Macromolecules **2000,** *33,* 6965−6969

A Polymer with Two Different Redox Centers in the π-Conjugated Main Chain: Alternate Combinations of Ferrocene and Dithiafulvene

Kensuke Naka,* Takashi Uemura, and Yoshiki Chujo*

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

Received March 6, 2000; Revised Manuscript Received July 5, 2000

ABSTRACT: A redox-active alternating π-conjugated copolymer of ferrocene with dithiafulvene was synthesized by cycloaddition polymerization of aldothioketene derived from 1,1′-bis(trimethylsilylethynyl)-ferrocene (**1**). The obtained polymer (**2**) was soluble in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, DMF, and DMSO. The structure of **2** was confirmed by IR, ^1H NMR, and ^{13}C NMR spectra compared with those of 2,6-bis(ferrocenyl)-1,4-dithiafulvene as a model compound (**3**). The cyclic voltammogram of **3** showed three oxidation peaks, which were originated from the two ferrocene units and the dithiafulvene unit. The polymer **2** showed only single-broad oxidation peak at 0.58 V vs Ag/Ag^+. This result was caused by an effective interaction between two different donors in **2**. Compounds **2** and **3** did not undergo oxidative dimerization to form extended tetrathiafulvalene during cyclic voltammetry. The polymer **2** formed a soluble charge-transfer (CT) complex with TCNQ in DMSO. The ratio of the dithiafulvene unit in **2** to TCNQ in the complex was 1:1, confirmed by ^1H NMR. The electrical conductivity of **2** was 3.6×10^{-3} S/cm after I_2 doping.

Introduction

The study of molecules comprising two different redox centers that are covalently linked is a developing area within supramolecular chemistry, with application in molecular electric devices, sensors, electrocatalysis, and energy conversion.[1] Current research in this area focuses on gaining control over charge-transfer (CT) interactions between combinations of organic and organometallic species, e.g., bipyridinium cations, quinones, metallocenes, and metal-coordinated macrocycles.[2] Combinations of ferrocene with multisulfur compounds offer new sulfur-based synthon for the preparation of molecular materials with unusual properties such as enhanced electrical conductivity, unusual magnetic behavior, and nonlinear-optical (NLO) effects.[3] Ferrocenyldithiafulvene compounds have been studied to achieve new attractive materials in such fields.[4] Ueno et al. reported that diferrocenyltetrathiafulvalene formed 1:1 CT complex with 2,3-dichloro-5,6- dicyanobenzo-1,4-quinone (DDQ), with an electrical conductivity of 1×10^{-3} S/cm.[4a]

Incorporation of dithiafulvene derivatives into π-conjugated polymer backbones is an attractive subject because of the enhanced processabilities of their charge-transfer salts and/or the anticipated high electrical conductivities.[5] We have developed the synthesis of new π-conjugated polymers having dithiafulvene and aryl units alternately in the main chain.[6] The UV−vis absorption spectra and cyclic voltammetry measurements of the polymers showed effective expansions of the π-conjugation systems in the polymers.[6a,b] These polymers formed soluble CT complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ).[6a,c]

In this paper, we describe the synthesis of an alternating copolymer of dithiafulvene with ferrocene units by cycloaddition polymerization of ferrocenyl thioketene. Both dithiafulvene and ferrocene units are electron donors. Incorporation of two different donors into main chains of π-conjugated system should be interesting. No example of the polymers containing the combination of dithiafulvenes and ferrocenes in π-conjugated systems has been reported. We found that electrochemical analysis for this new polymer showed an interesting behavior compared with its model compound.

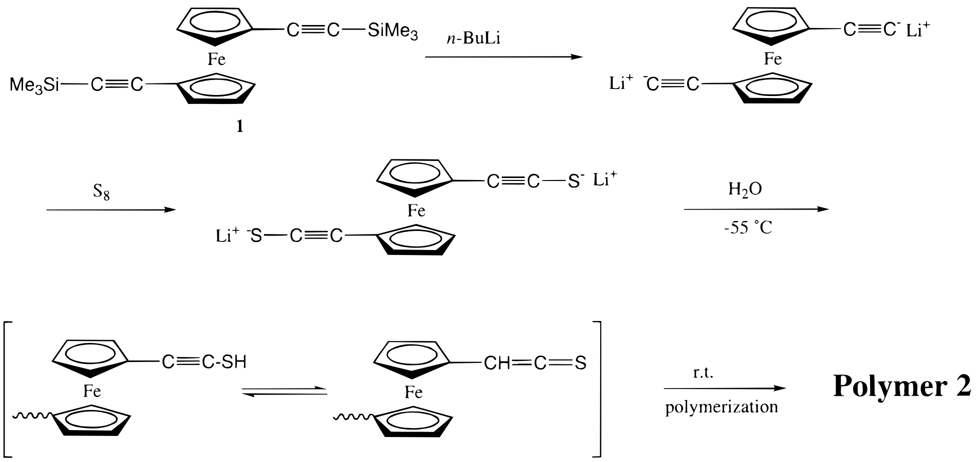
Results and Discussion

Polymerization. 1,1-Diethynylferrocene, which is an ideal monomer to generate an aldothioketene reactant, is too unstable to be isolated. A stable trimethylsilane derivative, **1**, can be prepared via an unstable diethynylferrocene by treatment of diacetylferrocene using Negishi's method.[7] **1** undergoes electrophilic substitution reactions to give various compounds in good yield, so that it was attempted to carry out the polymerization reaction from **1** instead of 1,1-diethynylferrocene. Scheme 1 provides the outline of polymerization by cycloadditon reaction of aldothioketene with alkynethiol tautomer derived from monomer **1**.[6a,b,8] To a solution of **1** in THF, *n*-butyllithium was added at −78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. After treated with sulfur and an equimolar of water as a proton source, the reaction mixture was stirred for 3 h to effect polymerization. The mixture was then poured into a large quantity of *n*-hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a brown-colored polymer, **2**, was obtained (50% yield). Polymer **2** was soluble in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, DMF, and DMSO. The molecular weight measurement was performed by GPC in eluent $CHCl_3$. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of **2** were $M_n = 1930$ and $M_w/M_n = 1.33$, respectively.

Characterization of the Polymer. The model compound **3** was prepared from ethynylferrocene to determine the structure of polymer **2**. The structure of **3** was confirmed by IR, ^1H and ^{13}C NMR spectra. In the IR

10.1021/ma0004054 CCC: $19.00

Scheme 1



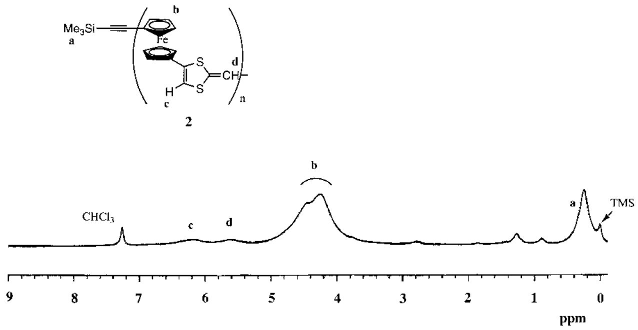
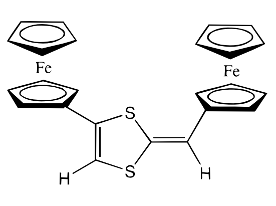
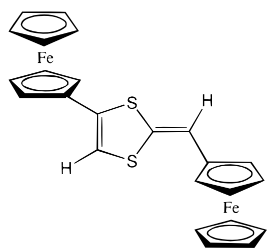


Figure 1. ^{1}H NMR spectrum of **2** in CDCl$_3$.

spectrum of **3**, a peak appeared at 1559 cm^{-1} was due to a C=C vibration of the dithiafulvene moiety. The ^{1}H NMR spectrum of **3** showed two peaks assigned to dithiafulvene protons at 5.60 and 6.10 ppm. The former peak corresponded to the ylidene proton; the latter is for the dithiole proton. In the ^{13}C NMR spectrum, eight peaks attributed to four dithiafulvene carbons were observed at 108.4, 109.0, 110.5, 110.9, 131.5, 131.7, 132.9, and 133.1 ppm, indicating that the model compound **3** was a mixture of *E* and *Z* isomers. The reaction mechanism of cycloaddition of aldothioketenes with their alkynethiol tautomer supports the predominant formation of *Z* isomers.[6b,8d,e] The ratio of the *E* to the *Z* isomer of **3** was estimated to be 1:2 from comparison of intensities of the peak area at 110.5 ppm with that at 110.9 ppm.

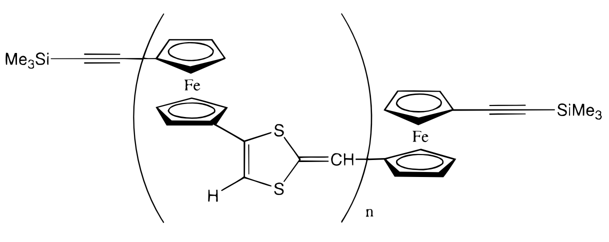


Z-3



E-3

The IR and ^{1}H NMR spectra of **2** were similar to those of **3**. The IR spectrum of **2** showed a peak at 1560 cm^{-1} assigned to the dithiafulvene unit. A weak peak at 2153 cm^{-1} was assigned to a C≡C vibration of the unreacted terminal trimethylsilylethynyl group. Figure 1 shows the ^{1}H NMR spectrum of **2**, which exhibited two extremely broad peaks around 5.6 and 6.2 ppm attributed to dithiafulvene protons. This type of broadening was also observed in the spectra of the π-conjugated poly(dithiafulvene)s previously reported.[6a,b] A broad peak was observed at 0.24 ppm, which was assigned to the terminal trimethylsilyl moiety. The degree of polymerization (DP) was estimated by the comparison of the intensities of the absorptions of the ferrocene protons in the repeating unit with those of the absorption of the terminal trimethylsilyl protons. The value of DP was 5.5 (M_n = 2020), which was consistent with the value from GPC data. In the ^{13}C NMR spectrum of **2**, broad peaks for the dithiafulvene carbons were recognized around 109 and 128 ppm, and a peak at 0.83 ppm due to the carbons of the terminal trimethylsilyl group was also observed. Table 1 summarizes the results of the polymerization under various conditions. When the reaction was attempted in Et$_2$O, no polymeric product was obtained (entries 1 and 2). The use of hexamethylphosphorus triamide (HMPT), which is a favorable solvent for nucleophilic substitution reactions,[7] decreased both the yield and the molecular weight of the product (entry 4). This relatively low reactivity of the trimethylsilylethynyl group toward *n*-BuLi caused the low molecular weight of polymer **2**.



2

UV−Vis Absorption Spectra. Figure 2 shows the UV−vis absorption spectra of **2** and **3** in CHCl$_3$. Compound **3** showed a peak at 450 nm, assignable to a d−d transition in the ferrocene unit[9] and a strong absorption peak due to the π−π* transition at 303 nm. Although the π−π* absorption band of **2** showed no obvious peak, a relatively broad absorption spectrum was observed in comparison with that of **3**. This might indicate some conjugative interaction within the unit structure.

Electrochemical Studies. The redox properties of **2** and **3** were studied by cyclic voltammetry. The model compound **3** exhibited three reversible oxidation peaks

Table 1. Preparation of Polymer 2 under Various Conditions

entry	solvent	nucleophile	yield (%)	M_n[b]	M_w[b]	M_w/M_n[b]
1	Et_2O	MeLi	no polymerization			
2	Et_2O	*n*-BuLi	no polymerization			
3	THF	*n*-BuLi	50	1930	2570	1.33
4	THF−HMPT[a]	*n*-BuLi	27	990	2200	2.23

[a] The ratio of THF to HMPT (hexamethylphosphorus triamide) was 1:0.3. [b] Determined from GPC.

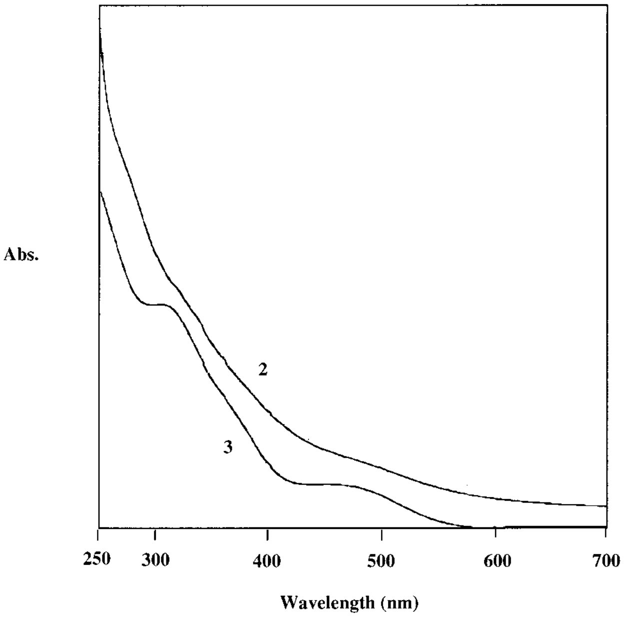
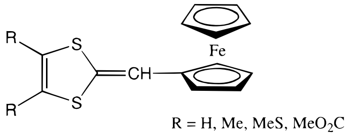


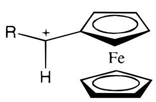
Figure 2. UV−vis absorption spectra of **2** and **3** in $CHCl_3$.

at 0.21, 0.50, and 0.85 V vs Ag/Ag^+, which originated from the two ferrocenes and the dithiafulvene. In the literature, the intermolecular oxidative dimerizations of 1,4-dithiafulvenes to yield the dication of the corresponding extended tetrathiafulvalene (TTF) systems were reported.[10] In these cases, a reversible wave appears at less positive potential during the reverse cathodic scan when the oxidation peak of the dithiafulvenes has been scanned beforehand. This result shows that during the scan, the oxidation of the dithiafulvenes led to the formation of the dimer TTFs, which are oxidized at less positive potentials than the dithiafulvenes. It should be noted that such a dimerization of ferrocene system **3** was not observed during cyclic voltammetry. On repeated cycling of the voltammogram of **3**, there was no marked change in the trace and no evidence was obtained for the formation of corresponding TTF. Moore et al. have reported that ferrocenyl dithiafulvenes (**4**) did not undergo the dimerization reaction during cyclic voltammetry.[4d] Both results were due to the ferrocenyl substituent of **3** and **4** increasing the stability of the derived cation radical to the extent that they were significantly more stable than anticipated. It is known that α-ferrocenylcarbonium cations **5** are unusually stable.[11] The electron-transfer level of **3** during the CV measurement was estimated from the electric current compared with that of ferrocene as a standard. The peaks *x*, *y*, and *z* involved 0.17, 0.67, and 0.20 electron transfer, respectively.

The redox behavior of **2** was found to be quite unique. As mentioned above, **3** exhibited three reversible oxidation peaks due to its three different redox sites. Compounds **4** showed the expected two oxidation peaks.[4d]



4



5

Although **2** had two kinds of donors in the main chain, the cyclic voltammogram of **2** showed only a single broad oxidation peak at 0.58 V vs Ag/Ag^+. A corresponding reduction peak occurs at 0.50 V vs Ag/Ag^+. This new observation should result from an effective interaction between two donors in **2** in contrast to the model compounds **3** and **4**. To the best of our knowledge, this was the first redox behavior resulted from such a combination of donors. The positive charge stored by the repeating unit during the CV scan was estimated by use of a ferrocene standard. The peak at 0.58 V involved 1.21 electron transfer, suggesting an effective charge transfer from the repeating unit during the scan. Nonconjugated dithiafulvenes are typically oxidized to the cation radical at between E^{ox} +0.9 and +1.4 V, depending on their substituents. The low potentials of the oxidation peaks of **2** and **3** are consistent with a highly delocalized π-electron system, as observed previously when π-conjugation of dithiafulvene derivatives is extended.[6a,b,9e,f,12] Similarly to the model compound **3**, no sign for the dimerization of dithiafulvene unit of **2** was obtained during cyclic voltammetry. This fact showed the high stability of **2** against the oxidation, resulting in no inter- and/or intramolecular dimerization of the dithiafulvene unit.

TCNQ Complex. Polymer **2** formed a CT complex with TCNQ in DMSO similar to the π-conjugated poly(dithiafulvene)s previously reported.[6a,c] The obtained CT complex was soluble in DMSO, DMF, acetonitrile, and acetone and partially soluble in THF. The ratio of dithiafulvene unit to TCNQ in the CT complex was determined by ^1H NMR spectrum of the sample. The ^1H NMR spectrum after an excess amount of TCNQ was added to the DMSO-d_6 solution of **2** showed a broad peak around aromatic region assignable to the protons of dithiafulvene unit of **2** and TCNQ. The reason for these broad signals might be due to the complex having paramagnetic species. The peaks for unreacted TCNQ hardly appeared in the ^1H NMR spectrum due to its limited solubility in DMSO. Comparison of the intensity of the absorption of the aromatic region with that of the ferrocenyl region showed the complex containing about 1:1 ratio of the dithiafulvene unit to TCNQ. The UV−vis absorption of the CT complex exhibited major maxima at 845, 762, and 745 nm, indicating an anion radical of TCNQ in the sample. The electrical conductivity of the CT complex was 5.0×10^{-6} S/cm at room temperature. After being doped with iodine, polymer **2** showed a conductivity of 3.6×10^{-3} S/cm.

Conclusions

New types of dithiafulvenes of **2** and **3** with appended ferrocenyl substituents were synthesized by cycloaddi-

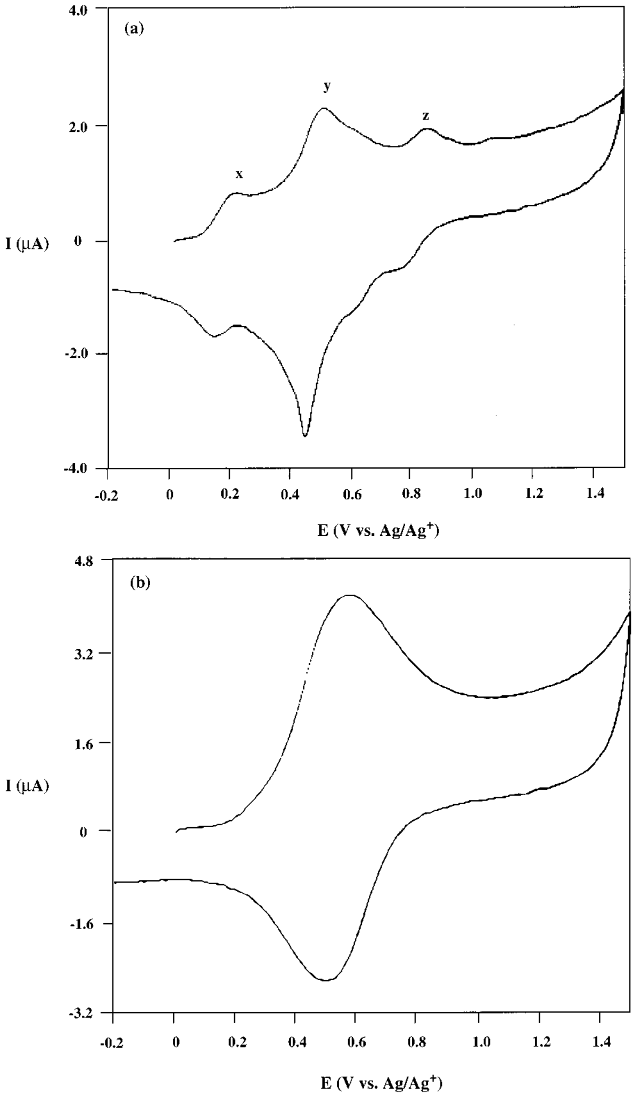
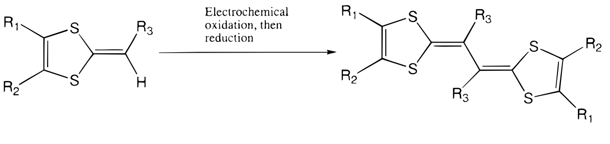


Figure 3. Cyclic voltammograms of (a) **3** and (b) **2**, measured in a CH_2Cl_2 solution of 0.2 M tetrabutylammonium hexafluorophosphate at 300 mV/s.

Scheme 2



tion of aldothioketenes. We succeeded to carry out the polymerization from **1** of which acetylene moieties were protected by trimethylsilane. In contrast to the previous report, the oxidative dimerizations of **2** and **3** were not observed during cyclic voltammetry. These results suggest that ferrocenyl substituents stabilized intermediate radical cations of dithiafulvenes in **2** and **3** for the oxidative dimerization. The cyclic voltammogram of **2** showed only one reversible potential due to effective interaction within the unit structure. The polymer **2** formed the soluble CT complex with TCNQ in DMSO. The conductivity of **2** showed a value of 3.6×10^{-3} S/cm after being doped with iodine.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2. 1,1′-Bis(trimethylsilylethynyl)ferrocene and ethynylferrocene were synthesized according to the literature.[7]

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. IR spectrum was recorded on a Perkin-Elmer 1600 spectrometer. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer. Gel permeation chromatography was carried out on a Shodex K-803 by using chloroform as an eluent after calibration with standard polystyrene samples. Cyclic voltammetry was recorded on a BAS CV-50W electrochemical analyzer. The experiments were carried out in CH_2Cl_2 solution of the compound containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 source meter.

Polymerization. To a solution of 1,1′-bis(trimethylsilylethynyl)ferrocene (189 mg, 0.50 mmol) in THF (1.0 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (0.65 mL, 1.04 mmol) at −78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. The temperature of the mixture was cooled to 0 °C. After addition of powder of sulfur (32 mg, 1.00 mmol), the reaction mixture was stirred for 2 h at 0 °C and then cooled at −55 °C, and water (18 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. The mixture was then poured into a large quantity of *n*-hexane. The obtained precipitate was washed with water to remove inorganic salts. After drying under reduced pressure, a brown-colored polymer **2** was obtained (74 mg, 50% yield). ^{1}H NMR ($CDCl_3$): δ 0.24 (−TMS), 3.8−4.9 (ferrocenyl protons), 5.6 (dithiafulvene), 6.2 (dithiafulvene). IR (KBr, cm^{-1}): 2153, 1560, 1548, 1434, 1252, 1038, 845.

Model Compounds. 2,6-Bis(ferrocenyl)-1,4-dithiafulvene (3). To a solution of ethynylferrocene (210 mg, 1.00 mmol) in THF (1.5 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (0.65 mL, 1.04 mmol) at −78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. The temperature of the mixture was cooled to 0 °C. After addition of powder of sulfur (32 mg, 1.00 mmol), the reaction mixture was stirred for 2 h at 0 °C and then cooled at −55 °C, and water (1 mL) was carefully added. The temperature of the mixture was allowed to rise at room temperature, and the reaction mixture was stirred for 0.5 h. The organic layer was extracted with CH_2Cl_2 and dried over $MgSO_4$. After evaporation of the solvent, the obtained solid was recrystallized from toluene/hexane. (123 mg, 51% yield). ^{1}H NMR (benzene- d_6): δ 3.97−4.23 (m, 14H), 4.31 (m, 2H), 4.42(m, 2H), 5.62 (s, 1H), 6.08 (s, 1H). ^{13}C NMR (benzene-d_6): 67.0, 67.2, 67.4, 68.5, 68.8, 69.0, 69.4, 70.2, 70.5, 78.7, 79.3, 83.9, 84.0, 108.4, 109.0, 110.5, 110.9, 131.5, 131.7, 132.9, 133.1. IR (KBr, cm^{-1}): 1559, 1410, 1242, 1001, 843. Anal. Calcd: C, 59.53; H, 4.16. Found: C, 59.02; H, 4.05.

References and Notes

(1) Reviews: (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Schneider, H.-J.; Dürr, H. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, Germany, 1991.

(2) (a) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goddnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vincent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193. (b) Wanger, R. W.; Brown, P. A.; Johnson, T. E.; Lindsey, J. S. *J. Chem. Soc., Chem. Commun.* **1991**, 1463. (c) Blauch, D. N.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 3323.

(3) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: Weinheim, Germany, 1995.

(4) (a) Ueno, Y.; Sano, H.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1980**, 28. (b) Moore, A. J.; Skabara, P. J.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K.; Daley, S. T. A. K. *J. Chem. Soc., Chem. Commun.* **1993**, 417. (c)Wilkes, S. B.; Butler, I. R.; Underhill, A. E.; Hursthouse, M. B.; Hibbs, D. E.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1995**, 897. (d) Moore, A. J.; Bryce, M. R.; Skabara, P. J.; Batsanov,

A. S.; Goldenberg, L. M.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3443. (e) Lee, H.-J.; Noh, D.-Y.; Underhill, A. E.; Lee, C.-S. *J. Mater. Chem*. **1999**, *9*, 2359.

(5) (a) Adam, M.; Müllen, K. *Adv. Mater*. **1994**, *6*, 439. (b) Bryce, M. R. *J. Mater. Chem*. **1995**, *5*, 1481. (c) Roncali, J. *J. Mater. Chem*. **1997**, *7*, 2307. (d) Frenzel, S.; Arndt, S.; Gregorious, M. R.; Müllen, K. *J. Mater. Chem*. **1995**, *5*, 1529. (e) Yamamoto, T.; Shimizu, T. *J. Mater. Chem*. **1997**, *7*, 1967.

(6) (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.

(7) Doisneau, G.; Balavoine, G.; Fillbeen-Khan, T.*J. Organomet. Chem*. **1992**, *425*, 113.

(8) (a) Raap, R. *Can. J. Chem*. **1968**, *46*, 2251. (b) Sukhai, R. S.; de Jong, R.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 368. (c) Harris, S. J.; Walton, D. R. M. *J. Organomet. Chem*. **1977**, *127*, C1. (d) Sukhai, R. S.; de Jong, R.; Brandsma, L. *Synthesis* **1977**, 888. (e) Sukhai, R. S.; Meijer, J. Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 179.

(9) (a) Togni, A.; Hobi, M.; Rihs, G.; Albinati, A.; Zanello, P.; Zech, D.; Keller, H. *Organometallics* **1994**, *13*, 1224. (b) Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 0, 5396.

(10) (a) Kirmse, W.; Horner, L. *Leibigs Ann. Chem*. **1958**, *614*, 4. (b) Cava, M. P.; Lakshmikantham, M. V. *J. Hetrocycl. Chem*. **1980**, *17*, S39. (c) Ohta, A.; Yamashita, Y. *J. Chem. Soc., Chem. Commun*. **1995**, 1761. (d) Benahmed-Gasmi, A.; Frére, P.; Roncali, J.; Elandaloussi, E.; Orduna, J.; Garin, J.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.* **1995**, *36*, 2983. (e) Lorcy, D.; Carlier, R.; Robert, A.; Tallec, A.; Lemaguerés, P.; Ouahab, L. *J. Org. Chem*. **1995**, *60*, 2443. (f) Hapiot, P.; Lorcy, D.; Tallec, A.; Carlier, R.; Robert, A. *J. Phys. Chem*. **1996**, *100*, 14823. (g) Ohta, A.; Yamashita, Y. *Heterocycles* **1995**, *40*, 123. (h) Ohta, A.; Yamashita, Y. *Heterocycles* **1997**, *44*, 263.

(11) Cais, M. *Organomet. Chem. Rev*. **1966**, *1*, 435.

(12) (a) Hansen, T. K.; Becher, *J. Adv. Mater*. **1993**, *5*, 288. (b) Moore, A. J.; Bryce, M. R. *Tetrahedron Lett*. **1992**, *13*, 1224.

MA0004054