

magnetization vs applied field was measured at various temperatures above and below the Neel temperature, $T_c = 12$ K (Figure 3). As the temperature is reduced, the isotherms become increasing sigmoidal. So, for instance, at 4 K, M varies linearly with H_A up to ca. 2000 G. At higher H_A , the field dependence of the magnetization departs from linearity and attains the value $M = 24\,800\text{ cm}^3\text{ G mol}^{-1}$ at the highest field employed (35 000 G). This value is close to that of the saturation magnetization M_S expected for a spin $S = S_{\text{Mn}} + S_{\text{Cu}} = 5/2$ per MnCu unit (the theoretical value of M_S for $S = 5/2$ and $g = 2$ is $28\,000\text{ cm}^3\text{ G mol}^{-1}$). The critical field is 4500 G. H_C is the value of the applied field for the crossing point of the isotherms (Figure 3). So H_C could be defined as the applied field which would induce the transition when $T \rightarrow 0$ K. Ac susceptibility measurements performed in the temperature range 4–20 K and at different frequencies show neither an out-of-phase signal nor frequency-dependent behavior. All these features are common to compounds 2 and 3, whose H_C and T_C values are 4000 G and 11.5 K for 2 and 2500 G and 9 K for 3.

The structures of 1–3 are likely to be very close as revealed by the similarity of their X-ray powder patterns. The most relevant feature of these patterns is the occurrence of two very strong diffraction peaks. One of them appears at ca. 7.1 Å for 1–3, whereas the other one is shifted toward higher d values when going from 1 to 3 (7.87, 8.34, and 9.32 Å, respectively) following the increasing size of the R group in this series. So, the most likely role of the R would be to separate the chains (or planes) from each other. Taking into account that $T_C \propto (J_{\text{intra}}J_{\text{inter}})^{1/2}$, where J_{intra} is the intrachain Cu(II)Mn(III) interaction and J_{inter} is the effective interchain interaction energy, an increase in the size of R would lead to a decrease of J_{inter} , in agreement with the observed trend $T_C(1) > T_C(2) > T_C(3)$ and $H_C(1) > H_C(2) > H_C(3)$.

Although the crystal structures of 1–3 are unknown, their stoichiometry, X-absorption studies, and IR and magnetic data strongly suggest that a ferromagnetic chain is formed with bridging oximate groups between Mn(III) and Cu(II) metal ions and that they present a metamagnetic behavior. Recently, a new family of metamagnets based on donor-acceptor charge-transfer salts ($[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNQ}]^{\text{1c}}$ and $[\text{Mn}(\text{C}_5\text{Me}_5)_2][\text{M}(\text{tfd})_2]^{\text{3b}}$ where $\text{M} = \text{Ni, Pd, Pt}$ and $\text{tfd} = \text{bis}(\text{trifluoromethyl})\text{ethylene-dithiolate}$) has been reported and a long-range magnetic order arising from one-dimensional donor-acceptor interactions has been demonstrated for them.

Finally, we show in this communication that the planar fragment Mn(III)–Cu(II) is a new ferromagnetic system similar to Cr(III)–Ni(II) and that the bis(glyoximate)-copper(II) monomeric complexes can be used as precursors of bimetallic alternating chains. This can be of particular interest to obtain molecular based-ferromagnets with high T_C values.

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Supplementary Material Available: Figures of Cu K-edge structures of an aqueous solution of Cu(II) nitrate and of a solid-state sample of 1 and Mn K-edge structures of an aqueous solution of Mn(II) nitrate and of a solid state sample of 1 (2 pages). Ordering information is given on any current masthead page.

Flagellenes: Nanophase-Separated, Polymer-Substituted Fullerenes

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It is becoming increasingly clear that more tractable and processable forms of fullerenes are going to be required to fully exploit the unique electronic and optical properties of C_{60} and its homologues. We have synthesized a new class of fullerene adducts which we designate "flagellenes", because they are comprised of several flexible polymer chains covalently attached to a fullerene "sphere" and have topologies similar to Flagellata-unicellular protozoa with snake-like appendages that give the cells motility. The particular flagellenes we report on are polymer adducts of C_{60} wherein linear polystyrene (PS) has been covalently attached to C_{60} , produced by reacting a living PS carbanion with C_{60} to give novel materials with the formula $\text{C}_{60}(\text{PS})_x$, where x ranges from 1 to ~ 10 . This class of materials represents a technologically significant advance in the functionalization chemistry of fullerenes: the $\text{C}_{60}(\text{PS})_x$'s are highly soluble and melt processable and as such they may be spin-coated, solvent cast, or melt extruded to give films and fibers having high concentrations of the fullerene covalently bound to the polymer matrix. Moreover, the unique topologies of flagellenes, in combination with the inherent chemical differences between the PS chain segments and the fullerene core, give rise to nanophase-separated solids analogous to those observed to occur spontaneously in diblock copolymers prepared from chemically distinct monomers. In this communication we describe the synthesis of flagellenes and their structural and morphological characterization using gel permeation chromatography (GPC), ^{13}C NMR, and transmission electron microscopy (TEM).

The salient features of living polymerizations—controlled molar mass,¹ narrow molar mass distribution,² and utility in creating functionalized polymers³—in conjunction with recent observations^{4,5} that carbanions could add across the carbon-carbon double bonds of C_{60} to give alkylated reaction products, prompted us to investigate the possibility that polymeric living carbanions might similarly add to C_{60} . Our synthesis of flagellenes is shown in Scheme I. The anionic living polymerization of styrene was accomplished using standard reaction conditions⁶ with

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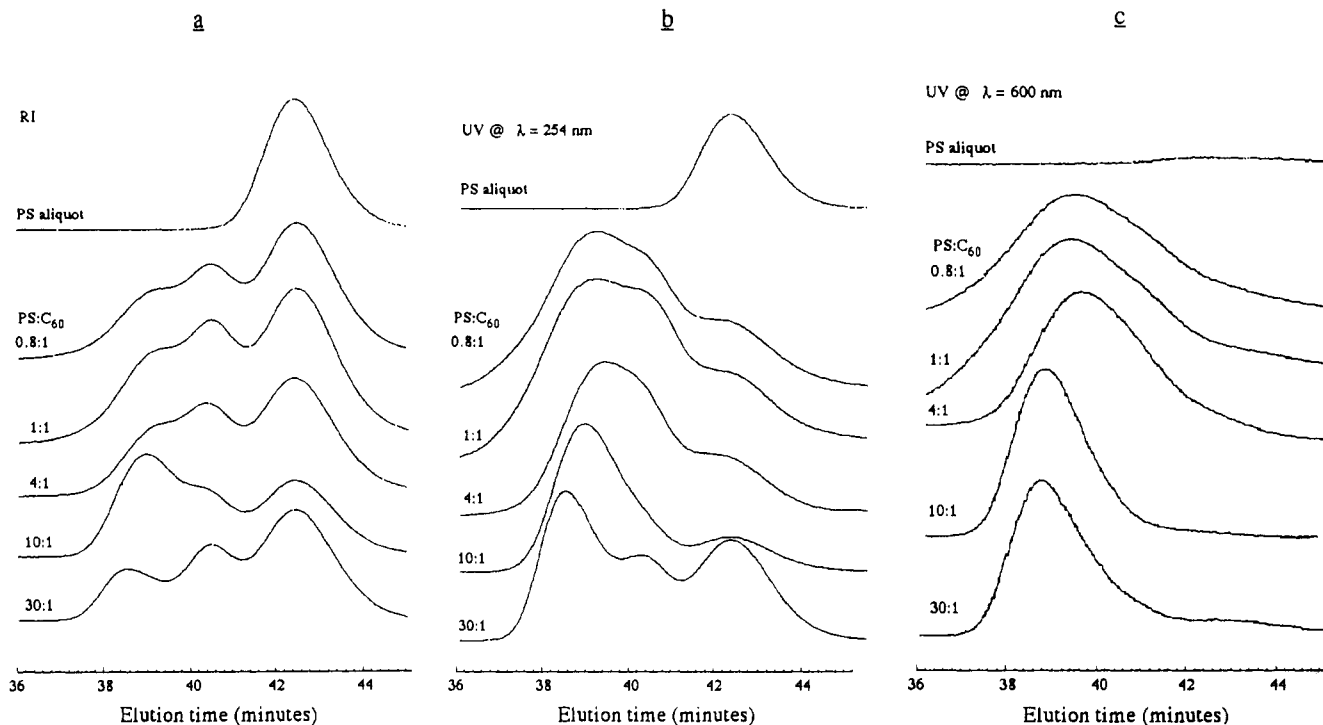


Figure 1. GPC chromatograms of PS aliquot and PS:C₆₀ crude products with the (a) refractive index detector, (b) UV-vis detector at $\lambda = 254$ nm, and (c) UV-vis detector at $\lambda = 600$ nm.

sec-butyllithium as the initiator in toluene under an inert atmosphere of argon. After complete consumption of the styrene monomer, the PS carbanion solution was sampled (referred to as the PS aliquot) to characterize its molar mass.⁸ The remaining PS carbanion solution was transferred anaerobically to a series of flasks containing C₆₀⁹ dissolved in toluene having 0.8:1, 1:1, 4:1, 10:1, and 30:1 mole ratios of PS anion to C₆₀. Upon addition of the red-orange PS carbanion solution, all of the C₆₀ solutions slowly (ca. 4 s) changed to a color ranging from burgundy to dark brown to black with increasing PS:C₆₀ ratio. After 30 min, 10-fold excess of iodomethane¹⁰ was added to each reaction flask; no color change was observed. The regiochemistry of addition is undetermined and its mechanism is unknown currently.¹¹

Figure 1 shows the series of GPC chromatograms for each detector¹² for the reactions having PS:C₆₀ mole ratios

(6) Toluene was distilled under argon from sodium. Styrene was degassed by three successive freeze-thaw cycles and vacuum distilled from dibutyl magnesium. *sec*-Butyllithium was generously supplied by the Lithium Division of the FMC Corp. The molar concentration was determined by the Gilman double titration method.⁷ The anionic polymerization was conducted in a one-neck 500-mL, round-bottomed flask equipped with a magnetic stir bar and rubber septa under a 6–8 psig argon atmosphere. The flask was charged with 11.0 mL of styrene in 100 mL of dry toluene. The polymerization was initiated with the addition of 3.63 mL of 1.38 M *sec*-butyllithium in cyclohexane. The resulting orange-red solution was allowed to stir for ~5 h at 0 °C.

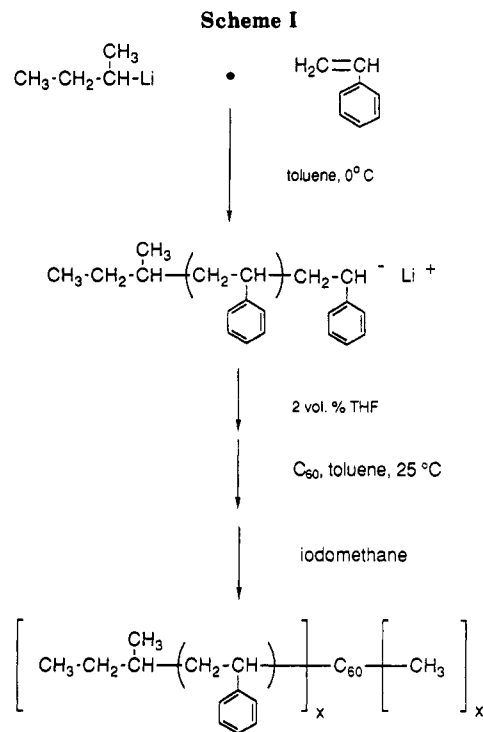
(7) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* 1964, 2, 447.

(8) Prior to sampling, 2.0 mL of tetrahydrofuran (distilled under argon from the purple sodium/benzophenone ketyl) was added to the PS carbanion solution. A small aliquot of the PS carbanion solution was removed using anaerobic techniques and was precipitated directly into ca. 40 mL of deoxygenated 2-propanol to terminate the polymerization and to precipitate the polymer. The precipitated polymer was isolated by filtration.

(9) The C₆₀ (Aldrich, 90%) was separated from residual C₇₀ on an alumina column with a solvent mixture of 95:5 hexanes:toluene. Five 25-mL round-bottom flasks each equipped with rubber septa and containing 10 mg of C₆₀ in 20 mL of dried toluene were deoxygenated with an argon purge.

(10) Iodomethane was protected from light and stirred over phosphorus pentoxide for 12 h and run through an activated alumina column under argon followed by deoxygenation with an argon purge for 5 min.

(11) Dixon, D. A.; Matsuzawa, N.; Fukunaga, T.; Tebbe, F. N. *J. Phys. Chem.* 1992, 96, 6107.



ranging from 0.8:1 to 30:1; the top trace in each series is the PS aliquot. The PS aliquot has a number average molar mass $\langle M_n \rangle = 1990$ g/mol with a molar mass distribution $\langle M_n \rangle / \langle M_w \rangle = 1.07$, where $\langle M_w \rangle$ is its weight average. The peaks at elution times shorter than 42.3 min correspond to species having a higher molar mass (i.e., larger hydrodynamic volume) than the PS aliquot. As seen

(12) A Waters 150-CV GPC equipped with Ultrastaygel columns of 100-, 500-, 10³-, 10⁴-, and 10⁵-Å porosities in tetrahydrofuran was utilized and the reported molar masses were determined relative to linear PS standards. The onset of the UV-vis absorption for flagellenes is the same (~850 nm) as it is for pure C₆₀ however the tail of the strong bands at $\lambda_{\text{max}} < 300$ nm are shifted to longer wavelength giving rise to appreciable absorption at $\lambda = 600$ nm where PS homopolymer absorption is negligible.

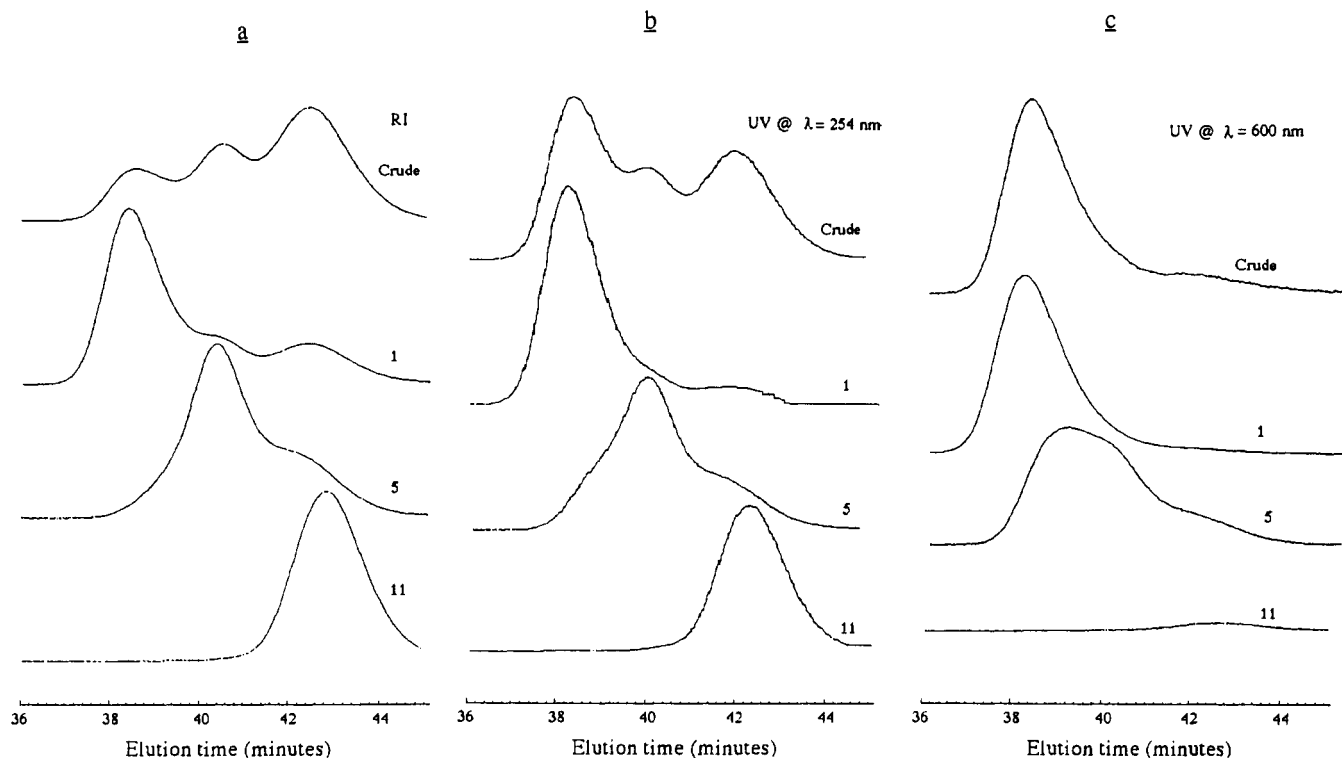


Figure 2. GPC chromatograms of 30:1 PS:C₆₀ crude product and representative purified fractions (fraction number indicated to the right of each trace) with the (a) refractive index detector, (b) UV-vis detector at $\lambda = 254$ nm, and (c) UV-vis detector at $\lambda = 600$ nm.

in the refractive index (RI) traces (Figure 1a), there is a trend toward increasing amounts of higher molar mass species as the PS:C₆₀ ratio in the reaction mixture increases going through an *apparent* maximum between 4:1 and 10:1. For the PS:C₆₀ = 30:1 reaction stoichiometry, the high concentration of species at ~ 42.3 min (bottom trace Figure 1a) merely reflects the large excess of (unreacted) PS carbanion in the reaction mixture which has been terminated in the "normal" fashion¹³ by iodomethane. The elution times of the highest molar mass peaks—the PS:C₆₀ adducts—correspond to equivalent PS molar masses of approximately 10^4 g/mol independent of the reaction stoichiometry. The UV chromatograms at $\lambda = 254$ nm (Figure 1b) are similar to the RI chromatograms (Figure 1a); both PS and C₆₀ absorb at $\lambda = 254$ nm. However, at $\lambda = 600$ nm (Figure 1c) where only the fullerene absorbs, only those species at the highest molar masses (lowest elution times) are observed indicating successful synthesis of a mixture of flagellenes.¹⁴ The material observed with both the RI and UV detector at $\lambda = 254$ nm and *not* observed at $\lambda = 600$ nm is attributed to free PS homopolymer. The chromatograms at $\lambda = 600$ for the 10:1 and the 30:1 reactions are essentially superimposable, and it is tempting to infer from elutions times relative to linear PS that the number of chains that can be accommodated on the fullerene core is roughly between 4 and 10. However, one needs to be cognizant of the inherent limitations of GPC for the measurement of molar masses of branched polymers—the increase in the polymer's radius of gyration (hydrodynamic volume) with increasing number of appendages in the flagellene is not the same as a comparable

change in mass for a linear polymer. Clearly a quantitative determination of the limiting stoichiometry of the flagellenes will require characterization that is sensitive to the molar mass itself (e.g., light scattering or colligative properties).

In an effort to isolate flagellenes with a narrower distribution of PS "arms", the 30:1 PS:C₆₀ reaction was fractionated.¹⁵ The first fractions precipitated contained the highest molecular weight species and the last fractions the lowest. Chromatograms from selected fractions are shown in Figure 2 along with the unfractionated material ("crude"). Both the RI (Figure 2a) and UV detector at $\lambda = 254$ nm (Figure 2b) show similar responses while the UV detector at $\lambda = 600$ nm (Figure 2c) shows that the first through fifth fractions contain flagellenes of varying molar mass. The eleventh fraction, which activates only the RI and UV ($\lambda = 254$ nm) detectors, is obviously PS homopolymer.

The purified flagellene (the first fraction from the 30:1 PS:C₆₀ reaction) was further characterized by using ¹³C NMR. It exhibits resonances between 28 and 35 ppm that are consistent with the addition of methyl groups to C₆₀ as suggested in Scheme I. Contrasting the aromatic region of the flagellene with the PS aliquot also shows additional resonances in the range 130–150 ppm; pure C₆₀ itself is a singlet (143.2 ppm).¹⁶ The rather small number of resonances in this chemical shift range (seven excluding the 145–146 ppm region masked by the styrene *ipso* carbon multiplet) is suggestive of a rather symmetric regiochemical substitution pattern on the fullerene.

TEM¹⁷ results on OsO₄ stained, thin-cast,¹⁸ flagellene

(13) The termination of anionic polymerizations of styrene with iodomethane leads to a certain amount of coupling reactions that proceed through a free radical mechanism, see: Teixeira-Barreira, S. R.; Mechin, R.; Tanielian, C. *Macromolecules* 1982, 15, 450. Moreover, a sample of the PS carbanion solution was terminated with iodomethane which confirmed this earlier reference and resulted in $\sim 35\%$ of coupled polymer.

(14) C₆₀ itself has negligible solubility in THF and no absorption due to free fullerenes could be observed in control experiments.

(15) The 30:1 crude product was dissolved in tetrahydrofuran and methanol was added dropwise until the onset of cloudiness. The solids were separated from the supernatant by centrifugation and this procedure was repeated to give 11 fractions.

(16) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* 1990, 1990, 1423.

(17) TEM analysis was performed using a JEOL 100CX transmission electron microscope at an accelerating voltage of 100 keV.

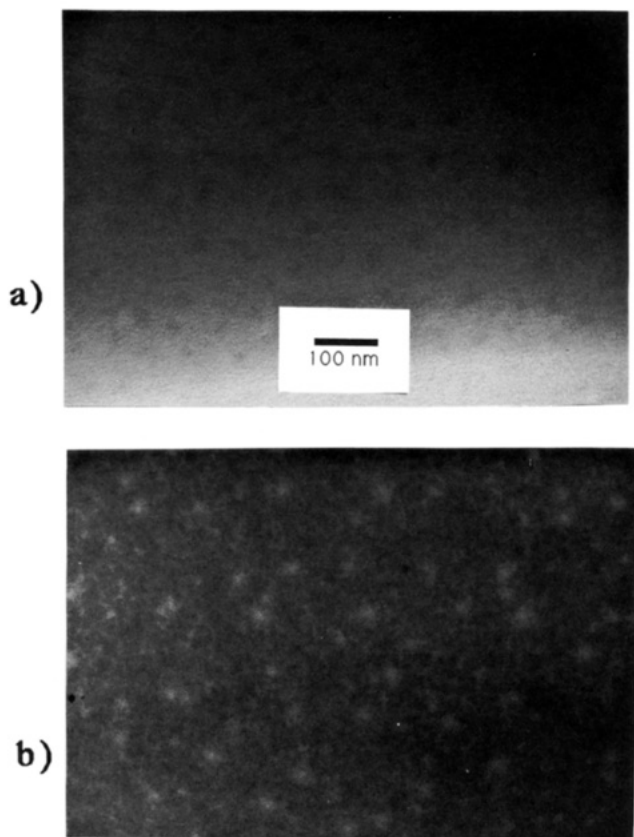


Figure 3. TEM micrograph of thin-cast films of the first (purified) fraction from the 30:1 PS:C₆₀ reaction: (a) OsO₄-stained having darkly contrasted, diffuse, fullerene-rich spherical domains; (b) RuO₄-stained having lightly-contrasted, diffuse, fullerene-rich spherical domains.

films show darkly contrasted diffuse spherical domains ~ 20 nm in diameter (Figure 3a). TEM results on the RuO₄ stained thin-cast film (Figure 3b) revealed lightly contrasted diffuse spherical domains also ~ 20 nm in diameter. In the case of block copolymers of poly(styrene)/poly(1,4-isoprene) (PS/PI), OsO₄ is known to preferentially stain phases rich in olefinic structures (PI) over PS-rich phases, while RuO₄ is known to preferentially react with and stain phases rich in PS over phases rich in olefinic structures.¹⁹ By analogy with TEM data on PS/PI block copolymers, and in conjunction with the low volume fraction of the fullerene component in the films, the observed preference of RuO₄ to stain PS and the preference of OsO₄ to stain the discrete minor phase implies that the dark (light) spherical domains in Figure 3a (Figure 3b) are fullerene-rich. The TEM morphology for thermally annealed, thick films²⁰ exhibited two distinct types of nanostructure: (1) a disordered, very diffuse morphology and (2) a highly ordered rodlike or lamellar morphology with

(18) Thin films were prepared by dissolving the polymer in chloroform at 5 w/w % concentration. A 0.05-mL drop of solution was deposited onto a distilled water substrate and the gold or silver areas of the film were selectively lifted onto TEM grids.

(19) Odell, J. A.; Dlugosz, J.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* 1976, 14, 861. Spitzer, U. A.; Lee, D. G. *J. Org. Chem.* 1974, 39, 2468; York, G. A.; DePorter, C. D.; McGrath, J. E.; Wilkes, G. L., submitted to *Polymer*.

(20) Bulk samples were thermally annealed at 50 °C above the T_g at 110 °C for 2 h and cooled to room temperature over a period of ~ 1 h. The bulk samples were microtomed at ambient temperature using a Reichert-Jung UltraCut E. Distilled water was used as a trough liquid and sections were picked up on a 600 mesh copper hex grid. The grids were placed in a vacuum oven at 50 °C to evaporate any excess water. The sections were then stained over a 0.5% aqueous ruthenium tetroxide vapor for 15 min.

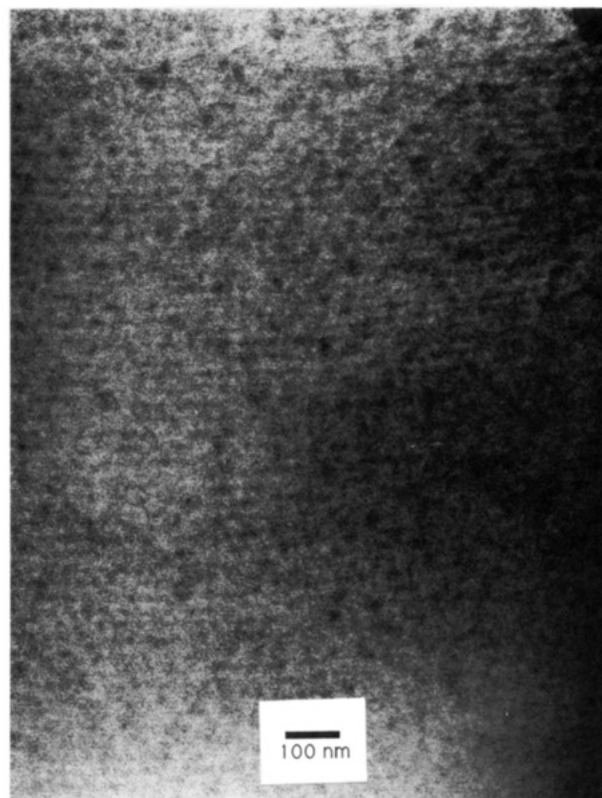


Figure 4. TEM micrograph of thermally annealed, RuO₄-stained film of the first (purified) fraction from the 30:1 PS:C₆₀ reaction exhibiting a rodlike or lamellar morphology.

PS-rich domains separated by 5.0–7.5 nm (Figure 4). Focusing on the latter, we recall that the domain size d in microphase-separated diblock copolymer systems is known to scale with the molar mass M of the chain [$d \sim (M)^{2/3}$]. The root-mean-square end-to-end distance of an unperturbed chain $(r^2)^{1/2}$ and the chain's contour length l scale as $(M)^{1/2}$ and $(M)^1$, respectively. Idealizing the PS oligomers in this way yields values for $(r^2)^{1/2}$, d , and l of 3.1, 3.9, and 9.4 nm, respectively (for $\langle M_n \rangle = 2000$ g/mol). The experimental interdomain spacing (5.0–7.5 nm) is, therefore, suggestive of a somewhat extended PS chain conformation.^{21,22} While the low molar mass of the PS and the starblock-like topology of the flagellenes should favor a more miscible system,²³ phase separation is unambiguous in the TEM micrographs of the flagellene films (Figures 3 and 4). Nanophase-separated morphologies at such low minor component compositions (6 wt % fullerenes) have been observed in systems which have low concentrations of strongly interacting ionic species.²⁴ At this time the nature of the interactions in the condensed phase of the flagellenes giving rise to nanophase separation is unknown.

Although the present C₆₀(PS)_x adducts consist of mixtures of flagellenes (variable polymer arm lengths and degree of substitution x on the C₆₀ core), the flagellene topology nevertheless confers unique supramolecular or-

(21) Hashimoto, T.; Shibayama, M.; Fujimura, M.; Kawai, H. In *Block Copolymers Science and Technology*; Meier, D. J., Ed.; MMI Press: Midland, MI, 1983.

(22) An increase in the scaling of domain size with molar mass to a power higher than two-thirds has been observed in systems with very strong ionic interactions; see: Gouin, J. P.; Williams, C. E.; Eisenberg, A. *Macromolecules* 1987, 20, 760.

(23) Sanchez, I. C.; Olvera de la Cruz, M. *Macromolecules* 1986, 19, 2501.

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ganization to fullerenes. Other 3-D nanostructural architectures can also be readily envisioned: reactions using polymer dicarbanions would be expected to yield networks having fullerene "cross-linkages"; reactions similar to those described here with carbon nanotubes²⁵ in place of fullerenes may yield novel, compatibilized reinforcements for polymer matrices. Our current efforts are focused on optimizing the synthesis²⁶ of C₆₀(PS)₁, anticipating that this

soluble and fusible monoflagellene will exhibit minimally perturbed, intrinsic, fullerene characteristics. It is conceivable that some (nonlinear) properties of monoflagellenes might be enhanced if they nanophase-separate into a spatially delineated glass.

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Reviews

Unusual Valences in Rare-Earth Halides[†]

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The *valence* of an atom in a particular compound is considered *unusual* when there is a difference between the "localized" valence and the oxidation number. The degrees of delocalization of electrons may be different. Total delocalization gives rise to a conduction band. There may also be partial delocalization with multicenter or cluster bonding. With such a definition, reduced rare-earth halides such as metallic LaI₂ or semiconducting Pr₂Br₅ and Gd₂Cl₃ with [Gd₆] clusters contain unusual valences but TmI₂ does not. In addition to the generalities of the synthesis and properties of reduced rare-earth halides, the electronic structures have been calculated making use of the extended Hückel algorithm. These calculations aim to yield a better understanding of bonding and the conductivity properties of these compounds.

Introduction

Valence determines the number of neighboring atoms with which an atom M can combine.¹ The *valence state* of this particular atom M is the arrangement of electron density around its core. The determination and theoretical description of the valence state in a discrete molecule are relatively easy tasks, even though bonding may be, although predominantly covalent, ionic or delocalized (as in the boranes or the fullerenes) to a certain degree. Molecular orbital calculations are a suitable method for the description and sometimes even understanding of bonding in molecules.

For solids with their three-dimensional infinite arrangement of atoms, the immediate problem is to determine where the neighborhood of atom M whose valence is under consideration ends. How many coordination spheres have to be taken into account: one, two, an infinite number? For predominantly ionic solids such as NaCl where the Coulomb (or Madelung) part of the lattice energy (MAPLE)² comes close to the total lattice energy, short-range order is much more important than long-range three-dimensional order, as a calculation for NaCl shows (Figure 1) where coordination number 1 (C.N.1) stands for a Na⁺Cl⁻ molecule, C.N.2 for an infinite one-dimensional

chain, C.N.3 for a double chain and, finally, C.N.6 for the three-dimensional network. Therefore, electron density is localized and the argument can only be how much covalency is involved in the bonding. For a complex compound such as K₂[PtCl₆], there is nothing wrong with the ionic description (K⁺)₂[(Pt⁴⁺)(Cl⁻)₆] as long as one takes into account that there is much covalency involved in the bonding of the complex anion [PtCl₆]²⁻ and less in K⁺-Cl⁻ bonding. The valence state of "Pt⁴⁺" may be described as ligand field or molecular orbital theory have taught us. There is *nothing unusual* about its valence, however.

The same is true for the valence of Xe²⁺ in XeF₂³ or In⁺ in InCl.⁴ Not even the valence of indium in In₂Br₇ is unusual. It is a mixed-valent bromide and contains according to a simple ionic formulation (In⁺)₃[(In₂)⁴⁺(Br⁻)₆](Br⁻) mono- and divalent indium.⁵ Divalent indium bound into the group [In₂Br₆]²⁻ is characterized by a covalent σ bond (so-called metal-metal bond) as is the case with isoelectronic monovalent cadmium in Cd₂(AlCl₄)₂.⁶

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[†] Dedicated to Professor Rudolf Hoppe on the occasion of his 70th birthday on October 29, 1992.