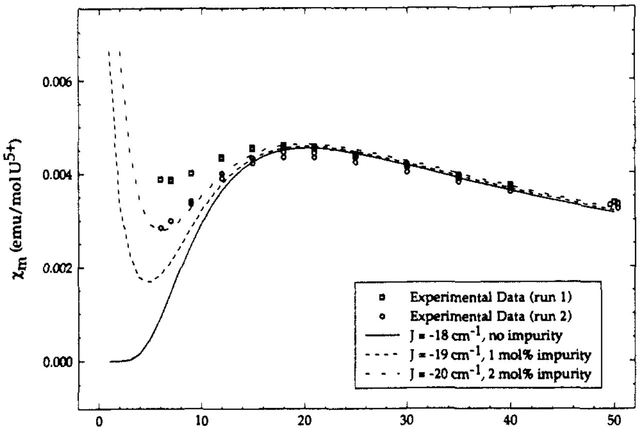


Figure 2. Comparison of experimental magnetic susceptibility data with calculated values for **1**. The calculations are with $g_\parallel = 2.6$. The impurity is assumed to be $(MeC_5H_4)_3U(thf)$, and three calculated curves are shown for $J = -18$ cm^{-1} (no impurity), $J = -19$ cm^{-1} (1 mol % impurity), and $J = -20$ cm^{-1} (2 mol % impurity).

The bimetallic molecule **1** can be considered to be two monomeric $(MeC_5H_4)U$ units that are connected by the diimide through which an intramolecular antiferromagnetic exchange takes place. Because of the steric bulk of the $(MeC_5H_4)_3U$ unit, intermolecular exchange is negligible, as shown by the data for **2**. The magnetism at low temperature in **1** and **2** is attributed to the population of the ground crystal field state only. Thus the Curie constant obtained from the plot of $1/\chi_M$ vs T at low temperature for **2** is directly related to the average g value. Since $g_\perp = 0$ with the assignment of the ground state as $\mu = \pm^3/_2$, $g_\parallel = 2.6$ for the $\mu = \pm^3/_2$ ground crystal field state of the U(V) ion. It is assumed that the ground state for **1** is the same as that for **2** in the absence of electron exchange, and that there is a one-dimensional exchange interaction along the 3-fold or z axis for **1** between the two U centers. With the second assumption, the exchange interaction in **1** may be treated with the model used for an isolated dimer.[1f,12] The Hamiltonian for such a dimer is written as

$$\mathcal{H} = -2JS_{z1}S_{z2} + g_\parallel \mu_B H_z(S_{z1} + S_{z2}) \qquad (2)$$

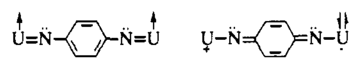
where S_{z1} and S_{z2} are effective spin $^1/_2$ operators, J is the exchange constant, and μ_B is the Bohr magneton. The magnetic susceptibility for a randomly oriented powder (per uranium ion) is (with $g_\perp = 0$)[1f]

$$\chi_{av} = {}^1/_3 \frac{N g_\parallel{}^2 \mu_B{}^2}{2kT}(1 + e^{-J/kT})^{-1} \qquad (3)$$

where N is Avogadro's number, k is the Boltzmann constant, and T is the absolute temperature. This model is applicable to **1** only for $T \lesssim 50$ K.

The calculated susceptibilities for **1** (with $g_\parallel = 2.6$) as a function of temperature for various values of J are shown in Figure 2. The experimental deviation from the theoretical model at low temperatures is assumed to be due to a small amount of a paramagnetic impurity as different preparations of **1** show differing susceptibilities in this temperature range. Assuming that the impurity is the starting material, $(MeC_5H_4)_3U(thf)$, then ca. 1-2 mol % is sufficient to cause the observed deviations at low temperature. It is concluded that $J \sim -19$ cm^{-1} and the antiferromagnetic state is lowest in energy.

The observation that the spins on each uranium center of **1** antiferromagnetically couple while those on **2** do not couple to 5 K may be rationalized by a superexchange pathway. The imido nitrogens in **1** are in the 1,4-positions of the benzene ring, and they can form a conjugated ring while those on **2** cannot. It is reasonable to postulate that the spin on each uranium center can communicate across the conjugated ligand in **1** though not in **2**. This may be illustrated by the two resonance structures shown below.



These two resonance structures imply that the two spins communicate by way of the ligand π-system and the electron on each uranium is in a π-symmetry orbital. A spin polarization model can be postulated, and this model also rationalizes the observation of antiferromagnetic coupling;[1c,8] we know of no simple way to distinguish between these two physical processes.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

(12) Baker, J. M.; Bleaney, B.; Brown, J. S.; Hutchison, C. A., Jr.; Leask, M. J. M.; Martineau, P. M.; Wells, M. R. *J. Magn. Magn. Mater.* **1983**, *657*, 31-34.

Helical and Nonhelical Palladium(II) Complexes of Oligopyridine Ligands: The Ligand-Directed Assembly of Polynuclear Complexes

Edwin C. Constable,* Susan M. Elder, John Healy, and Michael D. Ward

University Chemical Laboratory, Lensfield Road
Cambridge CB2 1EW, United Kingdom

Derek A. Tocher*

Department of Chemistry, University College London
20 Gordon Street, London WC1H OAJ, United Kingdom

Received January 12, 1990

There has been considerable recent interest in the design of ligands that facilitate the spontaneous self-assembly of complexes[1] and host–guest compounds[2] with novel chemical, biological, or topological properties. The assembly of double-helical polynuclear complexes has been studied by several groups.[3,4] We have investigated the ability of the oligopyridines to assemble flexible but nonlabile double-helical ligand environments with a view to

---

(1) Stoddart, F. *Nature (London)* **1988**, *334*, 10. Libman, J.; Tor, Y.; Stanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880. Stuckmeier, G.; Thewalt, U.; Furhop, J.-H. *J. Am. Chem. Soc.* **1976**, *98*, 278. Blake, A. J.; Dietrich-Buchecker, C. O.; Hyde, T. I.; Sauvage, J.-P.; Schöder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1663 and references therein. Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 189 and references therein.

(2) Ortholand, J.-Y.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1394. Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396.

(3) Lehn, J.-M.; Rigault, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095. Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci., U.S.A.* **1987**, *84*, 2565. Lehn, J.-M.; Sauvage, J.-P.; Simon, J.; Ziessel, R.; Piccinni-Leopardi, C.; Germain, G.; Declercq, J.-P.; Van Meerssche, M. *Nouv. J. Chim.* **1983**, *7*, 413. Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccinni-Leopardi, C.; Arrieta, J. M.; Germain, G.; Van Meerssche, M. *Nouv. J. Chim.* **1984**, *8*, 661. Struckmeier, G.; Thewalt, U.; Fuhrhop, J.-H. *J. Am. Chem. Soc.* **1976**, *98*, 278. Lippert, B. *Nachr. Chem., Tech. Lab.* **1990**, *38*, 186.

(4) Constable, E. C.; Drew, M. G. B.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1600. Constable, E. C.; Holmes, J. M. *Inorg. Chim. Acta* **1987**, *126*, 187. Barley, M.; Constable, E. C.; Corr, S. A.; Drew, M. G. B.; McQueen, R. C. S.; Nutkins, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1988**, 2655. Constable, E. C.; Drew, M. G. B.; Forsyth, G.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1450. Constable, E. C.; Drew, M. G. B.; Forsyth, G.; Ward, M. D. *Polyhedron* **1989**, *8*, 2551. Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1256. Cathey, C. J.; Constable, E. C.; Hannon, M. J.; Tocher, D. A.; Ward, M. D. *J. Chem. Soc., Chem. Commun.*, in press.

0002-7863/90/1512-4590$02.50/0

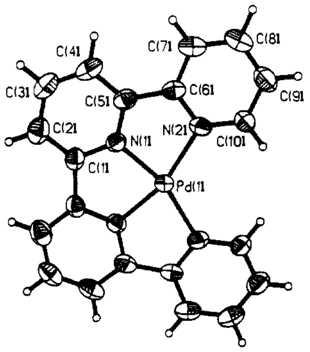


Figure 1. A view of the $[Pd(quaterpy)]^{2+}$ cation in $[Pd(quaterpy)][PF_6]_2$; Pd(1)–N(1), 1.928 (4) Å; Pd(1)–N(2), 2.057 (4) Å; ∠N(1)–Pd–N(2), 80.5 (2)°; ∠N(1)–Pd–N(1A), 81.2 (2)°; ∠N(1A)–Pd–N(2), 161.7 (2)°; ∠N(2)–Pd–N(2A), 117.7 (2)°.

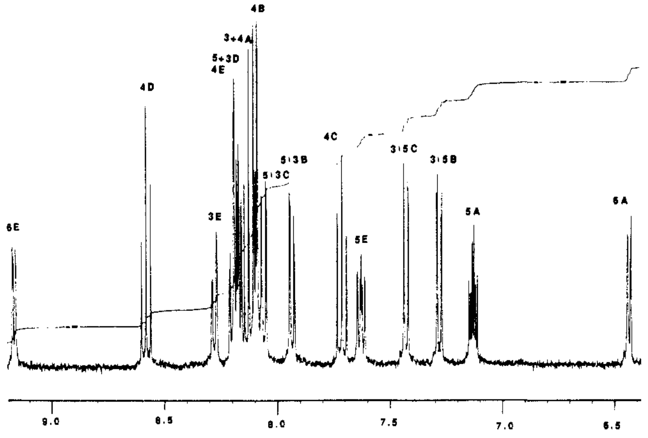


Figure 2. ^1H NMR spectrum (400 MHz) of $[Pd_2(quinquepy)_2][PF_6]_4$·$(CD_3CN)$; assignments based on a double quantum filtered COSY experiment.

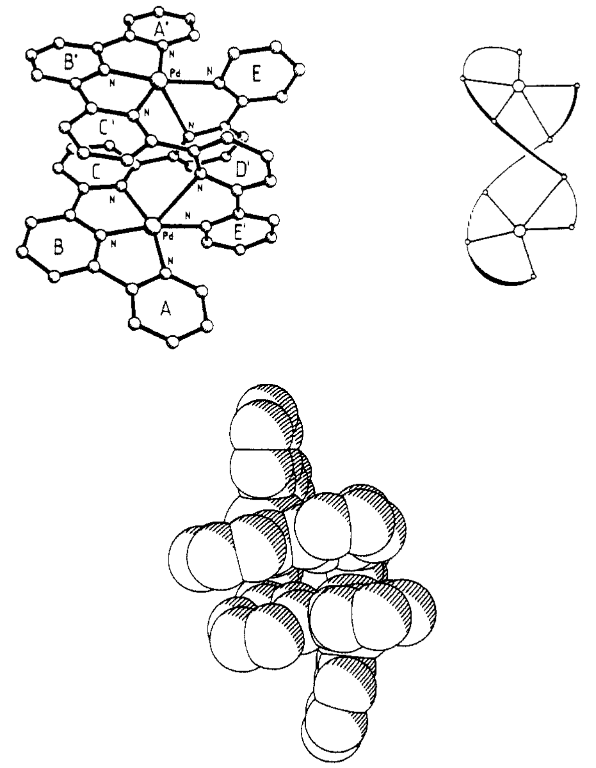


Figure 3. Alternative views of the $[Pd_2(quinquepy)_2]^{4+}$ cation in $[Pd_2(quinquepy)_2][PF_6]_4$·4MeCN.

designing photoactive and redox-active binuclear complexes.[4] In order to probe the features dictating the formation of the double-helical array, we have investigated the behavior of a metal ion with a strong preference for the adoption of a planar nonhelical coordination geometry.

The reaction of 2,2′:6′,2″:6″,2‴-quaterpyridine (quaterpy) with $[\{Pd(OAc)_2\}_3]$ in methanol results in the formation of a pale yellow solution, from which $[Pd(quaterpy)][PF_6]_2$ may be isolated.[5] The FAB mass spectrum indicated the formation of only a 1:1 complex, while the ^1H NMR spectrum indicated a complex with C_2 symmetry.[6] This is consistent with a square-planar mononuclear formulation, and we have confirmed this by determining the crystal structure of the complex.[7] The molecular structure of the $[Pd(quaterpy)]^{2+}$ cation is shown in Figure 1. The quaterpy ligand is planar and presents a distorted square-planar donor set to the palladium; the distortions from the idealized 90° N–M–N angles are similar to those reported in other quaterpy complexes.[5,8] The palladium exhibits short contacts to the two $[PF_6]^-$ counterions of 3.10 (1) Å, which are distorted from the "idealσqt axial sites in the same way that the *pseudo*axial substituents are in $[Ni(quaterpy)(MeCN)_2]^{2+}$ (∠F–Pd–F, 164.6 (7)°).[5] The $[Pd(quaterpy)]^{2+}$ cation is a 'normal' square planar palladium complex.

A yellow solution was obtained from the reaction of 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (quinquepy) with $[\{Pd(OAc)_2\}_3]$, from which a yellow salt of the stoichiometry $[Pd(quinquepy)][PF_6]_2$·2MeCN was obtained. The FAB mass spectrum exhibits highest mass peaks at *m/z* 493 ($\{Pd(quinquepy)\}^+$) and 638 ($\{Pd(quinquepy)(PF_6)\}^+$), and the ^1H NMR spectrum (Figure 2) indicates 17 proton environments. These data are consistent with five independent pyridine rings and a mononuclear structure analogous to that for $[Pd(quaterpy)]^{2+}$, with one additional noncoordinating pyridine. This formulation does not account for the large upfield shift of the doublet of doublets centered at δ 6.43, and we accordingly determined the crystal structure of the compound.

Alternative views of the molecular structure of the cation are shown in Figure 3. A double-helical binuclear cation, $[Pd_2(quinquepy)_2]^{4+}$, is present. Each palladium is in an irregular five-coordinate environment with four short contacts (1.941–2.085 Å) to a "terpyridyl" fragment of one ligand and a terminal pyridine from the other ligand. The coordination sphere is completed by a long contact (≈2.6 Å) to the remaining pyridine of the second ligand. The palladium–palladium distance is 4.96 (1) Å, and there are no metal–metal interactions. The large metal–metal distance is achieved by a twisting (≈70°) about the C–C bond between the "terpyridyl" and "bipyridyl" fragments of each ligand. The structure is maintained by stacking interactions between the two ligands; the shortest approximately coplanar contacts are between rings D and E′ (3.38 Å) and rings E and D′ (3.49 Å), using the numbering of the nitrogen atom to describe the ring. The anomalous upfield shift of one of the H_6 protons and of the ligand is now seen to be due to H_6 of rings A and A′, which are lying in the shielded regions ≈2.6 Å above rings E′ and E, respectively.

---

(5) Constable, E. C.; Elder, S. M.; Healy, J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.*, in press.

(6) ^1H NMR (CD_3CN, 400 MHz): δ 8.64 (1 H, ddd, H_6), 7.92 (1 H, ddd, H_5), 8.41 (1 H, td, H_4), 8.37 (1 H, dd, H_3), 8.34 (1 H, dd, $H_{3'/5'}$), 8.51 (1 H, t, $H_{4'}$), 8.26 (1 H, dd, $H_{5'/3'}$). FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m/z* 561 ($\{Pd(quaterpy)(PF_6)\}^+$), 416 ($\{Pd(quaterpy)\}^+$) (based on ^{106}Pd).

(7) Crystal data for $C_{20}H_{14}N_4F_{12}P_2Pd$: monoclinic, $C2/c$, $a = 17.485$ (2) Å, $b = 11.714$ (1) Å, $c = 14.261$ (2) Å, $\beta = 127.60$ (1)°, $V = 2314$ Å^3, $Z = 4$, $D_{calcd} = 2.03$ g cm^{-3}, λ (Mo Kα) = 0.71073 Å (graphite monochromator), $\mu = 10.4$ cm^{-1}, Nicolet R3m/V diffractometer, 4104 reflections (5° ≤ 2θ ≤ 55°) on an off-white crystal 0.40 × 0.15 × 0.15 mm, 2645 independent, 2046 $[I \geq 3\sigma(I)]$, $R = 0.0445$, $R' = 0.0511$. Crystal data for $C_{54}H_{40}N_{12}F_{24}P_4Pd_2$: triclinic, $P\bar{1}$, $a = 12.594$ (7) Å, $b = 15.046$ (9) Å, $c = 17.237$ (9) Å, $\alpha = 87.64$ (7)°, $\beta = 77.34$ (5)°, $\gamma = 75.13$ (6°), $V = 3080$ Å^3, $Z = 2$, $D_{calcd} = 1.78$ g cm^{-3}, λ (Mo Kα) = 0.71073 Å (graphite monochromator), $\mu = 7.97$ cm^{-1}, Nicolet R3m/V diffractometer, 11185 reflections (5° ≤ 2θ ≤ 50°) on an orange crystal 0.25 × 0.30 × 0.50 mm, 10658 independent, 4151 $[I \geq 3\sigma(I)]$, $R = 0.0970$, $R' = 0.0966$. All computations used SHELXTL-PLUS: Sheldrick, G., University of Göttingen, Federal Republic of Germany, 1986.

(8) Henke, W.; Kremer, S.; Reinen, D. *Z. Anorg. Allg. Chem.* **1982**, *491*, 124. Maslen, E. N.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 323.

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.

Acknowledgment. We thank the Science and Engineering Research Council for support.

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.

---

(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"?

Young H. Kim* and Owen W. Webster

Central Research and Development Department
E. I. du Pont de Nemours & Co., Inc.†
Experimental Station, P.O. Box 80328
Wilmington, Delaware 19880-0328

Received January 16, 1990

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.

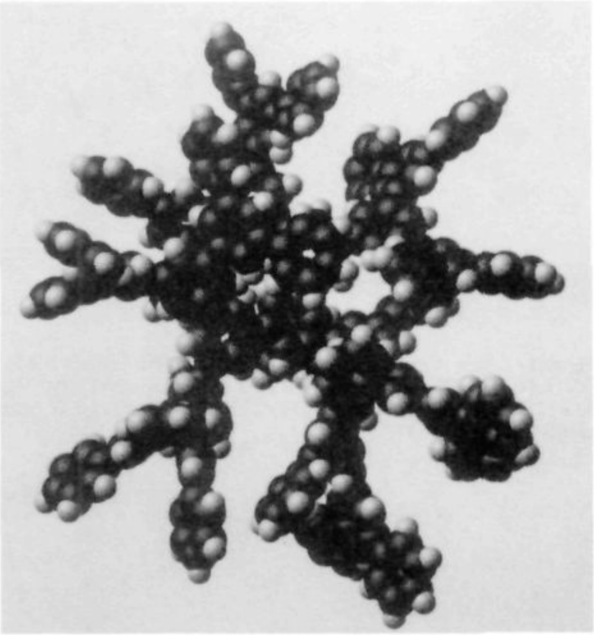
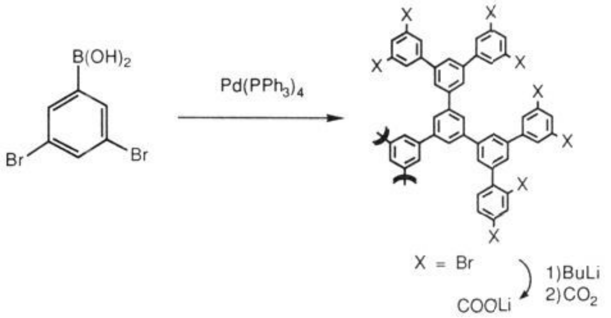


Figure 1. Computer-generated molecular model of an ideal fully branched hyperbranched polyphenylene with 46 phenyl units. The terminal functional group was eliminated from the model for clarity.

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

---

† 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.

0002-7863/90/1512-4592$02.50/0