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Poly(dithiafulvene)s containing alkoxy groups and mesogenic moiety in the side chain: synthesis, properties and their charge-transfer complex

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Summary

Poly(dithiafulvene)s having alkoxy group and mesogenic moiety in the side chain were prepared by cycloaddition polymerization. The effects of the side chains on the structural and optical properties of poly(dithiafulvene)s in solution were investigated. Furthermore, the film state properties of the polymers and their charge transfer complex with electron acceptor were studied before and after annealing.

Introduction

π-Conjugated polymers have superial physical properties such as photonic and electronic properties, derived from the delocalization of π-electrons throughout the polymer chain. These properties strongly depend on the second structure of the polymers, especially on the planarity of the polymer main chain [1]. Indeed, theoretical studies have shown that coplanality along the chain π-orbitals leads to better electrical properties [2,3]. Many reports on the control of planar structure of the π-conjugated polymers have been published. Regioregular poly(3-alkylthiophene)s are actively studied [4-7] because of the unusual electronic and optical properties of the polymers caused by their planar and stacked structure, which was accomplished by the alignment of the alkyl side chains. Planarization of polymer backbones by means of weak interactions (e.g., intrachain hydrogen bonds) resulted in fine-tuning of optical and conducting properties of the polymers [8-10]. The introduction of mesogenic moieties into the side chain of π-conjugated polymers to make use of the alignment of the mesogenes succeeded in developing new concept for π-conjugated polymers [11-13].

Recently, we have succeeded in preparing novel π-conjugated polymers containing dithiafulvene unit in the main chain [14-16]. The polymerization procedure is based on cycloaddition polymerization of thioketenes and its alkynethiol tautomers derived from diyne monomers. The poly(dithiafulvene)s are new class of π-conjugated polymers, showing strong electron-donating property measured by cyclic voltammetry. Further, the poly(dithiafulvene)s formed charge transfer (CT) complexes with electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a DMSO solution [17]. The conductivities of the polymers were improved after forming the CT complexes compare to the neutral polymers. In our previous paper, we mentioned briefly about side-chain effect on optical properties of the poly(dithiafulvene)s in solution by UV-vis analysis [16].

Here we prepared a series of π-conjugated poly(dithiafulvene)s having several alkoxy groups and mesogenic groups in the side chains by cycloaddition polymerization procedure. We investigated the effect of the side chains on the structural and physical properties of the polymers in solution. In addition, we studied the solid-state properties before and after annealing. This is the first report on the synthesis of mesogene-introduced poly(dithiafulvene)s and their properties.

Experimental

Materials

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under nitrogen atmosphere. 1,4-Diethynyl-2,5-bis(hexyloxy)benzene (**1b**) [18], 1,4-diethynyl-2,5-bis(dodecyloxy)benzene (**1c**) [18], 4'-(6-bromohexyloxy)-4-cyanobiphenyl [19] and 2,5-dibromo-4-dodecyloxyphenol [20] were synthesized according to the literatures. **1e** was prepared analogously to compound **1d** (described below).

Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography (GPC) of **2a** was carried out on a TOSOH 8020 (TSK-gel α-3000 column) with DMF as an eluent after calibration with polystyrene standards. GPC of **2b**-**2d** was performed on a Shodex K-803 with $CHCl_3$ as an eluent after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 °C min^{-1} in air. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, SEIKO Instruments, Inc., with heating rate of 10 °C min^{-1} under nitrogen.

Synthesis

4'-[6-(2,5-Dibromo-4-dodecyloxyphenoxy)-hexyloxy]-biphenyl-4-carbonitrile

The solution of 2,5-dibromo-4-dodecyloxyphenol (1.506 g, 3.16 mmol), 4'-(6-bromohexyl)-4-cyanobiphenyl (1.134 g, 3.16 mmol), potassium carbonate (0.508 g, 3.68 mmol) and sodium iodide (15 mg, ..mmol) in acetone (80 ml) was refluxed for 24 h. The solvent was removed in vacuo and the resulting solid was dissolved in water, and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$and evaporated to give a white powder (2.10 g, 2.94 mmol, yield 93%): ^{1}H NMR ($CDCl_3$, ppm) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz , 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 4.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.95 (m, 4H), 1.7-1.9 (m, 6H), 1.47 (m, 2H), 1.2-1.4 (m, 22H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, ppm) δ 159.25, 149.75, 149.56, 144.86, 132.17, 130.89, 127.93, 126.68, 118.74, 118.09, 114.69, 110.76, 109.65, 69.94, 69.73, 67.59, 31.60, 29.34, 29.32, 29.26, 29.23, 29.03, 29.98, 28.79, 28.71, 25.61, 25.42, 22.39, 13.83; Anal. Calcd: C, 62.28; H, 6.64; N, 1.96; O, 6.73; Br, 22.39. Found: C, 62.09; H, 6.69; N, 1.89; O, 6.57; Br, 22.69.

4’-[6-(4-Hexyloxy-2,5-bis-trimethylsilanylethynylphenoxy)-hexyloxy]-biphenyl-4-carbonitrile

4’-[6-(2,5-Dibromo-4-dodecyloxyphenoxy)hexyloxy]-biphenyl-4-carbonitrile (1.335 g, 1.87 mmol), trimethylsilylacetylene (5.0 ml), $PdCl_2(PPh_3)_2$ (273 mg, 0.39 mmol), PPh_3 (204 mg, 0.78 mmol), and CuI (75 mg, 0.39 mmol) were dissolved in THF (40 ml) and NEt_3 (10 ml). The mixture was stirred at 75 ^oC for 20 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filterate was evaporated in vacuo. The residue was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give a yellow powder (1.212 g, 1.62 mmol, yield 87%): ^{1}H NMR ($CDCl_3$, ppm) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 2.7 Hz, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 3.95 (m, 4H), 1.7-1.9 (m, 6H), 1.47 (m, 2H), 1.2-1.4 (m, 22H), 0.88 (t, *J* = 6.0 Hz, 3H), 0.23 (s, 18H); ^{13}C NMR ($CDCl_3$, ppm) δ 155.58, 154.08, 153.87, 145.29, 132.55, 131.29, 128.31, 127.85, 127.08, 119.17, 117.18, 115.08, 113.95, 110.96, 110.03, 82.25, 79.32, 69.42, 69.19, 68.02, 31.91, 30.59, 29.67, 29.62, 29.43, 29.35, 29.33, 29.24, 29.20, 26.02, 25.82, 25.79, 22.71, 22.68, 14.11; Anal. Calcd: C, 75.45; H, 8.76; N, 1.87. Found: C, 75.45; H, 8.76; N, 1.59.

4’-[6-(2,5-Diethynyl-4-dodecyloxyphenoxy)-hexyloxy]-biphenyl-4-carbonitrile (1d)

To a stirred solution of 4’-[6-(4-hexyloxy-2,5-bis-trimethylsilanylethynylphenoxy)-hexyloxy]-biphenyl-4-carbonitrile (250 mg, 0.33 mmol) in THF (20 ml), tetrabutylammonium fluoride (1.0 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. After removal of the solvent, the crude product was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give a yellow powder (108 mg, 0.18 mmol, yield 55%): ^{1}H NMR ($CDCl_3$, ppm) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.6 Hz 2H), 6.98 (d, *J* = 8.8 Hz 2H), 6.95 (d, *J* = 2.7 Hz 2H), 3.9-4.1 (m, 6H), 3.33 (s, 1H), 3.30 (s, 1H), 1.7-1.9 (m, 6H), 1.46 (m, 2H), 1.2-1.4 (m, 22H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, ppm) δ 159.65, 153.95, 153.76, 145.17, 132.49, 131.21, 128.25, 128.17, 127.00, 119.06, 117.62, 115.01, 114.96, 113.16, 109.97, 82.46, 82.43, 79.73, 79.70, 69.59, 69.37, 67.92, 31.92, 29.65, 29.58, 29.36, 29.19, 29.11, 29.03, 25.89, 25.76, 25.72, 22.70, 14.15; Anal. Calcd: C, 81.55; H, 8.18; N, 2.32; O, 7.95. Found: C, 81.29; H, 8.21; N, 2.32; O, 7.66.

Polymerization

A typical experimental procedure is as follows. To a solution of 1,4-diethynylbenzene (126 mg, 1.0 mmol) in a solvent (Et_2O or THF, 1.0 ml), 1.6 M solution of *n*-butyllithium in *n*-hexane (1.25 ml, 2.0 mmol) was added at 0 ^oC. After stirring for 30 min, the powder of sulfur (64 mg, 2.0 mmol) was added to the solution. The reaction mixture was stirred for 2 h, then cooled at -55 ^oC and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.3 ml) and stirred for 30 min. The mixture was then poured into a large quantity of Et_2O or THF. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, an orange-colored polymer was obtained.

2a [14] Yield: 75%. ^{1}H NMR (DMSO-d_6, ppm) δ 1.2-1.6 (CH_2 of piperidine unit), 3.6 (N-CH_2 of piperidine unit), 4.2 (N-CH_2 of piperidine unit), 4.3 (-$CH_2C(=S)N<$), 6.7 (benzylidene proton), 7.1-7.7 (aromatic and 1,3-dithiole ring protons).

2b Yield: 61%. ^{1}H NMR ($CDCl_3$, ppm) δ 0.9 (-OC_5H_{10}-$\mathit{CH_3}$), 1.1-1.5 (-OC_2H_4-$\mathit{C_3H_6}$-CH_3 and CH_2 of piperidine unit), 1.8 (-OCH_2-$\mathit{CH_2}$-C_4H_9), 3.6 (N-CH_2 of piperidine unit), 3.9-4.1 (-O$\mathit{CH_2}$-C_5H_{11} and N-CH_2 of piperidine unit), 4.3 (-$CH_2C(=S)N<$), 6.8 (benzylidene and aromatic protons), 6.9-7.1 (aromatic and 1,3-dithiole ring protons).

2c [16] Yield: 58%. ^{1}H NMR ($CDCl_3$, ppm) δ 0.9 (-$OC_{11}H_{22}$-$\mathit{CH_3}$), 1.1-1.6 (-OC_2H_4-$\mathit{C_9H_{18}}$-CH_3 and CH_2 of piperidine unit), 1.8 (-OCH_2-$\mathit{CH_2}$-$C_{10}H_{21}$), 3.6 (N-CH_2 of piperidine unit), 3.9-4.1 (-O$\mathit{CH_2}$-$C_{11}H_{23}$ and N-CH_2 of piperidine unit), 4.3 (-$CH_2C(=S)N<$), 6.8 (benzylidene and aromatic protons), 6.9-7.2 (aromatic and 1,3-dithiole ring protons).

2d Yield: 52%. ^{1}H NMR ($CDCl_3$, ppm) δ 0.9 (-$OC_{11}H_{22}$-$\mathit{CH_3}$), 1.0-1.7 (-OC_2H_4-$\mathit{C_9H_{18}}$-CH_3 and -OC_2H_4-$\mathit{C_2H_4}$-C_2H_4O- and CH_2 of piperidine unit), 1.7-1.9 (-OCH_2-$\mathit{CH_2}$-$C_{10}H_{21}$ and -OCH_2-$\mathit{CH_2}$-C_2H_4-$\mathit{CH_2}$-CH_2O-), 3.6 (N-CH_2 of piperidine unit), 3.8-4.2 (-O$\mathit{CH_2}$-$C_{11}H_{23}$ and -O$\mathit{CH_2}$-C_4H_8-$\mathit{CH_2}$O- and N-CH_2 of piperidine unit), 4.3 (-$CH_2C(=S)N<$), 6.8-7.1 (benzylidene and aromatic protons of main chain and aromatic protons of biphenyl moiety), 7.3-7.7 (aromatic protons of biphenyl moiety and 1,3-dithiole ring protons).

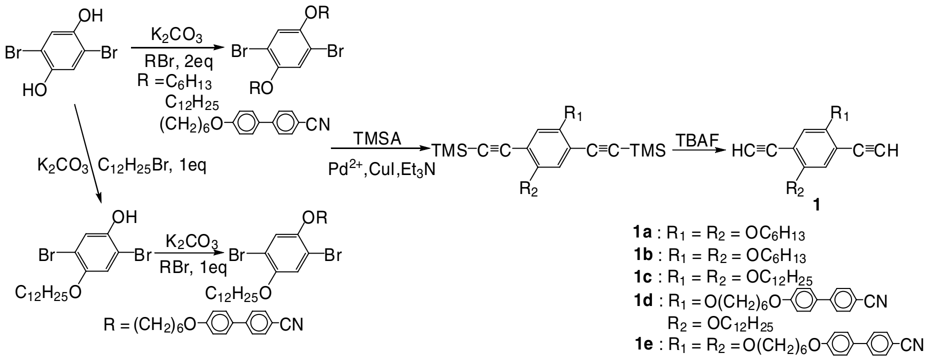
2e Yield: 76%. Obtained as an insoluble powder in any organic solvents.

Results and Discussion

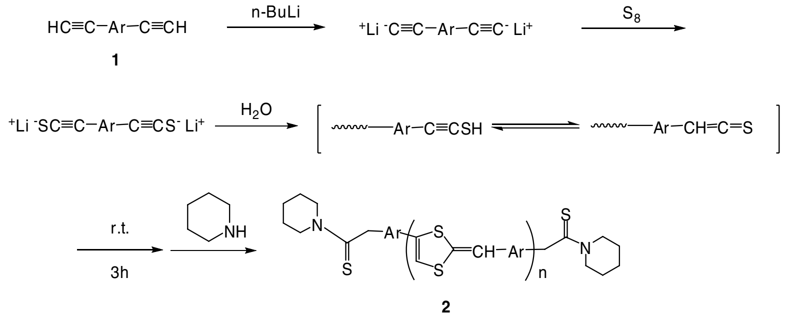
Synthesis of Monomers and Polymerization

Cycloaddition polymerization procedure for the poly(dithiafulvene) is generally carried out using diyne compounds as monomers. We prepared several diethynylbenzene derivatives having dialkoxy chains or mesogenic moieties (Scheme 1). **1e** with two mesogenic moieties had low solubility in THF, used as a solvent in polymerization. On the other hand, **1a**-**1d** were easily soluble in Et_2O or THF. The polymerization was performed by general procedure (Scheme 2). After the Et_2O or THF solution of the diyne monomer was treated with *n*-butyllithium, powder of sulfur was added to the reaction mixture. Protonation of the resulting alkynyl thiolate was performed by adding an equimolar amount of water to the mixture at –78 $^\circ$C. Alkyne thiol and its tautomer, thioketene formed five-membered ring structures by cycloaddition. The reaction mixture was stirred for further 3 h at room temperature. Finally, piperidine was added to the mixture to quench the terminal thioketenes. After the reprecipitation into Et_2O or THF, an orange powder was obtained.

The results of polymerization are summarized in Table 1. The polymer **2e** was insoluble in any organic solvent because of high crystallinity caused by the two mesogenic chains, composed of cyanobiphenyl (CB) group. It was not possible to determine its structure by NMR analysis. On the other hand, **2a**-**2d** were soluble in common organic solvents such as $CHCl_3$ and DMSO. From gel permeation chromatographic analysis ($CHCl_3$ or DMF, calibrated with polystyrene standards), the number-average molecular weights of the polymers were estimated as 4000 to 6170. The degree of polymerization was estimated by NMR data by comparing the integration ratio of the terminal benzyl protons and the protons on the thio-cyclic repeating unit. This estimation from the NMR data should be more reliable than that from the GPC data because the poly(dithiafulvene) has a rigid structure compared to polystyrene standards. The values of DP indicate that these polymers have almost the same number of the repeating units in the main chain.



Scheme 1. Preparation of diethynyl compounds **1a**-**1e**



Scheme 2. Cycloaddition polymerization

Table 1. Results of polymerization

Polymer	Yield (%)	M_n	DP[a]	Solubility	λ_{max} (nm)
2a	75	5440[b]	15	DMSO	400
2b	61	4590[c]	15	$CHCl_3$, DMSO	421
2c	58	4000[c]	12	$CHCl_3$, DMSO	446
2d	52	6170[c]	18	THF, $CHCl_3$	421
2e	76			Insoluble	

[a] Degree of polymerization determined by NMR

[b] GPC ($CHCl_3$, polystyrene standards)

[c] GPC (DMF, polystyrene standards)

Optical Properties of the Polymers in Solution

The effect of the side chain on optical properties of the polymers in solution was studied by UV-vis absorption analysis (Figure 1). In the spectrum of **2a**, a π-π^* transition absorption is observed at 400 nm. This peak is located at longer wavelength than that of the model compound, which is composed of one dithiafulvene unit. This fact indicates efficient π-electron delocalizations in the polymer systems [14]. When a dihexyloxy side chain was introduced into poly(dithiafulvene) (**2b**), the absorption maximum showed a bathochromic shift to 431 nm. In the case of **2c** with longer alkoxy chains than **2b**, the absorption maximum was shifted to longer wavelength (446 nm) than that of **2b**. The introduction of the alkyl side chains into the poly(dithiafulvene)s prompted them to stack the π-conjugated main chain in $CHCl_3$. Actually, the UV-vis absorption maximum of **2c** in $CHCl_3$ was a superposition of that in film state. When a more bulky CB unit was introduced (**2d**), a hypsochromic shift occurred comparing to the absorption of **2c**. The bulky CB unit seemed to interrupt the stacking of the π-conjugated polymer main chain. From these results, the optical properties were tuned by modifying the substituent of the polymer side chains. That is, the arrangement of the size and length of the side chain leads to control the conformation of the polymer chain in solution.

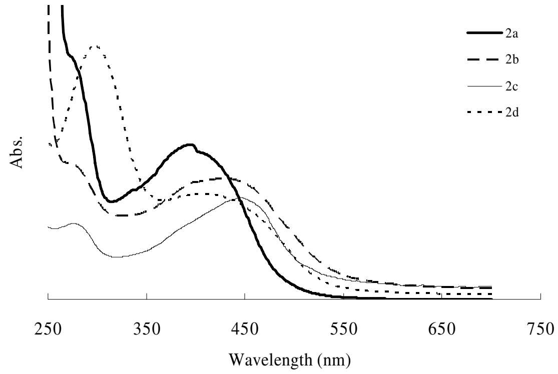


Figure 1. UV-vis spectra of the side-chain substituted poly(dithiafulvene)s in DMSO (**2a**) and in $CHCl_3$ (**2b**-**2d**).

Film Properties

Polymer **2d** with the mesogenic moieties has a potential to change its morphology by stimuli such as heat or magnetic field. Thermal properties of **2d** were studied by TGA and DSC measurements to confirm its thermal stability and glass transition temperature (T_g) (Figure 2).

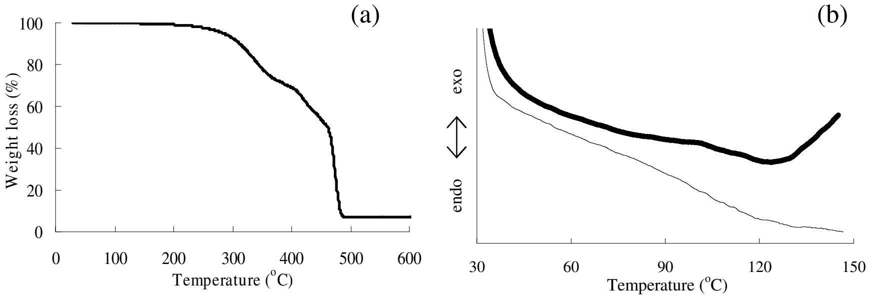


Figure 2. (a) TGA analysis of **2d** in air and (b) DSC thermograms of **2d** (bold) and **2c** (plane).

From the TGA chart in Figure 2a, it is obvious that **2d** has high thermal stability and shows no weight loss below 200 °C. The temperature of 10 % decomposition of the polymer was confirmed at 300 °C. From the DSC thermograms of **2d** and **2c** shown in Figure 2b, T_g of polymer **2d** was observed at 105 °C and no T_g appeared in the thermogram of **2c**.

Polymers **2c** and **2d** showed a good film forming property. Cast films of **2c** and **2d** were easily prepared from the $CHCl_3$ solutions. These samples were annealed at 100 °C for 15 min., then cooled to room temperature. Second annealing was carried out at 150 °C, and the samples were cooled. UV-vis spectra of these samples on each step were measured (Figure 3). In the case of **2c**, there are no significant changes in the shape of the spectra and in the wavelength of the absorption maximum. This fact indicates that the poly(dithiafulvene)s are thermodynamically stable under 150 °C annealing. And it also suggests that no stuructural change in the film of **2c** occurred during annealing. On the other hand, in the spectra of **2d**, decreasing of the absorption maximum was observed when it was annealed at 150 °C (above T_g). From this result, a conformational change occurred after annealing on the film of **2d**. As a consequence, π-plane of the polymer was disturbed and effective conjugation length was shortened. The conjugation length might be controlled by modifying the density of the mesogenic unit in the polymer.

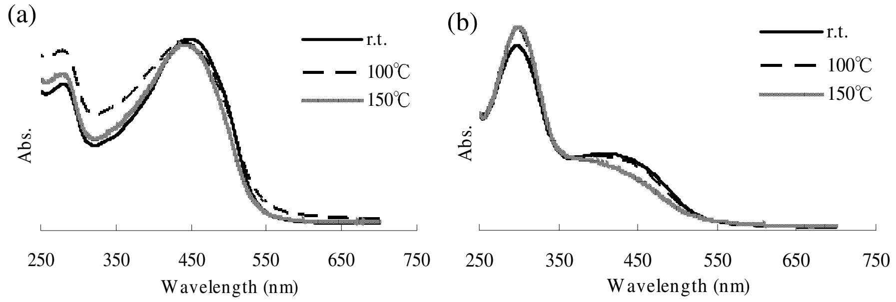


Figure 3. UV-vis spectra of (a) **2c** and (b) **2d** in solid state after annealed at each temperatures.

CT Complex with TCNQ

To the solution of polymer **2c** and **2d** in $CHCl_3$, an excess TCNQ was added and the reaction mixture was stirred for 5 min at room temperature. The color of the solutions changed from orange to green, suggesting that polymers formed CT complex with TCNQ in $CHCl_3$. The unreacted TCNQ was removed by filteration to give green precipitations following evaporation. The conductivities of the polymers and their CT complexes were measured by two probe technique on cast films from $CHCl_3$ solutions. The results are summarized in Table 2. When the polymers formed the CT complexes, conductivities of **2c** and **2d** were slightly increased. The long alkyl chains in the polymers prevented intermolecular electron hopping because of their nature as insulator, resulted in showing slight increase of the conductivity even after forming CT complexes. The films of the CT complexes were annealed at 190 °C for 15 min. Both of them had no gravimetric loss during annealing. Although **2c** showed no significant change in the value of the conductivity after annealing, **2d** exhibited a quite different behavior, that is, the conductivity of the CT complex was highly increased (50 times) after annealed. By doping with iodine, the conductivity of **2d** was also improved before (1×10^{-6} S/cm) and after (3×10^{-4} S/cm) annealing at 190 °C. The conformational change of **2d** by the thermal treatment, which was observed in Figure 3b, also occurred in the CT complex. This probably improved the mobility of charge carriers by hopping the disordered alkyl insulators and resulted in the increasing of the conductivity.

Table 2. Conductivity data of polymer CT complex

Polymer	Neutral (S/cm)	CT complex (S/cm)	Annealed CT complex[a] (S/cm)
2c	4 x 10^{-7}	3 x 10^{-6}	1 x 10^{-6}
2d	3 x 10^{-7}	2 x 10^{-6}	1 x 10^{-4}

[a] annealed at 190 °C for 15 min

Conclusions

We succeeded in introducing various alkoxy and mesogenic side chains into poly(dithiafulvene)s via cycloaddition polymerization. From UV-vis analysis in solution, the optical properties of the polymers were tuned by modifying the substituent of the polymer side chains. That is, the arrangement of the size and length of the side chain leads to control the conformation of the polymer chain in solution. The mesogen-introduced poly(dithiafulvene) (**2d**) exhibited a structural change after annealing. Conductivity of the CT complex of **2d** with TCNQ was increased after annealing at 190 °C, while that of the control polymer (**2c**) with TCNQ did not show significant change by thermal treatment.

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