Found: C, 31.76; H 2.06; S, 7.95. X-ray quality single crystals were obtained by slowly evaporating a solution of **12** in CH_3CN in an open air container.

Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-3,5-epoxy-1,4-cyclohexadiene (13). Furan (140 mg) gave by the above procedure 0.58 g (73%) of **13**: mp 118–119 °C dec; IR (CCl_4, cm^{-1}) 3093, 3065, 1566, 1472, 1445, 1279, 1242, 1168, 1021, 885, 868; ^1H NMR (δ, CD_3CN) 5.62 (br s, 2 H, H-3 and H-6), 6.75 (br s, 2 H, H-4 and H-5), 7.62 (m, 2 H, Ph), 7.81 (m, 1 H, Ph), 8.05 (m, 2 H, Ph); ^{19}F NMR (δ, CD_3CN) −77.85 (s, CF_3); ^{13}C NMR (δ, CD_3CN) 90.8 (C-3 and C-6), 121.2 (quart, J = 319 Hz, CF_3), 112.4, 133.6, 134.5, 137.1 (Ph), 139.2 (C-1 and C-2), 142.7 (C-4 and C-5). Anal. Calcd for $C_{20}H_{14}F_6I_2O_7S_2$: C, 30.09; H, 1.77; S, 8.03. Found: C, 30.22; H, 1.78; S, 8.08.

2,3-Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]-1,4-epoxy-1,4-diphenylnapthalene (14). Benzofuran **11** (540 mg) gave by the above procedure 0.47 g (47%) of **14**: mp 93–95 °C dec; IR (CCl_4, cm^{-1}) 3082, 3055, 1469, 1455, 1445, 1294, 1216, 1163, 1019, 987, 902; ^1H NMR (δ, CD_3CN) 7.05–7.15 (m, 4 H, C_6H_4), 7.3 (m, 10 H, 2Ph), 7.6–7.9 (m, 10 H, $2PhI^+$); ^{19}F NMR (δ, CD_3CN) −76.52 (s, CF_3); ^{13}C NMR (δ, CD_3CN) 98.5 (C-1 and C-4), 121.0 (quart, J = 319 Hz, CF_3), 113.8, 123.8, 127.8, 128.4, 130.5, 131.6, 131.9, 133.5, 134.4, 136.8 (Ar), 145.7 (C-2 and C-3), 150.1 (C-5 and C-10); mass spectrum (FAB) m/z (%) 499 (25), $[M + H^+ - 2TfO^- - PhI]^+$; 295 (100), $[M + H^+ - 2TfO^- - 2PhI]^+$; HRMS for $C_{28}H_{19}IO$ $[M + H^+ - 2TfO^- - PhI]^+$ calcd 499.05581, found 499.05581.

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Supplementary Material Available: Tables of X-ray crystal and structural data for compounds **8** and **12** (35 pages); tables of observed and calculated structure factors for **8** and **12** (28 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Novel *p*-Terphenoquinone Analogues Involving a Central Dihydrothiophenediylidene Structure

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Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan, Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai 980, Japan, and Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan. Received August 15, 1990

Abstract: The title quinones, 2,5-bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene and its tetraalkyl derivatives, were synthesized via 2-(4-alkoxyphenyl)thiophene and 2,5-bis(4-alkoxyphenyl)thiophene conveniently prepared by using palladium(0)-catalyzed cross coupling reaction of 4-alkoxyaryl halides and thienylzinc chloride. The ground-state structures and redox properties of these quinones were fully characterized based on spectroscopic data (IR, ^1H NMR, ^{13}C NMR, UV–vis, and MS), X-ray analysis, cyclic voltammetry, CNDO/2 calculation, and EPR spectroscopic investigation. These quinones show an intense absorption maximum in the region of 531–558 nm of their electronic spectra. Despite their three-ring system, these quinones exist in a coplanar conformation in the solid state in which the terminal six-membered rings incline 9.1° and 11.1°, respectively, from the central five-membered ring, and the twisting angle between the mean planes of the two terminal rings is 1.8°. Rotation about the intercyclic bonds does not take place at ordinary temperatures in solution. Noticeably, these quinones exhibit a half-wave oxidation potential (E_1^{ox} value) of 1.26–1.46 V along with half-wave reduction potentials (E_1^{red} value) of −0.11 to −0.52 V and (E_2^{red} value) of −0.20 to −0.67 V vs SCE, so that they have been proven to be a new type of quinones exhibiting an amphoteric redox property undergoing two-stage one-electron reduction up to the dianions and one-electron oxidation up to the radical cations. The reduction and oxidation potentials of these quinones are in good correspondence with the calculated energy levels of the HOMO and the LUMO. Decrease in the HOMO–LUMO gap is mainly ascribed to the destabilized HOMO lying at a higher level by 0.97 eV than that of diphenoquinone. Both the cation and anion radicals were generated by the electrochemical reduction and oxidation of these amphoteric quinones and have been definitely characterized by EPR spectroscopy.

Benzoquinonoid compounds have hitherto played a most important role in the development of organic redox chemistry due to their multistage redox properties[1,2] and have attracted a great deal of attention currently not only from the scientific but also from industrial points of view since redox systems could be used for functional materials with high technological potential such as electroconductors,[3] optoelectronic display devices,[4] catalysts for electron-transfer reaction,[5] artificial photosynthetic systems,[6] and so on. Therefore, the molecular design and synthesis of novel quinonoid compounds having a different skeletal structure from the traditional ones and having unique redox properties may provide an impetus for the versatile and ensuing development of material science and material technology of topical interest.

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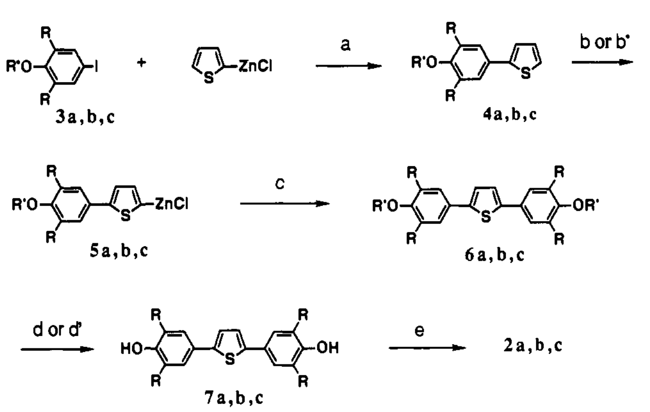
Scheme I[a]

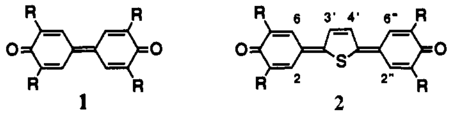


a: R=H, R'=Me, b: R=R'=Me, c: R=*t*-Bu, R'=Me$_3$Si

[a] Reagents and conditions: (a) $Cl_2Pd(PPh_3)_2$, THF, *i*-Bu_2AlH, hexane, room temperature, 1 h, 78.4% (**4a**), 75% (**4b**), 85% (**4c**); (b) (**4a,b** → **5a,b**) *n*-BuLi, ether, 0 °C, 1 h; $ZnCl_2$, THF; (d′) (**4c** → **5c**) *t*-BuLi, hexane, −20 °C, 1 h; $ZnCl_2$, THF; (c) $Cl_2Pd(PPh_3)_2$, THF, *i*-Bu_2AlH, hexane, room temperature 10 min; **3a–c**, THF, room temperature, 1 h, 47% (**6a**), 87% (**6b**), 67% (**6c**); (d) (**6a,b** → **7a,b**) BBr_3, CH_2Cl_2, reflux 3 h, 99.5% (**7a**), room temperature, 4 h, 99% (**7b**); (d′) (**6c** → **7c**), 1 M HCl, MeCN, room temperature, 5 h, 83% (**7c**); (e) $K_3[Fe(CN)_6]$, CH_2Cl_2 (**7a,b** → **2a,b**), benzene (**7c** → **2c**), 0.1 M aqueous KOH, room temperature, 1 min, 61% (**2a**); 5 min, 91% (**2b**); 4 h, 91% (**2c**).

An important concept in the design of novel quinones with multistage redox properties is to stabilize thermodynamically and kinetically the radical ions and to maintain good coplanar conformation both in the neutral and in the ionic states.[2,7] Moreover, the quinones exhibiting an intense absorption maximum in the visible or near-infrared region in their electronic spectra and/or showing reversible and remarkable color change on application and removal of an electric voltage or current would be more favorable since such quinones have high potential for use in electrochromic display devices or in optical storage media[8] or in other materials with extended performances. Of course such quinones should be stable and synthesized conveniently starting from easily accessible basic compounds. Indeed, hitherto unknown *p*-terphenoquinones might be candidates for such compounds; however, they would be unstable since the quinonoid structure is formed by missing the aromaticity of three benzenoid rings of the corresponding reduced form, and the molecular coplanarity could hardly be maintained due to the nonbonded atom interaction between the biphenylic ortho hydrogen atoms. Apparently, the quinones well investigated and widely used so far have been limited to the dioxo derivatives of aromatic hydrocarbons.

With this in mind, we have here designed a *p*-terphenoquinone type of compounds **2** involving a central heterocyclic quinonoid ring as a key skeletal component. Coplanarity would be expected in **2** since nonbonded atom interaction between the biphenylic ortho hydrogen atoms (H-6 and H-3′; H-6″ and H-4′) should be significantly diminished in **2** compared with diphenoquinone **1** or terphenoquinone on considering the larger exocyclic bond angles of dihydrothiophenediylidene (thienoquinonoid) than those of benzoquinonoid ring systems. Furthermore, **2** is expected to provide a stable radical ion by considering the conjugation between the carbonyl groups and the central sulfur atom[9,10] and by the aromaticity of the thiophene ring created upon the redox reaction. We have already designed and synthesized a variety of cyclic cross-conjugated compounds extended with a thienoquinonoid structure[11-13] and have clarified that the introduction of such a moiety as an integral conjugative component is one of the most effective strategies to stabilize both the closed-shell and open-shell species with coplanar conformation.[11,13]



a: R=H, b: R=Me, c: R=*t*-Bu

To this end, we report here the synthesis of novel quinones **2a–c** and their structural and electrochemical properties. Quite interestingly, these quinones have proven to have amphoteric redox properties; namely, they are both reducible and oxidizable through a multistage electron-transfer fashion. A series of benzoquinones has been most thoroughly investigated in electrochemistry, but there has been no report referring to their amphoteric property except only particular examples of tetrakis(dimethylamino)-*p*-benzoquinone and others.[14] This is also true for the extended quinones such as diphenoquinones, stilbene quinones, and others[1a] including bis(4-oxo-2,5-cyclohexadien-1-ylidene)ethene[15] and tetrakis(4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutane[16] derivatives. Thus, quinones **2** provide a new mode of amphoteric redox system constructed from an extended *p*-benzoquinonoid structure.

Results and Discussion

Synthesis. The synthetic procedure for quinones **2a–c** is outlined in Scheme I. The Pd(0)-catalyzed aryl–heteroaryl cross-coupling reaction[17] has now been proven to be a convenient method for the synthesis of 2-(alkoxyphenyl)thiophenes **4** and 2,5-bis(alkoxyphenyl)thiophenes **6**, key synthetic precursors of quinones **2**. Thus, thienylzinc chloride, obtained by the reaction of thienyllithium with zinc chloride, reacted readily with iodoanisole **3a** in the presence of 5 mol % of $Pd(PPh_3)_4$ generated in situ by treating $Cl_2Pd(PPh_3)_2$ with *i*-Bu_2AlH to give **4a** in 78% yield. Organozinc chloride **5a** prepared from lithiated **4a** and zinc chloride was allowed to react again with **3a** to produce **6a** in 47% yield by the Pd(0)-catalyzed cross-coupling. Demethylation of **6a** with boron tribromide yielded quantitatively bisphenol **7a** which was subsequently oxidized with potassium ferricyanide dissolved in 0.1 M KOH solution to afford **2a** in 61% yield as black crystals. This is the first synthesis and isolation in solid state of a terpheno-

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Table I. Selected Spectroscopic Parameters of **2a–c** and Diphenoquinones **1a–c**

	^{1}H NMR chemical shifts[a] δ, ppm					^{13}C NMR chemical shifts[b] δ, ppm				IR[c]	UV–vis[d]
compd	2,2″	6,6″	3,3″	5,5″	3′,4′	4,4″	2,2″	6,6″	3′,4′	ν_{CO}, cm^{-1}	λ_{max}, nm (log ε)
2a	7.54	7.67	6.61	6.55	7.78	*e*				1614	531 (4.57)
2b	7.32	7.45			7.69	186.6	131.4	128.8	134.4	1589	546 (4.87)
2c	7.28	7.43			7.69	185.8	128.0	125.4	133.9	1591	558 (4.90)
1a	7.91	7.91	6.63	6.63						1630	395 (4.80)[f]
1b	7.74	7.74				187.3	129.7	129.7		1589	421 (4.86)[f]
1c	7.71	7.71				186.5	126.2	126.2		1602	420 (4.85)[f]

[a] In CDCl$_3$, **2a** in 400 MHz, **2b** and **2c** in 200 MHz: The chemical shift assignment of H-6,6″ and H-2,2″ was confirmed through the NOE enhancement of the signal of H-6,6″ on decoupling of H-3′,4′. [b] In CDCl$_3$, 50.3 MHz: The assignment was confirmed through the two-dimensional ^{13}C NMR spectroscopic method. [c] In KBr disk: The most intense band in the region 1700–1500 cm^{-1}. Similar IR bands occurred in CHCl$_3$. [d] In MeCN. [e] Not determined due to poor solubility. [f] In EtOH.

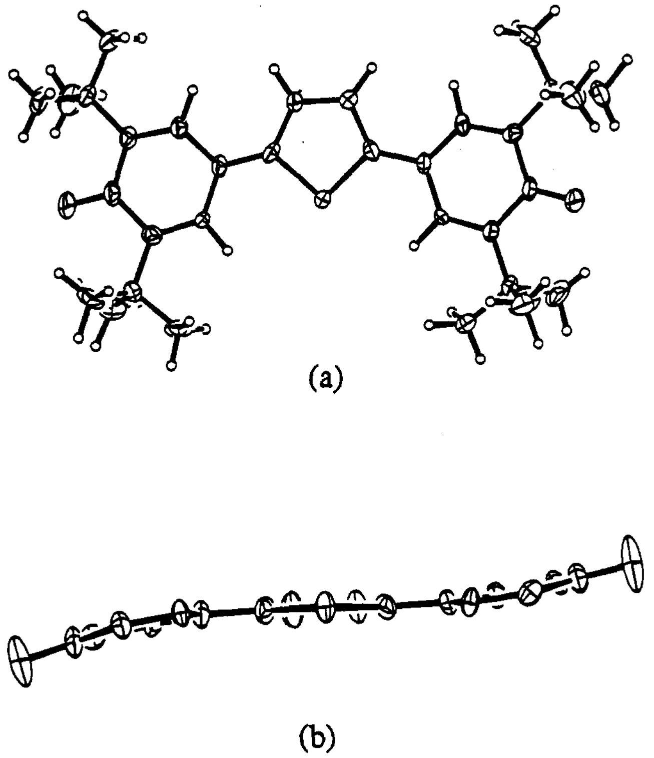

Figure 1. ORTEP drawings of **2c**: (a) top view and (b) side view (*tert*-butyl groups have been omitted for clarity).

quinone analogue where the central cyclohexadienylidene is replaced with a dihydrothiophenediylidene moiety. The quinone **2a** is stable in the solid state for about 1 month at room temperature and for a longer period in a refrigerator but thereafter degenerates gradually at room temperature and decomposes more quickly on a silica gel column.

Tetramethyl derivative **2b** was also prepared as greenish-black crystals in a better overall yield by a similar procedure by using 2,6-dimethyl-4-iodoanisole **3b**[18] as an arylhalide partner. The synthesis of tetra-*tert*-butyl derivative **2c** was achieved by a route similar to **2a** and **2b**, but the phenolic hydroxy groups were protected as trimethylsilyl ether, since the corresponding methyl ether was difficult to cleave with acid or Lewis acid.

Iodide **3c** gave **4c** in an excellent yield, whereas the corresponding bromide gave the same product only in 14% yield. Compound **6c** was readily desilylated with 1 M HCl in aqueous MeCN to give **7c** in 83% yield, which was then oxidized with potassium ferricyanide to quinone **2c**[19] as shining green needles or black fine crystals, in 91% yield. Quinones **2b** and **2c** are stable in the solid state at room temperature[20] and in solution in common organic solvents or on contact with silica gel. Quinones **2a–c** were reduced quantitatively with Na$_2$S$_2$O$_4$ to **7a–c**, respectively.

Table II. Selected Bond Distances and Angles for **2c**

Bond Distances (Å)

atom 1	atom 2	1/Å	atom 1	atom 2	1/Å
S1	C2′	1.766 (9)	S1	C5′	1.762 (9)
O1	C4	1.211 (14)	O1″	C4″	1.225 (14)
C1	C2	1.442 (13)	C1	C6	1.434 (14)
C1	C2′	1.355 (14)	C2	C3	1.331 (14)
C3	C4	1.496 (14)	C4	C5	1.482 (14)
C5	C6	1.322 (14)	C2′	C3′	1.403 (14)
C3′	C4′	1.364 (14)	C4′	C5′	1.416 (14)
C5′	C1″	1.391 (14)	C1″	C2″	1.438 (13)
C1″	C6″	1.399 (14)	C2″	C3″	1.337 (13)
C3″	C4″	1.486 (14)	C4″	C5″	1.482 (14)
C5″	C6″	1.333 (14)			

Bond Angles (deg)

atom 1	atom 2	atom 3	angles	atom 1	atom 2	atom 3	angles
C2′	S1	C5′	92.3 (5)	C2	C1	C6	115.3 (8)
C2	C1	C2′	122.8 (9)	C6	C1	C2′	121.9 (9)
C1	C2	C3	124.0 (9)	C2	C3	C4	118.3 (9)
O1	C4	C3	120.8 (10)	O1	C4	C5	120.8 (10)
C3	C4	C5	118.4 (9)	C4	C5	C6	117.4 (9)
C1	C6	C5	126.0 (9)	S1	C2′	C1	122.4 (8)
S1	C2′	C3′	108.1 (7)	C1	C2′	C3′	129.3 (9)
C2′	C3′	C4′	116.8 (9)	C3′	C4′	C5′	112.7 (9)
S1	C5′	C4′	110.0 (7)	S1	C5′	C1″	121.6 (7)
C4′	C5′	C1″	128.4 (9)	C5′	C1″	C2″	121.6 (9)
C5′	C1″	C6″	121.7 (9)	C2″	C1″	C6″	116.6 (9)
C1″	C2″	C3″	123.2 (8)	C2″	C3″	C4″	118.4 (9)
O1″	C4″	C3″	120.8 (10)	O1″	C4″	C5″	121.2 (10)
C3″	C4″	C5″	118.0 (9)	C4″	C5″	C6″	117.4 (9)
C1″	C6″	C5″	125.5 (9)				

Structural Identification. The selected spectroscopic data of **2a–c** are listed in Table I together with those of **1a–c** for reference. The ^{1}H NMR chemical shifts of H-2,2″ and H-3,3″ are different from those of H-6,6″ and H-5,5″, respectively, in **2a**. The ^{1}H and ^{13}C NMR chemical shifts of H-2,2″ and C-2,2″ are also different from those of H-6,6″ and C-6,6″, respectively, in **2b** and **2c**. Judging from the nonequivalency of the six-membered ring protons and carbons between those in the same side and the opposite side to the central sulfur atom, the rotation of the terminal six-membered rings about the intercyclic bonds does not take place in **2a–c** at ordinary temperatures in solution.

X-ray crystallographic analysis disclosed the precise geometry of **2c**. The ORTEP view is shown in Figure 1, where the mean planes of the terminal six-membered rings incline 9.1° and 11.1°, respectively, from that of the central five-membered ring, and the twisting angle between the mean planes of the two terminal rings is 1.8°. From these observations, the quinones **2a–c** are shown

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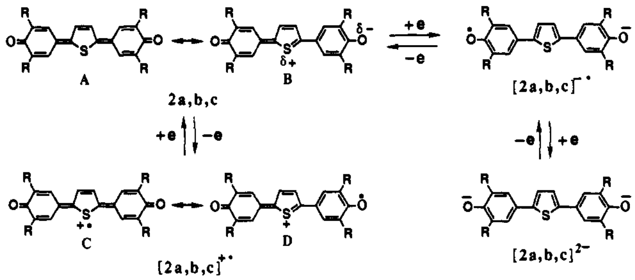
(20) Tetra-*tert*-butyl derivative **2c** is quite stable in the solid state on exposure to light and air and storable safely for a long time at room temperature. Tetramethyl derivative **2b** appears to be less stable than **2c**, degenerating slowly at room temperature within 1 year.

Scheme II



to retain essentially a coplanar conformation for the whole molecule. On the basis of this molecular geometry, these quinones are promising models to clarify the conjugative electronic structure and redox properties of extended types. The interatomic bond distances and bond angles are listed in Table II. The single and double bond distances in **2c** do not deviate substantially from the standard values, and the bond distances of the six-membered rings are close to the values found in tetra-*tert*-butyldiphenoquinone (**1c**).[21] The pronounced bond alternation is attributable to the appreciable contribution of the quinonoid structure A (Scheme II) to the ground state of **2c**. However, the contribution of a polarized structure consisting of negatively charged phenoxy and positively charged thiophene groups (the structure B in Scheme II) should not be disregarded even though slight, since the C3′–C4′ bond is slightly longer by 0.021 Å and the C2′–C3′ (C4′–C5′) bond is slightly shorter by 0.02 (0.003) Å than the corresponding bonds in 2,2′-(2,5-dihydrothiophene-2,5-diylidene)bis(1,3-dithiolane).[22] The contribution of structure B is also suggested from the spectroscopic data, namely the ^{1}H NMR signals of the six-membered ring protons of **2a–c** appear at higher field than those of **1a–c**, and the ^{13}C NMR resonances of carbonyl carbons (C-4,4″) and C-6,6″ unaffected by the anisotropy of the sulfur atom of **2c** appear also at higher field by 0.66 and 0.80 ppm, respectively, than those of **1c**. The carbonyl frequency in the IR spectrum of **2a** is lower by about 16 cm^{-1} than that of **1a** (Table I). The tetraalkylquinones **2b** and **2c** exhibit a weak and a very weak IR band at 1624 and 1630 cm^{-1}, respectively, and the most intense band at 1589 and 1591 cm^{-1}, respectively. In the case of unsubstituted **2a**, no band is observed in the region around 1630 cm^{-1}, and the most intense band occurs at 1614 cm^{-1} accompanied with other strong bands at 1597 and 1587 cm^{-1}. Of these characteristic bands, the most intense band can be tentatively assigned to the carbonyl stretching for the same reason attributed to diphenoquinones.[23]

Another feature of interest in **2** is a pronounced decrease in the HOMO–LUMO energy split compared with **1**, which may correlate closely to the amphoteric electrochemical properties of **2** mentioned below. The small HOMO–LUMO gap in **2** is actually demonstrated by the electronic absorption spectra, in which the first excitation bands of **2a–c** (531–558 nm), assigned to the π_{10} (HOMO) → π_{11} (LUMO) transition by PPP-CI calculations,[24] are shifted remarkably to the longer wavelength region by 125–138 nm from those of the respective **1a–c** in acetonitrile.

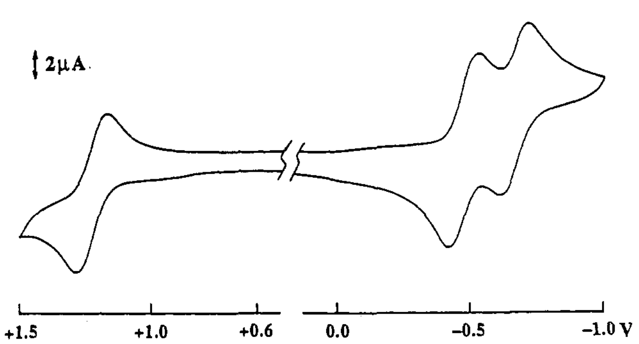


Figure 2. Cyclic voltammogram of **2c**, 0.1 mM in C_6H_5CN/0.1 M $(n\text{-}Bu)_4NClO_4$ at room temperature (scan rate: 50 mV/s; reference electrode: SCE).

Table III. Oxidation and Reduction Potentials[a] and Their Numerical Sum of **2a–c** and **1a–c**

compd	solvent	E_1^{red}	E_2^{red}	E_1^{ox}	E_{pa}^{ox}	E_1^{sum}
2a	C_6H_5CN	−0.12[b]	−0.22[b]	1.46[c]	1.49	1.58
2a	EtCN	−0.12[b]	−0.21[b]	1.43[c]	1.46	1.55
2a	DMF	−0.11	−0.20	1.44[c]	1.47	1.55
1a	MeCN	−0.23	−0.52			
2b	C_6H_5CN	−0.37[b]	−0.44[b]	1.21[c]	1.24	1.58
2b	MeCN	−0.35[b]	−0.45[b]	1.21[c]	1.24	1.56
2b	DMF	−0.34	−0.48	1.22[c]	1.25	1.56
1b	MeCN	−0.44	−0.77			
2c	C_6H_5CN	−0.47	−0.67	1.23	1.28	1.70
2c	MeCN	−0.46	−0.60	1.20	1.24	1.66
2c	CH_2Cl_2	−0.51	−0.61	1.26	1.32	1.77
1c	MeCN	−0.52	−0.89			

[a] Potentials are given in volt (V) vs SCE and were determined with 0.1 M $(n\text{-}Bu)_4NBF_4$ as supporting electrolyte at room temperature (scan rate, 50 mV/s; reference electrode, SCE). E^{ox} and E^{red} values were calculated by averaging the anodic and cathodic peak potentials: $E = (E_{pa} + E_{pc})/2$. [b] Divided from a reversible coalescent peak according to the Myers–Shain method: Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980. [c] Deduced 30 mV from E_{pa}^{ox} (irreversible).

Electrochemistry. The cyclic voltammograms (CV) of **2c** in benzonitrile containing $n\text{-}Bu_4NClO_4$ (TBAP) recorded at a voltage sweep rate of 50 mV s^{-1} are shown in Figure 2. The molecule can be reduced in two successive one-electron-tranfer reactions up to the dianion. More interestingly, in the anodic direction one-electron oxidation takes place up to the radical cation. The one-electron nature of the oxidation wave is indicated by the peak height of the oxidation wave equal to that of each reduction wave. The formation of both a stable radical anion and a radical cation as well as a dianion according to the redox reaction sequence shown in Scheme II is proved by the complete reversibility of all three redox waves for **2c**.

Whereas two separate reduction waves are observed for **2b** in DMF, **2a** and **2b** (in other solvents) tend to give one coalescent reduction wave, even if measurements are carried out at different sweep speeds. Such a difference between **2c** and **2a** (**2b**) may be ascribed to a lower rate of the electron-transfer reaction in **2c** than **2a** or **2b**, due to the steric hindrance of the *tert*-butyl substituents located at adjacent positions to the carbonyl groups. The *tert*-butyl groups may also prevent the radical ions from the reaction with a trace of air or water in the solvent, resulting in a good reversibility of the redox reaction, although the measurements were performed under argon atmosphere by using carefully dried solvents.[25] No second oxidation to the dications of **2a–c** was observed up to a potential range of 2.0 V.

The electrochemical data obtained by the CV are summarized in Table III along with those of diphenoquinones **1a–c**. The first half-wave reduction potentials (E_1^{red}) of **2a–c** appear in a slightly more positive region by 0.10–0.06 V than **1a–c**, and correspondingly the electron-accepting ability increases. The E_2^{red} of **2a–c** are much more positive by 0.29–0.32 V than those of **1a–c**; in this respect the ΔE^{red} ($E_2^{red} - E_1^{red}$) values of **2a–c** become apparently smaller than those of **1a–c**, demonstrating the diminished Coulomb repulsion in the dianion state of the former.

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(21) Khan, M. A.; Osman, A.; Dennis, G. T. *Acta Crystallogr.* **1986**, *C42*, 1399.

(22) Takahashi, K.; Nihira, T. to be published.

(23) For diphenoquinones **1a–c** with D_{2h} symmetry, the most intense band has been assigned to the out-of-phase $(C{=}O)_2$ stretching since this stretching mode belonging to the B_{3u} species is allowed and in-phase $(C{=}O)_2$ stretching belonging to the A_g species is forbidden in the IR. The molecular symmetry of **2a–c** differs from **1a–c** in that they have C_{2v} symmetry in which both out-of-phase $(C{=}O)_2$ stretching belonging to the B_1 species and in-phase $(C{=}O)_2$ stretching belonging to the A_1 species are allowed in the IR. However, for 3,3′-dimethyl-5,5′-di-*tert*-butyldiphenoquinone exhibiting C_{2v} symmetry, the most intense band has also been assigned to out-of-phase $(C{=}O)_2$: (a) Nyquist, R. A. *Appl. Spectrosc.* **1982**, *35*, 533. (b) Gordon, J. M.; Forbes, J. W. *Appl. Spectrosc.* **1961**, *15*, 19.

(24) (a) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466, 767. (b) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

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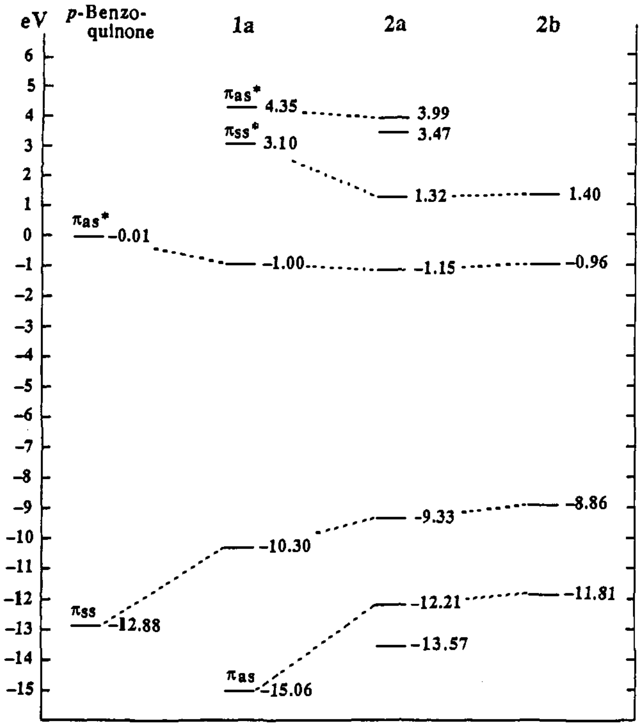

Figure 3. Correlation diagram for the molecular orbital levels of *p*-benzoquinone, **1a**, **2a**, and **2b** obtained from CNDO/2 calculations.

It is rather surprising that **2a–c** exhibit an E_1^{ox} value of 1.26–1.46 V, on considering the poor electron-donating ability of the corresponding diphenoquinones **1a–c** and highly extended quinones such as bis(4-oxo-2,5-cyclohexadien-1-ylidene)ethenes[15] and tetrakis(4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutanes[16] whose E_1^{ox} values lie out of the range readily accessible for studies by cyclic voltammetry. The enhancement of the electron-donating ability of **2a–c** can be attributed to the conjugative effect of the 3pπ electrons on the sulfur atom stabilizing effectively the corresponding radical cation[9,10] and to the high-energy level of the HOMO of **2** (vide infra) which results from the conjugation extension. Indeed, the π AO coefficient at the sulfur atom in **2** is larger than those at any other atoms in the HOMO, while it nearly vanishes in the LUMO. Moreover, the radical cation may be stabilized by the contribution of the structure D[26] (Scheme II) equivalent to galvinoxyl.

Thus, **2a–c** are characterized as a new type of quinones exhibiting an amphoteric three-stage redox behavior capable of acting, in principle, not only as an electron acceptor but also as an electron donor depending on the ionization potential and electron affinity of their partner.[27] The numerical sum (E_1^{sum}) of the first oxidation (E_1^{ox}) and first reduction (E_1^{red}) potentials, a convenient measure to evaluate the amphotericity of a specified molecule,[28] is determined to be 1.55–1.77 V for **2a–c**, which is almost comparable to the E_1^{sum} value (1.66 V) of *p*-tricyanovinyldimethylaniline[29] whose amphotericity has been demonstrated by the formation of solid complexes with 2,4,7-trinitrofluorene and dimethylaniline. Amphoteric compounds are of special interest as promising potential candidates to build up single-component or three-component organic electroconductors.

The electrochemically obtained redox potentials listed in Table III are in good correlation with the energy levels of the frontier orbitals of **1** and **2** calculated by the CNDO/2 method[30] utilizing the bond lengths and bond angles determined by X-ray analysis.[31] As seen in Figure 3, **2a** exhibits a significantly destabilized HOMO which lies at a higher level by 0.97 eV than that of **1a**.

Table IV. Hyperfine Splitting Constants (a in mT) for the Radical Anions and Radical Cations of Thienoquinonoid-Extended Quinones **2a–c** in MeCN at Room Temperature

radical	$a^{H_{3',4'}}$	$a^{H_{2,2'',6,6''}}$	$a^{H_{3,3'',5,5''}}$	*g* value
$\mathbf{2a}^{\bullet-}$	0.228	0.028	0.167	2.0036
$\mathbf{2a}^{\bullet+}$	0.220	0.081	0.180	2.0056
$\mathbf{2b}^{\bullet-}$	0.208	0.018	0.166 (Me)	2.0037
$\mathbf{2b}^{\bullet+}$	*a*	*a*		2.0054
$\mathbf{2c}^{\bullet-}$	0.205	<0.045		2.0037
$\mathbf{2c}^{\bullet+}$	0.130	0.130		2.0055

[a] Unresolved.

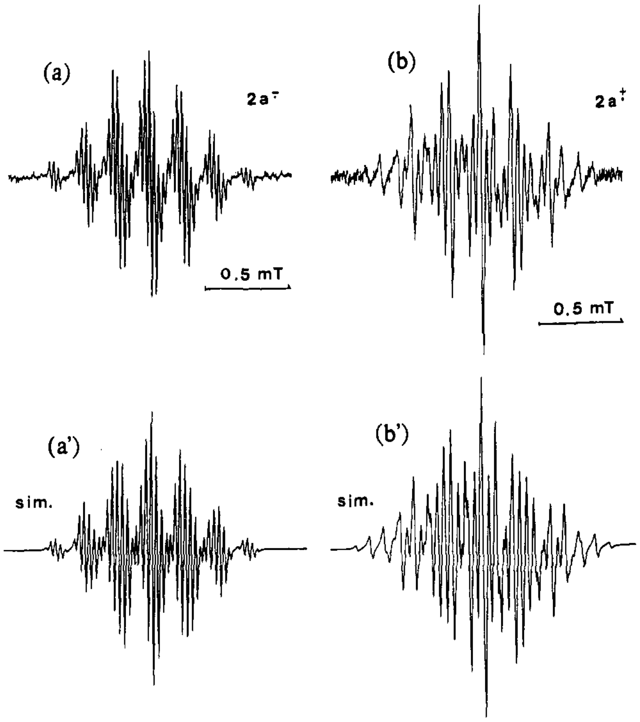

Figure 4. EPR spectra of the radical anion (a) and radical cation (b) of **2a** generated by electrolysis in MeCN at room temperature and the corresponding simulated spectra (a′) and (b′), respectively.

The extent of destabilization in the HOMO is much larger than that of stabilization in the LUMO of **2a** which lies lower by 0.15 eV than that of **1a**.[32] As a result of this, the HOMO–LUMO separation decreased significantly in **2a**, which can surely be ascribed to the amphoteric behavior of **2a–c**. In agreement with the more negative reduction potentials and lower oxidation potentials of **2b** and **2c** compared with **2a** (Table III), the HOMO and the LUMO of **2b** are calculated to be higher by 0.47 and 0.19 eV, respectively, than the corresponding MOs of **2a**. This can be ascribed to the electron-releasing effect of the alkyl groups.

EPR Spectroscopy. As mentioned above, the introduction of the thienoquinonoid moiety to the diphenoquinone system provides a novel property, that is, accounting for the amphotericity. Generation of both anion and cation radicals are definitely assigned by the EPR observation as follows.

The EPR spectra due to the radical anions of quinones **2a–c** in acetonitrile were obtained by cathodic reduction. Each spectrum appeared at around $g = 2.003$ region, where usual radical anions

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(26) The structure D has been suggested by a referee to whom the authors are indebted.

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(28) (a) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Hagenbruch, B.; Hesse, K.; Hunig, S.; Klug, G. *Liebigs Ann. Chem.* **1981**, 256. (c) Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1982**, *104*, 1432. (d) Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136.

(29) Sandman, D. J.; Richter, A. F. *J. Am. Chem. Soc.* **1979**, *101*, 7079.

(30) Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1966**, *44*, 3289: The 3d orbitals of sulfur atom were not included in the calculations.

(31) The bond lengths and bond angles determined by X-ray analysis were averaged to attain a C_{2v} symmetry.

(32) The HOMO and LUMO of **2a** belong to the symmetry species b_1 and a_2, exhibiting large bonding and antibonding 2pπAO's on the intercyclic bonds, respectively.

of quinone derivatives were observed. Essentially identical spectra were also obtained by the one-electron reduction with Na metal in THF.

Figure 4a shows the EPR spectrum of the radical anion formed by the electrolysis of **2a** in acetonitrile. Three splitting constants, 0.028 (4 H), 0.167 (4 H), and 0.228 mT (2 H), are obtained from the hyperfine structure. The constants were confirmed by spectral simulation, giving the spectrum included in Figure 4a′. Well-resolved EPR spectra were also obtained by the electrolyses of **2b** and **2c** and were easily assigned to the corresponding radical anions considering the results of the spin density calculated by means of McLachlan method. The values were slightly smaller than those of diphenoquinones[33] indicating the delocalization of the unpaired electron over the thiophene moiety. The hyperfine splitting (hfs) constants thus obtained are summarized in Table IV.

Electrochemical oxidation of quinones **2a–c** in acetonitrile brought about the EPR spectra at $g = 2.0055$. Figure 4b shows the EPR spectrum observed during the electrolysis of **2a** in a degassed solution. The spectrum was analyzed by using three sets of hfs constants, 0.081 (4 H), 0.180 (4 H), and 0.220 mT (2 H). The simulated spectrum using the hfs values is shown in Figure 4b′. EPR spectra obtained under the electrolysis of **2b** and **2c** were characterized reasonably as those arising from the corresponding radical cations. The assignment to the hfs constants listed in Table IV was given tentatively according to the type of splitting and by comparing them with those of the cation radical of **2a**. In the case of **2b**, however, the EPR spectrum was too broad to analyze, which may come from the small hfs constants induced by twelve equivalent protons of the four methyl groups.

The unpaired electron distribution differs distinctly between the radical anion and the radical cation. The larger g values of the radical cations indicate that the unpaired electron localizes considerably on the sulfur atom, since the HOMO has the largest π AO coefficient and the LUMO has an almost vanished one at the sulfur atom as mentioned in the preceding section. However, the structure D[26] (Scheme II) should also be responsible for the radical cations since the g values ($\sim$2.0055) are not so large as that (2.008) of TTF. Whereas H-2.2″ are magnetically inequivalent to H-6,6″, they are equivalent in the EPR spectra, and two sets of hfs constants were obtained for the phenoxy ring protons in **2a**. The radical cation and the radical anion of **2c** persist with undiminished intensity of the EPR signal for at least 30 min after the current is turned off. Thus, the substitution of *tert*-butyl groups at the β positions relative to the oxygen atoms stabilizes the radical ions in solution.

Conclusion

The quinones **2a–c**, in which the inner cyclohexadienediylidene of the corresponding terphenoquinones are replaced by a dihydrothiophenediylidene moiety, have been synthesized by an advantageous method by using Pd-catalyzed cross-coupling reactions and proved to be stable compounds exhibiting essentially planar conformation both in the solid state and in solution. Electrochemical behavior of the dihydrothiophenediylidene-extended quinones **2a–c** has been investigated by using cyclic voltammetry and EPR spectroscopy, demonstrating that these quinones show a novel amphoteric property consisting of two-stage one-electron reduction up to the dianion and one-electron oxidation up to the semiquinone radical cation. The coplanarity of the molecule and the 3pπ orbitals of the central sulfur atom may contribute effectively to the stabilization of the radical cation as well as their high-lying HOMO. The stabilization effect of the 3pπ orbitals is revealed by the large g values of the radical cations. Quinones **2a–c** exhibit an intense absorption maximum at 531–558 nm in the electronic spectra which is bathochromic by 125–138 nm from those of the corresponding diphenoquinones. Due to the deep coloration and novel redox properties, **2a–c** would have a high utility potential for the extended performances of materials of topical interest. The idea of the heterocyclic extension of a conjugated π-electron system could be widely applicable to the design and synthesis of a functionally new type of molecules capable of developing significant novel properties.

Experimental Section

General Procedures. Melting points were obtained by using an electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded on either a Varian XL-200 or JEOL GX-400 spectrometer. All ^{1}H and ^{13}C chemical shifts are recorded relative to TMS as internal standard. Chemical shift assignments were confirmed through spin decoupling and two-dimensional carbon-proton chemical shift correlation experiments. Infrared (IR) spectra were recorded on either a HORIBA FT-300 spectrophotometer or a Shimazu IR-27G spectrophotometer. Mass (MS) spectra were recorded on either a JEOL-JMS-HX110 or DX-303 spectrometer. Ultraviolet (UV) spectra were recorded on a Hitachi No. 323 spectrophotometer. ESR spectra were measured with a Varian E-109E EPR spectrometer. The sample solution for an electrolysis was prepared by using a vacuum line system. Elemental analyses were performed at Instrumental Analysis Center for Chemistry, Tohoku University.

2-Thienylzinc Chloride. To a stirred solution of thiophene (719 mg, 8.55 mmol) in dry ether (11 mL) was added dropwise a 1.57 M solution of *n*-butyllithium in hexane (5.44 mL, 8.55 mmol) at 0 °C under argon atmosphere. After being stirred for 1 h at 0 °C, the resulting solution was added to anhydrous zinc chloride (1.17 g, 8.55 mmol) dissolved in dry THF (11 mL). The mixture was stirred for an additional 1 h at 0 °C, giving thienylzinc chloride (8.55 mmol) as a solution.

2-(4-Methoxyphenyl)thiophene (4a). To a Pd(0) catalyst prepared by treating $Cl_2Pd(PPh_3)_2$ (300 mg, 0.427 mmol) suspended in dry THF (11 mL) with 1 M solution of *i*-Bu_2AlH in hexane (0.855 mL, 0.855 mmol) were added at room temperature first a solution of *p*-iodoanisole (2.00 g, 8.55 mmol) in dry THF (20 mL) and then a THF solution of thienylzinc chloride (8.55 mmol) prepared as described above. After the reaction mixture was stirred at room temperature for 1 h, it was quenched with water and extracted with ether. The combined extracts were washed with brine and dried over Na_2SO_4. Solvent evaporation and chromatography of the residue on silica gel by eluting with hexane afforded **4a** which was recrystallized from methanol to obtain pure **4a** as colorless crystals (1.28 g, 78%): mp 106–107 °C; IR (KBr) 3105–2845 (w), 1610 (m), 1576 (w), 1536 (w), 1500 (s), 1294 (m), 1262 (s), 1248 (s), 1184 (s), 1036 (s), 856 (m), 828 (s), 816 (s), 708 (s) cm^{-1}; ^{1}H NMR (200 MHz CDCl$_3$) δ 3.84 (s, 3 H, OMe), 6.91 (dm, 2 H, $J = 8.8$ Hz, ArH-3,5), 7.05 (dd, 1 H, $J = 5.0$ and 3.8 Hz, ThiH-4′), 7.19 (dd, 1 H, $J = 3.8$ and 1.3 Hz, ThiH-3′), 7.21 (dd, 1 H, $J = 5.0$ and 1.3 Hz, ThiH-5′), 7.54 (dm, 2 H, $J = 8.8$ Hz, ArH-2,6); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 55.36 (OMe), 114.30 (ArC-3,5), 122.09 (ThiC-3′), 123.82 (ThiC-5′), 127.25 (ArC-2,6), 127.36 (ArC-1), 127.90 (ThiC-4′), 144.37 (ThiC-2′), 159.23 (ArC-4); MS (25 eV) m/z (rel intensity) 190 (M$^+$, 96), 175 (100). Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.30; S, 16.85. Found: C, 69.40; H, 5.51; S, 16.45.

2-(3,5-Dimethyl-4-methoxyphenyl)thiophene (4b). In a manner similar to **4a**, a solution of thienylzinc chloride (45.79 mmol) in dry ether (60 mL) and dry THF (60 mL) was treated at room temperature for 1 h with a solution of 2,6-dimethyl-4-iodoanisole (10.0 g, 38.15 mmol) in dry THF (60 mL) in the presence of Pd(0) catalyst prepared from a solution of $PdCl_2(PPh_3)_2$ (1.339 g, 1.908 mmol) in dry THF (60 mL) and a 1 M solution of *i*-Bu_2AlH in hexane (3.82 mL, 3.82 mmol). Pure **4b** was isolated as colorless crystals (6.25 g, 75.0%) after the purification by chromatography (SiO_2–hexane) and recrystallization (MeOH): mp 46–47 °C, IR (KBr) 3100–2800 (w), 1590 (w), 1530 (w), 1480–1420 (m), 1355 (w), 1300 (w), 1240 (s), 1218 (m), 1158 (s), 1012 (s), 880 (s), 864 (s), 832 (s), 822 (s), 760 (m), 720 (s), 704 (s) cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.32 (br s, 6 H, Me), 3.74 (s, 3 H, OMe), 7.03 (dd, 1 H, $J = 4.9$ and 3.7 Hz, ThiH-4′), 7.21 (dd, 1 H, $J = 4.9$ and 1.3 Hz, ThiH-5′), 7.22 (dd, 1 H, $J = 3.7$ and 1.3 Hz, ThiH-3′), 7.26 (br s, 2 H, ArH-2,6); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 16.14 (Me), 59.75 (OMe), 122.54 (ThiC-5′), 124.19 (ThiC-3′), 126.51 (ArC-2,6), 127.84 (ThiC-4′), 130.05 (ArC-1), 131.30 (ArC-3,5), 144.34 (ThiC-2′), 156.72 (ArC-4); MS (25 eV) m/z (rel intensity) 218 (M$^+$, 100), 203 (M$^+$ − 15, 88). Anal. Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46; S, 14.69. Found: C, 71.46; H, 6.63; S, 14.80.

Zinc Derivative 5a. To a stirred solution of **4a** (800 mg, 4.20 mmol) in dry ether (18 mL) was added dropwise a 1.57 M solution of *n*-BuLi in hexane (2.68 mL, 4.20 mmol) at 0 °C under argon atmosphere. After being stirred for 1 h, the resulting solution was added to anhydrous zinc chloride (573 mg, 4.20 mmol) dissolved in dry THF (10 mL) at 0 °C. The reaction mixture was warmed gradually to room temperature, giving **5a** as a solution.

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2,5-Bis(4-methoxyphenyl)thiophene (6a). To a Pd(0) catalyst prepared by treating $Cl_2Pd(PPh_3)_2$ (148 mg, 0.21 mmol) in dry THF (10 mL) with 1 M solution of *i*-Bu_2AlH in hexane (0.42 mL, 0.42 mmol) were added sequentially at room temperature under argon atmosphere a solution of *p*-iodoanisole (984 mg, 4.20 mmol) in dry THF (12 mL) and a solution of **5a** (4.20 mmol) described above. After being stirred for 1 h, the resulting mixture was worked up as usual and crude reaction products were chromatographed on silica gel by eluting with a mixture of 1:1 hexane–CH_2Cl_2 to give **6a** as colorless crystals (0.55 g, 46.6%): mp 216–217 °C; IR (KBr) 3080–2850 (w), 1604 (m), 1502 (s), 1282 (m), 1250 (s), 1180 (s), 1032 (s), 838 (s), 800 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.85 (s, 6 H, Me), 6.93 (dm, 4 H, J = 9.5 Hz, ArH-3,3″,5,5″), 7.15 (s, 2 H, ThiH-3′,4′), 7.55 (dm, 4 H, J = 9.5 Hz, ArH-2,2″,6,6″); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 55.39 (OMe), 114.35 (ArC-3,5), 122.90 (ThiC-3′,4′), 126.86 (ArC-2,6), 127.41 (ArC-1), 142.64 (ThiC-2′), 159.18 (ArC-4); MS (25 eV), m/z (rel intensity) 296 (M^+, 100), 281 (M^+ − 15, 100). Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44; S, 10.82. Found: C, 72.68; H, 5.49; S, 10.66.

2,5-Bis(3,5-dimethyl-4-methoxyphenyl)thiophene (6b). In a manner similar to **6a**, a solution of **5b** prepared from **4b** (1.00 g, 4.580 mmol) in dry ether (6 mL), a 1.57 M solution of *n*-BuLi in hexane (2.92 mL, 4.580 mmol), and zinc chloride (624 mg, 4.580 mmol) in dry THF (6 mL) was treated with a solution of 2,6-dimethyl-4-iodoanisole (1.20 g, 4.580 mmol) in dry THF (12 mL) in the presence of Pd(0) catalyst prepared from a solution of $PdCl_2(PPh_3)_2$ (161 mg, 0.229 mmol) in dry THF (6 mL) and a 1 M solution of *i*-Bu_2AlH in hexane (0.458 mL, 0.458 mmol). Pure **6b** was isolated as colorless crystals (0.884 g, 86.6%) after chromatographic purification (SiO_2–95:5 hexane–AcOEt): mp 110–111 °C; IR (KBr) 2980–2825 (w), 1588 (w), 1476 (s), 1454 (s), 1408 (m), 1240 (s), 1208 (s), 1160 (s), 1014 (s), 866 (s), 806 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 12 H, Me), 3.75 (s, 6 H, OMe), 7.15 (s, 2 H, ThiH-3′,4′), 7.27 (s, 4 H, ArH-2,2″,6,6″); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 16.17 (Me), 59.79 (OMe), 123.33 (ThiC-3′,4′), 126.09 (ArC-2,2″,6,6″), 130.06 (ArC-1,1″), 131.32 (ArC-3,3″,5,5″), 142.94 (ThiC-2′,5′), 156.68 (ArC-4,4″); MS (25 eV) m/z (rel intensity) 352 (M^+, 100), 337 (M^+ − 15, 98). Anal. Calcd for $C_{22}H_{24}O_2S$: C, 74.96; H, 6.86; S, 9.10. Found: C, 75.10; H, 6.92; S, 8.87.

2,5-Bis(4-hydroxyphenyl)thiophene (7a). To a solution of **6a** (220 mg, 0.674 mmol) in dry CH_2Cl_2 (40 mL) was added BBr_3 (0.128 mL, 1.350 mmol), and the reaction mixture was refluxed for 3 h. Water was added, and the mixture was extracted with ethyl acetate. After usual workup, the crude reaction products were chromatographed on silica gel by eluting with a 3:1 mixture of CH_2Cl_2–AcOEt to give **7a** as colorless crystals (180 mg, 99.5%): mp 255–257 °C; IR (KBr) 3300 (s), 1730 (w), 1608 (m), 1548 (m), 1504 (s), 1444 (m), 1384 (m), 1254 (s), 1178 (m), 1114 (m), 834 (s), 804 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.84 (dm, 4 H, J = 8.8 Hz, ArH-3,5), 7.14 (s, 2 H, OH), 7.20 (s, 2 H, ThiH-3′,4′), 7.50 (dm, 4 H, J = 8.8 Hz, ArH-2,6); ^{13}C NMR (50.3 MHz, CD_3CN) δ 116.81 (ArC-3,3″,5,5″), 123.97 (ThiC-3′,4′), 127.31 (ArC-1,1″), 127.79 (ArC-2,2″,6,6″), 143.31 (ThiC-2′,5′), 157.73 (ArC-4,4″); MS (25 eV) m/z (rel intensity) 269 (M^+ + 1, 31), 268 (M^+, 100); UV (MeCN) λ_{max} nm (log ϵ) 335 (4.37), 242 sh (3.85), 218 sh (4.23). Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51; S, 11.95. Found: C, 71.48; H, 4.55; S, 11.72.

2,5-Bis(3,5-dimethyl-4-hydroxyphenyl)thiophene (7b). In a manner similar to **7a**, a solution of **6b** (2.50 g, 7.092 mmol) in dry CH_2Cl_2 (100 mL) was treated with BBr_3 (1.34 mL, 14.18 mmol) at room temperature for 4 h. Pure **7b** was isolated as colorless crystals (2.30 g, 100%) after chromatographic purification (SiO_2–1:1 hexane–ether): mp 194–196 °C; IR (KBr) 3330 (s), 2950–2860 (w), 1600 (w), 1482 (s), 1386 (m), 1352 (m), 1320 (m), 1240 (s), 1204 (s), 1166 (s), 796 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (br s, 12 H, Me), 4.65 (br s, 2 H, OH), 7.10 (s, 2 H, ThiH-3′,4′), 7.25 (br s, 4 H, ArH-2,2″,6,6″); ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 15.95 (Me), 122.59 (ThiC-3′,4′), 123.42 (ArC-3,3″,5,5″), 126.00 (ArC-2,2″,6,6″), 126.92 (ArC-1,1″), 142.66 (ThiC-2′,5′), 151.85 (ArC-4,4″); MS (25 eV) m/z (rel intensity) 325 (28), 324 (M^+, 100); UV (MeCN) λ_{max} nm (log ϵ) 339 (4.44), 240 sh (4.08), 218 sh (4.39). Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21; S, 9.88. Found: C, 73.71; H, 6.25; S, 9.93.

2,5-Bis(4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene (2a). To a solution of **7a** (25 mg, 0.093 mmol) in CH_2Cl_2 (100 mL) were added a 0.1 M aqueous KOH solution (100 mL) and then potassium ferricyanide (123 mg, 0.373 mmol) at room temperature, and the mixture was stirred vigorously for 1 min. The reaction mixture was extracted with CH_2Cl_2, and the combined extracts were washed with brine, dried over Na_2SO_4, and concentrated. The residue was washed with dry acetonitrile to afford **2a** as black crystals (15 mg, 60.6%): degenerating point 183–185 °C (turn to a brown solid without melting): IR (KBr) 3100 (w), 3008 (w), 1614 (vs), 1597 (s), 1587 (s), 1570 (s), 1535 (m), 1504 (s), 1436 (w), 1359 (w), 1263 (w), 1155 (m), 1095 (w), 941 (w), 850 (s), 796 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, 2 H, J = 10.0 and 2.0 Hz, ArH-5,5″), 6.61 (dd, 2 H, J = 9.8 and 2.0 Hz, ArH-3,3″), 7.54 (dd, 2 H, J = 9.8 and 2.8 Hz, ArH-2,2″), 7.67 (dd, 2 H, J = 10.0 and 2.8 Hz, ArH-6,6″), 7.78 (s, 2 H, ThiH-3′,4′); DEI-MS m/z (rel intensity) 269 (M^+ + 1, 16), 268 (M^+, 100), 85 (43), 83 (66); UV-vis (MeCN) λ_{max} nm (log ϵ) 278 (3.37), 288 (3.27), 340 (3.65), 500 sh (4.23), 531 (4.57). Anal. Calcd for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.79; S, 12.04. Found: C, 72.24; H, 3.67; S, 11.89.

2,5-Bis(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene (2b). In a manner similar to **2a**, a solution of **7b** (200 mg, 0.616 mmol) in CH_2Cl_2 (100 mL) was treated with a 0.1 M aqueous KOH solution (100 mL) and potassium ferricyanide (406 mg, 1.233 mmol) at room temperature for 5 min. Pure **2b** was obtained as greenish black crystals (180 mg, 90.6%) after chromatography (SiO_2–CH_2Cl_2); mp 189–201 °C (turns to a red solid at 150–154 °C); IR (KBr) 2900 (w), 1624 (w), 1589 (vs), 1565 (m), 1533 (w), 1508 (s), 1376 (m), 1335 (m), 1201 (m), 1041 (m), 885 (w), 850 (w), 789 (w) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.13 (d, 6 H, J = 1.1 Hz, ArMe-5,5″), 2.15 (d, 6 H, J = 1.1 Hz, ArMe-3,3″), 7.32 (dq, 2 H, J = 2.6 and 1.1 Hz, ArH-2,2″), 7.45 (dq, 2 H, J = 2.6 and 1.1 Hz, ArH-6,6″), 7.69 (s, 2 H, ThiH-3′,4′); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 16.84 (Me), 16.94 (Me), 127.68 (ArC-1,1″), 128.84 (ArC-6,6″), 131.39 (ArC-2,2″), 134.37 (ThiC-3′,4′), 136.03 (ArC-3,3″), 138.41 (ArC-5,5″), 152.37 (ThiC-2′,5′), 186.64 (ArC-4,4″); DEI-MS m/z (rel intensity) 326 (M^+ + 2, 10), 325 (M^+ + 1, 28), 324 (M^+, 100), 323 (M^+ − 1, 9); UV-vis (MeCN) λ_{max} nm (log ϵ) 334 (4.03), 348 (4.08), 508 sh (4.46), 546 (4.87). Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63; S, 9.95. Found: C, 74.32; H, 5.79; S, 9.84.

2,6-Di-*tert*-butyl-4-iodo-1-[(trimethylsilyl)oxy]benzene (3c). To a solution of 2,6-di-*tert*-butyl-4-iodophenol[34] (25.0 g, 75.25 mmol) in dry THF (90 mL) was added dropwise a 1.64 M solution of *n*-BuLi in hexane (45.9 mL, 75.25 mmol) at −78 °C under argon atmosphere. After stirring for 10 min, trimethylsilyl chloride (19.1 mL, 150.50 mmol) was added at −78 °C. The resulting mixture was stirred for 10 min at −78 °C, poured into H_2O, and extracted with ether. The combined extracts were washed with brine and dried over Na_2SO_4. Solvent evaporation and chromatography of the residue on silica gel by eluting with hexane provided **3c** which was recrystallized from methanol to give pure **3c** as colorless crystals (26.78 g, 88%): mp 127–130 °C; IR (KBr) 3040–2875 (m), 1404 (s), 1360 (m), 1260 (s), 1228 (s), 1200 (m), 1118 (m), 916 (s), 844 (s), 780 (m), 768 (m) cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 0.38 (s, 9 H, SiMe), 1.37 (s, 18 H, *t*-Bu), 7.33 (s, 2 H, ArH); MS (25 eV) m/z (rel intensity) 404 (M^+, 100), 389 (76). Anal. Calcd for $C_{17}H_{29}OSiI$: C, 50.49; H, 7.23; I, 31.38. Found: C, 50.35; H, 7.20; I, 31.11.

2-(3,5-Di-*tert*-4-[((trimethylsilyl)oxy)phenyl]thiophene (4c). In a manner similar to **4a**, a solution of thienylzinc chloride (41.97 mmol) in dry ether (50 mL) and dry THF (50 mL) was treated with a solution of **3c** (13.0 g, 32.15 mmol) in THF (100 mL) in the presence of Pd(0) catalyst prepared from a solution of $PdCl_2(PPh_3)_2$ (1.13 g, 1.607 mmol) in dry THF (50 mL) and a 1 M solution of *i*-Bu_2AlH in hexane (3.22 mL, 3.215 mmol). Pure **4c** was isolated as colorless crystals (9.90 g, 85.4%) after the purification by chromatography (SiO_2–hexane) and recrystallization (MeOH): mp 88–89 °C; IR (KBr) 3000–2850 (m), 1485 (m), 1473 (m), 1442 (m), 1416 (s), 1390 (m), 1361 (m), 1345 (m), 1256 (s), 1230 (s), 1119 (m), 918 (s), 840 (s), 765 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.43 (s, 9 H, SiMe), 1.45 (s, 18 H, *t*-Bu), 7.04 (dd, 1 H, J = 4.5 and 4.5 Hz, ThiH-4′), 7.21 (mc, 2 H, ThiH-3′,5′), 7.49 (s, 2 H, ArH-2,6); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 3.93 (SiMe), 31.17 (C*Me*), 35.19 (*C*Me), 121.91 (ThiC-3′), 123.58 (ThiC-5′), 123.77 (ArC-2,6), 127.22 (Thi-4′), 126.54 (ArC-1), 141.22 (ArC-3,5), 145.46 (ThiC-2′), 153.05 (ArC-4); MS (25 eV) m/z (rel intensity) 361 (M^+ + 1, 68), 360 (M^+, 100), 345 (100), 73 (100). Anal. Calcd for $C_{21}H_{32}OSSi$: C, 69.94; H, 8.95; S, 8.89. Found: C, 69.77; H, 8.84; S, 8.63.

Zinc derivative 5c was prepared in a similar manner to **5a**, except that **4c** was lithiated at −20 °C with a 1.5 M solution of *t*-BuLi in hexane (1.2 mol equiv to **4c**).

2,5-Bis(3,5-di-*tert*-butyl-4-[((trimethylsilyl)oxy)phenyl]thiophene (6c). The same procedure described for the preparation of **6a** and **6b** was followed with **5c** (8.319 mmol), **3c** (3.35 g, 8.319 mmol), $PdCl_2(PPh_3)_2$ (292 mg, 0.416 mmol), and *i*-Bu_2AlH (0.8319 mmol). Purification by chromatography (SiO_2–hexane) and recrystallization (MeOH) gave pure **6c** as colorless crystals (3.21 g, 66.7%): mp 175–176 °C; IR (KBr) 3050–2880 (s), 1600 (w), 1490 (w), 1470 (w), 1424 (s), 1416 (s), 1395 (m), 1365 (m), 1272 (s), 1260 (s), 1238 (s), 1125 (m), 926 (s), 852 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.57 (s, 18 H, SiMe), 1.94 (s, 36 H, *t*-Bu), 7.13 (s, 2 H, ThiH-3′,4′), 7.50 (s, 4 H, ArH-2,2″,6,6″); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 3.94 (SiMe), 31.21 (C*Me*), 35.22 (*C*Me), 122.65 (ThiC-3′,4′), 123.33 (ArC-2,2″,6,6″), 126.73 (ArC-1,1″), 141.22

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(ArC-3,3″,5,5″), 143.50 (ThiC-2′,5′), 152.92 (ArC-4,4″); MS (25 eV) *m/z* (rel intensity) 636 (M^+, 100); UV (CH_2Cl_2) λ_{max} nm (log ϵ) 242 (4.16), 342 (4.50). Anal. Calcd for $C_{38}H_{60}O_2SSi$: C, 71.64; H, 9.49; S, 5.03. Found: C, 71.32; H, 9.60; S, 4.95.

2,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)thiophene (7c). To a solution of **6c** (2.00 g, 3.139 mmol) in acetonitrile (440 mL) were added 12 M HCl (40 mL) and H_2O (8 mL) at room temperature. After stirring for 5 h, the reaction mixture was concentrated under reduced pressure. Water was added, and the mixture was extracted with ether. After usual workup and chromatographic separation (SiO_2–98:2 hexane–CH_2Cl_2) of the reaction products, pure **7c** was isolated as colorless crystals (1.61 g, 99.8%): mp 91–93 °C; IR (KBr) 3640 (s), 2960–2875 (s), 1436 (s), 1236 (s), 1154 (m), 880 (w), 798 (w), 700 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.49 (s, 36 H, *t*-Bu), 5.25 (s, 2 H, OH), 7.11 (s, 2 H, ThiH-3′,4′), 7.43 (s, 4 H, ArH-2,2″,6,6″); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 30.28 (Me), 34.40 (*C*Me), 122.54 (ThiC-3′,4′), 122.78 (ArC-2,2″,6,6″), 126.17 (ArC-1,1″), 136.32 (ArC-3,3″,5,5″), 143.70 (ThiC-2′,5′), 153.53 (ArC-4,4″); EI-MS (70 eV) *m/z* (rel intensity) 494 ($M^+ + 2$, 11), 493 ($M^+ + 1$, 36), 492 (M^+, 100), 410 (27); UV (MeCN) λ_{max} nm (log ϵ) 242 sh (4.16), 342 (4.50). Anal. Calcd for $C_{32}H_{44}O_2S$: C, 78.00; H, 9.00; S, 6.51. Found: C, 77.88; H, 9.15; S, 6.47.

2,5-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene (2c). In a manner similar to **2a**, a solution of **7c** (1.45 g, 2.942 mmol) in benzene (240 mL) was treated with a 0.1 M aqueous KOH solution (480 mL) and potassium ferricyanide (9.63 g, 29.42 mmol) at room temperature for 5 h. Pure **2c** was obtained as shining green or black fine crystals (1.318 g, 91.4%) after chromatography (SiO_2–95:5 hexane–ether) and recrystallization (MeCN): mp 270–273 °C; IR (KBr) 2960–2845 (w), 1630 (vw), 1591 (vs), 1556 (w), 1510 (w), 1454 (w), 1360 (m), 1332 (w), 1257 (w), 1146 (w), 1088 (w), 1030 (m), 991 (w), 893 (w), 852 (m), 818 (w), 785 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.36 (s, 18 H, *t*-Bu), 1.38 (s, 18 H, *t*-Bu), 7.28 (d, 2 H, J = 2.5 Hz, ArH-2,2″), 7.43 (d, 2 H, J = 2.5 Hz, ArH-6,6″), 7.69 (s, 2 H, ThiH-3′,4′); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 29.68 (Me), 35.63 and 35.89 (*C*Me), 125.35 (ArC-6,6″), 127.28 (ArC-1,1″), 128.04 (ArC-2,2″), 133.94 (ThiC-3′,4′), 147.71 (ArC-3,3″), 150.32 (ArC-5,5″), 152.64 (ThiC-2′,5′), 185.81 (ArC-4,4″); EI-MS (70 eV) *m/z* (rel intensity) 494 ($M^+ + 4$, 11), 493 ($M^+ + 3$, 36), 492 ($M^+ + 2$, 100), 491 ($M^+ + 1$, 10), 490 (M^+, 21); UV–vis (MeCN) λ_{max} nm (log ϵ) 272 (3.72), 282 (3.71), 294 (3.68), 349 (3.85), 558 (4.90). Anal. Calcd for $C_{32}H_{42}O_2S$: C, 78.32; H, 8.63; S, 6.53. Found: C, 77.99; H, 8.63; S, 6.68.

Single-Crystal X-ray Structure Determination of 2c. The crystals of **2c** belong to a monoclinic system with cell dimensions a = 19.918 (5) Å, b = 24.394 (9) Å, c = 5.971 (2) Å, β = 92.93 (2)°, and V = 2897.4 (17) $Å^3$. The space group is $P2_1/a$ and $Z = 4$. The empirical formula is $C_{32}H_{42}O_2S$, molecular weight is 490.72, and calculated density is 1.125 g/cm^3. The three-dimensional X-ray data were collected by the use of graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Syntex R3 automatic four-circle diffractometer up to a maximum 2θ of 50°. The intensity data of 5222 independent reflections were collected and 1884 with $|F_o| > 4\sigma|F_o|$ were used in the present X-ray analysis. The structure was solved by the direct method (MULTAN 78). All non-hydrogen atoms were located on the initial E synthesis. Remaining hydrogens were located by the difference Fourier map and included in the further calculations. Block-diagonal least-squares refinements with anisotropic 35 non-hydrogen atoms and 42 isotropic hydrogens have converged to a conventional R factor of 0.078. All the calculations were done on a HITAC M-680H computer of Hiroshima University by using a structure analysis program system UNICS3 [Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *56*, 69].

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Supplementary Material Available: Tables of hydrogen atom coordinates, fractional coordinates, anisotropic thermal parameters, mean square displacement tensor of atoms, and bond angles and bond distances (5 pages). Ordering information is given on any current masthead page.

One-Step Synthesis of Hyperbranched Dendritic Polyesters

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Abstract: The one-step synthesis of a hyperbranched polyester possessing a dendritic structure has been achieved by thermal self-condensation of 3,5-bis(trimethylsiloxy)benzoyl chloride. The hyperbranched polyesters are obtained in yields of 80% or greater and with polystyrene equivalent weight average molecular weights in the range 30 000 to almost 200 000. The polydispersity and the molecular weights of the polyesters were found to vary greatly with the temperature of the polymerization. Characterization of the polymers was readily accomplished by NMR spectroscopy with the help of model compounds. The degree of branching of the polyesters as determined from NMR experiments was between 55 and 60%. The polyesters, which contain reactive functional groups at all chain extremities, are glassy materials that show a very high thermal stability comparable to that of analogous linear materials. In contrast, the excellent solubility properties of the hyperbranched polyesters influenced by their shape and functionalization are at variance with those of their linear polyester analogues.

Introduction

Polycondensation reactions leading to highly branched polymers, with branches at almost every repeating unit, have been a neglected subject until recently. Initial interest dates back to the early 1950s with publication of a theoretical paper by Flory[1] on polymers made from AB_x-type monomers containing a single reaction group A and at least x reactive groups B ($x \geq 2$). In such systems, growth occurs through direct reactions involving the two different functionalities without requring separate activation or deprotection steps. Early examples of such processes include the Friedel–Crafts condensation of benzyl halides[2] and the condensation of 2,5,6-tribromophenol under basic conditions.[3] These AB_x polycondensation reactions generally led to the formation of highly irregular and frequently ill-characterized structures,[1-3] with few reports of purposeful attempts to control molecular architecture found in the literature until recently. The preparation of polybenzyl has been reinvestigated[4,5] and remains largely unexpioited

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