Synthesis of π-Conjugated Poly(dithiafulvene) by Cycloaddition Polymerization of Aldothioketene with Its Alkynethiol Tautomer

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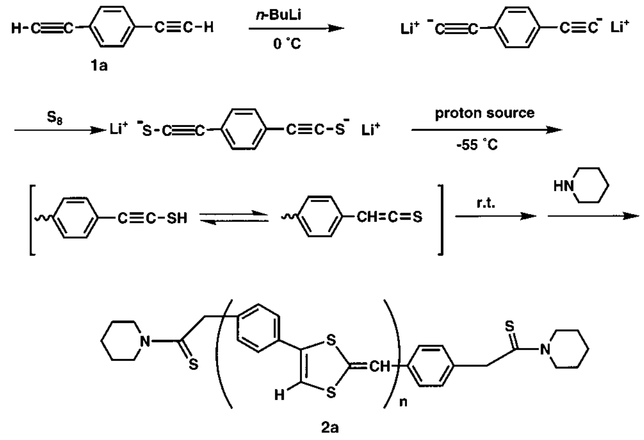
Thioketenes are highly reactive and short-lived species similar to their ketene analogues.[1] The chemistry of ketenes has been developed since the beginning of this century, and ketenes and bis(ketene)s can be used as the monomer in several different types of polymerizations.[2] Although understanding of the reactions of thioketenes has been highly improved within the last several decades, the direct use of thioketenes in polymer synthesis has been very limited to date. We have begun a project that is focusing on the polymerization of bis(thioketene)s to produce novel sulfur-containing polymers.

Among numerous preparation methods, thioketenes can be derived from alkynethiolates.[3] Alkynethiolates can be regarded as aldothioketene anions and are accessible via addition of sulfur to acetylide anions. Protonation of alkynethiolates yields the thiols that tautomerize to aldothioketenes. The usual result of the reaction between aldothioketenes and their alkynethiol tautomer is the formation of 1,3-dithiafulvenes.[4] If a π-conjugated diyne was used for polymerization, a new π-conjugated polymer having electron-donating 1,3-dithiafulvene units in the main chain might be produced.

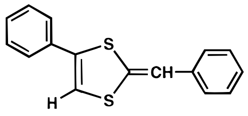
Derivatives of 1,3-dithiafulvene, including tetrathiafulvalenes (TTF), act as electron donors and form stable charge-transfer complexes and radical ion salts with a wide range of organic and inorganic acceptor species.[5] These molecules are components of organic metals. Since the first polymer containing a TTF moiety was prepared via a polycoupling process,[6] several attempts to incorporate such donor molecules into a polymeric framework have been carried out.[7] Polymers containing 1,3-dithiafulvene units were prepared by polymerization of vinyl derivatives[8a] or polycondensation of substituted 1,3-dithiafulvenes with diacid chlorides, *p*-phenylene diisocyanate, and terephthalaldehyde.[8b] Examples of polymers containing dithiafulvene derivatives in the π-conjugated main chain have been limited, however. We now report the synthesis of a new π-conjugated polymer having electron-donating 1,3-dithiafulvene units in the main chain by the cycloaddition polymerization of the aldothioketene derived from 1,4-diethynylbenzene with its alkynethiol tautomer.

Scheme 1 provides an overview for the polymerization. To a solution of 1,4-diethynylbenzene (**1a**) in Et_2O, a 1.6 M solution of *n*-butyllithium was added at 0 °C. After stirring for 0.5 h, the powder of sulfur was added to the solution. The reaction mixture was stirred for 2 h, and an equimolar amount of water was carefully added to the mixture at −55 °C. The temperature of the mixture was allowed to rise to room temperature and the reaction mixture was stirred for 3 h to effect polymerization. Finally, piperidine was added to the mixture to quench terminal thioketenes and the reaction mixture was stirred for 30 min. The mixture was then poured into a large quantity of Et_2O. The precipitate was washed with Et_2O several times to remove unreacted piperidine, followed by washing with water to remove inorganic salts. After drying under reduced pressure, an orange polymer (**2a**)[9] was obtained in 76% yield. Polymer **2a** was soluble in DMSO and DMF and partially soluble in acetone and methanol. Polymer **2a** was dissolved in DMSO and was subjected to GPC measurement. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of the polymer were M_n = 11 000 and M_w/M_n = 1.22, respectively.[10]

Scheme 1



The structure of **2a** was confirmed by IR and ^{1}H NMR spectroscopies compared with those of model compounds. 2-Benzylidene-4-phenyl-1,3-dithiole (**3**),[11] which was quantitatively obtained by the treatment of lithium 2-phenylethynethiolate with water in Et_2O, was used as a model compound for the 1,3-dithiafulvene unit. An almost quantitative model compound for the terminal thioamide (**4**) was also obtained from lithium 2-phenylethynethiolate with an excess of piperidine.[12] The reaction between a thioketene and a secondary amine is a very efficient process and appears to be quantitative.[1,3b,c] The IR spectrum of polymer **2a** showed a strong peak at 1578 cm^{-1} due to a C=C vibration of the dithiafulvene unit. The IR spectrum also showed peaks at 1502 and 1290 cm^{-1}, which were assigned to the terminal thioamide group. The ^{1}H NMR spectrum of **2a** was similar to that of the model compounds. In the ^{1}H NMR spectrum of **2a**, a broad peak for the benzylidene proton appeared at 6.7 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.2 ppm. In the ^{1}H NMR spectrum of **4**,[11] two triplets (4.28 and 3.57 ppm) assigned to $N-CH_2-$ appeared due to hindered rotation around the C−N bond.[4b,c] The peak at 4.35



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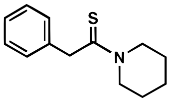

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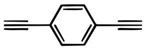
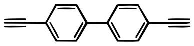
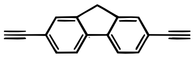
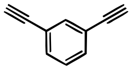
10.1021/ma980969w CCC: $15.00

Table 1. Synthesis of Poly(1,3-dithiafulvene)s Using Various Aromatic Diynes[a]

Diynes	polymer	Yield (%)[b]	M_n[c]	UVλmax (nm)[d]
	**2a**	76	5440	398
	**2b**	55	1900	379
	**2c**	66	2900	401
	**2d**	54	3880	359

[a] Polymerization was carried out in Et_2O at room temperature for 3 h. [b] Isolated yields after washing with water. [c] Determined from ^1H NMR. [c] Absorption spectra were recorded in dilute acetonitrile solutions at room temperature.

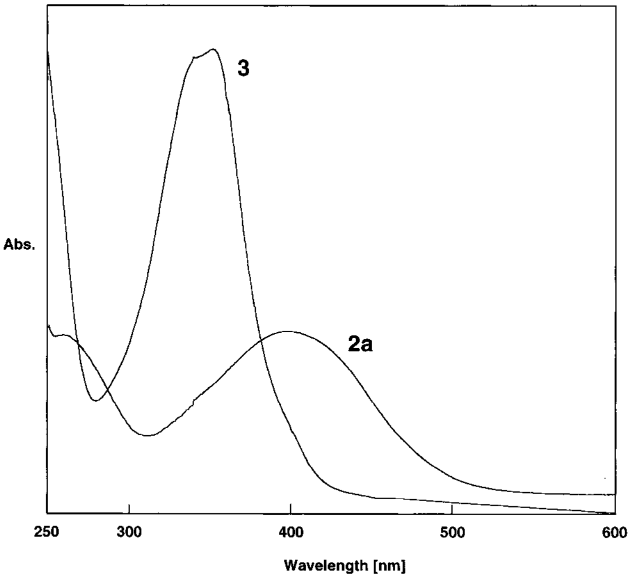


Figure 1. UV−vis spectra of **2a** and **3** in acetonitrile.

ppm was assigned to Ph−CH_2−C(=S)−N in **4**. The ^1H NMR spectrum of **2a** also shows two broad peaks at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. Comparison of the intensities of the absorptions of the 1,3-dithiafulvene protons in the repeating unit with those of the absorptions of the terminal thioamide protons results in the estimation of the number-average degree of polymerization (DP) as 26 (M_n = 5440).

Thermogravimetric analysis (TGA) was recorded for **2a** under nitrogen. The small weight loss of the polymer started at 250 °C. Subsequently, a rapid weight loss begins at about 430 °C and is completed at 540 °C.

The results of the polymerization with various diyne monomers[13] are summarized in Table 1. In every case, the corresponding polymer was obtained in good yield. The structures of the polymers were supported by IR and ^1H NMR spectra. The UV−vis absorption spectra data for the diluted acetonitrile solutions of **2a**−**d** are also shown in Table 1. Figure 1 shows the spectrum of **2a**, in which the peak due to the $\pi-\pi^*$ transition of the polymers is observed at 398 nm. The value was largely bathochromic shifted in comparison with the model compound **3**. This red-shift is ascribed to effective expansion of the π-conjugation system in **2a**. The smaller bathochromic shift of **2b** from the λ_{max} of **3**, compared with the bathochromic shifts observed with **2a** and **2c**, was due to a steric distortion of the biphenyl moiety. In the case of **2d**, the absorption maximum was the same as that of **3**. This result was caused by the fact that the π-conjugation is not expanded through 1,3-disubsituded benzene.

It is known that 2-benzylidene-4-phenyl-1,3-dithiole (**3**) readily forms 1:1 charge-transfer (CT) complexes with electron acceptors such as tetracyanoquinodimethane (TCNQ).[8a] In DMSO, all polymers **2** reacted with TCNQ to produce a dark green homogeneous solution. CT complex formation was shown by the appearance of a major maximum in the visible region of the spectrum at 840 nm and minor bands at 744, 760, 680, and 665 nm, which are responsible for the anion radical of TCNQ. Anion-radical formation of TCNQ was also confirmed by the ^1H NMR spectrum after TCNQ was added to the DMSO-d_6 solution of **2a**. Integration of the spectrum showed a formation of a complex containing a 1:1 ratio of 1,3-dithiafulvene unit to TCNQ. These results indicate that **2** formed soluble CT complexes with TCNQ. The CT complex of this π-conjugated polymer having 1,3-dithiafulvene unit is a new class of π-conjugated CT complexes. Further detailed properties of this polymer are now under investigation.

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(9) The elemental analysis agreed. Found: C, 63.09; H, 4.45; N, 1.50; S, 30.96. Calcd: C, 63.07; H, 4.10; N, 1.44; S, 31.39.
(10) Gel permeation chromatography was carried out on Shodex K-803 plus K-804 columns by using DMSO as an eluent at 50 °C after calibration with standard poly(8-oxa-6-azabicyclo-[3.2.1]octan-7-one) samples.
(11) Model compound **3** was prepared according to ref 4a: mp 204−205 °C (lit.[8a] mp 197−199 °C); IR (KBr) 1578, 1556, 1484 cm^{-1}; ^1H NMR (270 MHz, $(CD_3)_2SO$) δ 6.73 (s, 1H), 7.19 (m, 1H), 7.30−7.55 (m, 10H).
(12) Mp 69.0−69.5 °C (lit.[14] mp 71−72 °C); IR (KBr) 1508, 1289 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (m, 2H), 1.65 (m, 4H), 3.57 (t, 2H), 4.28 (t, 2H), 4.35 (s, 2H), 7.33 (m, 5H).
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