Liquid Crystalline Regioregular Semifluoroalkyl-Substituted Polythiophenes

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Control of the molecular architecture of conjugated polymers by substitution with side chains[1] affords polymers that are electronically conductive upon doping, semiconductive, and electroluminescent. Approaches to self-assembled conjugated polymers include the substitution of the backbones with side chain mesogens,[2] preparation of amphiphilic monomers,[3] and polymerization in organized media.[4] However, these approaches introduce bulky side chains and counterions which disrupt packing and planarity of the polymer backbone.

We have previously reported the synthesis of regiorandom (i.e., nonregular, **Np**) poly(3-(semifluoroalkyl)-thiophene)s[5] and copolymers bearing alternating alkyl and semifluoroalkyl side chains[6] which assemble by virtue of the amphiphilicity of the semifluorinated chains.[7−9] We have now prepared regioregular analogues **Rp(Th-*m*,*n*)** to enhance the order of the polymers and to assess the potential for development of liquid crystalline poly(3-alkylthiophene)s.[10,11]

Bromination of **1**[5] with *N*-bromosuccinimide gave the corresponding 2,5-dibromo-substituted thiophene, **2** (Figure 1). The dibromide was treated with methylmagnesium bromide in THF,[12] followed by addition of a catalytic amount of Ni(dppp)Cl_2 to afford the regioregular head-to-tail coupled polymer **Rp(Th-11,4)**. Gel permeation chromatography (THF as eluent, polystyrene calibration) of the hexane soluble fraction gave an average number molecular weight of 10 500 g/mol and a polydispersity of 1.2. NMR spectroscopy reveals that the polymer has a high content of head-to-tail couplings between 3-substituted 2,5-thiophenediyl units. The ratio of the integrals of signals at 2.8 ppm (assigned to the α-methylenes of head-to-tail linkages) and 2.5 ppm (head-to-head) indicates ca. 95% of head-to-tail couplings. (This analysis ignores the influence of end groups which were not observed as separate peaks in the NMR spectra.) Regiorandom **Np(Th-11,4)** was prepared by oxidative polymerization of **1** ($FeCl_3$, $CHCl_3$).

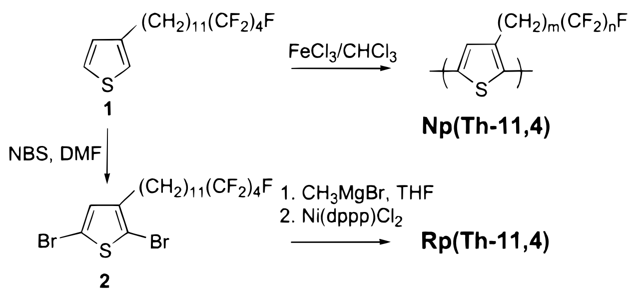

Figure 1. Synthesis of **Rp(Th-11,4)** and **Np(Th-11,4)**.

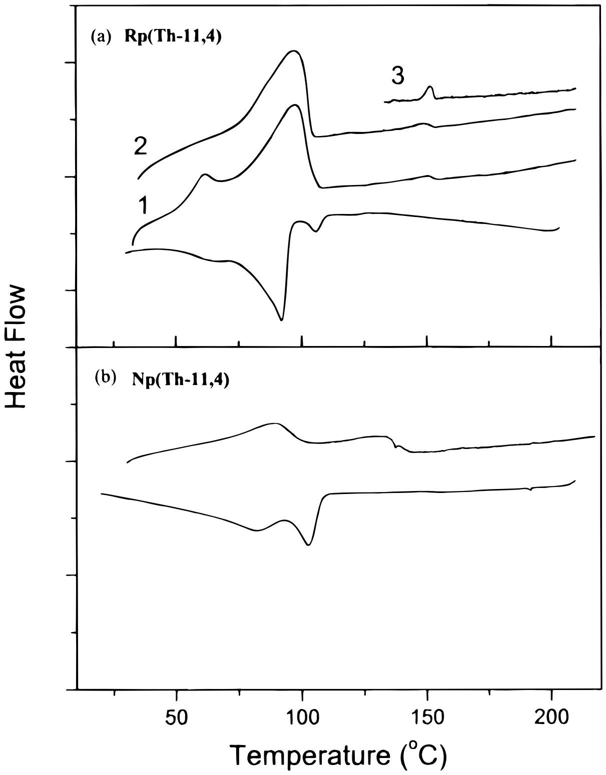

Figure 2. Differential scanning calorimetry (10 °C/min) thermograms of (a) **Rp(Th-11,4)** (1, first heating and cooling scans; 2, second heating; 3, heating after annealing at 125 °C for 5 h) and (b) **Np(Th-11,4)**.

Differential scanning calorimetry of a pristine sample of **Rp(Th-11,4)** exhibits three endothermic peaks (Figure 2). The peak at 60 °C only appears on the first heating scan or after annealing the sample at room temperature for more than 5 h. A broad peak at 97 °C ($\Delta H = 17$ J/g, i.e., 7.73 kJ/mol repeat unit) corresponds to a transition from a solid to a fluid liquid. A small third peak appears at ca. 150 °C. This endotherm becomes more defined (150 °C, $\Delta H = 0.24$ J/g) after annealing the sample at 125 °C for 5 h. The cooling curve shows two exothermic peaks at 108 °C ($\Delta H = 0.4$ J/g, i.e., 0.18 kJ/mol repeat unit) and 92 °C ($\Delta H = 14$ J/g, i.e., 6.4 kJ/mol repeat unit). Thus, there appears to be an enantiotropic mesophase. The transformation from the isotropic liquid into the mesophase is supercooled, but the polymer rapidly crystallizes from the mesophase upon further cooling. Polarized optical microscopy of **Rp(Th-11,4)** indicates a melting point of 100 °C with no indication of birefringence, consistent with only a weakly ordered phase and the high adsorption of visible light displayed by this polymer.[13]

The X-ray diffractogram of a solvent cast film of **Rp(Th-11,4)** at room temperatue (Figure 3) has sharp reflections at $2\theta = 2.89°$, 5.60°, 8.31°, and 13.8° which can be assigned to the (100), (200), (300), and (500) planes of a lamellar phase with a spacing of 32.6 Å. A peak at 23.7° (3.8 Å) corresponds to thiophene face-to-face stacking distance. The interlayer distance for **Rp(Th-11,4)** corresponds to the width of a diad in an anti conformation with extended side chains. Between 90 and 100 °C there is a dramatic change in the appearance of the diffractograms. The diffraction peaks from the (200) and (300) reflections are very small and broad up to 140 °C. Above 140 °C this residual order is lost, and only a broad amorphous peak is observed.

Thermochromism of poly(3-alkylthiophene)s has previously been correlated with melting transitions.[14] The absorption maximum of a spin-coated film of **Rp(Th-11,4)** shifts to lower wavelength upon heating (not

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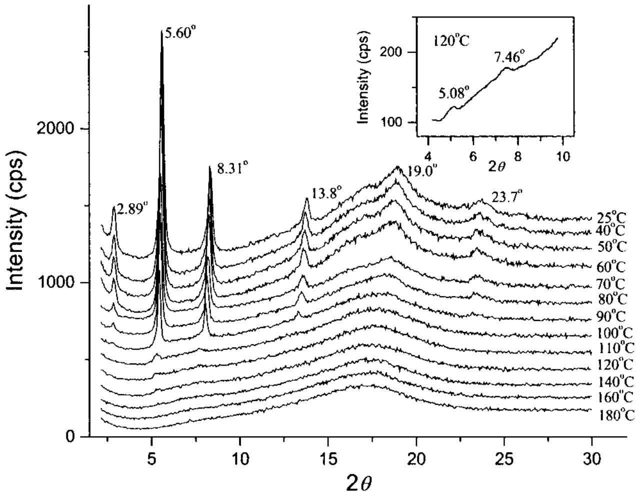

Figure 3. X-ray diffractograms of **Rp(Th-11,4)** film at various temperatures. Inset: expansion of diffractogram obtained at 120 °C.

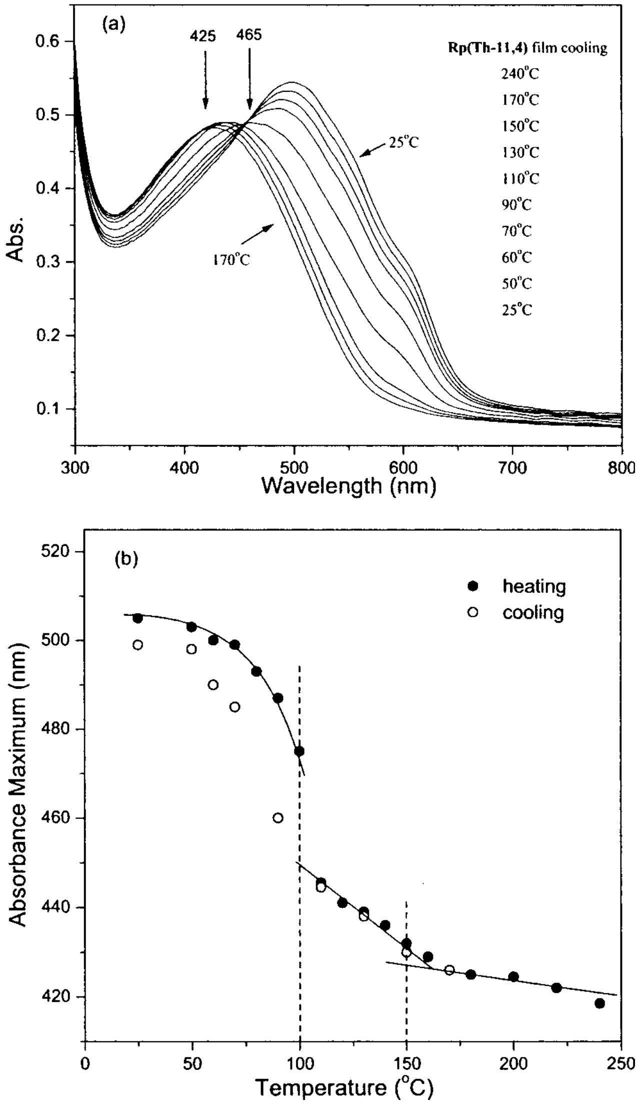

Figure 4. (a) UV–vis spectra of a film of **Rp(Th-11,4)** (cooling from 240 to 25 °C). (b) λ_{max} of UV–vis spectra of **Rp(Th-11,4)** film versus temperature on heating and cooling.

shown). Upon cooling, the spectra shift back to higher wavelength with some hysteresis (Figure 4b). There is a gradual decrease in λ_{max} between room temperature and 90 °C followed by a large decrease at approximately 100 °C. The value of λ_{max} then decreases slowly as the temperature is raised to 150 °C (which correlates to the highest transition observed by DSC) and then decreases even more slowly in the isotropic phase.

The appearance of isosbestic points in the temperature- or solvent-dependent UV–vis spectra of poly(3-alkylthiophene)s has been attributed to the equilibrium between two distinct conformational forms of the polymer backbone.[15] Careful examination of spectra reveals that there are two isosbestic points. The first isosbestic point at 465 nm is defined by spectra obtained between room temperature and 100 °C. Spectra collected between 130 and 170 °C define a second isosbestic point at 425 nm.

The evidence presented above suggests that **Rp(Th-11,4)** forms a weakly ordered fluid thermotropic phase between a semicrystalline phase (<100 °C) and the isotropic liquid (>150 °C). Although the transformation from the solid phase into the liquid crystalline phase is associated with a decrease in conjugation length, as shown by the decrease in λ_{max}, the polymer backbones retain some orientational order. While semifluorinated alkanes form smectic-like phases, **Rp(Th-11,4)** forms a weakly ordered thermotropic mesophase. Thus, rather than considering these partially fluorinated alkyl groups as side chain mesogens, it appears as though they simply undergo conformational disordering prior to isotropization of the main chains with formation of a nematic phase. The role that the fluorocarbon chains play on the ordering of polythiophenes and the design of other liquid crystalline polymers are under investigation.

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