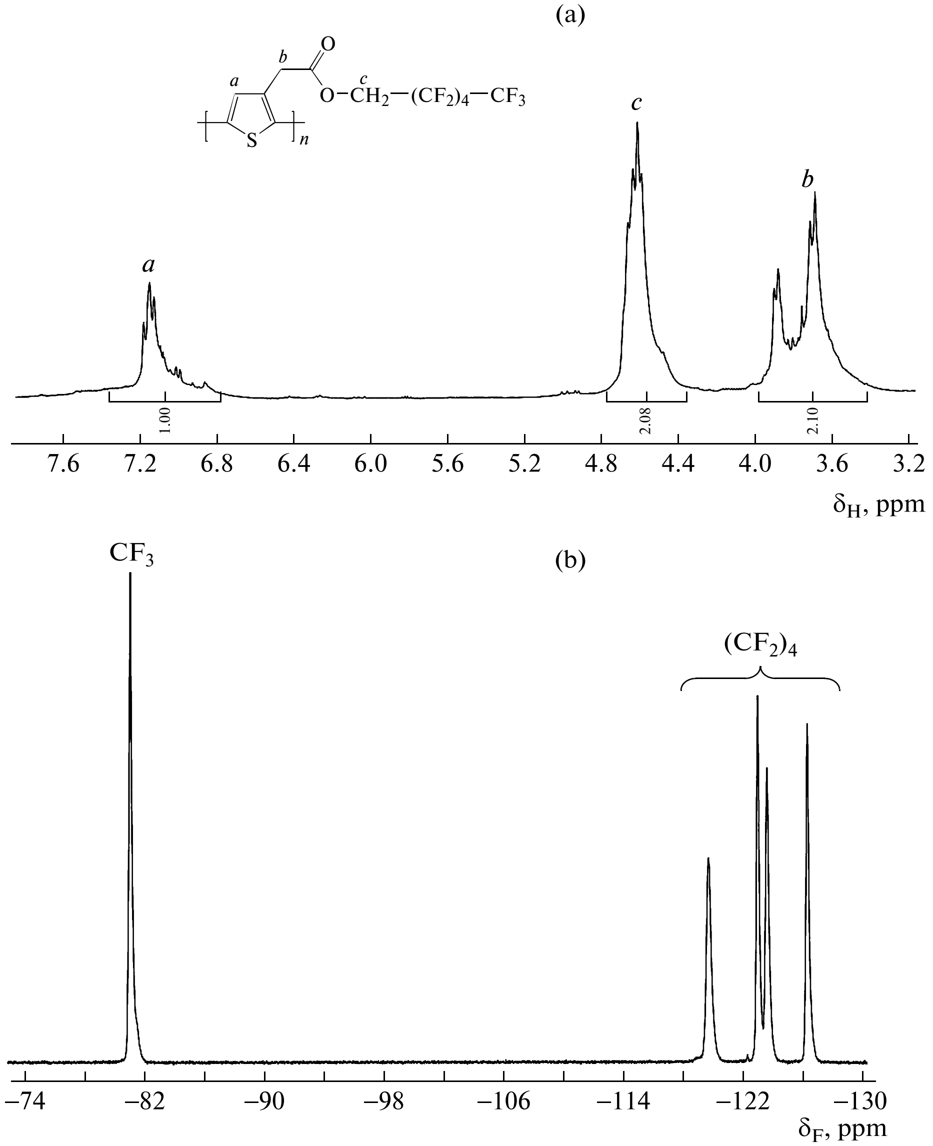


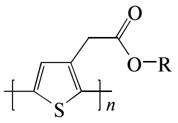
Fig. 1. (a) ^{1}H and (b) ^{19}F NMR spectra of polymer **I**.

ring is split into two peaks, which confirms the regiorandom character of the bond. Regioregularity (the ratio of head-to-tail, head-to-head, or tail-to-tail) was calculated from the intensity ratio of two peaks of the methylene group directly bound to the thiophene ring. As it was expected, the majority of polymers obtained in sc-CO_2 have the regiorandom bond character. The same values were also obtained for PFTs synthesized in chloroform, which indicates the similar effect of solvents on the stereoregularity of polymerization.

The molecular weights and polydispersity of polymers **I**–**V** obtained in sc-CO_2 and chloroform vary in the range 3950–5880 and 8040–12420 (M_n), 21720–11200 and 19880–38120 (M_w), 2.71–3.69 and 2.47–3.07 (M_w/M_n), respectively (Table 3). Table 3 shows that, although the molecular weights of the polymers obtained in both solvents are almost equal, the polydispersity of polymers obtained in sc-CO_2 is much higher than that of polymers obtained in chloroform. This fact may result from the different solubility of the monomers in sc-CO_2 and chloroform.

All the polymers are soluble in common organic solvents such as DMF, toluene, THF, chloroform, and acetone. The thermal characteristics of polythiophenes **I**–**V** were studied by TMA and TGA, the results are given in Table 3. The glass transition temperatures of the polymers (T_g) determined from TMA curves are rather low and fall in the range of 54–82°C. The polymers show good thermal stability. The temperature of 10% weight loss ($T_{10\%}$) determined by TGA

Table 2. Spectral characteristics of polythiophenes of general formula

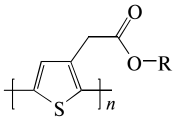


Polymer	R	IR, cm^{-1}	NMR; δ, ppm		λ_{abs}, nm	λ_{fl}, nm
			^{1}H	^{19}F		
I	$CH_2(CF_2)_4CF_3$	1758	6.72–7.25 (m, 1H) 4.51–4.77 (m, 2H) 3.71–4.00 (m, 2H)	–126.44 (2F) –123.74 (2F) –123.11 (2F) –119.80 (2F) –80.93 (CF_3)	402	526
II	$CH_2(CF_2)_5CF_3$	1762	6.87–7.21 (m, 1H) 4.41–4.79 (m, 2H) 3.50–3.97 (m, 2H)	–126.31 (2F) –123.51 (2F) –122.97 (2F) –122.26 (2F) –119.73 (2F) –80.96 (CF_3)	386	512
III	$(CH_2)_3(CF_2)_5CF_3$	1740	6.75–7.25 (m, 1H) 4.10–4.32 (m, 2H) 3.52–3.91 (m, 2H) 1.18–2.31 (m, 4H)	–126.37 (2F) –123.54 (2F) –123.07 (2F) –122.12 (2F) –114.52 (2F) –81.04 (CF_3)	381	506
IV	$CH_2(CF_2)_7CF_3$	1757	6.67–7.23 (m, 1H) 4.48–4.75 (m, 2H) 3.51–3.92 (m, 2H)	–126.25 (2F) –123.44 (2F) –122.35 (2F) –122.04 (6F) –119.72 (2F) –80.83 (CF_3)	395	525
V	$(CH_2)_2(CF_2)_7CF_3$	1737	6.60–7.25 (m, 1H) 4.15–4.53 (m, 2H) 3.82–3.93 (m, 2H) 2.28–2.58 (m, 2H)	–126.26 (2F) –123.62 (2F) –122.26 (2F) –122.05 (6F) –113.73 (2F) –80.89 (CF_3)	398	525

in argon atmosphere and in air are within 248–294 and 270–300°C for the polymers obtained in sc-CO_2 and chloroform, respectively. The data of Table 3 indicate that the introduction of additional CF_2 groups in to the polymer chain leads to increase in the glass transition temperature and thermal stability of the polymers.

Ultraviolet absorption and fluorescence spectra provide further understanding of the conjugation extent of the polymer, the structure and effect of fluoroalkyl ester substituents on the polymer chain and electronic effects in PFT obtained in sc-CO_2. The photophysical properties of the polymers were studied by UV and fluorescence spectroscopy, the results are presented in Fig. 2 and Table 2. The maxima of absorption spectra of polymers **I**–**V** obtained in sc-CO_2 are in the range of λ = 381–402 nm and shifted to the blue region as compared with poly(3-octylthiophene) (λ = 437 nm) due to decrease in the conjugation length of poly(fluoroalkyl 3-thienylacetate) chain. These spectra are identical to those of polymers **I**–**V** obtained in chloroform. All the polymers exhibit fluorescence in the blue region with emission maxima in the range 506–526 nm (Fig. 2). There is a marked difference in the Stokes shift. Fluorescence maxima are shifted to the right by 124–130 nm relative to the absorption maxima with minimal overlapping. Such a trend in fluorescence takes place for the polymers obtained in both sc-CO_2 and chloroform.

Table 3. Certain characteristics of obtained in sc-CO_2 polythiophenes of general formula



Polymer	R	Solvent	Yield, % [b]	M_n	M_w	M_w/M_n	T_g, °C (DMF)	$T_{10\%}$, °C [c] (THF)
I [a]	$CH_2(CF_2)_4CF_3$	$CHCl_3$	86	9230	25780	2.77	82	$\frac{285}{305}$
I	$CH_2(CF_2)_4CF_3$	sc-CO_2	73	5810	19180	3.30	74	$\frac{270}{285}$
II [a]	$CH_2(CF_2)_5CF_3$	$CHCl_3$	91	12420	38120	3.07	82	$\frac{303}{317}$
II	$CH_2(CF_2)_5CF_3$	sc-CO_2	79	5880	21720	3.69	79	$\frac{294}{300}$
III [a]	$(CH_2)_3(CF_2)_5CF_3$	$CHCl_3$	80	11730	31670	2.70	62	$\frac{282}{305}$
III	$(CH_2)_3(CF_2)_5CF_3$	sc-CO_2	71	5070	17240	3.40	58	$\frac{263}{280}$
IV [a]	$CH_2(CF_2)_7CF_3$	$CHCl_3$	80	8040	19880	2.47	72	$\frac{275}{280}$
IV	$CH_2(CF_2)_7CF_3$	sc-CO_2	70	4140	11200	2.71	63	$\frac{260}{278}$
V [a]	$(CH_2)_2(CF_2)_7CF_3$	$CHCl_3$	82	8430	24370	2.89	68	$\frac{260}{295}$
V	$(CH_2)_2(CF_2)_7CF_3$	sc-CO_2	72	3950	13230	3.35	63	$\frac{248}{270}$

[a] Polymers were obtained in chloroform.
[b] Polymerization conditions: 2 h at 40°C at monomer to catalyst ratio of 1 : 4.
[c] The temperature of 10% weight loss of polymers in air in the numerator and that in argon in the denominator.

Experimental results show that sc-CO_2 has no effect on the conformational distribution of polymers in the course of polymerization.

Thus, we have prepared a series of novel fluoroalkyl ester-containing polythiophenes **I**–**V** by oxidative polymerization in sc-CO_2 and chloroform. The poly-

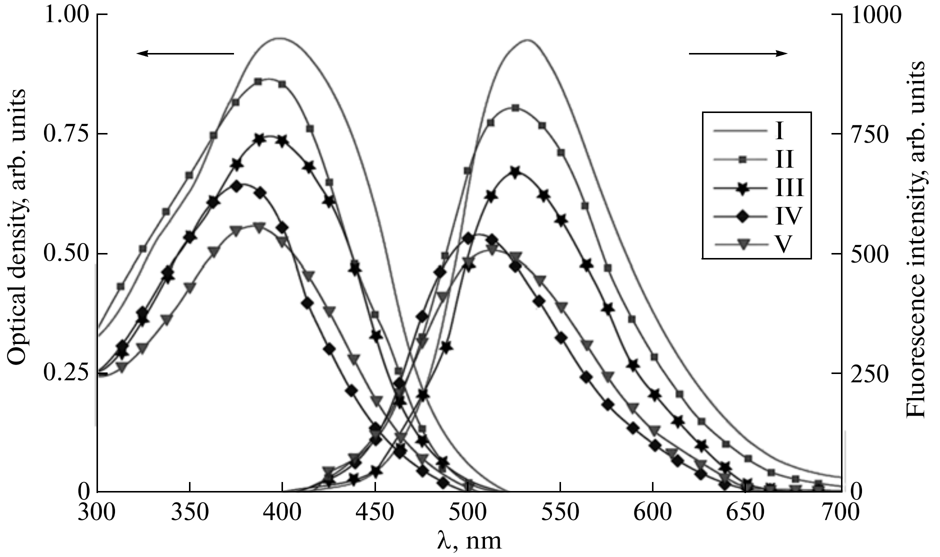


Fig. 2. Absorption and fluorescence spectra of polymers **I**–**V** in chloroform ($c = 10^{-5}$ M).

mers were obtained in both solvents in high yields and with high molecular weights.

The properties of the polymers obtained in sc-CO_2, such as molecular weight, polydispersity, conjugation, UV absorption, are similar to the properties of poly(fluoroalkyl 3-thienylacetate)s obtained in chloroform. The unique combination of fluoroalkyl and carbonyl groups makes the poly(fluoroalkyl 3-thienylacetate)s highly soluble in sc-CO_2. Our studies show that sc-CO_2 is an alternative promising solvent for the oxidative polymerization of fluoroalkyl 3-thienylacetates.

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