The formation of the binuclear complex and the forcing of the irregular five-coordinate geometry on the palladium center is indicative of the stability of the double-helical ligand array (although other five-coordinate palladium complexes containing nitrogen donors are known[9]). The adoption of the double-helical geometry is dictated by the stacking of aromatic rings; in all of the double-helical complexes that we have structurally characterized, there are contacts between approximately coplanar pyridine rings in the range 3.2–3.5 Å.[4,5] The distance between the metal centers in the ligand array may be varied by the degree of twisting about one of the interannular C–C bonds (between the "terpyridyl" and "bipyridyl" fragments in the case of quinquepy). The greater the twisting, the longer the metal–metal distance. The double-helical ligand array derived from two quinquepyridine ligands can accommodate metal–metal distances in the range 3.9–5.0 Å[4] and should prove to be a versatile host for hetero- and homobinuclear complexes with first-, second-, and third-row transition metals. We are currently extending these studies to the preparation of metal–metal bonded systems.

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Supplementary Material Available: Details of the crystal structure determinations and tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for $[Pd(C_{20}H_{14}N_4)][PF_6]_2$ and $[Pd_2(C_{25}H_{17}N_5)_2][PF_6]_4 \cdot 2CH_3CN$ (17 pages); listing of observed and calculated structure factors for $[Pd(C_{20}H_{14}N_4)][PF_6]_2$ and $[Pd_2(C_{25}H_{17}N_5)_2][PF_6]_4 \cdot 2CH_3CN$ (49 pages). Ordering information is given on any current masthead page.

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[9] Chieh, P. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1643. Hinamoto, M.; Ooi, S.; Kuroya, H. *J. Chem. Soc., Chem. Commun.* **1972**, 356. Weighardt, K.; Schoffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877.

Water-Soluble Hyperbranched Polyphenylene: "A Unimolecular Micelle"?

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Whereas host–guest interactions by hydrophobic binding to preorganized molecular cavities[1] can be highly specific, the flexible binding sites of micelles are nonspecific yet solubilize apolar substances by complexation in water.[2] Only a few publications have appeared describing attempts that mimic micelle structure.[3,4]

We report here a fully aromatic water-soluble hyperbranched polymer[5] that complexes with small organic molecules in water.

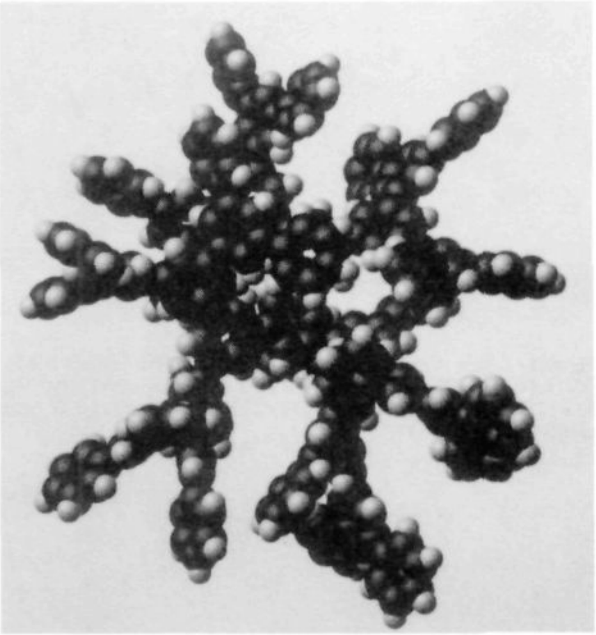
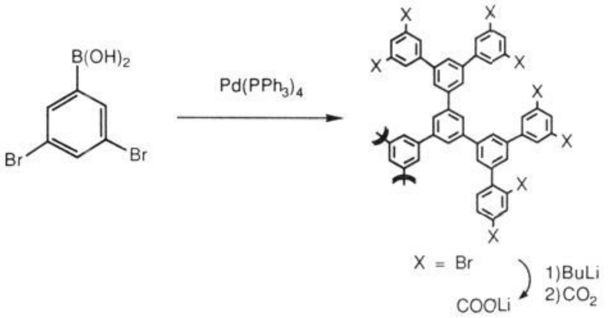


Figure 1. Computer-generated molecular model of an ideal fully branched hyperbranched polyphenylene with 46 phenyl units. The terminal functional group was eliminated from the model for clarity.

The substance was prepared by homocoupling of (3,5-dibromophenyl)boronic acid[6] under modified Suzuki conditions,[7] in a mixture of an organic solvent and an aqueous Na_2CO_3 solution with a catalytic amount of $Pd(PPh_3)_4$.[8] The polyphenylene is freely soluble in THF and *o*-dichlorobenzene, but insoluble in CH_2Cl_2 and ether.



The molecular weight of the polymer depends on the organic solvent and temperature employed during polymerization. The polymers formed in 1-methylnaphthalene or diphenyl ether had higher $\bar{M}_n$ values than the polymer formed in xylene. Addition of more monomer at the end of polymerization did not increase the molecular weight nor give a bimodal distribution. De Gennes et al. predicted that a perfect multiple-tiered polymer would grow

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[†] Contribution No. 5393.

[1] (a) Diederich, F.; Dick, K.; Griebel, D. *J. Am. Chem. Soc.* **1986**, *108*, 2273. (b) Gutsher, C. D. *Acc. Chem. Res.* **1983**, *16*, 61. Gutsher, C. D. In *Host Guest Complex Chemistry/Macrocycles*; Springer-Verlag: Berlin, 1985; p 375. (c) Canceill, J.; Lacombe, L.; Collet, A. *J. Chem. Soc., Chem. Commun.* **1987**, 219. (d) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer: Berlin, 1978. (e) For polymeric host molecules, see: Shea, K. J.; Sasaki, D. Y. *J. Am. Chem. Soc.* **1989**, *111*, 3442 and references therein.

[2] Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilization by Surface Active Agents*; Chapman and Hall: New York, 1968.

[3] (a) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676; **1981**, *78*, 676. (b) Menger, F. M.; Doll, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1109. (c) Butcher, J. A., Jr.; Lamb, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 1217.

[4] (a) Menger, F. M.; Takeshita, M.; Chow, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5938. (b) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849. (c) Tamalia, D. A.; Hall, V. B. M.; Hedstrand, D. M. *Macromolecules* **1987**, *20*, 1164. (d) Naylor, A. M.; Goddard, W. A., III; Kelfer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (e) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138 and references therein.

[5] (a) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 271. (b) Maciewjewski, M. *J. Macromol. Sci., Chem.* **1982**, *A17*, 689–703. (c) Klein, D. J. *J. Chem. Phys.* **1981**, *75*, 5186.

[6] It was prepared from the monolithiate of 1,3,5-tribromobenzene (Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1983**, *251*, 149) with trimethyl borate in 80% yield.

[7] Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

[8] Typically about 3.0 g of phenylboronic acid was reacted in 50 mL of an organic solvent and 20 mL of sodium carbonate with 30 mg of $Pd(PPh_3)_4$. Yield: 80–95%. ^1H NMR ($CDCl_3$): a broad peak between 7.0–8.5. GPC (PS standard): $\bar{M}_n = 3820$, $\bar{M}_w = 5750$. The degree of branching, determined by ^{13}C NMR: ca. 70%. IR: 847 and 740 cm^{-1} (1,3,5-trisubstituted aromatics). Tg: 280 °C, no melting point. Inherent viscosity in THF ($c = 2$ g/dL): 0.031 dL/g. Anal. Calcd for C_6H_3Br: C, 46.49; H, 1.95; Br, 51.55. Obsd: C, 48.00; H, 2.27; Br, 49.67. This polymer was also obtained by a $Ni(PPh_3)_2Cl_2$-catalyzed coupling reaction (Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091) of (3,5-dibromophenyl)magnesium bromide. The polymer obtained by this method has $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of 3910 and 1.81, respectively, but has only 40% branching.

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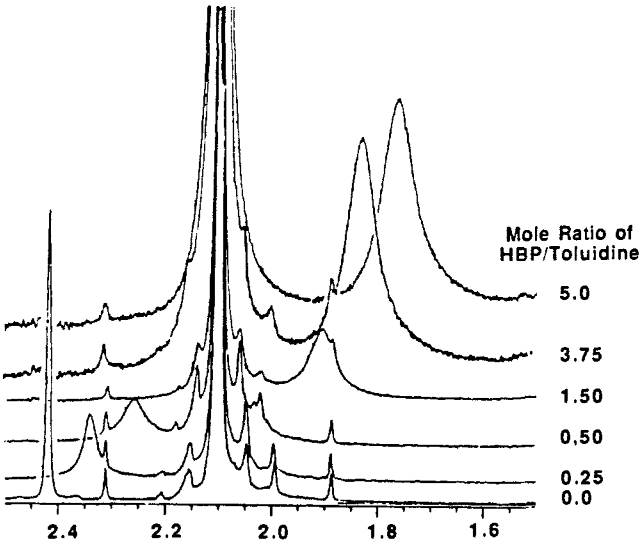

Figure 2. The NMR spectra of the methyl group region of the *p*-toluidine in 1 M NaCl at 30 °C. The concentration of *p*-toluidine is 3.8×10^{-3} M. The large peak at 2.10 is due to sodium acetate, and the small peaks at both sides of this peak are spinning sidebands and carbon satellite peaks.

to a maximum molecular weight.[9] The repeat unit of our polymer is not flexible, and branching is imperfect;[10] thus, no definite steric saturation point at the surface could be found based on a molecular model. We cannot explain what causes the molecular growth to stop.

A molecular model[11] of the polymer (Figure 1) reveals a globular structure with many cavities, The average opening size of the cavities was measured to be in the range of 5 Å.

A water-soluble derivative of the polymer was prepared by metalation with *n*-BuLi at −78 °C in THF, followed by reaction with CO_2.[12] The polymer was isolated as its Li salt. The titration curve of this salt with 0.1 M HCl showed a broad pK_a value for the acid group, ranging from 3.0 to 5.0. The conversion to carboxylate was estimated to be 70% of theory based on elemental analysis and the NMR spectrum after the carboxy group had been reduced to a hydroxymethyl function with borane. The carboxylate form of the polymer is very soluble in water (greater than 1 g/mL), without much change in the viscosity of the solution. The carboxylic acid ended polymer is water insoluble. The NMR spectrum of the acid-ended polymer in THF shows several well-resolved groups of peaks in the aromatic region, but the carboxylate polymer in an aqueous solution gives only a broad peak. This might be due to the ordered structure of the water in the cavities restricting the rotation of the phenyl rings more than a loosely bound organic solvent does.

The complexation with *p*-toluidine, a guest molecule, was studied by NMR.[13] All *p*-toluidine NMR peaks shifted upfield and broadened as the polymer was added. The effect is strongly dependent on the ionic strength of the media, namely, with a polymer to *p*-toluidine ratio of 0.53, the chemical shift of the methyl group was 1.76[14] in 1.28 M and 2.03 in 0.13 M Na_2SO_4 solution. When the ratios were higher than 2.5 in a 1.9 M solution, the chemical shift reached a limiting value of 1.59. The equilibrium constant of the complex was determined in 1 M NaCl solution. At a 0.5 molar ratio of polymer to *p*-toluidine, the chemical shift change ($\Delta\delta$) of the methyl group and AB quartets of the phenyl ring were 0.08, 0.08 (ortho proton), and 0.10 (meta proton) ppm, respectively; at a molar ratio of 10, $\Delta\delta$ values of 0.66, 0.72, and 0.84 were found (Figure 2). An accurate equilibrium constant is difficult to obtain, since the polymer could form multiple complexes with *p*-toluidine when the ratio of host to guest is low. If we make two approximations, (1) only a 1:1 complex is formed and (2) the chemical shift for the methyl group of the complexed *p*-toluidine is 1.59, then an equilibrium constant of 510 (±150) M^{-1} is estimated.[15]

In conclusion, an array of aromatic polymeric chains was able to generate an environment that resembles a micellar structure.[16] This microenvironment resembles a Flory-Dill model[3a] in the sense that all of the chains are pointing toward the center of the globular structure, but the accessibility of the cavity to water and connectivity of the chains is applicable to a Menger model.[3b]

Acknowledgment. We are very grateful to J. Calabrese for helping with the computer modelling.

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(9) De Gennes, P. G.; Hervet, H. *J. Phys.* (*Paris*) **1983**, *44*, L351-L360.

(10) If the polymer (DP > 24, equivalent to three tiers) is fully branched, the ratio of the number of carbons (4-position) between two carbons connected to bromide to the number of carbons (1-position) connected to phenyl ring is 0.25. In the ^{13}C NMR spectrum, the peaks due to these two kinds of carbon are well separated, and the branching factor was found to be in the range of 70%. The NMR spectrum was obtained by 20-s pulse delay while NOE was suppressed. The relaxation time of the quaternary carbon was found to be less than 5 s.

(11) Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England.

(12) In a small-scale reaction, the yield of the lithiation was confirmed to be over 95% by quenching of the anion with trimethylchlorosilane. When the anion was quenched with MeOH, IR peaks at 700 and 799 cm^{-1}, due to monosubstituted benzene, appeared in addition to the peaks corresponding to trisubstituted benzene.

(13) This polymer solution also showed dissolution ability. A 10% solution of the lithium carboxylate polymer in water dissolves 1.1 mg of naphthalene in 1 mL of solution. The same amount of polymer in 0.1 M K_2HPO_4 solution also enhanced the solubility of methyl red and methyl orange 30 times and twice, respectively.

(14) Sodium acetate was used as an internal standard with the chemical shift 2.100. The chemical shift of sodium acetate was invariable relative to the water peak in addition of the polymer. The pH of the solution was 9.6.

(15) The 10 data points were plotted to an equation $R/r = 1 + 1/[Kt(1 - r)]$ where R is the molar ratio between the polymer and *p*-toluidine, r is the ratio between the $\Delta\delta$ at the given R and the maximum $\Delta\delta$, and t is the concentration of *p*-toluidine. The correlation factor for the fit was 0.82.

(16) The term micelle was introduced in 1858 by a Swiss botanist, C. van Naegeli, who described a cell as an aggregate of 9000 molecules of starch packed in a crystalline array. Polymers were believed to have micellar structures (the micellar theory) until the 1920s.

Multiple-Bond Character between Two Carborane Polyhedra: The Two-Electron Reduction of Biscarborane

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In an effort to extend the chemistry and possibly determine the molecular structure of the $[nido\text{-}C_2B_{10}H_{12}]^{2-}$ anion,[1-3] a valuable synthon for numerous metallacarboranes,[4-8] biscarborane[9] was

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(1) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128.

(2) Zakharkin, L.; Kalinin, V.; Podvisotskaya, L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *10*, 2310.

(3) Stanko, V.; Gol'typin, Y. V.; Brattsev, V. *Zh. Obshch. Khim.* **1969**, *39*, 1175.

(4) Dunks, G. B.; McKown, M. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 2541.

(5) Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 1109.

(6) Dustin, D. F.; Evans, W. J.; Jones, C. J.; Wiersema, R. J.; Gong, H.; Chan, S.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 3085.

(7) (a) Salentine, C. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 426. (b) Lo, F. Y.; Strouse, C. E.; Callahan, K. P.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 428. (c) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872. (d) Salentine, C. G.; Hawthorne, M. F. *J. Am. Chem. Soc., Chem. Commun.* **1975**, 848.

(8) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1805.

(9) The term biscarborane here refers to 1-1′-(*closo*-1′,2′-$C_2B_{10}H_{11}$)-*closo*-1,2-$C_2B_{10}H_{11}$. (a) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1643. (b) Paxson, T. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 708.

0002-7863/90/1512-4593$02.50/0