erization and verification of the type of chemistry[6] portrayed in Scheme Ib were established in solution by ^{1}H NMR spectroscopy.[12] Cured films were typically 4 μm in thickness as measured by profilometry. Corona poling and final polymerization (curing) of the I-polyimide films was carried out under N_2 at various temperatures for 1.0 h in the in situ SHG instrumentation described previously.[2,4] The corona needle-to-film distance was 1.0 cm and the applied potential was +5.0 to +6.0 kV. Poled films were cooled to room temperature over 0.5 h before removing the poling field, and the initial measurement of storage SHG properties made within 15 min of field removal. SHG measurements on the films ($\lambda = 1.064$ μm) were made at room temperature in the p-polarized geometry and were referenced against quartz using procedures and instrumentation detailed elsewhere.[13] Film specimens for time-dependent SHG decay studies were stored in air in a thermostated tube furnace at 85 °C. Films were removed from the furnace and allowed to cool to ambient temperature before SHG measurements were performed. Transmission optical spectroscopic measurements indicated only minor changes in film optical properties through the poling/curing process, arguing for minimal if any thermal decomposition.[14]

In Figure 1 is shown the relationship between the I-polyimide curing temperature and the ultimate, DSC-determined T_g value. The approximate linearity of this relationship is further indication that the polymerization process is well-behaved. The apparent T_g value of 236 °C is to our knowledge, the highest yet reported for a chromophore-functionalized NLO polymer of any type.[1-5,15] Second harmonic indexes, d_{33}, for the poled I-polyimide were found to be in the range (11–13) × 10^{-9} esu. These values are reasonable for a nitroaniline chromophore of the present architecture and estimated matrix chromophore number density (~7 × 10^{20} cm^{-3}).[1-5] They are comparable in magnitude to d_{33} values of similar chromophore-functionalized NLO polymers.

SHG temporal stability data at 85 °C for three I-polyimide films precured and poled under differing thermal conditions are shown in Figure 2. It was found that increases in the prepoling temperature (T_{precure}) are accompanied by increases in the achievable poling temperature (T_{cure}), above which SHG signal loss and film damage are apparent. Importantly, Figure 2 reveals only minor (~ 10–15%) decay in SHG efficiency over the first 24 h at 85 °C and, within the precision of the measurements, *negligible to very minor decay* over the following month at 85 °C. Also noteworthy is the small sensitivity of the $d_{33}(t)$ characteristics to the nature of the precure/cure protocol. Attempts to fit the $d_{33}(t)$ data by nonlinear least-squares methods to either a biexponential[2,4,16] or Kohlrausch-Williams-Watts stretched exponential expression[17,18] were inconclusive (τ values diverged) owing to the small observed d_{33} temporal dependence.

These results demonstrate that NLO chromophore-functionalized polyimide structures can be prepared which, after appropriate thermal polymerization and electric field poling, exhibit very high T_g values, efficient SHG characteristics, and unprecedented SHG temporal stability. Efforts are continuing to further decrease matrix mobility and to introduce higher β chromophores.

Acknowledgment. We thank NSF (Grant DMR 8821571) through Northwestern University Materials Research Center and AFOSR (Contract 90-0071) for support of this research. J.T.L. thanks Academia Sinica (ROC) for a sabbatical leave, and M.A.H. thanks the AFOSR for a Laboratory Graduate Fellowship.

Registry No. I, 143969-94-2; II (copolymer), 143969-95-3; II (SRU), 143969-96-4.

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(12) A solution of I and II in DMSO-d_6 (1:1 stoichiometry, ca. 27 mM in each) was heated at 127 °C and monitored by ^{1}H NMR until no further changes were observed in the spectra (35 h). During the course of the experiment, resonances at δ = 7.17 and 4.81 disappeared while a resonance appeared at δ = 5.21. These resonances are attributed to the olefinic protons in II, the primary amine protons in I, and the secondary amine protons in the addition product, respectively. No spectral changes were observed in solutions of I or II heated alone under the same conditions.

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(14) (a) Films exhibited $\lambda_{\max}$ = 432 nm before precuring, 440 nm after precuring, and 450 nm after poling. Such small shifts in spectra of poled NLO polymers are common and attributable to dichroic,[14b] electrochromic,[14b] and/or interchromophore π–π overlap[14c] effects. (b) Mortazavi, M. A.; Knoesen, A.; Kowel, S. F.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733–741. (c) DiBella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.*, **1992**, *114*, 5842–5849 and references therein.

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(16) $d_{33}(t) = Ae^{-1/\tau_1} + (1 - A)e^{-t/\tau_2}$.

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(18) $d_{33}(t) = Ae^{(-t/\tau)^{\beta}}$.

Metamagnetic Properties of a Family of Ferromagnetic Alternating Spin Chains: Bis(dimethylglyoximato)(carboxylato)manganese(III)copper(II)

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The interaction between unpaired electrons are most often of the up–down type. The parallel spin alignment (ferromagnetic interaction) remains exceptional in molecular chemistry and requires the fulfillment of quite peculiar conditions. That is why one of the main challenges in the field of molecular materials is the design of molecular-based ferromagnets[1-4] and several approaches

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† Universitat de Valência.

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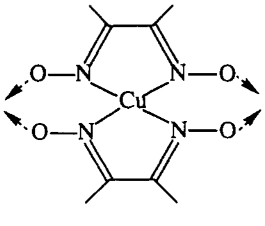
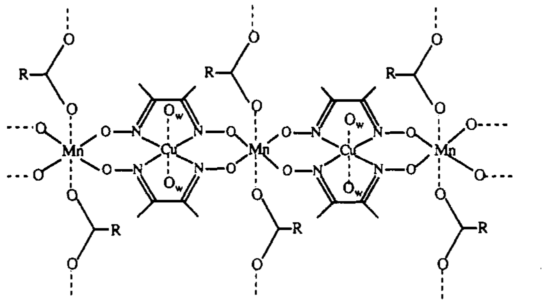
Chart I



$[Cu(dmg)_2]^{2-}$



$[Mn^{III}Cu^{II}(dmg)_2(H_2O)_2(RCOO)]_n$

based on ferrimagnetism[5] (e.g., alternating Cu(II)–Mn(II) or organic radical–Mn(II) linear chains)[2,4] have been proposed as an alternative to achieve such ferromagnets.

Other strategies have been proposed to favor the ferromagnetic interaction,[5] one of them being the orthogonality of the magnetic orbitals.[6] VO(II)–Cu(II),[6a] Cr(III)-Cu(II),[6b] and Cr(III)–Ni(II)[6c] heteropolynuclear species are classical examples of such a situation. Among them, the $Cr^{III}(d^3)$–$Ni^{II}(d^8)$ pair would be the most appropriate to prepare a ferromagnet with a high T_c value owing the highest spin multiplicity of this pair ($S = {}^5/_2$). Very recently was obtained the compound $Cs[NiCr(CN)_6]\cdot 2H_2O$[7] which orders ferromagnetically at T_c = 90 K. The $Mn^{III}(d^4)$–$Cu^{II}(d^9)$ pair would be as interesting as this latter system: owing to the Jahn–Teller effect, which is operative in both metal ions, it is possible to achieve strict orthogonality between the magnetic orbitals of Mn(III) (d_{xy}, d_{xz}, d_{yz}, and d_{z^2}) and the one of Cu(II) ($d_{x^2-y^2}$) if both metal ions are located in the xy plane, leading to $S = {}^5/_2$ as in the Cr(III)–Ni(II) pair.

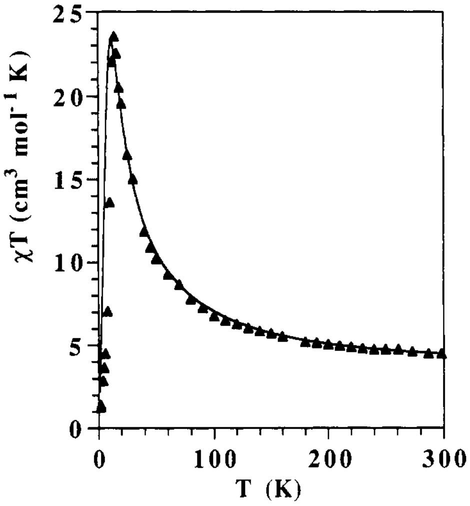


Figure 1. Temperature dependence of the product of the molar magnetic susceptibility with temperature for **1** at H = 500 G. Experimental points are shown as triangles. The curve was calculated as discussed in the text.

During the course of our attemps to synthesize ferrimagnetic oximato-bridged Mn(II)–Cu(II) alternating linear chains (e.g., using $Cu(dmg)_2^{2-}$ as a precursor; see Chart I), we found that the oxygen oxidizes Mn(II) to Mn(III) in the reaction of $Cu(Hdmg)_2$ with manganese(II) carboxylate, yielding the compounds $[MnCu(dmg)_2(RCOO)]\cdot 2H_2O$ (R = methyl (**1**), ethyl (**2**) and phenyl (**3**)). These compounds revealed ferromagnetic Mn(III)–Cu(II) alternating linear chains[8] which exhibit a metamagnetic behavior. We report herein the synthesis, structural characterization, and magnetic behavior of these compounds.

1–3 were synthesized by air oxidation of the methanolic solutions of manganese(II) carboxylate in presence of $Cu(Hdmg)_2$.[9] The products were obtained as black polycrystalline powders. IR data strongly support the presence of bis(dimethylglyoximato)copper(II) and its coordination to Mn(III) through oxygen oxime atoms,[10] as well as the coordination of the carboxylate oxygen atoms in an equivalent fashion.[11]

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(9) These syntheses are highly reproductible even in other solvents such as MeCN, CH_2Cl_2, or CH_3Cl. Indeed, it is possible to obtain the same compounds in a a high yield by reaction of $[Mn^{III}_3(RCOO)_6(py)_3]ClO_4$ with $Cu(Hdmg)_2$ in MeCN. Elemental analysis (C, H, N, Cu, Mn) are in agreement with the proposed formulation. Anal. Calcd (found) for $MnCuC_{10}H_{19}N_4O_8$ (**1**): C, 27.19 (26.95); H, 4.34 (4.49); N, 12.68 (12.64); Cu, 14.38 (14.22); Mn, 12.44 (12.35). Anal. Calcd (found) for $MnCuC_{11}H_{21}N_4O_8$ (**2**): C, 28.99 (28.58); H, 4.64 (4.59); N, 12.29 (12.11); Cu, 13.94 (14.12); Mn, 12.05 (12.15). Anal. Calcd (found) for $MnCuC_{15}H_{21}N_4O_8$ (**3**): C, 35.76 (35.92); H, 4.20 (4.23); N, 11.12 (10.89); Cu, 12.61 (12.12); Mn, 10.90 (10.65). Thermogravimetric analysis of **1–3** shows a loss of weight at 65 °C which corresponds to two water molecules per CuMn unit.

(10) The IR bands at 1550 (ν(CN)) and 1220 cm^{-1} (ν(NO)) in the starting $Cu(Hdmg)_2$ precursor are shifted to 1580 and 1200 cm^{-1}, respectively in **1–3**. These features are common to a series of polynuclear oximato-bridged compounds that have been characterized by single crystal X-ray diffraction. See the following references: (a) Chaudhuri, P.; Winter, M.; Della Vĕdova, B. P. C.; Bill, E.; Trautwein, A.; Gehering, S.; Fleischhauer, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 2148. (b) Okawa, H.; Koikawa, M.; Kida, S.; Luneau, D.; Oshio, H. *J. Chem. Soc., Dalton Trans.* **1990**, 469. (c) Lloret, F.; Ruiz, R.; Julve, M. Manuscript in preparation.

(11) The occurrence of ν_{as}(COO) and ν_s(COO) stretching vibrations of carboxylate groups at 1570 and 1400 cm^{-1} for **1–3** ($\Delta = (\nu_{as}(COO) - \nu_s(COO)) = 170\ cm^{-1}$) clearly indicate that both oxygen carboxylate atoms are coordinated in an equivalent fashion; however, we cannot distinguish between the carboxylate chelating and bridging coordination modes because the difference of the frequencies in the two types of coordination is too small. See the following references: (a) Deacon, G. B.; Philips, R. J. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 337.

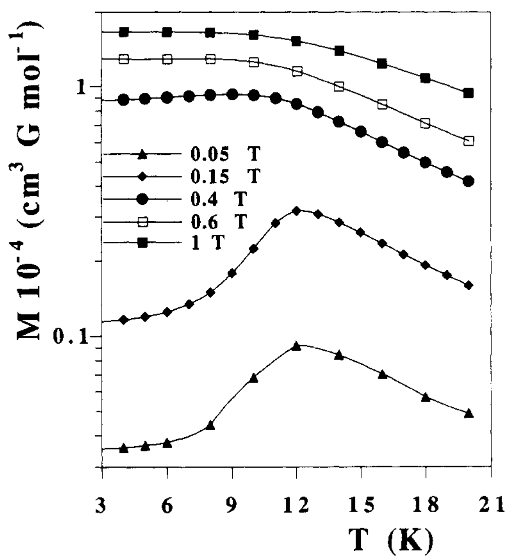

Figure 2. Field-cooled magnetization data for 1 in applied fields. The magnetic field was held constant when decreasing the temperature.

In the absence of single crystals suitable for X-ray diffraction, an X-ray absorption study was undertaken. The preliminary results at room temperature are consistent with a distorted octahedral environment for both metal ions and divalent and trivalent oxidation states for copper and manganese, respectively. The EXAFS data, and particularly the Fourier transforms, allow us to put in evidence the first coordination sphere metal-to-ligand distances: four N atoms (1.99 Å) and two O atoms (2.03 and 2.28 Å, $\sigma = 0.07$) around Cu(II), and six O atoms (four at 1.94 Å ($\sigma = 0.05$) and two at 2.06 Å ($\sigma = 0.08$)) around Mn(III).[12]

The magnetic properties of 1–3 have been studied in the 1.8–300 K temperature range under different external fields (5–35 000 G) with a SQUID (Mētronique Ingēnierie) magnetometer and a pendulum-type apparatus.[13] Low-field measurements were performed on an ac susceptometer measuring both the real and imaginary component of the molar susceptibility, χ_M. The values of susceptibility were corrected for the diamagnetism from Pascal's constants. The thermal dependence of $\chi_M T$ for 1 is shown in Figure 1 (analogous behavior is observed for 2 and 3). $\chi_M T$ is equal to 4.44 cm^3 mol^{-1} K at 290 K ($\mu_{eff} = 5.96\ \mu_B$), a value which is higher than the spin-only value ($\mu_{eff} = 5.20\ \mu_B$) of the magnetically noninteracting Mn(III)–Cu(II) pair and very close to that expected for a sextuplet state ($\mu_{eff} = 5.92\ \mu_B$). On a lowering of the temperature, $\chi_M T$, increase up to 23.5 cm^3 mol^{-1} K at 14 K. This behavior is indicative of a relatively strong ferromagnetic coupling between Cu(II) and Mn(III) ions. Below 14 K, $\chi_M T$ decreases rapidly and a maximum of χ_M is observed at 12 K (for applied fields lower than 4000 G; see Figure 2). The $\chi_M T$ data down to ca. 30 K can be fitted with the formula appropriate to one-dimensional $S_1 = 2$ and $S_2 = {}^1/_2$ ferromagnet,[14] with $g_{Mn} = 2.0$, $g_{Cu} = 2.21$, and $J = 52.1$ cm^{-1} (the Hamiltonian in the form $\hat{H} = -J\hat{S}_1\hat{S}_2$).[15] The agreement factor is $R = 1.3 \times 10^{-4}$.

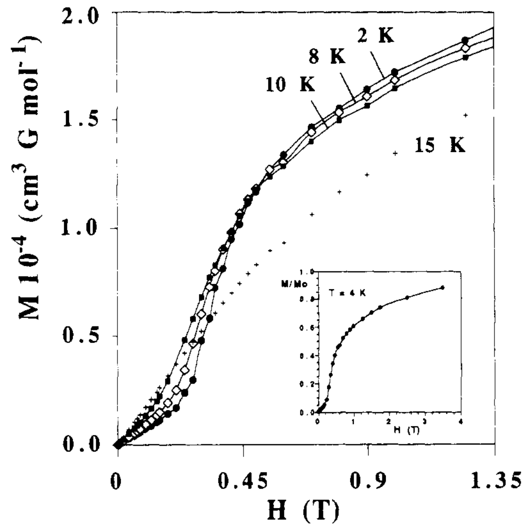

Figure 3. Magnetization isotherms for 1 at temperatures as indicated. Experimental data were obtained as indicated in Figure 2. The insert shows the magnetization measurements at 4 K in the form M/M_0 vs H ($M_0 = Ng\mu_\beta S$).

The observed maximum in the χ_M vs T plot is a clear indication of an antiferromagnetic interchain coupling. We suggest that this may be due to carboxylate bridging between Mn(III) ions (see Chart I). According to this structural scheme, compounds 1–3 would be two-dimensional, with a large ferromagnetic coupling within the chain and a weak antiferromagnetic coupling between the chains. Consequently, we can treat this two-dimensional magnet as a "chain of chains".[16] The best fit for 1 gives $J_{inter} = -0.078$ cm^{-1}, a value which agrees with a very weak coupling between chains.

At low temperatures, 1–3 exhibit peculiar magnetic properties which are consistent with metamagnetic behavior.[17] As shown in Figure 2, χ_M for 1 reaches a maximum at 12 K for low applied fields, which broadens as H_A is increased, and finally disppears for $H_A > 4000$ G, demonstrating that a field-induced transition from an antiferromagnetic to a feromagnetic ground state occurs.[17,18] To confirm this metamagnetic behavior, the

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[12] Castro, I., Verdaguer, M., work in progress at LURE, Orsay, the French Synchroton Radiation Facility. The Fourier transforms at room temperature do not detect the presence of heavy neighbors beyond the first coordination sphere. Low-temperature measurements, are planned to get information about intramolecular Cu–Mn or intermolecular distances.

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[16] At a given temperature we associate to the ferromagnetic oximato bridged chain an effective total spin, S_{eff}, which can be calculated from: $S_{eff}(S_{eff} + 1) = 2\chi_{fc}T$ (where χ_{fc} is the susceptibility calculated for this ferromagnetic chain from the classic-quantic spin model[14]). The susceptibility for the two-dimensional magnet (1) is then calculated from the classic spin model for antiferromagnetic linear chains (Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343) with total spin S_{eff}. See also the following references: (a) Caneschi, A.; Gatteschi, D.; Melandri, M. C.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1990**, *29*, 4228. (b) Lloret, F.; Julve, M.; Ruiz, R.; Journaux, Y.; Nakatani, K.; Kahn, O.; Sletten, J. *Inorg. Chem.*, in press.

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magnetization vs applied field was measured at various temperatures above and below the Neél 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 cm^3 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 $S = S_{Mn} + S_{Cu} = {}^5/_2$ per MnCu unit (the theoretical value of M_S for $S = {}^5/_2$ and $g = 2$ is 28 000 cm^3 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 $T_C \propto (J_{intra}J_{inter})^{1/2}$, 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 oximato 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 ([Fe(C_5Me_5)$_2$][TCNQ][1c] and [Mn(C_5Me_5)$_2$][M(tfd)$_2$],[3b] where M = Ni, Pd, Pt and tfd = bis(trifluoromethyl)ethylenedithiolate) 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(glyoximato)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 $C_{60}(PS)_x$, where x ranges from 1 to ~10. This class of materials represents a technologically significant advance in the functionalization chemistry of fullerenes: the $C_{60}(PS)_x$'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 polymers[3]—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 conditions[6] with

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