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A Carborane-Based Analogue of Poly(*p*-phenylene)

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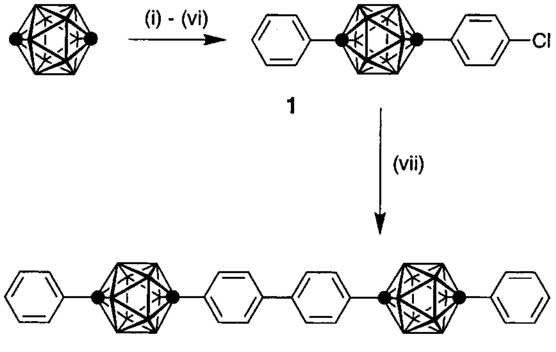
Since the successful development of elastomeric poly(carborane−siloxane)s with very high thermal and chemical stability (*Dexsils, Ucarsils*),[1] many attempts have been made to extend the range of useful carborane-based polymers.[2] Current research is focused on the synthesis and characterization of materials containing carborane icosahedra linked either by direct carbon−carbon bonds [3] or by aromatic systems.[4] Poly(arylene−carboranes) are of particular interest because of their extreme resistance to combustion,[5] giving them potential value as components of fire-retardant and oxidation-resistant coatings. The remarkable combustion resistance exhibited by these materials appears to stem both from a high-temperature cross-linking reaction between aromatic and carborane units, which prevents the formation of volatile thermolysis products, and from the production of a cohesive surface-coating of boron(III) oxide, B_2O_3, which serves to limit further oxidation.[6] All previous syntheses of linear poly(arylene−carborane)s have focused on the *indirect* linking of diarylcarborane units by functional groups such as ester, amide, imide and ether/ketone, but in view of the extreme chemical stability of *directly*-bonded aromatic materials such as poly(1,4-phenylene),[7] we have begun to explore the synthesis of analogous materials in which carborane icosahedra alternate with directly bonded aromatic nuclei. Here we report preliminary characterization data for the first polymer of this type to be synthesized.

Transition metal-catalyzed coupling of dihalogenoarenes is a versatile route to polymers with biaryl linkages,[8] but to establish the viability of this chemistry for carborane-based systems, a model compound, 1-(4-chlorophenyl)-12-phenyl-1,12-dicarbadodecaborane (**1**), was synthesized [9] and coupled in dimethylacetamide (DMAc) solution using $Ni(PPh_3)_4$ as catalyst (Figure 1). The resulting "dimer" **2,** a novel, carborane-based analogue of *p*-sexiphenyl, was isolated in good yield by column chromatography. Thermal analysis of compound **2** by DSC showed not only a strong crystal-melting transition at 419 °C, but also a series of weak, lower-temperature endotherms at 260, 312, and 328 °C. Although the extended, rodlike structure of **2** appears to suggests potential nematic character, hot-stage polarizing microscopy in fact demonstrated that the weaker endotherms are associated with solid state (crystal−crystal) transitions rather than with any form of liquid crystalline behavior.



(i) BuLi, (ii) CuCl, (iii) 1,4-ClC_6H_4I, (iv) BuLi, (v) CuCl, (vi) C_6H_5I, (vii) Zn, $Ni(PPh_3)_4$

Figure 1. Synthesis and nickel-catalyzed coupling of 1-(4-chlorophenyl)-12-phenyl-1,12-dicarbadodecaborane (**1**).

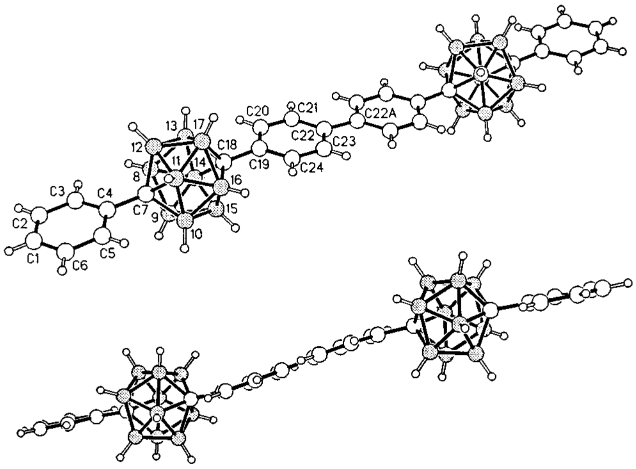


Figure 2. X-ray structure of the centrosymmetric dimer **2**, with atom numbering (upper view). The lower view illustrates the marked "sinusoidal" distortion of this molecule in the solid state. Selected molecular parameters: C(4)−C(7) = 1.512(4), C(18)−C(19) = 1.516(4), C(22)−C(22A) = 1.503(5), B−B(mean) = 1.771(5), B−C(mean) = 1.722(4) Å; C(3)−C(4)−C(5) = 117.8(3), C(20)−C(19)−C(24) = 117.3(3), C(21)−C(22)−C(23) = 116.5(3)°.

The structure of dimer **2** was solved by single-crystal X-ray diffraction,[11] which revealed a centrosymmetric molecular structure featuring a marked "sinusoidal" distortion of the expected collinear configuration (Figure 2). *Ab initio* calculations at the HF/6-31G level (*Gaussian 94*) revealed no intramolecular basis for this distortion, so that the observed deviations from collinearity must result from anisotropic crystal-packing forces.

Following the successful model reaction, catalytic polycondensation of the bifunctional monomer 1,12-bis-(4-chlorophenyl)-1,12-dicarbadodecaborane (**3**) was attempted under similar conditions (Figure 3). The resulting rodlike polymer (**4**) crystallized spontaneously from the reaction solution, and was found to be very similar in its physical properties to poly(*p*-phenylene).[7] Thus, it failed to dissolve in a wide range of organic solvents, even at high temperatures, and showed no evidence of melting or softening up to 600 °C. The

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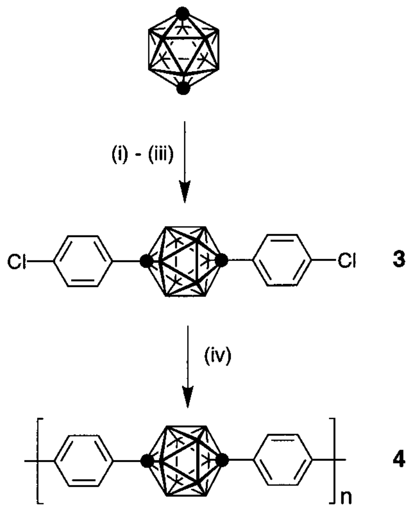

(i) BuLi, (ii) CuCl, (iii) 1,4-ClC$_6$H$_4$I, (iv) Zn, Ni(PPh$_3$)$_4$

Figure 3. Synthesis and catalytic polycondensation of 1,12-bis(4-chlorophenyl)-1,12-dicarbadodecaborane.

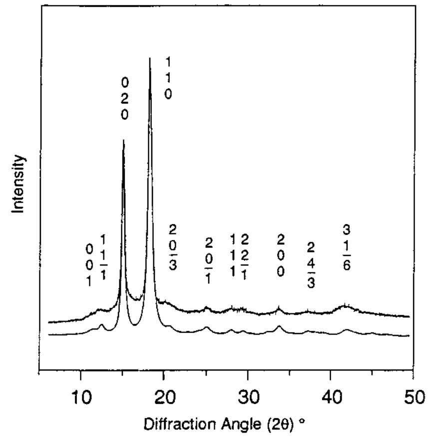

Figure 4. Experimental (upper trace) and simulated (lower trace) X-ray powder diffraction patterns (Cu Kα) for poly(4,4′-biphenylene-1,12-dicarbadodecaborane) and the current structural model (Figure 5), respectively.

extreme insolubility of polymer **4** suggests that only a relatively low degree of polymerization is achieved before the polymer precipitates from solution. The polymer does however give a very well-defined X-ray powder diffraction pattern (Figure 4), confirming that its intractability stems from a high crystal melting point and not from any cross-linking or other side reaction associated with its synthesis. Since the dimer **2** melts only above 400 °C, a crystalline melting point for polymer **4** of >600 °C (i.e., above its decomposition temperature) does not seem at all unreasonable. Thermogravimetric analysis of polymer **4**, to 1000 °C under argon, indicates a very high ceramic yield indeed (ca. 92%). In view of this result, we are currently exploring the possibility that the polymer may undergo direct thermal conversion to graphitic boron carbide.

The X-ray powder pattern of polymer **4** (Figure 4, upper trace) could be indexed in terms of a *C*-face-centered monoclinic unit cell with dimensions $a = 9.11$ Å, $b = 11.77$ Å, $c = 13.33$ Å, $\beta = 144.4°$. The c dimension was fixed by reference to the "polymer-repeat length" represented by the distance C(7)–C(18A) in the structure of dimer **2** (Figure 2). Using the standard convention for polymer crystals, the c-axis is thus oriented parallel to the direction of the polymer chain. A more detailed structural analysis of polymer **4** was carried out using the software package *Cerius-2* (Molecular Simulations Inc.), using an idealized chain-structure based on that found experimentally for oligomer **2**. Crystallographic inversion centers were located at the center of the carborane cage and at the center of the biphenyl linkage, defining a polymer chain in which the aromatic rings are effectively coplanar, leaving only the torsion angle between the carborane cage and its associated aromatic rings to be determined.

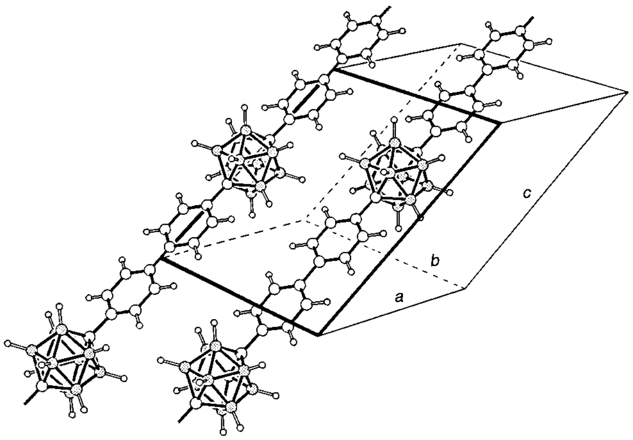

Figure 5. Final model for the crystal and molecular structure of polymer **4**.

Ab initio calculations for phenyl-*o*-carborane show that the energy-barrier to rotation about the phenyl–carborane (C–C) bond is very low indeed (ca. 2.1 kJ/mol).[10] For the polymer considered here, the higher symmetry of the phenyl-*p*-carborane linkage must reduce this torsional barrier even further, so that the ring-cage torsion angle H–C–B–H (defined here as Δ) will be strongly influenced by crystal packing forces. The rotational potential has 10-fold symmetry (36° from minimum to minimum), so that the actual range of Δ over which the potential varies is only 18°. Crystal packing calculations were therefore undertaken for polymer chains with Δ-values ranging from 0 to 18°, and the resulting crystal structures were evaluated in terms of their lattice energy, density, and simulated X-ray powder diffraction patterns. These calculations identified a number of possible unit cells of similar energy and density ($E = 32-33$ kcal per chain, $\rho = 1.18-1.20$), but the original, *C*-centered monoclinic unit cell provided the best fit to the experimental powder pattern. This cell was found to represent the crystal-energy minimum for a chain conformation in which $\Delta = 18°$. A powder diffraction pattern simulated, with appropriate broadening parameters, from this structure is shown in Figure 4 (lower trace), superimposed on the experimental powder pattern. The experimental density for polymer **4** of 1.19 g cm^{-3}, measured by flotation, may be compared to a value of 1.18 g cm^{-3} calculated for the simulated unit cell.

In the final model (Figure 5) the polymer chain has a mirror plane parallel to *ac* and inversion symmetry about the centers of the icosahedron and the biphenyl linkage. All aromatic rings in the crystal are essentially parallel, and an analysis of interchain contact distances suggests that the crystal packing is dominated by arene–carborane (H···H) contacts. A slight sinusoidal distortion of the polymer chain, as found in the structure of oligomer **1**, leaves the chain symmetry unchanged but significantly improves both the density of the simulated crystal and the calculated fit to the experimental X-ray powder pattern.

Currently available X-ray data do not permit a more quantitative refinement of this structure, but it may be noted that the symmetry elements of the model are consistent with space group $C2/m$. Perhaps surprisingly, the present work appears to be the first in which a well-defined crystal structure is proposed for *any* carborane-based polymer system.

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Supporting Information Available: Tables of crystal data and structure refinement for oligomer **2**, and atomic coordinates, thermal parameters, and hydrogen atom coordinates for **2**; crystal packing diagram and intermolecular contacts for **2**, a table of peak-broadening parameters used in the diffraction-modeling study of polymer **4**, and views of the final model for the crystal structure of polymer **4** (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Peters, E. N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *C17*, 173.

(2) Plešek, J. *Chem. Rev.* **1992**, *92*, 269, and references therein.

(3) (a) Yang, Y.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (b) Muller, J.; Baše, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.

(4) (a) Vinogradova, S. V.; Valetskii, P. M.; Kabachi, Y. A. *Russ. Chem. Rev.* **1995**, *64*, 365. (b) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 3056. (c) Colquhoun, H. M.; Herbertson, P. L.; Wade, K. *J. Polym. Sci., Part A, Polym. Chem.* **1996**, *34*, 2521. (d) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.

(5) Kabachii, Y. A.; Valetskii, P. M. *Int. J. Polym. Mater.* **1990**, *14*, 9.

(6) (a) Colquhoun, H. M.; Daniels, J. A.; Stephenson, I. R.; Wade K. *Polym. Commun.* **1991**, *32*, 272. (b) Colquhoun, H. M.; Lewis, D. F.; Daniels, J. A.; Herbertson, P. L.; MacBride, J. A. H.; Stephenson, I. R.; Wade K. *Polymer* **1997**, *38*, 2447.

(7) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10934.

(8) Ueda, M.; Seino, Y.; Sugiyama, J. *Polym. J.* **1993**, *25*, 1319.

(9) Coult, R.; Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K. *J. Organomet. Chem.* **1993**, *462*, 19.

(10) Brain, P. T.; Cowie, J.; Donohoe, D. J.; Hnyk, D.; Rankin, D. W. H.; Reed, D.; Robertson, H. E.; Welch, A. J.; Hofmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 1701.

(11) Crystals of dimer **2** were grown from hexane−acetonitrile. Crystal data: $C_{28}H_{38}B_{20}$, $M = 590.78$, monclinic, space group $P2_1/n$, $a = 9.794(1)$ Å, $b = 10.642(1)$ Å, $c = 15.931(2)$ Å, $\beta = 95.31(1)°$, $Z = 2$, $U = 1653.2(3)$ Å^3, $D_c = 1.187$ g cm^{-3}, μ(Cu Kα) = 0.41 mm^{-1}, $F(000) = 612$. The structure was solved by direct methods and the non-H atoms were refined anisotropically by full-matrix least-squares methods, based on F^2, the H atoms being refined isotropically (riding model) to give $R_1 = 0.060$, $wR_2 = 0.141$ for 1684 independent observed reflections [$I > 2\sigma(I)$, $2\theta \leq 124°$].

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