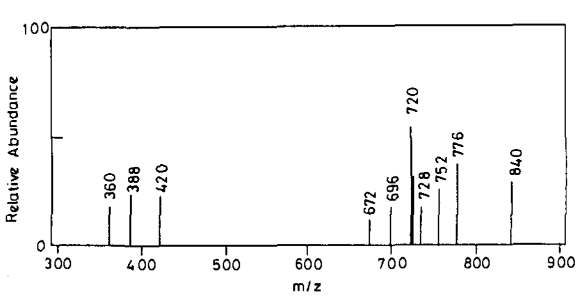

Figure 1. Mass spectrum of FeC$_{60}$ (I) (in mixture with C$_{70}$) from the gas-phase reaction. Peaks at 840, 720, 696, and 672 arise from the parent fullerenes.

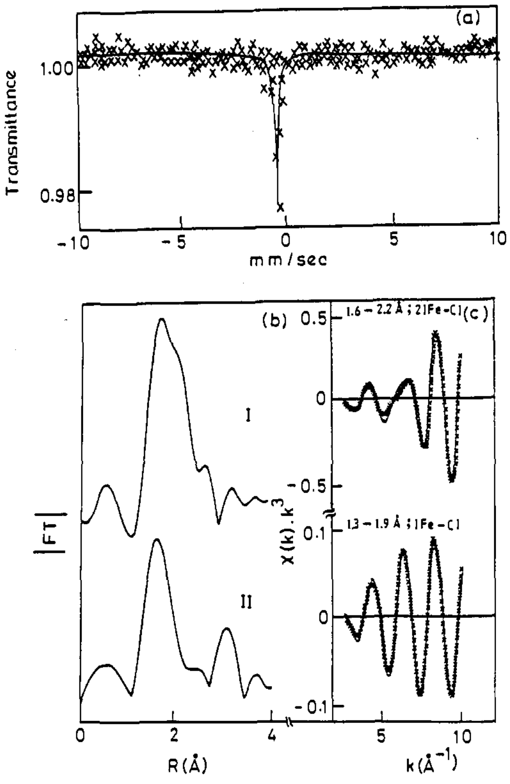

Figure 2. ^{57}Fe Mössbauer spectrum of FeC$_{60}$ (I) (a); Fourier transforms of the Fe-K EXAFS of FeC$_{60}$ (I and II) (b); inverse-transformed EXAFS data (c).

the half-mass of FeC$_{60}$. The presence of peaks due to C$_2$ and C$_4$ losses in the decreasing order of intensity suggests that Fe may be internally bound to the C$_{60}$ frame. Similar C$_2$ losses found in HeC$_{60}$ and LaC$_{60}$ have been attributed to the entrapment of He and La in the hollow cage.[5,6] The ^{57}Fe Mössbauer spectrum[9] of the adduct[12] shows a singlet with an isomer shift of −0.083 mm/s with respect to α-Fe (Figure 2a), characteristic of iron in a near-zero oxidation state. The sharpness of the spectrum suggests a strongly bound Fe species. The compound was paramagnetic over the 10–300 K range, and its electronic absorption spectrum showed a slight red shift relative to that of C$_{60}$. The IR spectrum showed little change from that of C$_{60}$.

Unlike the FeC$_{60}$ (I) prepared by the gas-phase reaction, solid FeC$_{60}$ (II) where Fe was bound externally to the fullerene[13] showed a doublet in the Mössbauer spectrum with an isomer shift of 0.45 mm/s due to Fe(III); magnetic susceptibility measurements showed evidence for antiferromagnetic interaction. Both the electronic and infrared spectra were different from those of C$_{60}$. Furthermore, the mass spectrum did not show C$_2$ losses.[14]

We have examined the structures of the two FeC$_{60}$ adducts (I and II) by means of Fe-K EXAFS measurements by employing a Rigaku spectrometer. Figure 2b shows the Fourier transforms of the EXAFS data obtained with $k_{\min}$ 3.0 and $k_{\max}$ 12.0 Å^{-1} after weighing the data by k^3. Analysis of the EXAFS data, including curve fitting of the inverse-transformed data (employing ferrocene as the reference), gave a good fit (Figure 2c) with two coordinations for Fe at Fe–C distances of 2.06 and 2.34 Å for FeC$_{60}$ (I) with lower Debye–Waller factors ($\Delta\sigma^2 = 0.0002$ Å^2). Two such short Fe–C distances can only be reconciled if Fe is in the cage. Any adduct with Fe bound externally would show a single short Fe–C distance, as indeed found by us from the analysis of the EXAFS of FeC$_{60}$ (II) prepared from solution reaction (Figure 2b). In this solid, where Fe is externally bound, we find Fe–C distances of 2.03 and 3.46 Å with $\Delta\sigma^2$ of 0.0003 and 0.001 Å, respectively.

The near-zero oxidation state of Fe, C$_2$ losses in the mass spectrum, the occurrence of the two Fe–C distances close to each other, as well as some of the other features indicate that FeC$_{60}$ (I) obtained by the gas-phase reaction during arc vaporization of graphite is likely to be an endohedral species with the Fe atom inside the cage of C$_{60}$. Further studies on the various FeC$_{60}$ adducts are in progress.

Registry No. Fe^{I}C$_{60}$, 137433-48-8; Fe(CO)$_5$, 13463-40-6; C$_{60}$, 99685-96-8; FeCl$_2$, 7758-94-3; NaC$_{60}$$^+$, 137718-24-2; Na, 7440-23-5; graphite, 7782-42-5.

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(12) The sample gave a single spot in TLC and satisfactory analysis for Fe (7.2%) and C (92%). A preliminary study of the powder X-ray diffraction pattern of FeC$_{60}$ (I) suggests that a primitive tetragonal structure (a = 15.43 Å, c = 9.08 Å) may be preferable over the FCC structure. The strongest (221) reflection could be simulated with Fe atoms in the cage 8 Å apart.

(13) The solid Na compound of C$_{60}$ prepared by the reaction of Na with C$_{60}$ in toluene solution was reacted with FeCl$_2$ in THF solution to obtain solid FeC$_{60}$ (anal. Fe 7.2%).

(14) We have sought to prepare (C$_{60}$)$_2$Fe by reacting the monosodium salt of C$_{60}$ with FeCl$_2$ in THF solution. A brown solid thus obtained has a different electronic spectrum. Electron-impact mass spectroscopy unfortunately seems to fragment the species. Fe–C distances in this ferrocene analogue cannot be distinguished from those of FeC$_{60}$ (II).

Nanoarchitectures. 1. Controlled Synthesis of Phenylacetylene Sequences

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Well-defined oligomeric sequences are valuable models for investigating how physical properties depend on molecular size and chemical structure. For example, controlled sequences have recently been used to study cooperative motions[1] and microphase separation[2] of copolymers. Monodisperse sequences have also been used to study the electronic properties of conjugated chains, such as optical nonlinearity[3] and band gap.[4] We have found that well-defined oligomers are valuable for preparing very large two- and three-dimensional molecular frameworks.[5] Outside the realm

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† Participant in the NSF Research Experience for Undergraduates program.

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(2) Wagener, K. B.; Matayabas, J. C.; Wanigatunga, S. *Macromolecules* **1989,** *22,* 3211.

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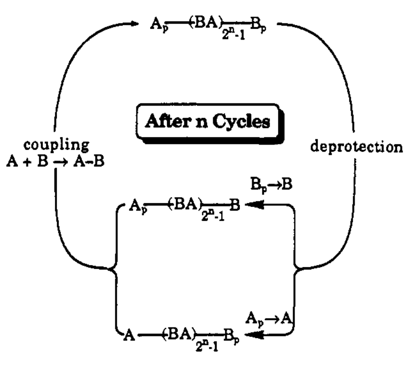
Scheme I. Repetitive Method for the Synthesis of Linear Sequences



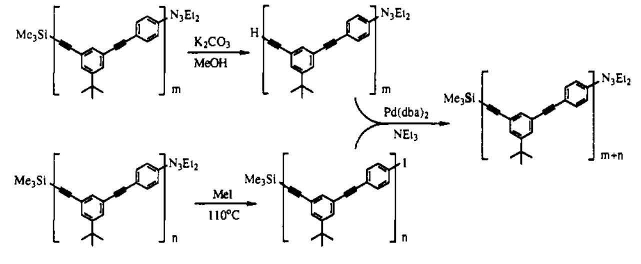
of biorelated oligomers,[6] however, very few methods are available for efficiently synthesizing sequences of precise structure. We report on a stepwise, repetitive approach in which chain growth follows a pattern of geometric progression.[7] The method should be broadly applicable beyond the phenylacetylene sequences described here.

Any repetitive methodology for assembling covalently linked sequences of monomeric units must be able to control chain length, sequence order of monomers, and end-group functionality. In addition, the method must be efficient and versatile. The solid-phase methods pioneered by Merrifield[6] remain the methods of choice for complex polypeptides, especially when each successive unit is different from the previous. However, it is clear that this approach is not necessarily the most attractive for other systems.[8]

For sequences that are periodic or sequences that have extensive periodic segments, the repetitive method shown in Scheme I is, in principle, considerably more efficient.[9] The cycle begins by selective deprotection at each of the two ends of the diprotected monomer A_pB_p, yielding the monoprotected intermediates A_pB and AB_p. These are then coupled to give the dimer, A_pBAB_p, protected in the same way as the original monomer, concluding one repetition. The process can be repeated *n* times to give a sequence of length 2^n. Sequences of length other than 2^n, as well as sequences having a particular arrangement of comonomer units, can be realized by merging parallel repetitive cycles. For example, a hexamer sequence is realized by combining tetramer and dimer sequences. These ideas are demonstrated below with a series of phenylacetylene sequences.

Table I provides a summary of yield and molecular weight data for a series of alternating phenylacetylene comonomer sequences. The chemistry involves palladium-catalyzed cross-coupling of terminal acetylenes with aryl iodides.[10,11] A key finding which has made this particular chemistry feasible is that (trimethylsilyl)acetylenes and 1-aryl-3,3-diethyltriazenes function very effectively as complementary protecting groups for terminal acetylenes[12] and aryl iodides,[13] respectively. Each of these protecting groups can be selectively removed in the presence of the other, and both protecting groups are stable to the cross-coupling conditions. The efficiency of this scheme can be seen by the excellent overall yields for the three-step cycles (Table I). Since all of these reactions are quite mild, we have been able to extend this chemistry to functionalized sequences as well.[14]

Table I.[a] Yield and Molecular Weight Data for a Series of Phenylacetylene Sequences



m	*n*	sequence length[b]	overall yield (%)[c]	mol wt (calcd)	mol wt (obsd)[d]	M_w/M_n
e	*f*	2	86	456	380	1.03
1	1	4	84	713	850	1.03
1	2	6	78	969	1420	1.02
2	2	8	78	1225	2030	1.02
4	2	12	70	1738	3300	1.02
4	4	16	67	2251	4650	1.02

[a] 1-Aryl-3,3-dialkyltriazenes are represented by N_3Et_2. [b] Total number of phenylacetylene units, i.e., $2(m + n)$. [c] Overall yield for the three-step repetitive cycle. [d] Molecular weight by SEC relative to polystyrene standards. [e] *p*-Ethynylphenylenetriazene. [f] 1-(Trimethylsilyl)-2-(3-bromo-5-*tert*-butylphenyl)acetylene.

Size-exclusion chromatography (SEC) data for the sequences in Table I demonstrate the high level of chain length control that can be realized by this method. The large gap between calculated and observed molecular weights is a consequence of the differences in the molecular weight dependence of radius of gyration for our sequences compared to polystyrene calibration standards.[15] We have presently achieved sequences with as many as 16 phenylacetylene units on gram-scale quantities.[16] The sequences shown in Table I are reasonably soluble amorphous or poorly crystalline solids.[17] We will soon report the use of these and related sequences to efficiently assemble nanoscale molecular frameworks.

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Supplementary Material Available: Experimental details and characterization data for all phenylacetylene sequences (9 pages). Ordering information is given on any current masthead page.

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(6) Merrifield, R. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 799.

(7) The synthesis of dendritic macromolecules also takes advantage of geometric progressive growth: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(8) The disadvantage of the Merrifield approach is that growth can only take place at one end, and thus an *n*-unit sequence usually requires at least 2*n* steps. In the method described here, sequences of length 2^n, where *n* is the number of repetitive cycles, can be assembled in a total of just 3*n* steps.

(9) The method in Scheme I can, however, suffer from solubility or purification problems that might be less severe by the Merrifield approach.

(10) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. (c) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.

(11) It is essential that solvents be thoroughly degassed and the reactions run under oxygen-free conditions in order to prevent oxidative dimerization.

(12) (a) Eastmond, R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4601. (b) Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1965**, *4*, 217.

(13) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465.

(14) For example, phenylacetylene backbones with ester side groups have recently been prepared. Moore, J. S.; Zhang, J. Unpublished results from this laboratory.

(15) Assuming universal calibration to hold, two polymers which differ in chemical composition but which have identical SEC retention times will have molecular weights related by eq a

$$M_1 = \left(\frac{K_2}{K_1}\right)^{(\alpha_1+1)^{-1}} M_2^{(\alpha_2+1)/(\alpha_1+1)} \qquad \text{(a)}$$

where M_i is the molecular weight of polymer *i* and K_i and α_i are the respective Mark–Houwink constants of the two polymers. See: Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979; pp 335–337.

(16) Attempts to obtain the 32-mer have thus far been hampered by poor solubility. The synthetic chemistry does not appear to have reached its limitation, but rather we have had difficulty purifying and characterizing this poorly soluble species.

(17) All sequences have been characterized as their α-iodo-ω-(trimethylsilyl)acetylene derivatives by SEC, ^{1}H NMR, ^{13}C NMR, elemental analysis, and MS.