Optical Properties and Dual Electrical and Ionic Conductivity in Poly(3-methylhexa(oxyethylene)oxy-4-methylthiophene)

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ABSTRACT: A new regioregular polythiophene derivative bearing side chains with exactly six oxyethylene units has been synthesized. From the thermochromic and ionochromic behavior of this polymer, it is concluded that the hexa(oxyethylene) side chains induce a more planar conformation of the polythiophene backbone than random-length oxyethylene side chains with on average seven oxyethylene units. It is further observed that the ionochromic transition from the planar to the nonplanar conformation is $[K^+]^2$ dependent, suggesting that solvation of K ions by adjacent side chains is required. The polymer is ionically as well as electronically conductive. The ionic conductivity is only measurable at 80 °C, i.e., above T_g and the order−disorder temperature of the polymer.

I. Introduction

Conjugated polymers (polyacetylene, polythiophene, polypyrrole, polyaniline, etc.) have been extensively studied for their conductive properties in the doped (oxidized, reduced or protonated) state.[1] These polymer materials have been made fusible and solvent processable with the introduction of flexible side chains on their backbone. Moreover, new interesting optical properties have been discovered for polythiophene derivatives in the neutral state.[2−4] These chromic phenomena are not exclusive to polythiophene derivatives and can also be observed in substituted polydiacetylenes,[5−9] polysilanes,[10−13] polygermanes,[14] and poly(alkylbithiazoles).[15−17] The latter is also an electroactive material.[17,18]

The chromic effect is associated with a planar/nonplanar conformational transition of the conjugated backbone and a lengthening/shortening of the effective conjugation in the backbone that affects the electronic transition in the UV−visible range. In regioregular (head-to-tail coupled) polythiophene derivatives, linear side chains seem to maintain the planar conformation of the polymer at low temperature and in marginal solvents.[19,20] Disordering of the side chains leads to a less planar conformation of the polythiophene backbone.[21] The disordering of the side chains and concomitant backbone twisting can be due to temperature (thermochromism), to solvent effects (solvatochromism), to light (photochromism) or to a range of specific molecular interactions with the side chains, e.g., the presence of specific ions associating with the side chains leads to ionochromism. In regioregular polythiophene derivatives, a discontinuous shift in the absorption spectrum with an isosbestic point is observed, indicating the presence of only two species.

Regioregular polythiophenes with oligo(oxyethylene) and crown ether side chains have been studied previously.[21−25] These polymers form noncovalent interactions with alkali-metal ions that cause modification of the optical and electrochemical properties.[23,26,27] Polythiophene with di(oxyethylene) substituents shows only a weak response to alkali-metal cations, K^+ actually stabilizing the planar form in THF.[21] On the other hand, poly(3-oligo(oxyethylene)-4-methylthiophene) (P350MT, Scheme 1), with on average seven oligoethylene units ($\bar{n} = 7$, $3 \leq n \leq 10$), shows a strong chromic response to the presence of selective alkali-metal ions.[22]

In this work, we describe the synthesis and properties of a new regioregular polythiophene with exactly six oxyethylene units in every monomer unit. Since all side chains are identical and are sufficiently long to be active in alkali-metal ion complexation, an improved ion sensitivity is expected. Furthermore, this polymer can act as a mixed conductor. The backbone is electroactive in the doped state and the oxyethylene side chains can solubilize alkali-metal cations and act as an ion-transporting polyelectrolyte. The polyelectrolyte properties of poly(*p*-phenylene)s and polypyrroles with oligo(oxyethylene) side chains have been recently reported.[28−30] Therefore, the ionic conductivity of polymer/salt blends as well as the electronic conductivity of the pure doped polymer has been determined. Eventually, these systems could be useful as separator membranes between the polymeric electrolyte and the electrode or act as the electrodes in solid-state lithium batteries.[28,30]

II. Experimental Section

Synthesis. 3-Hexa(oxyethylene)oxy-4-methylthiophene (**1**) was synthesized (Scheme 2) from 3-bromo-4-methylthiophene and hexaethylene glycol, according to previously described methods.[31,32] Under Ar atmosphere, 1.37 g (0.060 mol) of Na was reacted completely (by heating slightly) with 50 g (0.177 mol) of hexaethylene glycol to produce the alcoholate. Then, 4.00 g (0.023 mol) of 3-bromo-4-methylthiophene, 4.40 g (0.024 mol) of CuBr and 20 mL of NMP were added to the reaction flask, and the mixture was heated to 110 °C for 43 h. The solution was allowed to cool to room temperature. The precipitate was filtered and rinsed with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2, filtered on cotton wool, and evaporated. The product was purified on silica gel using ethyl acetate as eluent (53% yield, light yellow oil). ^1H NMR ($CDCl_3$, 400 MHz, ppm): 2.05 (s, 3H), 2.82 (b, 1H), 3.55 (m, 2H), 3.60 (m, 16H), 3.68 (m, 2H), 3.81 (m, 2H), 4.06 (m, 2H), 6.12 (d, 1H), 6.77 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 12.61, 61.57, 69.50, 69.57, 70.19, 70.43(2C), 70.49(2C), 70.51 (2C), 70.73, 72.44, 96.43, 119.77, 129.02, 155.75. Anal. Calcd for $C_{17}H_{30}O_7S$: C, 53.95; H, 7.99; S, 8.47. Found: C, 53.44; H, 8.33; S, 8.29.

3-Methylhexa(oxyethylene)oxy-4-methylthiophene (**2**) was obtained from **1** (Scheme 2). A 3.1 g (0.055 mol) sample of KOH was partly dissolved in 24 mL of dimethyl sulfoxide. Then,

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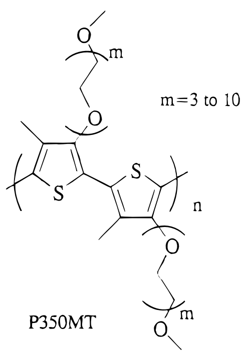
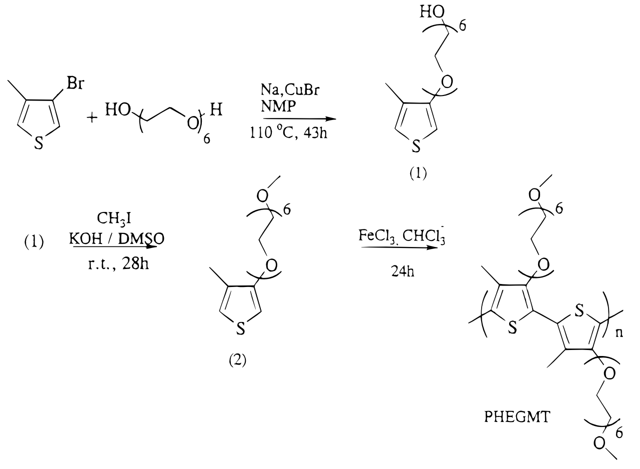
Scheme 1. Poly(3-oligo(oxyethylene)-4-methylthiophene) (P350MT)



Scheme 2. Synthesis of Poly(3-methylhexa(oxyethylene)O*xy*-4-methylthiophene) (PHEGMT)



4.41 g (0.0116 mol) of **1** was added to the solution, and the mixture was reacted for 50 min. An excess of methyl iodide (13 g (0.091 mol)) was added to the alcoholate. After the mixture was stirred for 28 h at room temperature, it was poured into 800 mL of water, the product was extracted with dichloromethane and filtered on cotton wool, and the crude product was dried under vacuum. The product was purified on silica gel using ethyl acetate and dried under vacuum at 45 °C (68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 2.08 (s, 3H), 3.36 (s, 3H), 3.52 (m, 2H), 3.63 (m, 16H), 3.66 (m, 2H), 3.84 (m, 2H), 4.09 (m, 2H), 6.15 (d, 1H), 6.79 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 12.60, 58.88, 69.49, 69.55, 70.37, 70.44 (2C), 70.46 (2C), 70.49 (2C), 70.51, 70.75, 71.79, 96.39, 119.77, 129.00, 155.73. Anal. Calcd for $C_{18}H_{32}O_7S$: C, 55.08; H, 8.22; S, 8.17. Found: C, 55.02; H, 8.47; S, 7.93.

Poly(3-methylhexa(oxyethylene)oxy-4-methylthiophene) (PHEGMT) (**3**) (Scheme 2) was obtained in $CHCl_3$ via chemical polymerization with iron trichloride as the oxidizing agent. The mixture was stirred for 24 h at room temperature, and the solution was precipitated in cold methanol. The resulting polymer was filtered on a Buechner funnel and washed with cold methanol. It was then washed for 24 h with water in a Soxhlet apparatus to extract the residual ferric chloride. The polymer was further rinsed with methanol at room temperature to eliminate the low molecular weight fraction. The high molecular weight fraction was dissolved in chloroform and filtered, the solvent evaporated, and the polymer dried at 40 °C for 1 day and stored under vacuum at room temperature. The polymer formed a violet free-standing film. It was completely soluble in chloroform and tetrahydrofuran at room temperature, and most of it was soluble in methanol when warmed.

Characterization and Physical Measurements. NMR spectra were obtained in deuterated chloroform with a Varian 400 MHz instrument. Differential scanning calorimetry (DSC) was performed with a DuPont model 2910, calibrated with ultrapure indium. The UV−visible absorption spectra were obtained on a Hewlett-Packard diode array model 8453 spectrometer. The measurements were performed in a 1 cm-path quartz cell. For temperature-dependent (10−65 °C) solution measurements the spectrophotometer was provided with a thermostated holder controlled by a water−ethylene glycol bath. Spectra were taken immediately after the temperature and spectra had stabilized (about 10 min). For the thermochromic and ionochromic measurements, the polymer concentration in methanol was approximately 1×10^{-4} M. The polymer−salt mixtures were prepared from identical volumes of a filtered methanol solution of the polymer and of the salt solution in methanol. The solutions were kept in the dark and left to stabilize for at least 12 h before performing the measurements. For measurements on solid samples a few drops of a concentrated chloroform solution of the polymer were evaporated on a quartz plate. A heating unit allowed for temperature control from room temperature to 250 °C with a maximum error of ± 2 °C.

Ionic conductivity measurements were made on polymer−salt mixtures. For each polymer−salt mixture, 12 mg of polymer was dissolved in approximately 1−3 mL of dry chloroform and exposed to hydrazine vapor to reduce the polymer and help solubilization. The solution was concentrated under a flow of Ar. Salt solutions were made from previously dried lithium triflate ($LiCF_3SO_3$, Aldrich) or lithium bis(trifluoromethanesulfonyl)imide ($LiN(CF_3SO_2)_2$, LiTFSI, 3 M), in dry acetonitrile. The required amount of salt solution was added to the concentrated polymer solution. The solution was left for 12 h in the dry atmosphere of a glovebox for the electrolyte to reach equilibrium. The mixture was then concentrated with an Ar flow. The concentrated electrolyte was then deposited drop by drop on microelectrodes (MB-4000, Windsor Scientific Ltd.), and the solvent was allowed to evaporate between each drop. The whole electrode was then dried under vacuum at 40 °C overnight and kept under vacuum until the measurements were made.

The microelectrodes coated with the polymer/salt blends were connected to a printed circuit board header and kept under He in a glass container. The container was heated to 80 °C using an ethylene glycol bath. The temperature was allowed to stabilize for 3 h before the measurements were made. Impedance measurements were performed using a Solartron frequency response analyzer 1260 instrument with the Zplot software (Scribner). The measurements were made from 100 Hz to 1 MHz at an oscillating amplitude of 10 mV. A measurement was performed for each combination of the four-band microelectrode. These microelectrodes have three band gaps separated by 10, 30, and 50 μm, respectively. The data were fitted to an equivalent circuit (see below) using the Z-view software. The conductivity was calculated according to the literature.[33] These microelectrodes allow us to overcome the use of the thickness of the films in the calculations. As previously seen for other microelectrodes, the results obtained had to be multiplied by a constant (4.5) in order to obtain the final conductivity results. This constant is due to the geometry of the electrodes.[34]

The electronic conductivity was measured by the four-probe technique on a polymer film cast from a chloroform or a mixture of dichloroethane and tetrachloroethane solution. The film was then doped with iodine vapor overnight. The film thickness was measured with a Dektak profilometer.

III. Results and Discussion

Preparation. The ^{1}H NMR spectrum of PHEGMT[3] (Figure 1a) shows a sharp and well-defined symmetric peak around 2.2 ppm and only four peaks are present in the aromatic region of the ^{13}C NMR (Figure 1b) spectrum. From these results, we can conclude that the oxidative polymerization has led to a regioregular polymer with more than 95% head to tail coupling.[35−38]

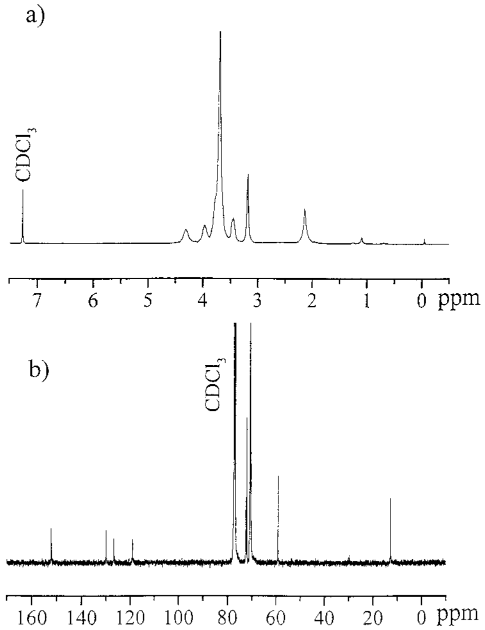


Figure 1. NMR spectra of PHEGMT in chloroform: (a) ^{1}H NMR; (b) ^{13}C NMR.

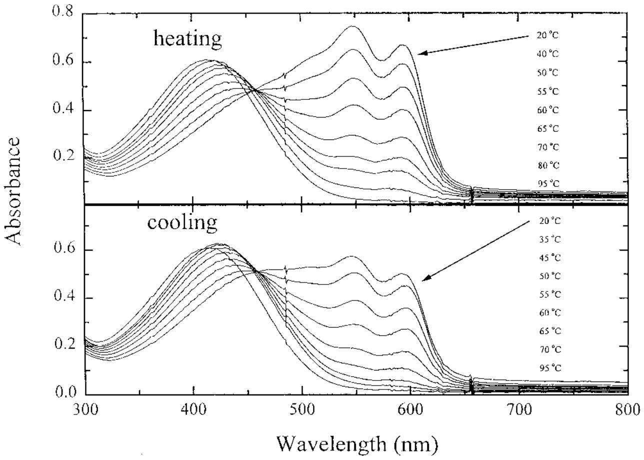


Figure 2. Temperature dependence of the UV−vis absorption spectrum of PHEGMT in the solid state. Top: heating scan. Bottom: cooling scan.

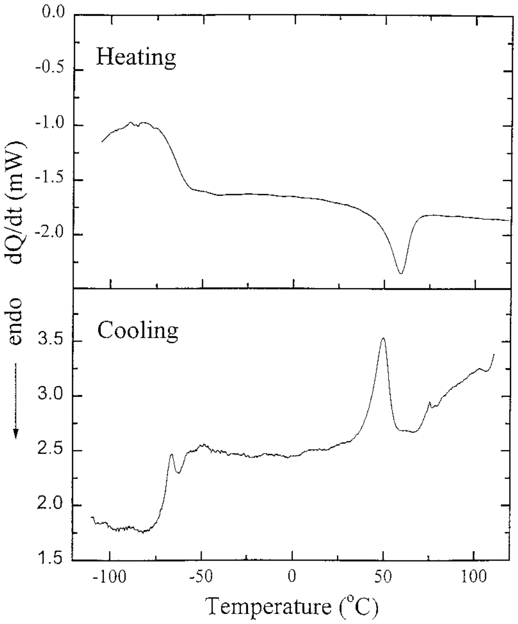


Figure 3. DSC thermograms of PHEGMT. Top: heating scan. Bottom: cooling scan.

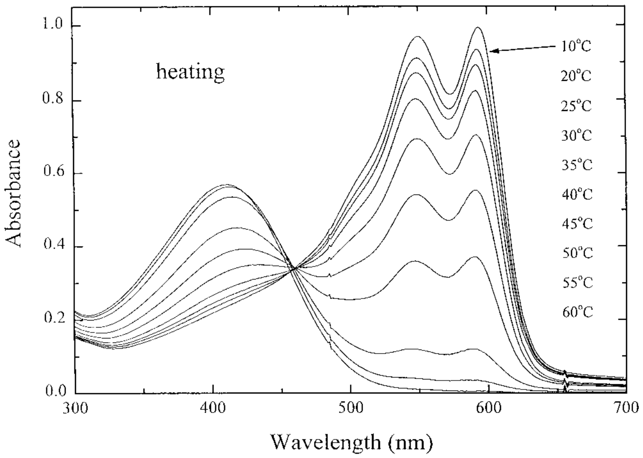


Figure 4. UV−vis absorption spectrum of PHEGMT in methanol (1 × 10^{-4}) as a function of temperature.

This regioregularity is the result of a difference of reactivity between the 2 and 5 positions of the 3,4-disubstituted thiophene monomer.[39] The absence of NMR signals due to end groups of the polymer and the easy formation of free-standing films indicate that the polymer has a high molecular weight. Size exclusion chromatography proved unreliable because the polymer was adsorbed on the column material even with the addition of tetrabutylammonium chloride to the eluent.

Thermochromism. PHEGMT (**3**) is thermochromic, both in the solid state and in solution. Figure 2 shows the UV−visible absorption spectra of the polymer film. At room-temperature PHEGMT has a λ_{max} at 550 nm related to the $\pi-\pi^*$ transition with at least two vibronic peaks. Upon heating, a new blue-shifted peak at 420 nm appears between 40 and 80 °C. The cooling scan is very similar to the heating scan, although there is some hysteresis. There is always an isosbestic point indicating that only two species are present. The DSC analysis reveals a glass transition around −64 °C which is probably due to the hexa(oxyethylene) side chains. See Figure 3. There is also a first-order endothermic transition at 59 °C with an enthalpy of 0.76 kcal/mol of repeat units. This transition is reversible and is observed at 49 °C on cooling. These results are very similar to those obtained with poly(3-oligo(oxyethylene)-4-methylthiophene).[22] For this polymer the glass transition is at −60 °C and the first-order transition is a little lower at 53 °C. The chromic and thermal transitions are obviously related to the same molecular process and assigned to an order−disorder transition in which the disordering of the side chains with increasing temperature drives a planar to nonplanar twisting of the thiophene backbone rings.[22,38,40] The discontinuous chromic transition observed in polysilanes is also accompanied by a thermal transition.[12,13]

Thermochromism can also be observed in solution. The polymer can be dissolved in methanol upon warming. The solution is then stable at room temperature when stored in the dark. The UV−visible spectra as a function of temperature in methanol are shown in Figure 4. At 10 °C the spectrum has maxima at 550 and at 590 nm and a shoulder at 520 nm as in the solid state. The latter two are due to vibronic fine structure. On warming between 20 and 50 °C, a strong blue shift with

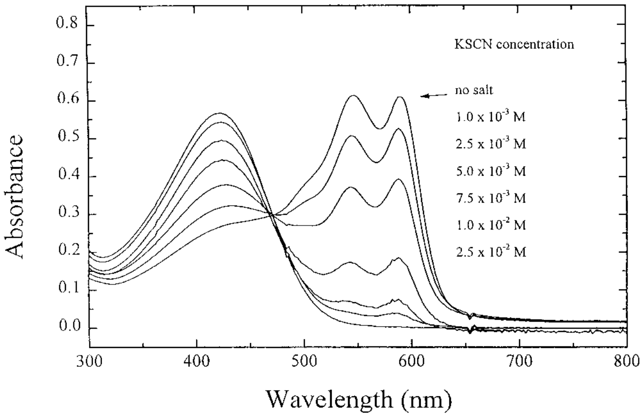


Figure 5. UV−vis absorptions spectra of PHEGMT (1×10^{-4} M) in methanol as a function of different KSCN concentrations at room temperature.

the appearance of a new maximum at 410 nm is observed. There is an isosbestic point.

On cooling, the spectral changes are reversed albeit with some hysteresis. We investigated the spectral change at 40 °C after temperature jumps from 20 and from 60 °C. About 75% of the change occurs over the first 20 s required for temperature stabilization. The remainder of the spectral change takes about 2−3 h. This behavior suggests that the spectral changes reflect two different molecular processes. The first one is most likely intramolecular. The second, slow one, may have an intermolecular origin, but it does not present any new spectral features. It is interesting to compare the thermochromism of PHEGMT with that of poly(3-oligo(oxyethylene)-4-methylthiophene.[22] The latter has a mixed spectrum even at low temperature (15 °C) and is completely converted to the 420 nm conformation at 45 °C. This suggests that the random-length oligo(oxyethylene) side chains destabilize the planar conformation slightly more than the uniform hexa(oxyethylene) side chains. Although there is no NMR evidence, the small difference between the two polymers could also be due to a slightly more regioregular composition of the PHEGMT sample.

Ionochromism. Methanol solutions of oxyethylene substituted polythiophenes also respond optically to the presence of alkali-metal ions. Figure 5 shows the spectral changes of PHEGMT on the addition of KSCN. The color change from red-violet to yellow is completed over a narrow concentration range at 0.05 M salt concentration. This color change is identical to the thermal change in solution and in the solid film. An isosbestic point can be clearly observed. It has been found that the planar/nonplanar polythiophene conformations are in equilibrium according to

$$[\text{planar}]_{548} + 2[\text{K}^+] \rightleftharpoons [\text{nonplanar } 2\text{K}^+]_{420}$$

where it is assumed that the planar conformation absorbs at 548 nm and the complexed nonplanar conformations absorb at 420 nm. Values of the equilibrium constant are summarized in Table 1. It should be remarked that the equilibrium constants are relative to the counterions solvated in methanol. It is also assumed that the salts are completely dissociated at the low concentrations in methanol. The ineffectiveness of Li salts is probably due in large part to the strong solvation of the Li cation by methanol.[41] The interaction with NH_4^+ ion is very moderate. The selectivity of K^+ and Rb^+ and, to a lesser extent, of Cs^+ over the smaller ions is clear. The size of the cations alone cannot account for the order of effectiveness in the planar to nonplanar transition. The effect of the counteranion is very small. The second order dependence of the spectral change on the cation concentration suggests either that two K^+ ions are required per thiophene unit or, more likely, that the complexation of neighboring side chains is required in order to twist the backbone into the nonplanar conformation. Results obtained under identical conditions on poly(3-oligo(oxyethylene)-4-methylthiophene)[42] lead to K values of 80 000 ± 20 000 $(\text{L/mol})^2$ for KCl and $(1.2 \pm 0.25) \times 10^5$ $(\text{L/mol})^2$ for KSCN, significantly higher than those for PHEGMT. This is in qualitative agreement with the higher tendency of the irregularly substituted polythiophene to disorder in methanol solution. Recent results on crown ether substituted polythiophene[23] show this polymer to have the opposite spectral behavior. The uncomplexed polymer has the nonplanar conformation and the K^+ complexed form becomes planar. In that case we find that the equilibrium is of the form

$$[\text{nonplanar}]_{420} + \text{K}^+ \rightleftharpoons [\text{planar K}^+]_{550}$$

with $K = 300$ L/mol. As a result of the first-order dependence on $[K^+]$, the complete conversion of the nonplanar to the planar conformation requires more than 2 decades range of the salt concentration.

Table 1. Solvation Constants, K $(\text{L/mol})^2$, of PHEGMT with Alkali-Metal Ions in Methanol at 22 °C

salt	K	salt	K	salt	K
LiCl					
NaCl	150 ± 50	NaSCN	300 ± 150	$NaCF_3SO_3$	200 ± 30
KCl	3300 ± 400	KSCN	6000 ± 1500		
RbCl	2600 ± 200				
CsCl	1000 ± 400				

Ionic Conductivity. The ionic conductivity has been studied on blends of PHEGMT with various concentrations of LiFSI and $LiCF_3SO_3$ in the range 60:1 to 3:1 oxyethylene (OE) per Li cation. In this ratio, we have taken six OE units per monomer and have assumed that the seventh oxygen atom adjacent to the thiophene ring does not participate in the interaction with lithium. First, the glass transition and order−disorder transitions of the blends have been investigated by DSC at 10 °C/min after erasing the thermal history by heating to 120 °C and cooling at 10 °C/min. The glass transition temperature increases with increasing salt concentration as shown in Figure 6. There is no evidence that a two-phase blend is produced. The increase is in good agreement with the 25 °C increase observed when poly(*p*-phenylene) (poly(PPP)) substituted with oligoethylene side chains is complexed with $LiCF_3SO_3$ and LiFSI at the OE:Li = 25 level.[28,29] Allcock et al. found that T_g increases slightly less in the case of polyphosphazenes with oligo(oxyethylene) when complexed with $LiClO_4$.[43] The presence of the salt also affects the first-order transition. In the case of LiTFSI the first-order transition temperature and the enthalpy decrease with increasing lithium salt and become undetectable when OE:Li ≤ 6. See Table 2. With $LiCF_3SO_3$ the first-order transition temperature stays constant, but the enthalpy of the process decreases but does not go to zero in the available salt concentration range. These trends are also clearly observed in poly(PPP) with oxyethylene side chains.[29]

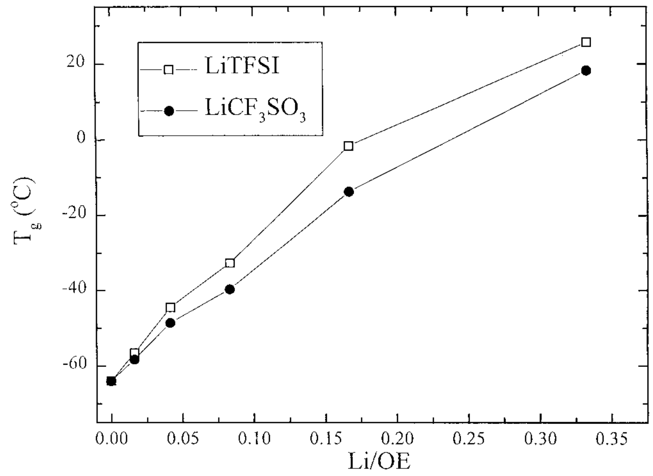


Figure 6. Glass transition temperature of PHEGMT as a function of different lithium salt concentrations for blends with LiTFSI and $LiCF_3SO_3$.

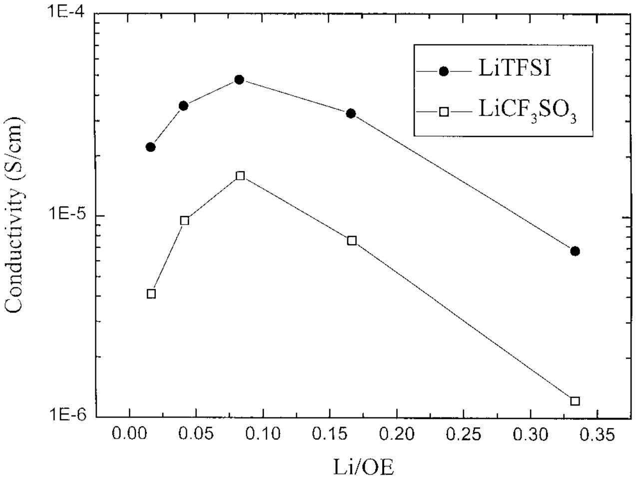


Figure 7. Variation of the ionic conductivity of PHEGMT as a function of salt concentration for blends with LiTFSI and $LiCF_3SO_3$.

Table 2. Transition Temperatures of PHEGMT with Lithium Salts

blend	T_g	T_t	ΔH (J/g)
pure polymer	−64	59	8.16
OE/LiTFSI			
60:1	−57	59	6.49
24:1	−44	58	3.91
12:1	−33	48	2.68
6:1	−1	-	-
3:1	26	-	-
OE/$LiCF_3SO_3$			
60:1	−58	59	6.27
24:1	−49	59	4.85
12:1	−40	62	5.40
6:1	−13	63	4.72
3:1	18	∼58	-[a]

[a] Not measurable due to interference of T_g.

At room temperature, the impedance of the blends is too high to be measured accurately. Attempts to obtain completely amorphous blends at room temperature by quenching blends to −190 °C were unsuccessful. Therefore, all impedance results have been obtained at 80 °C well above T_g in the amorphous disordered state. At this temperature all the blends are yellow films. The evolution of the ionic conductivity with the Li:OE ratio is shown in Figure 7. The maximum conductivity for both salts is obtained at Li:OE = 0.083, i.e., when OE:Li = 12:1 or one Li for every two thiophene units. The conductivity of blends with LiTFSI is between 3 and 5 times higher than the conductivity of the corresponding $LiCF_3SO_3$ blend. The maximum conductivity of LiTFSI (4.76×10^{-5} S/cm) is about 3 times higher than for $LiCF_3SO_3$. Since the glass transition temperature of the LiTFSI blend is slightly higher at OE:Li = 12:1, the higher LiTFSI conductivity is probably due to the higher mass fraction and to the higher ionic dissociation of this salt.[44] It is also interesting to compare the ionic conductivity of the 24:1 PHEGMT−lithium salt blends with data obtained at 80 °C on 25:1 blends of the same salts with oxyethylene-substituted poly(PPP).[28] The poly(PPP) with equimolar penta- and hexa(oxyethylene) side chains is most appropriate for comparison with PHEGMT. In agreement with our results, LiTFSI has a 3-fold higher conductivity than the blend with $LiCF_3SO_3$. Furthermore, the poly(PPP)−lithium salt blends have a 3-fold higher conductivity than the PHEGMT−lithium salt blends. The reasons for this last difference are not obvious because poly(PPP) has only one oxyethylene side chain on every second phenyl ring and a T_g at −39 °C, higher than the T_g of the PHEGMT lithium salt blends (−44 and −48 °C, respectively; see Figure 6). When OE:Li ≤ 12 the ionic conductivity decreases. Since the maximum conductivity is reached when the [Li^+] times the ion mobility are at a maximum, part of the decrease of the conductivity at high lithium loading may be due to decreased mobility due to an increased glass transition temperature. Other reasons, like the formation of triple ions cannot be excluded. A maximum conductivity in the salt concentration dependence has also been observed with oxyethylene substituted polyphosphazenes.[43]

Electronic Conductivity. The electronic conductivity of cast films of PHEGMT doped with iodine is 3×10^{-2} S/cm at room temperature. This result is reproducible and has been obtained with films of different thicknesses. The electronic conductivity seems to be comparable to that of other alkoxy ether substituted polythiophenes.[45,46] Alkoxy-substituted regioregular polythiophenes have conductivities between 1 and 100 S/cm.[36,47] Other ether substituted polythiophenes bearing a methylene function in the α position usually show higher conductivities ranging from 500 to 1000 S/cm.[37] In addition to the polymer chain structure the quality of the films plays an important role in the conductivity. The cast films of PHEGMT are porous. Furthermore, at room temperature the neutral polymer does not have a perfect planar conformation. (See Figure 2.) PHEGMT films doped with $FeCl_3$ have a very low conductivity of 10^{-6} S/cm. This may be related to complexation of Fe^{3+} with the ether side chains.

IV. Conclusions

Poly(3-methylhexa(oxyethylene)oxy-4-methylthiophene) has been successfully synthesized. A comparison of this polymer with P350MT, which has oxyethylene side chains with a distribution of lengths shows that the regular side chain length introduces a more planar conformation in the polythiophene backbone. This is reflected in the higher order−disorder transition temperature (59 vs 53 °C) in the solid polymer. In methanol solution, PHEGMT has a UV−vis spectrum consistent with 100% planar conformation at 10 °C, while P350MT is estimated to contain 15−20% nonplanar conformations at that temperature. On addition of K ions, spectral changes typical of the conversion to nonplanar conformations are observed between 1.0 and 1.5×10^{-2} M in PHEGMT but are already found sooner at 2.5×10^{-3} M for P350MT. In both cases the full transition to disordered polythiophenes occurs within 1 decade in $[K^+]$ and appears to be $[K^+]^2$ dependent. Therefore, a subtle change from a polymer with a distribution of side chains lengths to a polymer with exactly six oxyethylene side chains makes the polythiophenes conformation sensitive to K^+ in different concentration ranges.

PHEGMT is a mixed ionic and electronic conductor. The ionic conductivity of blends of PHEGMT with lithium salts has a maximum at a ratio OE:Li = 12 at 80 °C i.e., when two oxyethylene chains are available for every lithium. The ionic conductivities are of the same order of magnitude as for oxyethylene substituted poly(PPP) and polyphosphazenes. The role of the glass transition and order−disorder transition for the ionic conductance may require further investigation. The electronic conductivity obtained on iodine doped samples without further treatment is 3×10^{-2} S/cm, typical of oxyether-substituted polythiophenes.

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Supporting Information Available: Figures showing (a) the NMR ^{1}H (400 MHz) spectrum of 3-hexa(oxyethylene)oxy-4-methylthiophene in $CDCl_3$, (b) the NMR ^{13}C (100Mz) spectrum of 3-hexa(oxyethylene)oxy-4-methylthiophene in $CDCl_3$, (c) the NMR ^{1}H (400 MHz) spectrum of 3-methylhexa(oxyethylene)oxy-4-methylthiophene in $CDCl_3$, and (d) the NMR ^{13}C (100Mz) spectrum of 3-methylhexa(oxyethylene)oxy-4-methylthiophene in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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