Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Nishide, Hiroyuki , Yoshioka, Naoki , Saitoh, Yukoh , Gotoh, Ritsuko , Miyakawa, Takeshi and Tsuchida, Eishun(1992) 'Synthesis and Magnetic Property of Polyacetylene Bearing πConjugated Bis(Diphenylene)Phenylallyl Radical', Journal of Macromolecular Science, Part A, 29: 9, 775 — 786

To link to this Article: DOI: 10.1080/10601329208054115

URL: http://dx.doi.org/10.1080/10601329208054115

J.M.S.—PURE APPL. CHEM., A29(9), pp. 775–786 (1992)

SYNTHESIS AND MAGNETIC PROPERTY OF POLYACETYLENE BEARING π-CONJUGATED BIS(DIPHENYLENE)PHENYLALLYL RADICAL†

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ABSTRACT

m- and *p*-Bis(diphenylene)propenylphenylacetylene (***m***-, ***p*-8**) were synthesized and polymerized with WCl_6, $MoCl_5$, and Rh catalyst, yielding solvent-soluble poly(phenylacetylene)s bearing a π-conjugated bis(diphenylene)propenyl groups (***m***-, ***p*-7a**). The polymers gave their polyanion derivatives, which were electrolytically and chemically oxidized to yield the corresponding polyradicals (***m***-, ***p*-7b**). The polyradicals were chemically very stable due to the resonance stabilization of an unpaired electron whose spin concentration could be increased up to ca. 2×10^{23} spins per molar monomer unit. ESR spectroscopy suggested an antiferromagnetic interaction between unpaired electrons.

INTRODUCTION

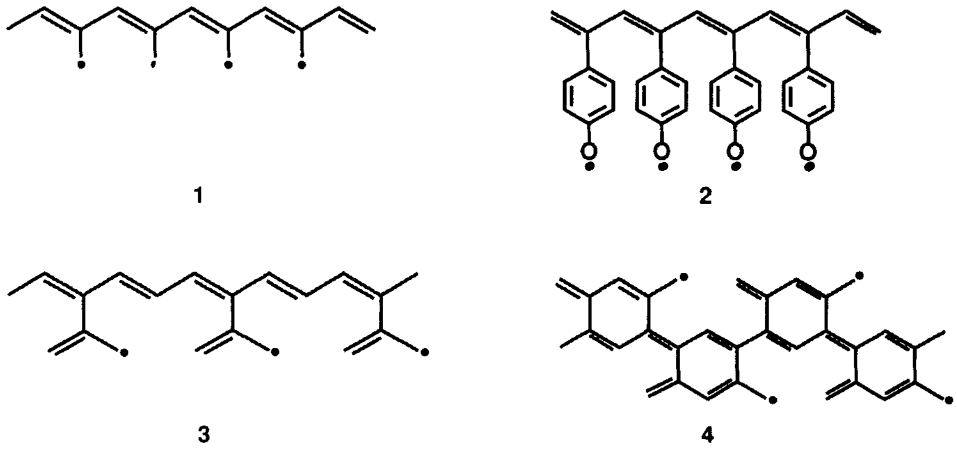
Stable polyradicals or polymer-bound radicals with various chemical structures have been synthesized, and their physicochemical and spectroscopic properties, redox behaviors, and radical reaction have been described [1]. Some of them were utilized as spin probes of polymers [2] and as nonfugitive antioxidants [3]. Much interest has recently been paid to the magnetic properties of organic polymers,

†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

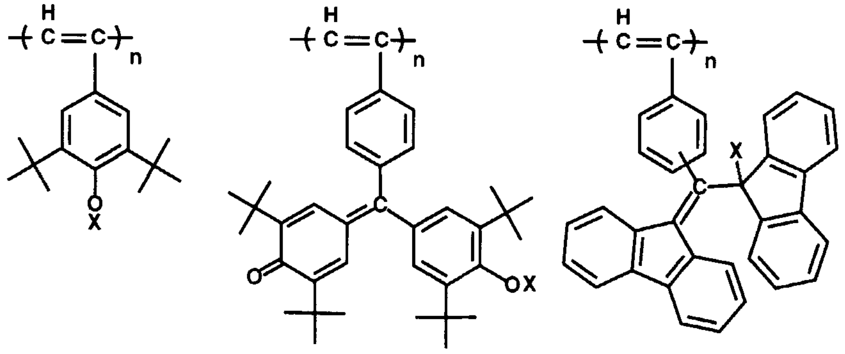
and the synthesis of new polyradicals is being spurred by the hope of discovering cooperative magnetic phenomena [4–11]. While magnetic interaction between unpaired electrons is governed by mutual arrangement in a crystal lattice of low molecular organic radicals, the accumulation of a great number of unpaired electrons in one molecule of a polyradical is expected to cause spin conduction through space and/or chemical bonds. Polyradicals are one of the key compounds in the construction of molecular-based magnetic materials [12–15].

Hypothetical polymers have been proposed to realize parallel (ferromagnetic) spin alignment, and their electronic structures have been estimated by computational chemistry (Scheme 1) [16–18]. These model polymers can be classified into two categories: delocalized spin model [16, 17] and localized spin model [18]. For polyradicals **1** and **2**, unpaired electrons formed in the side-chain groups delocalize over the whole molecule and their spins are ferromagnetically aligned [16]. On the other hand, unpaired electrons are localized within the side-chain allyl moiety for polyradicals **3** and **4** and interact indirectly. The interaction is explained by a spin polarization mechanism through π-conjugated main-chain bonds, which corresponds to a superexchange interaction in inorganic magnetic compounds [18]. There are only a few papers [4–9] on the syntheses of polyradical polymers bearing π-conjugated electronic structures because of the difficulties in monomer syntheses and polymerization procedures.

We recently synthesized polyradicals **5b** [4] and **6b** [5] (Scheme 2). They possess a π-conjugated polyene backbone which allows spin conduction through delocalization and/or polarization of the unpaired electrons. While the chemical structure of **5b** is equivalent to that of **2** and the unpaired electrons in **5b** were almost delocalized along the polyacetylene main chain, a long-range magnetic ordering was not observed, probably because segmentation of the conjugated main chain caused by quinoid structure formation [6–8] and magnetic interaction between unpaired electrons resulted in antiferromagnetic coupling. On the other hand, unpaired electrons were localized within the side-chain galvinoxyl unit in **6b**, and the paramagnetic state was predominant up to 50 mol% in spin concentration. At the higher



SCHEME 1.



5

6

a:X=H
b:X=•
c:X=⊖

m-, p-7

SCHEME 2.

spin concentration, intrachain exchange narrowing and interchain dipole broadening were observed in the ESR spectra of **6b** [5, 8]. In any case, magnetic interaction between the unpaired electrons was strongly influenced by the chemical structure of side-chain radical moieties.

This paper describes the synthesis and physicochemical properties of stable polyacetylene radicals *m*-, *p*-**7b** bearing the bis(diphenylene)phenylallyl radical, which is the most stable hydrocarbon radical known [19], in connection with the magnetic interaction between polymer-bound radical groups.

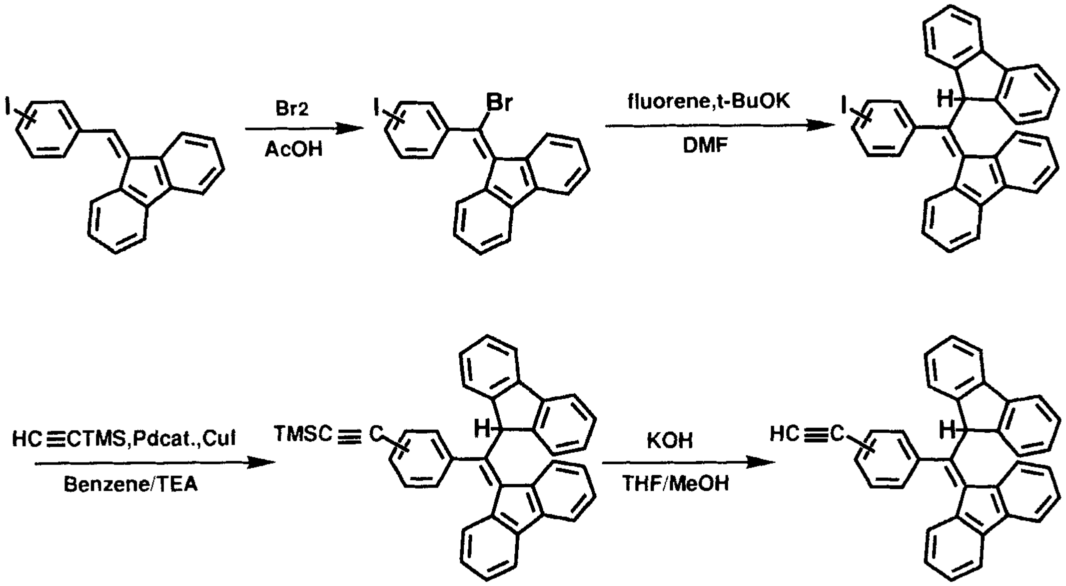
RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization

α,γ-Bisdiphenylene-β-phenylallyl is one of the most stable hydrocarbon radicals, and, in contrast to other carbon-centered radicals, it remains monomeric even in a concentrated solution and chemically inert to oxygen in the solid state [19]. The synthesis of the monomers *m*-, *p*-**8** is presented in Scheme 3. They were synthesized by a palladium coupling reaction [20] between an aromatic iodide and trimethylsilylacetylene, followed by desilylation with methanolic KOH. This coupling reaction did not proceed when aromatic bromides were used instead of iodides.

Substituted acetylenes are known to be polymerized with chlorides of Group 5 or 6 transition metals [21] or Rh complexes [22], and to yield poly(phenylacetylene)s with high molecular weights. Table 1 lists results for *m*-, *p*-**8** polymerization. While *p*-**8** was polymerized with WCl_6, $MoCl_5$, and $Rh[(C_8H_{12})(P(C_6H_5)_3)_2]PF_6$, *m*-isomer *m*-**8** was not polymerized with the Rh catalyst, probably because of steric hindrance of the bulky substituent. Both *m*- and *p*-**8** were effectively polymerized by WCl_6 to give polymers with an average molecular weight of 2-3 × 10^4.

The polymerization proceeded very slowly (Fig. 1). The polymer yield for *p*-**7** peaked at ca. 10 mol% after 24 h, suggesting that the propagation species is unsta-



m-,*p*-**8**

SCHEME 3.

ble. The yield for *m*-**8** continued to increase after 72 h, suggesting a longer lifetime of propagation for the *m*-isomer compared with the *p*-isomer; the steric effect of the *m*-isomer probably prevents backbiting and intrachain cyclization reactions [23]. Under the same conditions, unsubstituted phenylacetylene was quantitatively converted to polymer within 48 h. The slow polymerization of monomer **8** is explained by steric hindrance of the bulky substituents in the propagation step.

TABLE 1. Polymerization of Monomers *m*-, *p*-**8**[a]

Monomer	Catalyst	Solvent	Yield, %	$\overline{M}_n \times 10^4$	$\overline{M}_w/\overline{M}_n$
m-**8**	WCl_6	Benzene	11	1.7	2.6
	$MoCl_5$	Benzene	4	0.5	2.0
	Rh complex[b]	THF	0	–	–
p-**8**	WCl_6	Benzene	9	2.0	2.5
	$MoCl_5$	Benzene	5	0.5	1.5
	Rh complex[b]	THF	4	0.3	2.1
PA[c]	WCl_6	Benzene	100	1.8	2.8

[a] Conditions: $[\text{monomer}]_0 = 0.1$ *M*, [catalyst] = 50 m*M*, 35°C. Polymerization time: 72 h.

[b] $Rh[(C_8H_{12})(P(C_6H_5)_3)_2]PF_6$.

[c] Phenylacetylene.

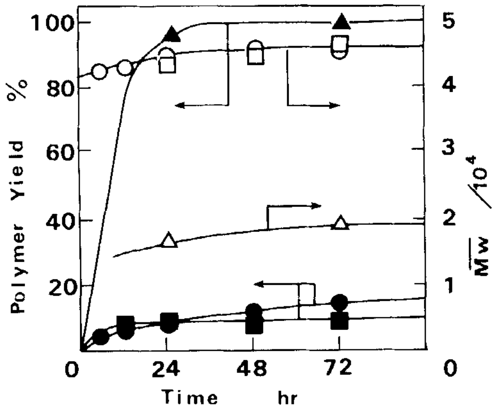


FIG. 1. Time course of the polymerization of *m*-, *p*-**8**, and phenylacetylene (PA) by WCl_6: (■, □) *p*-**8**; (●, ○) *m*-**8**; (▲, △) PA (in benzene, 35°C, $[\text{monomer}]_0 = 0.1$ *M*, [catalyst] = 50 m*M*).

Structural Analysis of Polymers

IR spectra of polymers *m*-, *p*-**7** showed complete disappearance of the stretching vibration of the C—C bond and C—H bond characteristic of monomer **8**. Other absorptions attributed to the bisdiphenylene residue were unchanged. These data indicate that the polymerization proceeds through the acetylene group. The polymers were soluble in common solvents such as benzene, THF, halogenated hydrocarbons, and alcohols. NMR data of the polymers also supported the polymer structure of **7**.

Polymer **7** was a yellow powder, in contrast to the deep red color of **5a** [4] and **6a** [5]. Every polymer possessed a maximum absorption at 225 nm in the UV region. A few shoulders were observed at longer wavelengths, and absorptions continued to ca. 550 nm, which is almost comparable with that of **5a**. The increase and decrease in π-conjugation of polyphenylacetylene derivatives are influenced by the steric effect of the substituent's side-chain phenyl ring. Steric repulsion between the very bulky bisdiphenylene substituents in **7a** may lead to a decrease in the π-conjugation length compared to that of poly(phenylacetylene).

The absence of a developed π-conjugation along the polyene chain was also supported by the ionization threshold estimated by ultraviolet photoelectron spectroscopy [8]. The ionization threshold of *p*-**7a**, 6.2 eV, was higher than those of **5a** (5.5 eV) and poly(phenylacetylene) (5.7 eV).

Formation of Polyanion and Polyradical

Polymers *m*-, *p*-**7a** were converted to the corresponding polyanions **7c** and polyradicals **7b** when their solutions were treated with a strong alkali and an oxidizing reagent, respectively (Table 2). Treatment of the methanolic solution of **7a** with excess KOH yielded the dark blue polyanion **7c**. Careful oxidation of polyanion **7c** with a small excess of $K_3Fe(CN)_6$ under an oxygen-free atmosphere gave a deep brownish solution. The broad absorption at ca. 495 nm increased with enhancement of the ESR signal intensity.

TABLE 2. Absorption Maxima and Redox Potential of Polymers *m*-, *p*-7

Sample	λ_{max} in nm (log ϵ) Anion	λ_{max} in nm (log ϵ) Radical	E^0 $(V)^a$ $(R^\cdot/R^-)$
m-7	612 (4.0)	464 (3.7)	−0.20
p-7	615 (4.3)	492 (3.9)	−0.27
[b]	593 (4.6)	489 (4.6)	−0.22
[c]	601 (7.4)	470 (5.6)	+0.24

[a] Redox potential vs Ag/AgCl in DMSO/tetrabutyl ammonium perchlorate.

[b] Bis(diphenylene)phenylpropene.

[c] Phenylhydrogalvinoxyl.

Polyradical **7b** was also generated by electrochemical oxidation. Figure 2 shows the cyclic voltammogram of *p*-**7c**. The oxidation peak is observed at ca. −0.2 V; **7c** is more easily oxidized to the polyradical in comparison with the corresponding phenol derivative, such as the phenylgalvinoxyl anion, probably due to the resonance stabilization effect derived from developed π-conjugation over the bis(diphenylene)allyl skeleton. The reduction current for the reduction of **7b** to **7c** was observed by a negative potential sweep and was comparable to that of the oxidation current. This cyclic voltammogram was drawn repeatedly by repeated potential sweeps. These results mean that radical generation is not accompanied with subsequent chemical side-reactions. Redox potentials determined by cyclic voltammetry are also listed in Table 2.

There was no distinct difference between the *m*- and *p*-isomers in spectral change during the polyanion and polyradical formation which was similar to those of low-molecular α,γ-bisdiphenylene-β-phenylallyl [24, 25]. It is suggested that the

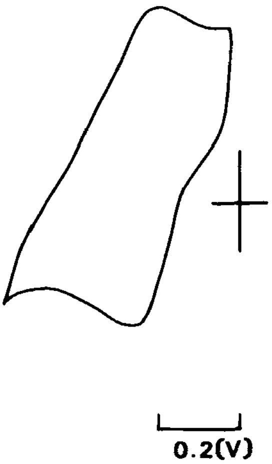


FIG. 2. Cyclic voltammogram of *p*-**7c** in DMSO in the presence of tetrabutylammonium perchlorate (vs Ag/AgCl).

electronic states of the bis(diphenylene)phenylallyl anion and radical are not influenced by the sterically crowded structure along the main chain for **7**.

Magnetic Property of Polyradical

It is reported that the solution ESR spectrum of α,γ-bisdiphenylene-β-phenylallyl gives a complicated hyperfine structure attributed to delocalization of unpaired spin over the bis(diphenylene)allyl moiety [25]. The ESR spectrum of the benzene solution of **7b** showed a broad singlet signal with a g-value of 2.0026. This is probably caused by dipole-dipole interaction derived from the relatively high local spin concentration along the main chain.

The spin concentration of the polyradical can be controlled by oxidative conditions up to ca. 2×10^{23} spins per molar monomer unit for ***p*-7b** and 6×10^{22} for ***m*-7b**. The polyradicals ***m*-**, ***p*-7b** were chemically very stable even in the solution state, and the ESR intensity decrease was less than 10% even after 1 week. This enormous stability of the polyradical **7b** is in contrast to the corresponding low-molecular α,γ-bisdiphenylene-β-phenylallyl with a half life time of ca. 1 h [26].

The magnetic property of polyradical **7b** in the solid state with different spin concentrations was analyzed by the temperature dependency of the relative ESR signal area (I_{ESR}) in the $\Delta m_s = \pm 1$ region. The I_{ESR} of **7b** normalized at 293 K is shown in Fig. 3. If there is no magnetic interaction between unpaired electrons, the temperature dependency of I_{ESR} is linear, obeying Curie's law.

Both ***m*-** and ***p*-7b** with spin concentrations of 9 mol% showed straight lines between 470 and 120 K. Up to 470 K, I_{ESR} was not irreversibly decreased, in contrast to those of **5b** and **6b** whose I_{ESR}'s were irreversibly decreased above ca. 330 K. The bisdiphenylene allyl moiety is also thermally stable. The straight line for **7b** almost coincided with that of low-molecular α,γ-bisdiphenylene-β-phenylallyl. On the other hand, the I_{ESR} of ***p*-7b** with a spin concentration of 28 mol% deviated negatively in the low temperature region, which suggests an antiferromagnetic coupling between localized unpaired spins.

Peak-to-peak linewidth (ΔH_{pp}) of the ESR spectra for ***m*-**, ***p*-7b** with a spin concentration of 9 mol% was ca. 7 G, and it was 3 G for ***p*-7b** with 28 spin mol%. This is attributed to an exchange narrowing derived from the through space electron interaction. For **7b**, effective packing between planar diphenylenephenyl groups leading to electron exchange is easily realized.

The absence of a characteristic visible absorption assigned to a nonfully developed π-conjugation and the relatively high ionization threshold energy mentioned above argue against a magnetic interaction through the polyene main chain. A possible magnetic coupling is attributed to a through space interaction between unpaired electrons delocalized over the bisdiphenylene moiety. Our data do not clearly show whether the through space antiferromagnetic coupling in ***p*-7b** with a spin concentration of 28 mol% is a result of an intra- or interchain interaction or their combination.

EXPERIMENTAL

p-Iodobenzalfluorene

To a solution of 33.0 g (0.2 mol) fluorene in 420 mL ethanol, sodium methoxide (1.46 g, 0.6 mol) was added and stirred. After a solution of *p*-iodobenzaldehyde (46.08 g, 0.2 mol) in 75 mL ethanol was added to the suspension and stirred for 12

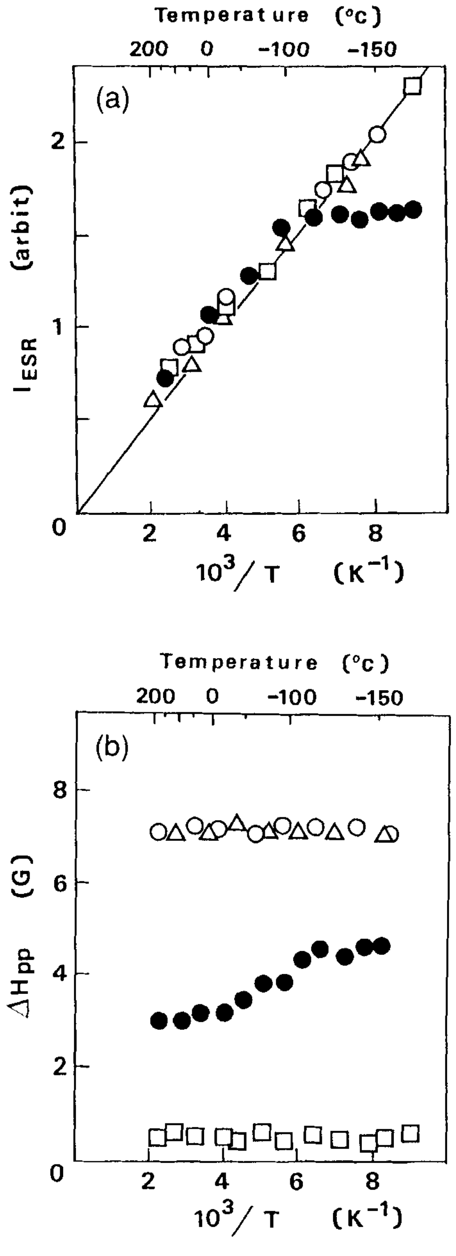


FIG. 3. Temperature dependency of (a) relative ESR signal intensity (I_{ESR}) and (b) peak to peak line width (ΔH_{pp}) of *m*-, *p*-**7b**, and low-molecular analogue (spin concentration in mol%): (○) *p*-**7b**(9); (△) *m*-**7b**(9); (●) *p*-**7b**(28); (□) α,γ-bisdiphenylene-β-phenylallyl(36).

h, it was poured into 5 *N* hydrochloric acid. The yellowish precipitate was filtered, washed with water, and recrystallized from chloroform and ethyl acetate (1:1), affording 51 g *p*-iodobenzalfluorene as a yellow crystal. Yield, 68%; mp, 119.6–120.3°C (Ref. 27, 120–122°C); ^{1}H-NMR ($CDCl_3$, Me_4Si standard): δ8.1–6.6 (m, aromatic, methine); MS: *m/z* 380.0 (M^+).

Analysis. Calculated for $C_{20}H_{13}I$: C, 63.2; H, 3.4%. Found: C, 62.8; H, 3.4%.

m-Iodobenzalfluorene

Sodium amide (0.39 g, 10.0 mmol) and fluorenone (1.51 g, 8.4 mmol) were added to a 200-mL benzene solution of *m*-iodobenzyltriphenylphosphine (4.46 g, 8.2 mmol) under nitrogen, and the mixture was refluxed for 8 h. After evaporation, the mixture was column separated with silica gel (chloroform:hexane = 1:4), and 2.27 g *m*-iodobenzalfluorene was obtained as a yellow crystal. Yield, 73%; mp, 104.6–105.3°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ7.8–6.4 (m, aromatic); MS: *m/z* 380.0 (M^+).

Analysis. Calculated for $C_{20}H_{13}I$: C, 63.2; H, 3.40%. Found: C, 62.8; H, 3.35%.

Iodobenzal-9-bromofluorene

Bromine (5.15 mL, 100 mmol) was added dropwise to *p*-iodobenzalfluorene (38.0 g, 100 mmol) in 500 mL acetic acid, and the mixture was stirred for half an hour. After refluxing for 1 h, the mixture was cooled and the precipitated yellow mass was recrystallized from benzene-hexane, yielding 30 g *p*-iodobenzal-9-bromofluorene. Yield, 66%; mp, 118.0–119.2°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ7.9–6.5 (m, aromatic); MS: *m/z* 457.9 (M^+).

Analysis. Calculated for $C_{20}H_{12}BrI$: C, 52.3; H, 2.6; Br, 17.4; I, 27.6%. Found: C, 52.3; H, 2.6; Br, 17.0; I, 28.0%.

m-Iodobenzal-9-bromofluorene was prepared by a method similar to the *p*-isomer. Yield, 76%; mp, 115.2–116.3°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.0–6.9 (m, aromatic); MS: *m/z* 457.9 (M^+).

Analysis. Found: C, 51.1; H, 2.5%.

Bis(diphenylene)-*p*-iodophenylpropene

To a DMF solution (100 mL) of *p*-iodobenzal-9-bromofluorene (4.58 g, 10 mmol), fluorene (1.82 g, 11 mmol), and potassium-*tert*-butoxide (2.80 g, 25 mmol) were added under nitrogen and the mixture was stirred for 1 h. It was acidified and poured into water. A light brownish precipitate was collected, redissolved in benzene, washed with water, and dried. Recrystallization from benzene-hexane gave 4.10 g bis(diphenylene)-*p*-iodophenylpropene as pale orange crystals. Yield, 75%; mp, 251.1–252.8°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.4–5.8 (m, aromatic); MS: *m/z* 544.0 (M^+).

Analysis. Calculated for $C_{33}H_{21}I$: C, 72.8; H, 4.0; I, 23.3%. Found: C, 72.6; H, 3.9; I, 23.3%.

m-Isomer: yield, 85%; mp, 198.0–199.2°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.5–6.4 (m, aromatic); MS: *m/z* 544.0 (M^+).

Analysis. Found: C, 73.3; H, 3.9%.

Bisdiphenylene(trimethylsilyletynylphenyl)propene

Bisdiphenylene-*p*-iodophenylpropene (5.44 g, 10 mmol) was dissolved in 70 mL benzene and 150 mL triethylamine. Under nitrogen atmosphere, $(Ph_3P)_2PdCl$ (141 mg, 0.20 mmol) and copper iodide (18.7 mg, 0.095 mmol) were added, and after that trimethylsilyl acetylene (2.9 mL, 20 mmol) was added dropwise to the solution. The mixture was stirred for 12 h at 60°C. After filtration of the deposited solid mass, the solution was washed with water and dried. Recrystallization from benzene-hexane afforded 2.55 g bisdiphenylene(*p*-trimethylsilylethynylphenyl)-propene as a light yellow crystal. Yield, 49%; mp, 201.1-202.0°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.5-5.8 (m, 21H, aromatic), 0.1 (s, 9H, $-Si(CH_3)_3$); MS: m/z 514.1 (M^+).

Analysis. Calculated for $C_{38}H_{30}Si$: C, 88.7; H, 5.9; Si, 5.4%. Found: C, 88.5; H, 6.0; Si, 5.2%.

m-Isomer: Yield, 85%; mp, 202.5-204.1°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.5-5.9 (m, 21H, aromatic), 0.1 (s, 9H, $-Si(CH_3)_3$); MS: m/z 514.1 (M^+).

Analysis. Found: C, 87.9; H, 5.5; Si, 5.3%.

Bis(diphenylene)propenylphenylacetylene

Potassium hydroxide (1.12 g, 30 mmol) was added to 5.14 g (10 mmol) bisdiphenylene(*p*-trimethylsilylethynylphenyl)propene in THF (100 mL) under nitrogen. After stirring for 8 h at room temperature, the solution was cautiously acidified using an excess of saturated ammonium chloride. After decoloring the mixture with aluminum oxide, the light yellow solid was recrystallized from benzene-hexane and gave 2.38 g *p*-bis(diphenylene)propenylphenylacetylene as a light yellow crystal. Yield, 54%; mp, 211.1-212.7°C; MS: m/z 442.3 (M^+), ^{1}H-NMR ($CDCl_3$, Me_4Si standard): 2.91 (s, 1H, $\equiv$CH), 5.84-8.37 (m, 21H, aromatic). ^{13}C-NMR: 77.4 ($\equiv$CH), 83.7 ($\equiv$C$-$R). IR (KBr pellet, cm^{-1}): 3300($\nu_{\equiv C-H}$), 2150($\nu_{C\equiv C}$).

Analysis. Calculated for $C_{35}H_{22}$: C, 95.0; H, 5.0%. Found: C, 94.6; H, 5.1%.

m-Isomer: Yield, 28%; mp, 215.9-217.2°C; ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ8.4-5.8 (m, 21H, aromatic), 2.9 (s, 1H, $\equiv$CH). ^{13}C-NMR δ77.0 ($\equiv$CH), 83.4 ($\equiv$C$-$R). MS: m/z 442.5 (M^+).

Analysis. Found: C, 94.8; H, 5.1%.

Poly[*p*-bis(diphenylene)propenylphenylacetylene] (*p*-7a)

Polymerization with Rh Complex

p-Bis(diphenylene)propenylphenylacetylene (0.45 g, 1.0 mmol) was dissolved in THF (10 mL) at 35°C under nitrogen. $Rh[(C_8H_{12})(PPh_3)_2]PF_6$ (8.5 mg, 0.01 mmol) was added and stirred for 72 h, then a little methanol was added to the mixture to stop the reaction. The catalyst was removed by GPC column using THF as a eluent. Yellow polymer was obtained by reprecipitation with benzene-methanol (3:7). ^{1}H-NMR ($CDCl_3$, Me_4Si standard) δ9-5 (broad singlet, aromatic and methine), peaks assignable to the ethynyl group in ^{1}H- and ^{13}C-NMR spectra in monomer had completely disappeared.

Analysis. Calculated for $C_{35}H_{22}$: C, 95.0; H, 5.0%. Found: C, 93.4; H, 5.2%.

Poly[*p*-bis(diphenylene)arylphenylacetylene] (*p*-7b)

Aqueous sodium hydroxide was slowly added to a DMF solution of *p*-bis(diphenylene)propenylphenylacetylene (4.4 mg, 0.01 mmol). After stirring for 15 min, $K_3[Fe(CN)_6]$ (40 mg, 0.1 mmol), which had been dissolved in the least water possible, was added to the mixture. It was poured into water very slowly, and the dark red precipitate of poly[*p*-bis(diphenylene)arylphenylacetylene] was collected.

Measurements

The molecular weight of the polymer was estimated by GPC (polystyrene gel column, eluent THF, polystyrene calibration). Cyclic voltammometry was carried out in dimethylsulfoxide using tetrabutylammonium perchlorate as the supporting electrolyte with a Nikko Keisoku DPG-3 potentiogalvanostat. IR and UV/vis spectra were measured with a JASCO IR-810 and a Shimadzu UV-240 spectrometer, respectively. ESR spectra were recorded using a JEOL JES-2XG ESR spectrometer with 100 kHz field modulation. The spin concentration of the sample was determined by careful integration of the ESR signal area of the benzene solution of 2,2,6,6-tetramethyl-1-piperindine oxide(TEMPO) with a known spin concentration (98%, Aldrich).

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 02650670, No. 02953052, and Priority Area of "Molecular Magnetism" No. 04242104) from the Ministry of Education, Science and Culture, Japan.

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Received January 8, 1992
Revision received February 25, 1992