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Synthesis of a π-Conjugated Poly(thioketene dimer) and Its Electron-Donating Property

Takashi Uemura, Kensuke Naka,*
Adriana Gelover-Santiago, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan

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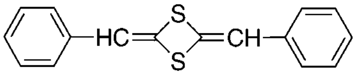
The reactivity of thioketenes shows features of the analogous ketene chemistry.[1] Thioketenes readily reacted with protic nucleophiles to give thiocarboxylic acid derivatives[2] or undergo cycloadditions across the C═C bond.[3] In addition to the ketene-type chemistry, the presence of sulfur atom allows thioketene reactions reminiscent of thiocarbonyl congeners; typical examples are the formation of *S*-oxides,[4] thiophilic attack of organometallics,[5] or cycloadditions across the C═S bond.[3a,6] Despite these synthetic advantages of thioketenes, few reports with the direct use of thioketenes in polymer synthesis have been published so far.[3a,7]

Recently, we reported on the synthesis of π-conjugated poly(dithiafulvene)s by cycloaddition polymerization of aldothioketenes with their alkynethiol tautomers.[8] The dithiafulvene analogues including tetrathiafulvalenes (TTF) have been intensively studied in attempt to prepare the novel organic materials, both low molecular weight and polymeric, since the discovery of the exceptional electric conductivity of charge-transfer (CT) complexes formed by TTF.[9] These poly(dithiafulvene)s formed soluble CT complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in DMSO, and the complexes had highly improved electrical conductivities compared with those of the uncomplexed poly(dithiafulvene)s.

Here we describe the synthesis of π-conjugated polymer with the 2,4-diylidene-1,3-dithietane unit by cycloaddition polymerization of bis(thioketene) derived from bis(phosphonium salt). The electric properties of the polymer were also studied. This is the first example of the polymer containing the thioketene dimer unit in the structure.



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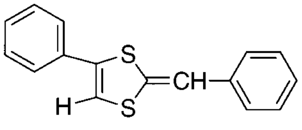

2

The most common example of (2 + 2) cycloadditions between thioketenes and C═S compounds is dimerization of thioketenes to give 2,4-bis(alkylidene)-1,3-dithietanes.[3a,10] Such dimers have been known for more than 100 years and synthesized by various methods. Although the structure of these dimer compounds is similar to that of the dithiafulvene derivatives, no research on the electric and magnetic properties of the thioketene dimers has been reported up to now.

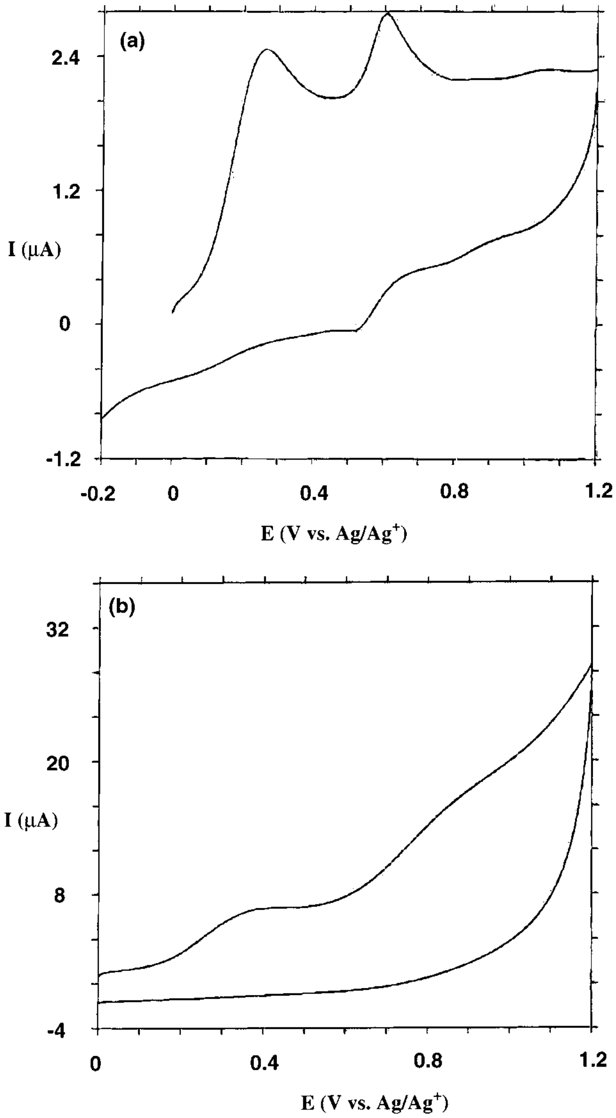

Figure 1. Cyclic voltammograms of (a) **1** and (b) cast film of **4**, measured in CH_3CN solution of 0.1 M $[NEt_4]BF_4$ at 100 mV/s.

An obvious approach to thioketenes is an olefination of carbon disulfide in a Wittig reaction.[10c,e,11] We carried out a basic dimerization of phenylthioketene derived from benzyltriphenylphosphonium chloride to yield 2,4-dibenzylidene-1,3-dithietane (**1**).[12] To elucidate the electric properties of **1**, cyclic voltammetry and UV−vis measurements were carried out. The cyclic voltammogram of **1** showed irreversible two-step oxidation peaks at 0.25 and 0.61 V vs Ag/Ag^+ (Figure 1a), indicating that **1** acts as a stronger electron donor than 2,6-bisphenyl-1,4-dithiafulvene (**2**)[8b] (E_{pa} = 0.40 V) and TTF (E_{pa} = 0.39 and 0.81 V). Compound **1** showed an absorption in the visible range with a peak at 364 nm in CH_3CN, due to the $\pi-\pi^*$ transition of **1**. This electron donor turned out to form CT complex with TCNQ in DMSO. The CT formation was shown by the appearance of CT band in the UV spectrum between 600 and 900 nm as well as by ^1H NMR and IR spectroscopies.[13] This CT complex contained a 1:1 ratio of **1** to TCNQ, determined by elemental analysis.

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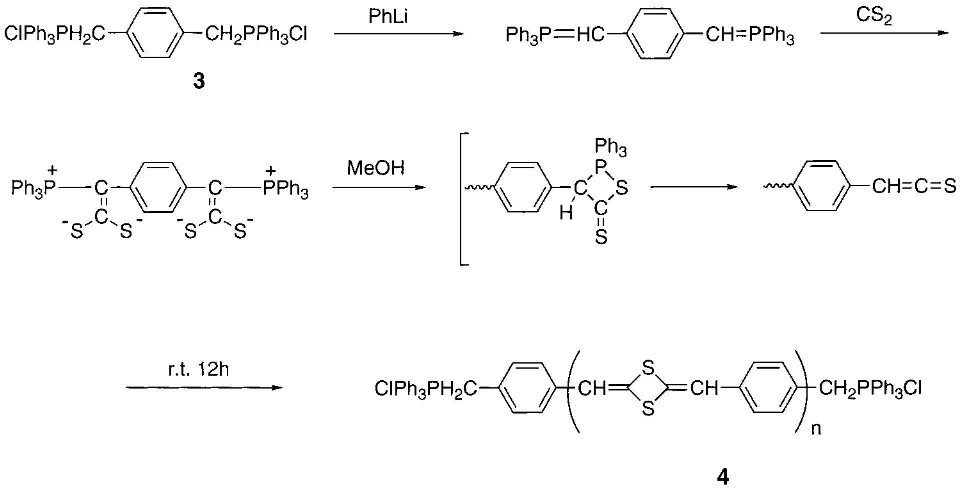
Scheme 1

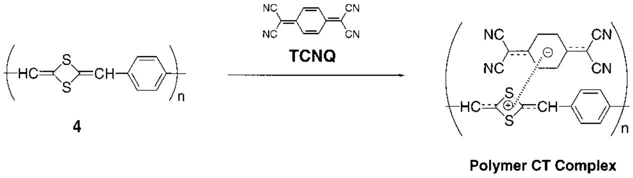


Scheme 1 provides an overview for the polymerization. *p*-Xylenebis(triphenylphosphonium chloride) (**3**) suspended in Et_2O was stirred while a solution of phenyllithium in cyclohexanes$-Et_2O$ was added dropwise. After 30 min, dry CS_2 was added to the mixture. After 5 h, the mixture turned yellow was poured into MeOH to afford bis(thioketene). The resulting mixture was stirred for 12 h to effect polymerization. The precipitate was washed with Et_2O several times to remove impurities. After drying under reduced pressure, a brown polymer (**4**) was obtained in 54% yield. The polymer **4** was soluble in DMSO and DMF. The molecular weight measurement was performed by GPC in eluent DMF with polystyrene standards. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were 10 280 and 2690, respectively. The molecular weight distribution (M_w/M_n) of the polymer was 3.82.

The structure of **4** was confirmed by IR and ^{1}H NMR spectroscopies, compared with those of **1** as a model compound. The IR spectrum of **4** showed a peak at 1653 cm^{-1} due to a C=C vibration of the ylidene unit as well as that of **1**. In the ^{1}H NMR spectrum of **4**, a broad peak for the benzylidene proton in the repeating unit appeared from 7.1 to 7.5 ppm. The spectrum also showed a peak due to the terminal benzyl protons at 5.1 ppm. Comparison of the intensities of the absorptions of the benzylidene and the aromatic protons in the repeating unit with that of the absorption of the terminal benzyl proton results in the estimation of number-average degree of polymerization (DP) as 8.3 ($M_n = 2290$), which is consistent with the value from GPC data. The low molecular weight of the polymer might result from the low reactivity of the monomer **3** toward phenyllithium, suggested by the remains of the benzyl moiety as the terminal group in the polymer. We carried out the polymerization under various conditions in order to improve the DP of the polymer. Any efforts, however, have not been effective so far.

The UV$-$vis absorption spectra of **4** were obtained for CH_3CN solution. The lower energy absorption edge of **4**, which was located at 550 nm, was largely bathochromic shifted in comparison with that of the model compound **1**, which was located at 420 nm. This red shift indicated an effective expansion of the π-conjugation system in **4**. The polymer **4** was electrochemically active, and its cast film gave irreversible two-step oxidation peaks at 0.39 and around 0.90 V vs Ag/Ag$^+$ in a cyclic voltammogram (Figure 1b). The cast film of the π-conjugated poly(dithiafulvene) previously reported gave an oxidation peak at 0.61 V vs Ag/Ag$^+$.[8] This fact indicated that **4** acts as a stronger electron donor than the poly(dithiafulvene). Since the electron-donating thioketene dimer moiety was incorporated into the π-conjugated main chain, the oxidation peaks of **4** were located at fairly high potentials compared with the model compound **1**.[8,14]

Scheme 2



Interestingly, the polymer **4** also formed a green CT complex with TCNQ in DMSO (Scheme 2). The UV$-$vis absorption of the polymer CT complex exhibited λ_{max} at 845, 762, and 745 nm, which were responsible for the anion radical of TCNQ. The ^{1}H NMR of the polymer CT complex in DMSO-d_6 showed a formation of the complex containing a 1:1 ratio of the repeating unit in **4** to TCNQ.[8d] The conductivity of the polymer was investigated at room temperature by conventional two-probe technique. The polymer CT complex showed the electrical conductivity of 9.5×10^{-5} S/cm at room temperature. The polymer **4** doped with iodine showed the conductivity of 1.8×10^{-3} S/cm.

In conclusion, we have prepared the polymer with thioketene dimer unit in the π-conjugated main chain by cycloaddition polymerization of aldothioketene. Our investigation demonstrated that this new polymer possessed the electron-donating property and formed the soluble CT complex with TCNQ. Further studies on the synthesis of the polymers with higher DP and from various monomers are in progress.

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(12) Model compound **1** was prepared according to ref 10c. IR (NaCl): 1652 (C═C vibration), 1398 cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6): d 6.99 (s, 2H), 7.13 (s, 2H, benzylidene proton), 7.38 (m, 4H), 7.57 (m, 4H).

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