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π-Conjugated Polymers with Electroactive Thioketene Dimer Unit

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ABSTRACT: New π-conjugated polymers (**2**) with the thioketene dimer unit were prepared by cycloaddition polymerization of bis(thioketene) derived from bis(triphenylphosphonium chloride) (**1**). The structures of the polymers were compared with that of 2,4-dibenzylidene-1,3-dithietane (**3**), which was prepared by dimerization of phenylthioketene derived from benzyltriphenylphosphonium chloride, by use of IR and ^{1}H NMR. The lower energy absorption edges of **2** were located at longer wavelengths than that of the model compound **3**, due to developments of π-conjugations in **2**. The cyclic voltammogram of **3** showed irreversible two-step oxidation peaks at 0.25 and 0.61 V vs Ag/Ag$^+$, indicating that the electron-donating ability of **3** is stronger than that of tetrathiafulvalene (TTF). The electron-donating properties of the polymers **2** were also confirmed by cyclic voltammetry and were found to depend on aromatic structures in **2**. The polymer **2** formed charge-transfer (CT) complexes with TCNQ (1:1 ratio of the repeating unit in **2** to TCNQ) in DMSO. The degrees of CT in the complex were investigated by UV and IR measurements. In the solid state, the complex of **2b** contained partially charge-transferred TCNQ (degree of CT = 0.59), resulting in higher conductivity than that of **2a**.

Introduction

Thioketenes are important and highly reactive intermediates. The reactivity of thioketenes shows features of the analogous ketene chemistry and has been extensively studied for a long time.[1] Recently, thioketene chemistry has noticeably grown in the field of the coordination of transition metals[2] and metabolism.[3] It has been suggested that thioketenes are potential biological reactive intermediates and induce DNA strand breaks.[4]

Thioketenes readily reacted with protic nucleophiles to give thiocarboxylic acid derivatives[5] or undergo cycloadditions across the C═C bond.[6] 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,[7] thiophilic attack of organometallics,[8] or cycloadditions across the C═S bond.[6a,9] The most common example of (2 + 2) cycloadditions between thioketenes and C═S compounds is a dimerization of thioketenes to give 2,4-bis(alkylidene)-1,3-dithietanes.[6a,10] Such dimers have been known for more than 100 years and synthesized by various methods.

There is a long-standing interest in the chemistry and properties of cyclic compounds containing sulfur atom in modern material chemistry due to their redox chemistry. Especially, the focus has been on dithiole derivatives, e.g., dithiafulvenes and tetrathiafulvalenes,[11] since the finding of metallic conductivity[12] and low-temperature superconductivity[13] in radical cation salts. The quite low oxidation potentials of 1,4-dithiin compounds have recently been reported.[14] Therefore, the potential electronic property of the thioketene dimer moiety is considerably attractive with the aim of application to a new and better π-donor. Even though these dimer compounds have been characterized spectroscopically, no physical investigation including electric and magnetic properties of the thioketene dimers has been reported up to date.

From a viewpoint of polymerizations, the direct use of thioketenes in polymer synthesis has been very limited,[6a,15] although ketenes have been employed in many kinds of polymerizations.[16] In the past few years, we have developed polymer syntheses by use of a cycloaddition reaction between an aldothioketene and its alkynethiol tautomer affording an electron-donating dithiafulvene moiety.[17] Recently, we reported initial studies on a synthesis of a new π-conjugated polymer with 2,4-diylidene-1,3-dithietane unit by cycloaddition polymerization of bis(thioketene)s derived from a bis(phosphonium salt).[18] That was the first example of a polymer containing the thioketene dimer unit in the structure. In this paper, we describe the synthesis, optical properties, and electrochemical analysis of π-conjugated polymers having electron-donating thioketene dimer units in the main chain. Formations of charge-transfer (CT) complexes of the polymers with tetracyanoquinodimethane (TCNQ) were also studied.

Polymerization

The π-conjugated poly(thioketene dimer)s were prepared by the cycloaddition polymerization of bis(thioketene)s derived from bis(triphenylphosphonium salt)s (**1**). Treatment of **1** with phenyllithium and carbon disulfide in Et$_2$O generated bis(betaine)s. The resulting mixture was poured into a large amount of MeOH to afford the bis(thioketene)s and left for 12 h to effect polymerization. An insufficient amount of MeOH led to a recovery of the monomer, suggesting that this reaction was much affected by the polarity of the reaction medium. Polymers **2** were obtained as yellow precipitates and soluble in DMF and DMSO. The molecular weight measurement of **2a** as a representative polymer 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 structures of **2** were confirmed by IR and ^{1}H NMR spectroscopies, compared with those of 2,4-dibenzylidene-1,3-dithietane (**3**) as a model compound. A model dimerization of phenylthioketene derived from benzyltriphe-

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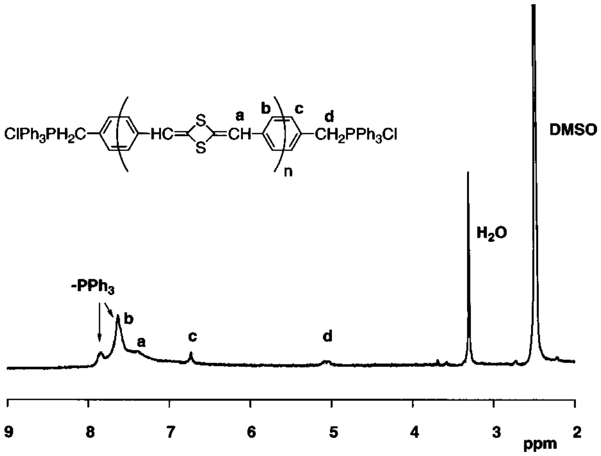
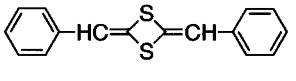


Figure 1. ^{1}H NMR spectrum of **2a** in DMSO-d_6.

nylphosphonium chloride gave **3** in a high yield.[10c] The IR spectrum of **3** showed a peak at 1652 cm^{-1} due to a C=C vibration of the ylidene unit. The polymer **2a**, for example, had the same peak at 1653 cm^{-1} in the spectrum, suggesting the thioketene dimer unit in the polymer. In the ^{1}H NMR spectrum of **2a** (Figure 1), 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. Therefore, it is possible to compare the peak intensities of the repeating unit with that of terminal moiety in order to estimate the degree of polymerization (DP) of polymer **2**. The DP values of **2a** and **2b** were determined as 8.3 (M_n = 2290) and 7.1 (M_n = 2700), respectively. These results are consistent with the values from GPC data.



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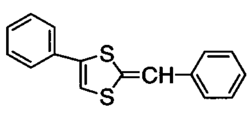

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Optical Study

Figure 2 shows UV–vis absorption spectra of the thioketene dimers. The model compound **3** had an absorption maximum due to the π–π* transition at 364 nm in CH_3CN. The spectrum of **2a** in the same solvent exhibited no absorption maximum; however, it was tailing beyond 550 nm. The lower energy absorption edge of **2a** was largely bathochromic shifted in comparison with that of the model compound **3**, which was located around 420 nm. This red shift indicated an effective expansion of the π-conjugation system in **2a**. The smaller bathochromic shift of **2b** than that of **2a** was due to a steric distortion of the biphenyl moiety.

Electrochemical Study

Cyclic voltammetry was performed in order to elucidate the electric property of the thioketene dimer **3**. The cyclic voltammogram of **3** showed irreversible two-step oxidation peaks at 0.25 and 0.61 V vs Ag/Ag$^+$ (Figure 3A). The first oxidation potential of **3** is remarkably lower than those of 2,6-bisphenyl-1,4-dithiafulvene (**4**)[17b] (E_{pa} = 0.40 V) and TTF (E_{pa} = 0.39 V) obtained in the same conditions, indicating that **3** acts as a stronger electron donor than the dithiafulvene and TTF. As shown in Figure 3B, the cast film of **2a** gave two-step broad oxidation peaks at 0.39 and 0.90 V vs Ag/Ag$^+$. The oxidation potentials of **2a** are higher and broader than those of **3**, indicating the apparent electronic interaction between the repeating thioketene dimer units in the π-conjugated system. Such anodic shifts and broadenings of the peaks have been observed in other electrochemically active π-conjugated polymers. The cast film of **2b** also gave similar broad oxidation peaks (E_{pa} = 0.43 and 0.92 V vs Ag/Ag$^+$) to those of **2a** (Figure 3C). An apparent broad oxidation peak for **2** compared with that of **3** suggested the interaction between thioketene dimer units along the π-conjugated polymer main chain.

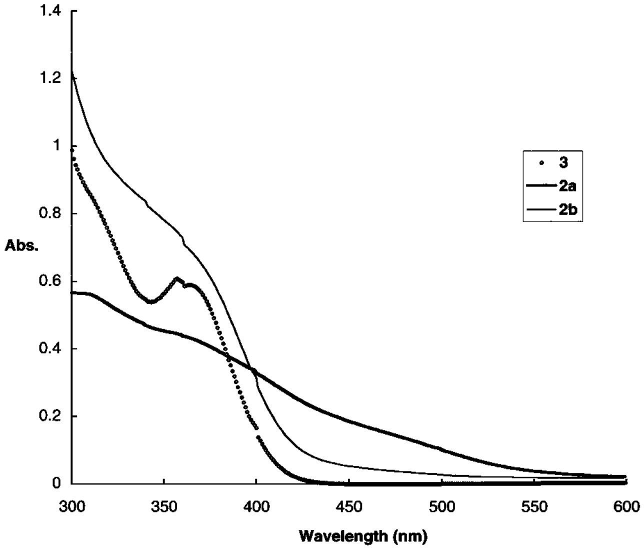


Figure 2. UV–vis absorption spectra of **2a** (bold line), **2b** (plain line), and **3** (○) in CH_3CN.

Charge-Transfer Complexes with TCNQ and Their Electrical Conductivities

Interestingly, DMSO solution of the model compound **3** turned to a clear green homogeneous solution after adding an excess amount of 7,7,8,8-tetracyanoquinodimethane (TCNQ) against **3**, indicating the formation of charge-transfer (CT) complex. Then the precipitated TCNQ, which was not reacted with **3**, was filtered off, and the filtrate was evaporated to give a green powder. This CT complex contained a 1:1 ratio of **3** to TCNQ, determined by elemental analysis. Polymers **2a** and **b** also formed green CT complexes with TCNQ in DMSO (Scheme 2), prepared in the same manner as **3**. The ^{1}H NMR spectra of the polymer CT complexes in DMSO-d_6 as well as the elemental analyses also showed the formation of the complex containing 1:1 ratio of the repeating unit in **2** to TCNQ.

The UV–vis absorption spectrum of the anion radical of TCNQ exhibits absorption at 420 nm and between 600 and 900 nm.[19] The neutral TCNQ shows a strong absorption at 392 nm. The UV–vis absorptions of the CT complexes of **2** and **3** with TCNQ in CH_3CN contained the total band assignable to the anion radical and the neutral TCNQ. The spectrum of the CT complex of **2a** is largely different from that of **2b** (Figure 4). Comparison of both spectra suggested that **2a** preferred the formation of anion radical TCNQ in the CT state; on the contrary, the CT complex of **2b** was mainly composed of the neutral TCNQ. The CT states of the complexes may be explained by the oxidation potentials of **2** determined by CV analysis. Predominant formation

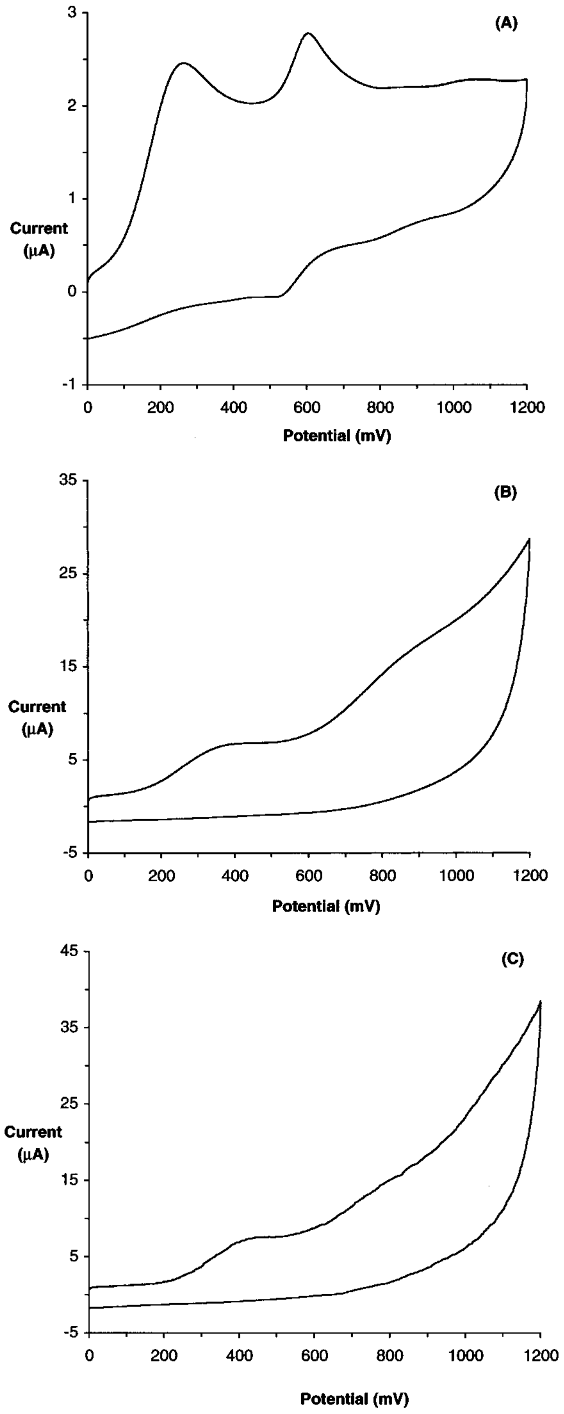


Figure 3. Cyclic voltammograms of **3** (A), a film of **2a** (B), and a film of **2b** (C) in CH_3CN solution of 0.1 M $[NEt_4]BF_4$ at 100 mV/s.

of TCNQ anion radical in **2a** complex is caused by the strong electron-donating ability of **2a**.

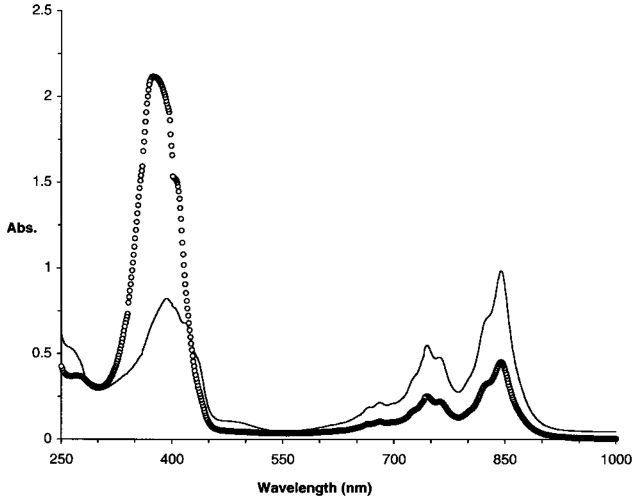
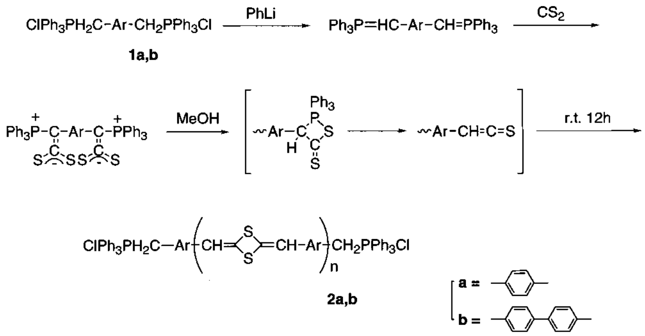
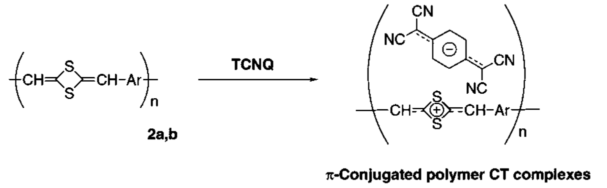


Figure 4. UV−vis absorption spectra of the **2a**−TCNQ complex (—) and **2b**−TCNQ complex (○) in CH_3CN.

Scheme 1



Scheme 2



The CT complexes of **2** and **3** were measured by FT-IR to investigate the degree of CT in the solid state. The degree of CT can be determined by the frequency of the nitrile stretching band of TCNQ in the complex.[20] The spectrum of the CT complexes of the model compound **3** showed a C≡N band at 2178 cm^{-1}. This value indicates a fully ionic state (anion radical) of TCNQ in the sample. As is similar to the model compounds, the IR spectrum of the complex of **2a** with TCNQ showed one C≡N band at 2178 cm^{-1}, which is characteristic of TCNQ anion radical. The polymer CT complex of **2b** with TCNQ had a major band at 2178 cm^{-1} and a minor band at 2202 cm^{-1}, showing that the complex contains two different species of charge-transferred TCNQ. The former peak is corresponding to the anion radical of TCNQ, and the latter was due to a partially charge-transferred TCNQ (degree of CT = 0.59).[20] As is similar to UV analysis, only the complex of **2b** contains the partially charge-transferred TCNQ in the solid state due to the weak electron-donating property. However, the degree of CT between 0.5 and 1.0 is necessary for such complexes to achieve a high conductivity.

The conductivity of the polymer was investigated at room temperature by the conventional two-probe technique. The polymer−TCNQ complexes of **2a** and **2b** showed the electrical conductivities of 9.5×10^{-5} and 2.0×10^{-3} S/cm, respectively, at room temperature. A higher conductivity of **2b** than that of **2a** might result from the existence of the partially charge-transferred TCNQ. Polymer **2a** doped with iodine showed a conductivity of 1.8×10^{-3} S/cm.

Summary

In conclusion, we have prepared the polymers with thioketene dimer unit in the π-conjugated main chain by cycloaddition polymerization of aldothioketene. The UV−vis study indicated effective expansions of the π-conjugation system in the polymers. The polymers generally behaved as strong electron donors and formed CT complexes with TCNQ. Oxidation potentials and the CT states of the polymers were dependent on the aromatic moieties of the polymers. The TCNQ complex of **2b**, which contained the partially charge-transferred TCNQ, had higher conductivity than that of **2a**. Possible applications of the new CT complexes composed of the thioketene dimers, including the low molecular weight model compound, to electronic, magnetic, and conducting materials are interesting, instead of the dithiafulvene-based compounds.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. The solvents were dried and distilled under N_2. Biphenyl-4,4′-bis(methyltriphenylphosphonium chloride) (**1b**) was synthesized according to the literature.[21]

Measurements. ^{1}H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin-Elmer 1600 spectrometer, respectively. GPC measurement was carried out on TSK gel a-3000 by using DMF as an eluent at 40 °C after calibration with standard polystyrene samples. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer. Cyclic voltammetry was carried out with a BAS CV-50W electrochemical analyzer in CH_3CN solution of 0.1 M $[NEt_4]BF_4$ as a supporting electrolyte. A platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurements. For the CV of the polymers, thin polymer films were prepared on indium tin oxide (ITO) coated glass electrodes by casting from their solutions. The electrodes were dried under vacuum. Electrical conductivity was measured at room temperature by the two-probe technique using a Keithley 2400 source meter. The polymer films were prepared by dropping of the polymer solutions onto glass plates equipped with platinum electrodes, followed by drying in vacuo.

Polymerization. To a mixture of a bis(triphenylphosphonium chloride) (1.0 mmol) and Et_2O (10 mL), a solution of phenyllithium in cyclohexane−Et_2O (ca. 17%, 1.1 mL) was added dropwise at room temperature. After 0.5 h, carbon disulfide (152 mg, 2.0 mmol) was added to the mixture. After 5 h, the resulting yellow mixture was poured into a large quantity of MeOH (200 mL) and then left at room temperature for 12 h to effect the polymerization. The precipitate was collected and washed with Et_2O several times to remove impurities. After drying under reduced pressure, a brown polymer was obtained.

2a. Yield: 138 mg (54%). ^{1}H NMR (270 MHz, DMSO-d_6): δ 5.1 ($-CH_2PPh_3Cl$, 4H), 6.7 (terminal benzene, 4H), 7.1−7.5 (repeating benzylidene proton, 2nH; $n = 8.3$), 7.6−7.8 (repeating benzene and triphenylphosphine, $(4n + 18)$H; $n = 8.3$), 7.9 (triphenylphosphine, 12H). IR (NaCl): 1653 cm^{-1}.

2b. Yield: 113 mg (30%). ^{1}H NMR (270 MHz, DMSO-d_6): δ 5.1 ($-CH_2PPh_3Cl$, 4H), 6.9−7.2 (repeating benzylidene proton, 2nH; $n = 7.1$), 7.2−7.9 (repeating benzene and triphenylphosphine, $(8n + 38)$H, $n = 7.1$). IR (NaCl): 1655 cm^{-1}.

2,4-Dibenzylidene-1,3-dithietane (3). The model compounds **3** were prepared according to ref 10c. ^{1}H NMR (270 MHz, DMSO-d_6): δ 6.98 (m, 2H), 7.14 (m, 2H), 7.3−7.5 (m, 4H), 7.5−7.7 (m, 4H). IR (NaCl): 1652 cm^{-1}.

CT Complexes of 2 with TCNQ. An excess amount of TCNQ against repeating unit of **2** was added to the solution of **2** in DMSO, and the mixture was stirred for 15 min. The solution gradually became dark green. After the unreacted TCNQ was filtered off, the solvent was evaporated to obtain a dark green powder.

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References and Notes

(1) (a) Schaumann, E. *Tetrahedron* **1988**, *44*, 1827. (b) Ma, N. L.; Wong, M. W. *Eur. J. Org. Chem.* **2000**, *8*, 1411.

(2) (a) Kim, Y.-J.; Lee, S.-C.; Cho, M. H.; Lee, S.-W. *J. Organomet. Chem.* **1999**, *588*, 268. (b) Wang, L. J. J.; You, S.-J.; Huang, S.-L.; Yang, Y.-L.; Lin, Y.-C.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1999**, 2243.

(3) (a) Dekant, W.; Urban, G.; Görsmann, C.; Anders, M. W. *J. Am. Chem. Soc.* **1991**, *113*, 5120. (b) Volkel, W.; Pahler, A.; Dekant, W. *J. Chromatogr., A* **1999**, *847*, 35. (c) Birner, G.; Werner, M.; Rosner, E.; Mehler, C.; Dekant, W. *Chem. Res. Toxicol.* **1998**, *11*, 750.

(4) Mueller, M.; Birner, G.; Sander, M.; Dekant, W. *Chem. Res. Toxicol.* **1998**, *11*, 464.

(5) (a) Raasch, M. S. *J. Org. Chem.* **1972**, *37*, 1347. (b) Raap, R. *Can. J. Chem.* **1968**, *46*, 2251. (c) Padwa, A.; Au, A.; Lee, G. A.; Owens, W. *J. Org. Chem.* **1975**, *40*, 1142. (d) Schaumann, E.; Scheiblich, S. *Tetrahedron Lett.* **1985**, *26*, 5269. (e) Sukhai, R. S.; de Jong, R.; Brandsma, L. *Synthesis* **1977**, 888.

(6) (a) Raasch, M. S. *J. Org. Chem.* **1970**, *35*, 3470. (b) Bestmann, H. J.; Schmid, G.; Sandmeier, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 53.

(7) Zwanenburg, B.; Lenz, B. G. *Methoden Org. Chem.* **1985**, *E11*, 941.

(8) Schaumann, E.; Walter, W. *Chem. Ber.* **1974**, *107*, 3562.

(9) (a) Ando, W.; Tsumuraya, T.; Goto, M. *Tetrahedron Lett.* **1986**, *27*, 5105. (b) Dickoré, K.; Wegler, R. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 970. (c) Raasch, M. S. *J. Org. Chem.* **1978**, *43*, 2500. (d) Raasch, M. S. *J. Org. Chem.* **1975** *40*, 161.

(10) (a) Raasch, M. S. *J. Chem. Soc., Chem. Commun.* **1972**, 577. (b) Pedersen, C. T.; Oddershede, J.; Sabin, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1062. (c) Purrello, G.; Fiandaca, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 692. (d) Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 7326. (e) Schönberg, A.; Frese, E.; Brosowski, K. *Chem. Ber.* **1962**, *95*, 3077.

(11) Hansen, T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 289.

(12) (a) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heegeer, A. J. *Solid State Commun.* **1973**, *12*, 1125. (b) Ferraris, J.; Cowan, D. O.; Walatka, V. V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

(13) (a) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555. (b) Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins, D. M.; Kommers, J. M.; Boryschuk, S. J.; Strieby-Crouch, A. V.; Kwok, W. K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3262.

(14) Nishinaga, T.; Wakamiya, A.; Komatsu, K. *Chem. Commun.* **1999**, 777.

(15) Staudinger, H.; Rathsam, G.; Kjelsberg, F. *Helv. Chim. Acta* **1920**, *3*, 853.

(16) Zarras, P.; Vogl, O. *Prog. Polym. Sci.* **1991**, *16*, 173.

(17) (a) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **1998**, *31*, 7570. (b) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **1999**, *32*, 4641. (c) Naka, K.; Uemura, T.; Chujo, Y. *Polym. J.* **2000**, *32*, 435. (d) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **2000**, *33*, 4733. (e) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **2000**, *33*, 6965.

(18) Uemura, T.; Naka, K.; Gelover-Santiago, A.; Chujo, Y. *Macromolecules* **2001**, *34*, 346.

(19) (a) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374. (b) Gong, J. P.; Kawakami, I.; Sergeyev, V. J.; Osada, Y. *Macromolecules* **1991**, *24*, 5246.

(20) (a) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442. (b) Skabara, P. J.; Müllen, K.; Bryce, M. R.; Howard, J. A. K.; Batsanov, A. S. *J. Mater. Chem.* **1998**, *8*, 1719.

(21) Subramaniam, G.; Gilpin, R. K. *Synthesis* **1992**, 1232.

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