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Responsive Gels with the Polymer Containing Alternating Naphthalene Diimide and Fluorinated Alkyl Chains: Gel Formation and Responsiveness as Well as Electrical Conductivity of Polymer Thin Films

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A new electroactive polymer **1** with alternating NDI (naphthalene diimide) moieties and fluorinated alkyl chains was prepared and characterized. Gels of polymer **1** were formed in several solvents. Interestingly, gels of polymer **1** exhibited responsiveness toward N_2H_4, F^- and CN^-. Absorption and ESR spectroscopic studies revealed that such responsiveness is owing to the reduction of NDI moieties into the respective $NDI^{\cdot -}$. In addition, thin films of polymer **1** were easily prepared with spin-coating technique and the electrical conductivity of thin films reached 52.4 S/m after exposure to N_2H_4 vapor.

Keywords responsive gels, naphthalene diimide, radical anion of naphthalene diimide, electroactive polymer, electrical conductivity

Introduction

Self-assembly of certain molecules, referred to as low-molecular weight gelators (LMWGs), through weak intermolecular interactions such as H-bonding, π-π stacking and van der Waals interactions, can lead to solvent gelation and formation of physical gels.[1,2] Because of the weak intermolecular interactions such physical gels are thermally reversible, namely, the gel-sol (solution) transition can be reversibly tuned by alternating heating and cooling. In comparison, chemical gels are usually formed through the covalent-linkage of polymer chains, and as a result the chemical gels cannot be redissolved. Note that polymer-based thermally reversible hydrogels are known by manipulating the interactions of polymer chains through supramolecular means.[3]

Physical gels have received increasing attentions recently as they may have potential applications in a number of areas including nanomaterials and delivery or modification agents for paints, inks, cleaning agents, drugs, *etc*.[1e-1g] Apart from studies on the gel formation and structures, extensive efforts have been made to investigate functional and stimuli responsive gels. Stimuli-responsive physical gels offer us promising opportunities for designing and constructing new functional materials, such as sensors, actuators, *etc*.[4] The molecular design rationale for these stimuli-responsive gels is to incorporate photoresponsive/electroactive/chemical reactive segments into the respective LMWGs derived from cholesterol, urea and other gelating moieties.[2,5-8]

For instance, organogels which respond to light irradiations have been achieved by incorporating photoresponsive moieties (*e.g.* azobenzene and stilbene)[1d,2b] into the corresponding LMWGs. By designing LMWGs with electroactive moieties, organogels showing responsiveness to redox reactions have been described.[5e,7]

In this paper we report physical gels based on polymer **1** (Scheme 1) which contains alternating naphthalene diimide (NDI) and fluorinated alkyl chains. The molecular design is based on the following considerations: (1) NDI is a planar conjugated moiety and thus tends to form stacks in the solid state via π-π interactions. In fact, NDI has been recently intensively investigated for developing organic semiconductors.[9] Moreover, NDI derived gelators and the resulting gels have been reported recently;[10] (2) the polymer with multiply NDI moieties would enhance the intermolecular π-π interactions. The intra-chain π-π interactions of NDI moieties may also exist as schematically depicted in Scheme 1; (3) NDI is an electron acceptor moiety which

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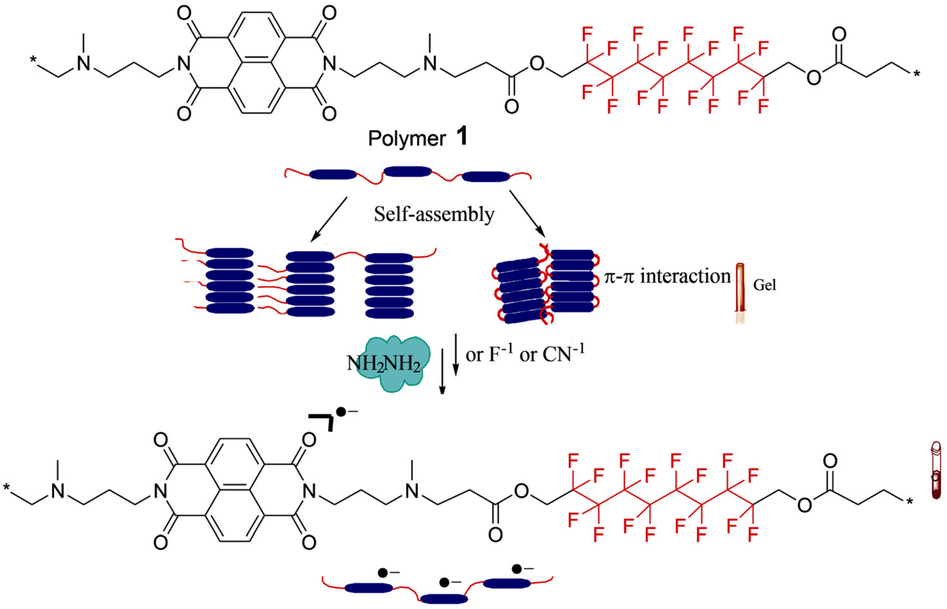
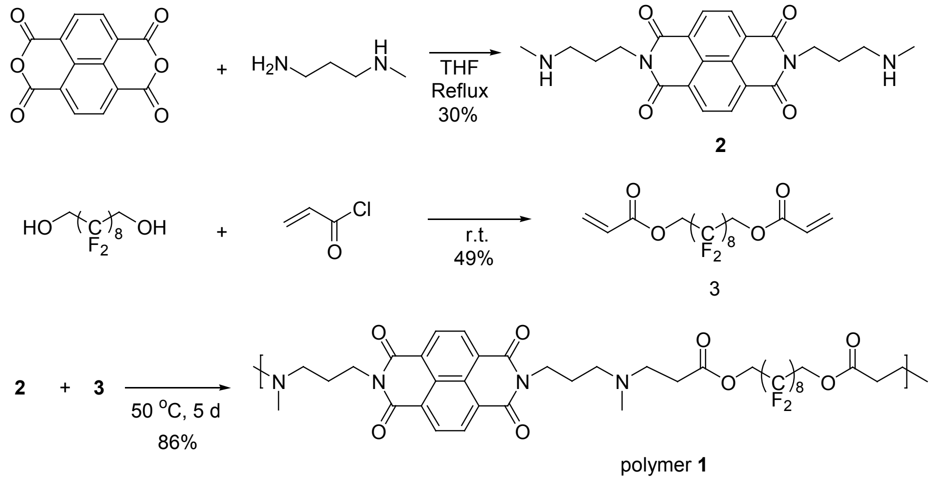
Scheme 1 Chemical structure of polymer **1** and schematic illustration intermolecular interactions and responsiveness toward N_2H_4, F^- and CN^-



Scheme 2 Synthetic approach for polymer **1**



can be easily transformed into $NDI^{\bullet-}$ by reduction.[11] The results reveal that polymer **1** can gel several solvents and the resulting gels show responsiveness toward either hydrazine or CN^- or F^-. Moreover, polymer can form thin films which exhibit semiconducting behavior upon exposure to hydrazine.

Experimental

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride, *N*-methylpropane-1,3-diamine, 1*H*,1*H*,10*H*,10*H*-perfluoro-1,10-decanediol, acryloyl chloride were purchased commercially from Alfa Aesar/Acros/Aldrich and used as received without further purification unless otherwise indicated. Compound **2** (Scheme 2) was synthesized according to the literature-reported procedures.[12]

Characterization techniques

The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-400 NMR spectrometer using tetramethylsilane as an internal standard. MS spectra were determined with BEFLEX III for TOF-MS. The gel permeation chromatography (GPC) measurements were performed on Waters 410 system against polystyrene standards with THF as an eluent. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Electronic absorption spectra were obtained on a Shimadzu UV-vis spectrometer model UV-1601PC. TGA (NETZSCH STA 409C), and DSC (Perkin-Elmer 7 series thermal analyzers) measurements were performed under nitrogen atmosphere at a heating rate of 10 ℃/min. ESR (Electron Paramagnetic Resonance) spectra were obtained by a Bruker-E500 spectrometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt wires of 2 mm diameter as working and counter electrodes, and an Ag/AgCl reference electrode on a computer-controlled CHI660C instruments at room temperature. For all scanning electron microscopy (SEM) experiments, a JOEL JSM 6700F field emission scanning electron microscope was used with a sample, which was sputtered with platinum; suspensions of xerogels were directly put onto the clean Si substrate for SEM measurements. X-ray diffraction data were collected with Rigaku D/max-γA 12 kW with Cu Kα radiation. Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) by cone and plate geometry in a peltier plate. The electrical conductivity of polymer **1** was measured with a two-electrode device; the polymer thin film of *ca.* 52 nm in thickness was at the bottom; the silver electrodes were 9 mm in length and 2 mm in width.

Gel formation

In a typical gelation experiment, a weighed amount of the polymer **1** and 1.0 mL of the solvent were placed in a test tube, which was sealed and then heated until the sample was dissolved. If the compound was unable to dissolve, it was noted as insoluble (I). After cooling down to 25 ℃ with water bath, if a stable and transparent gel was formed when inverting the vial, it was noted as gelation (G_t); if a stable and opaque gel was formed, it was noted as gelation (G_o); if solution was formed, it was noted as soluble (S). Repeated heating and cooling confirmed the thermo-reversibility of the gelation process. The critical gelator concentration (CGC) of the organogelator was determined by measuring the minimum amount of gelator required for the formation of a stable gel at room temperature (25 ℃). For the determination of gel-sol phase-transition temperature, DSC (differential scanning calorimetry) analysis of the gel was carried out. 6.0 mg of the gelled sample in THF (25 mg/mL) was carefully added to the aluminum crucible, sealed and heated from −10 to 50 ℃; the heating rate was 5.0 ℃/min. During the measurement, the oven was flushed with 20 mL/min nitrogen as protective gas and 50 mL/min nitrogen as purge gas.

Synthesis of compound 2

1,4,5,8-Naphthalene-tetracarboxylic dianhydride (3.0 g, 11.2 mmol) and *N*-methyl-1,3-propane diamine (30.0 mL, 0.24 mol) in THF (40.0 mL) were stirred and refluxed for 8.0 h. After being cooled down to room temperature, the reaction mixture was left overnight. The precipitate formed was filtered and taken up in $CHCl_3$. The undissolved material was filtered off, and the solvents were evaporated under reduced pressure. The desired material was obtained as a deep brown needle after recrystallization from ethanol (1.34 g, yield 30%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.76 (s, 4H), 4.29 (t, J=7.1 Hz, 4H), 2.70 (t, J=6.8 Hz, 4H), 2.45 (s, 6H) 1.92—2.00 (m, 4H) 1.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 162.9, 131.0, 126.7, 126.6, 49.3, 39.0, 36.4, 28.2; MS (MALDI-TOF) *m*/*z* $(M+1)^+$: calcd for $C_{22}H_{24}N_4O_4$ 409.2, found 409.1.

Synthesis of compound 3

1*H*,1*H*,10*H*,10*H*-Perfluoro-1,10-decanediol (2.0 g, 4.33 mmol) and triethylamine (7.0 mL, 50.4 mmol) were dissolved in 150 mL of THF. Acryloyl chloride (4.0 mL, 49.48 mmol) was added dropwise into the solution at 0 ℃. The solution was then stirred at room temperature overnight. The precipitate was filtered and the solvent was evaporated. The product was obtained by column chromatography on silica gel using petroleum ether∶CH_2Cl_2 （4∶1） as eluent to afford compound **3** as colorless oil with a 49% yield (1.2 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.52 (d, J=17.3 Hz, 2H), 6.18 (dd, J=17.3, 10.5 Hz, 2H), 5.98 (d, J=10.5 Hz, 2H), 4.66 (t, J=13.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 164.3, 133.2, 126.6, 60.0, 59.6, 59.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −120.1, −122.5, −124.0; HRMS (High resolution mass spectrometry) calcd for $C_{16}H_{10}F_{16}O_4$ 570.0324, found 570.0328.

Synthesis of polymer 1

Compound **2** (0.60 g, 1.47 mmol) and compound **3** (0.84 g, 1.47 mmol) were charged in a dry flask containing 15.0 mL of chloroform at room temperature, and then the reaction mixture was stirred at 50 ℃ for 5 d. The mixture was poured into hexane to precipitate the solid product. The product was collected by filtration. Then, the crude polymers were extracted by acetone in Soxhlet for 24 h to afford the desired polymer **1** (1.2 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.73 (s, 4H), 4.59 (t, J=13.6 Hz, 4H), 4.22 (t, J=6.7 Hz, 4H), 2.74—2.76 (m, 4H), 2.61—2.54 (br, 8H), 2.27 (s, 6H), 1.90—1.92 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 171.0, 162.8, 130.9, 126.6, 126.6, 59.8, 59.5, 59.1, 55.0, 52.6, 41.5, 39.2, 32.1, 25.6; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −120.1, −122.4, −123.9; IR (KBr) v: 3081, 2949, 2870, 2803, 1734, 1705, 1661, 1455, 1342, 1244, 769 cm^{-1}; GPC (THF, PS standard) M_n=7000, M_w=10000, PDI=1.47.

Results and Discussion

Synthesis and characterization

The synthesis of polymer **1** is shown in Scheme 2. Condensation of 1,4,5,8-naphthalene-tetracarboxylic dianhydride with *N*-methyl-1,3-propane diamine in THF at 60 ℃ led to compound **2** in 30% yield after separation. Reaction of 1*H*,1*H*,10*H*,10*H*-perfluoro-1,10-decanediol with acryloyl chloride yielded compound **3** in 49% yield after separation. Polymer **1** was obtained by the Michael reaction between compounds **2** and **3** (in 1∶1 molar ratio). After workup, polymer **1** was characterized with ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy. These NMR data are in good agreement with the repeating-moieties of polymer **1**. Polymer **1** exhibits two reversible reduction waves with $E^{1/2}_{\mathrm{red1}}=-0.58$ V and $E^{1/2}_{\mathrm{red2}}=-0.99$ V as expected for the NDI moieties (see Figure S1). The resulting polymer was found to be soluble in common organic solvents, such as toluene, dichloromethane, chloroform, and THF. Based on the GPC (gel permeation chromatography) analysis with THF as the eluent and polystyrene as the calibration standard, the weight-average molecular weight (M_w) of polymer **1** was determined to be *ca.* 10000 with a narrow molecular weight distribution (1.47). Polymer **1** melts above 172 ℃ (T_m) based on the DSC data, and starts to decompose at 230 ℃ (T_d) on the basis of TGA analysis (Figure S2).

Gel formation and responsiveness

The gelation ability of polymer **1** was examined in different solvents at 25 ℃, and the results were listed in Table 1. Among the solvents tested, polymer **1** can gel several organic solvents including THF, dioxane, toluene and chlorobenzene. The corresponding critical gelation concentrations (CGCs) at 25 ℃ were also measured (see Table 1). As demonstrated in Figure 1, a transparent yellow gel was formed by cooling a hot THF solution of polymer **1** (30 mg/mL) to 25 ℃. The gel-sol transition was also investigated with differential scanning calorimetry (DSC). As depicted in Figure S2, the gel-sol transition occurred at *ca*. 20 ℃ for the gel of polymer **1** (25 mg/mL in THF) and the transition took place gradually. Of note is the fact that gels of polymer **1** are thermally reversible and the sol-gel interconversion can be repeated by alternating heating and cooling as for typical physical gels. Figure 2 shows the SEM images of xerogel of polymer **1** formed in THF. Fibers and sheets of various sizes were interconnected to form porous structures. The intermolecular π-π interactions due to NDI moieties and those among fluorinated alkyl chains as well may be the driving-forces for the gelation process. Figure 3 shows the ^{1}H NMR spectra of polymer **1** at different concentrations in d_8-THF. When the concentration of polymer **1** increased, the corresponding signal at *δ* 8.66 owing to NDI moieties was gradually up-shifted, as shown in Figure 3. For instance, the signal at *δ* 8.66 was shifted to *δ* 8.62 by increasing the concentration of polymer **1** from 5.0 to 60 mg/mL. Such ^{1}H NMR spectral shifts manifest the π-π interactions among NDI moieties which can be operated in either intra-chain or inter-chain ways as illustrated in Scheme 1. For comparison, the polymer ($M_w=11000$) with alternating naphthalene diimide and alkyl chains was prepared (see page S4 of Supporting Information). But, gelation was not observed with this polymer under the same conditions as for polymer **1**.

Table 1 The gelation experimental results with polymer **1** in different solvents at 25 ℃[a]

Solvent	Gelation examination
THF	G_t (25 mg/mL)
Dioxane	G_t (50 mg/mL)
Chlorobenzene	G_o (20 mg/mL)
Toluene	G_o (50 mg/mL)
DMF	P
Methanol	I
Ethanol	I
Hexane	I
Cyclohexane	I
n-Heptane	I
Dichloromethane	S
Chloroform	S

[a] G_t: transparent gel; G_o: opaque gel; I: insoluble; P: precipitate; S: solution. The CGCs of the corresponding gels were measured at room temperature (25 ℃) and listed in the parentheses. The T_{gel} for the corresponding organogels under CGC condition were 25 ℃.

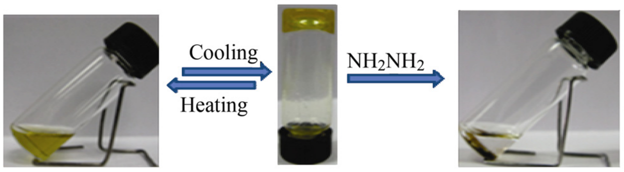


Figure 1 Illustration of gel formation with polymer **1** (30 mg/mL) in THF and disappearance of the gel phase after addition of hydrazine hydrate.

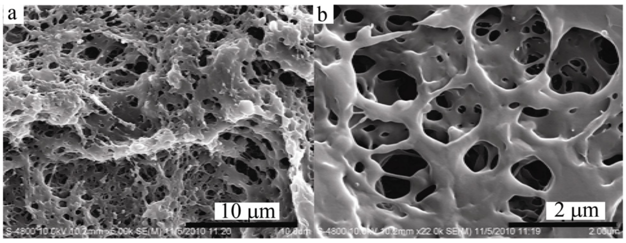


Figure 2 SEM image of the xerogel of polymer **1** from THF.

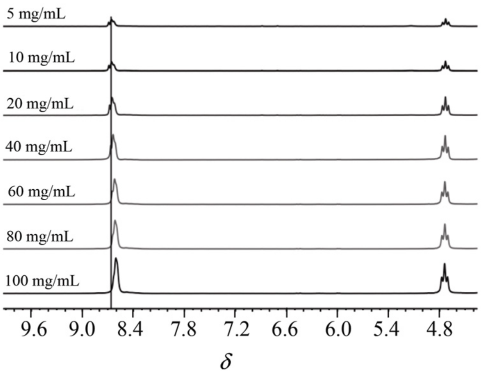


Figure 3 Partial ^{1}H NMR spectra for the polymer **1** of different concentrations (5.0—100 mg/mL) in d_8-THF.

Notably, gels of polymer **1** can be destroyed after the addition of hydrazine hydrate. For example, in the presence of hydrazine hydrate, the gel at the contact surface

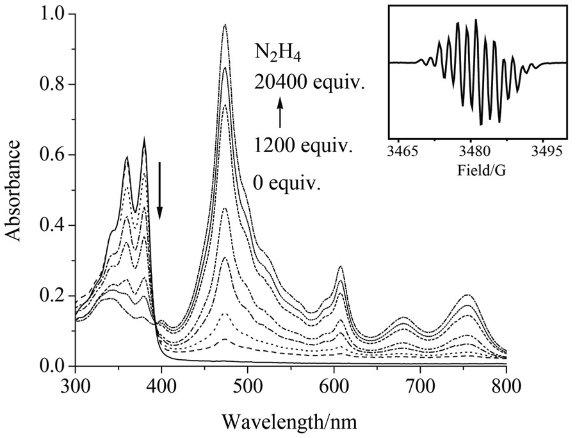


Figure 4 UV-vis absorption spectra of polymer **1** (3.0×10^{-5} mol/L in DMF) in the presence of different amounts of N_2H_4 (0—20400 equiv. vs. NDI moieties); the inset shows the ESR spectrum of polymer **1** (3×10^{-4} mol/L in DMF) in the presence of N_2H_4 (20400 equiv. vs. NDI moieties, $g=2.0058$).

collapsed immediately. But, it took about 1.0 h or more for the transformation of the whole gel due to the slow diffusion of hydrazine into the gels. As illustrated in Figure 1 the gel of polymer **1** in THF was transformed into fuscous precipitates suspended in the solution after the addition of hydrazine hydrate. Similar phenomena were also observed for gels of polymer **1** after the addition of either F^- or CN^-. Rheological studies also demonstrate such responsiveness for polymer **1**. For instance, the viscosity of polymer **1** (200 mg/mL) in DMF/dioxane (*V*/*V*, 1/4) at 50 ℃ was measured to be 47 Pa•s; but, the viscosity decreased to 4.0 Pa•s after the addition of hydrazine hydrate (0.5 equiv. vs. NDI moieties) within 10 s as shown in Figure S3. However, the viscosity could not be restored (reaching 17 Pa•s) after further addition of excess $NOPF_6$ (see Figure S3). This is indeed in agreement with the observation that gels of polymer **1** that have been treated by either hydrazine hydrate or F^- or CN^- cannot be recovered by further addition of excess oxidants such as $NOPF_6$.[13] The responsiveness of gels of polymer **1** is ascribed to the reduction of NDI moieties into the respective radical anions in the presence of either hydrazine hydrate or F^- or CN^-, and as a result the π-π interactions among NDI moieties are destabilized due to the electrostatic repulsions.

Figure 4 shows the absorption spectrum of polymer **1** and those after addition of hydrazine hydrate. Polymer **1** exhibits typical absorptions of NDI moieties at 344 nm, 360 and 380 nm. New absorptions around 474, 608, 678, 754 nm emerged gradually after introducing hydrazine hydrate to the solution (Figure 4). The appearance of these new absorptions is consistent with the formation of $NDI^{\cdot-}$ according to previous reports.[11] The solution of polymer **1** was ESR inactive, but, nine ESR signals were observed after addition of hydrazine hydrate as depicted in the inset of Figure 4. These spectral data reveal the reduction of NDI moieties into the respective $NDI^{\cdot-}$ in the presence of N_2H_4. Accordingly, the transformation of the gel of polymer **1** in the presence of hydrazine hydrate can be attributed to the generation of $NDI^{\cdot-}$ as discussed above. Similarly, new absorptions around 474, 608, 678, 754 nm were observed for polymer **1** after addition of either F^- or CN^- (see Figures S4 and S5). ESR signals were also detected (see the insets of Figures S4 and S5). These spectral data also indicate the formation of $NDI^{\cdot-}$ for the solution of polymer **1** in the presence of either F^- or CN^-. Again, this is understandable for the responsiveness of gels of polymer **1** toward either F^- or CN^-.

Thin-film formation and electrical conductivity

Thin films of polymer **1** can be prepared with spin-coating technique. Figure S6 shows the XRD pattern and AFM image for the thin film of polymer **1** on the modified SiO_2 substrate. The thin film was found to be smooth based on AFM image, but no XRD diffraction peaks were detected, indicating that polymer chains of **1** were not orderly arranged. However, diffraction peaks at 21.2° and 23.5° appeared after the thin film was annealed at 180 ℃ under vacuum. The diffraction peaks correspond to d-spacing of 3.8 and 4.2 Å, which may indicate the π-π interactions of NDI moieties. Simultaneously, morphological changes occurred for thin films of polymer **1** after annealing; non-continuous domains were formed after annealing (see Figure S6).

The conductivity of the as-prepared thin film of polymer **1** was measured to be about 1.7—1.8 S/m in air, and it kept almost unaltered in the temperature range of −30—50 ℃ (Figure 5). Interestingly, the conductivity increased after the thin-film was exposed to the saturated hydrazine vapor; moreover the conductivity further increased by increasing the temperature as shown in Figure 5. After treatment with saturated hydrazine vapor, the conductivity of the thin film of polymer **1** reached 19.7 S/m at 25 ℃ and 52.4 S/m at 50 ℃. Such conductivity enhancement can be attributed to reduction of NDI moieties into the respective $NDI^{\cdot-}$ and as a result

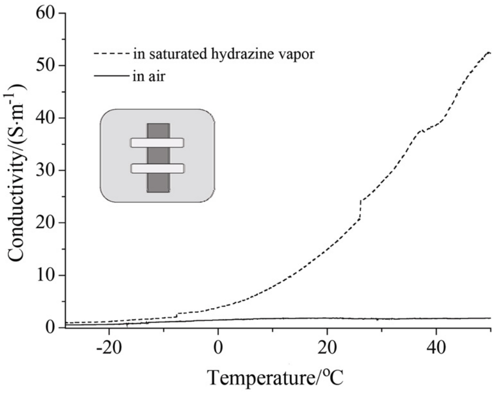


Figure 5 Variation of the conductivity vs. temperature for the thin film of polymer **1** (50 nm in thickness) in air or in saturated hydrazine vapor; the inset shows the schematic illustration of the two-electrode device fabricated on a SiO_2 substrate.

the carrier concentration increases.[14] Therefore, the thin film of polymer **1** is potentially useful for sensing N_2H_4 and other reducing agents.

Conclusions

In summary, a new electroactive polymer **1** with alternating NDI moieties and fluorinated alkyl chains was prepared and characterized. Polymer **1** can gel several organic solvents and the resulting gels show responsiveness toward N_2H_4, F^- or CN^-. Absorption and ESR studies reveal that such responsiveness is owing to reduction of NDI moieties in polymer **1** into the respective NDI$^{\bullet-}$ in the presence of either N_2H_4 or F^- or CN^-, and as a result the π-π interactions among NDI moieties may be altered. Thin films of polymer **1** can be prepared with the spin-coating technique. Moreover, the conductivity of the thin films of polymer **1** increases upon exposure to N_2H_4 vapor reaching 19.7 S/m at 25 ℃. The results of current research demonstrate the potential application of such electroactive polymer in developing new responsive materials.

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