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13. ABSTRACT *(Maximum 200 words)*

Described is the synthesis of oligo(2-ethylphenylene-ethynylene)s and oligo(2-(3'-ethylheptyl)phenylene-ethynylene)s via an iterative divergent convergent approach. Synthesized were the monomer, dimer, tetramer, and octamer of the ethyl derivative and the monomer, dimer, tetramer, octamer, and 16-mer of the ethylheptyl derivative. The 16-mer is 128 Å long. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence; an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and by mass spectrometry. The optical properties are presented which show the stage of optical absorbance saturation. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. These oligomers may act as molecular wires in molecular electronic devices and they also serve as useful models for understanding related bulk polymers.

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Jeffry S. Schumm, Darren L. Pearson, and James M. Tour*

Abstract

Described is the synthesis of oligo(2-ethylphenylene-ethynylene)s and oligo(2-(3'-ethylheptyl)phenylene-ethynylene)s via an iterative divergent convergent approach. Synthesized were the monomer, dimer, tetramer, and octamer of the ethyl derivative and the monomer, dimer, tetramer, octamer, and 16-mer of the ethylheptyl derivative. The 16-mer is 128 Å long. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence; an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and by mass spectrometry. The optical properties are presented which show the stage of optical absorbance saturation. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. These oligomers may act as molecular wires in molecular electronic devices and they also serve as useful models for understanding related bulk polymers.

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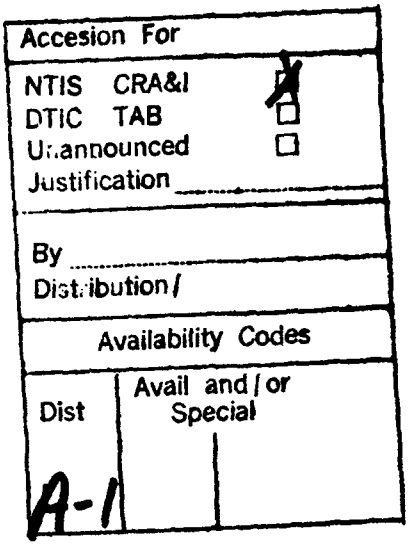

Text for the table of contents.

Described is the synthesis of phenylene-ethynylene oligomers up to 128 Å long. We have used an iterative divergent then convergent approach to rapidly synthesize the oligomers with controlled length and constitution. The molecular length doubles at each iteration. Once the key monomer was synthesized, only three sets of reaction conditions were needed to double the molecular length; namely, a an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. Four iterations provided the 128 Å long 16-mer.

{See figure at end}

The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.[1] Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime,[2] the issue of electronic conduction based upon single or small packets of molecules has not been addressed and the feasibility of molecular electronics remains theoretically controversial.[1,3] In an attempt to assess the possibility of molecular wire[4] conduction by spanning the 100 Å probe gaps with small packets of molecules, we describe here the synthesis of phenylene-alkynylene oligomers that remain in a near-linear conformation due to 1,4-phenylene-substitution patterns and alkyne linearity. This linear arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. Our approach to such a molecular framework involves a rapid iterative method that doubles molecular length at each iteration[5] to provide an air and light-stable linear conjugated oligomer that is 128 Å long that could also serve as a useful model for understanding bulk polymeric material properties.[4i,j,6] Moreover, the product could easily permit independent functionalization of the ends to serve as "molecular alligator clips" that might be required for surface contacts to metal probes for molecular electronics study.[7]

The synthesis of the ethyl-containing monomer **1** is shown in eqs 1 and 2.[8] The iterative divergent/convergent approach to molecular length doubling is shown in Scheme I. Notice how just three different reactions are needed at each stage to double the molecular length.[5c,d,9] We initially conducted the synthesis starting from the monomer **1** with the notion that the ethyl group would provide sufficient solubility to permit formation of a 16-mer that has a length sufficiently long to bridge between lithographically-derived probe gaps. Unfortunately, the octamer **19** was nearly insoluble. Therefore, we were only able to obtain a UV-visible spectrum and a direct exposure mass spectrum (MS) (Table 1).

In an effort to insure the solubility of the linear rigid rod oligomer through to the 16-mer, we prepared the monomer **2** as shown in Scheme II. We tried numerous methods to concomitantly reduce both the ketone and the nitro moieties, however, all methods failed, including the Pd-C/H_2/HCl reduction that worked for in the synthesis of **1** (eq 1 and 2). Therefore the multi-step reaction

sequence shown in Scheme II had to be utilized which also required a *tert*-BuONO-promoted[10] formation of the intermediate diazonium species. In addition to possessing a longer alkyl chain than **1**, **2** also has a stereogenic center which, upon successive dimerization, will afford numerous diastereomers that will retard crystallization and thereby increase the likelihood of solubility. Indeed, we were delighted to discover that both the octamer **20** as well as the 16-mer **23** (Scheme I) were quite soluble and they could be adequately spectroscopically characterization. While **1**, **2**, **7**, **8**, **13**, **14**, and **19** were characterized by direct exposure via electron impact MS, in order to obtain MS data on **20** and **23**, it was necessary to use matrix assisted laser desorption/ionization (MALDI) MS (Table 1). **23** was 128 Å long as determined by a conformational minimization using MMX with extended π-Hückel and multiconformational parameters.

The optical spectra are interesting in that a saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused no change in the position of the absorbance maximum (Figure 1, 2). We also noticed that the π-extended triazene substituent shifted the absorbance maxima bathochromically.

The results of the size exclusion chromatography (SEC) are shown in Figure 3 and compared with the actual molecular weights (MW) of the oligomers. SEC is not a direct measure of MW, but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_n) of rigid rod polymers are usually greatly inflated relative the actual molecular weights. Accordingly, the SEC recorded M_n values of the octamer (**20**) (M_n = 2,800, actual MW= 1,981) and 16-mer (**23**) (M_n = 6,650, actual MW= 3,789) were much greater than the actual MWs. These results further confirm the formation of the 16-mer (**23**). Also, as we would predict, the monomer (**2**), dimer (**8**), and tetramer (**14**) had M_n values that were reasonably close to the actual MWs (slope ~1.0 in Figure 3) because they are in the low MW region, prior to significant polystyrene coiling. In all cases, the SEC-determined values of M_w/M_n = 1.04-1.07. Thus Figure 3 can serve as a useful calibration chart for very rigid linear oligomers as they compare to polystyrene standards by SEC.

Thus we have prepared rigid linear conjugated oligomers by an iterative divergent/convergent doubling approach. These oligomers may be well-suited for molecular wire testing in nanopatterned assemblies.

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Legends for figures and schemes.

(1) 128 Å long linear oligomer for the table of contents.

(2) Equations 1 and 2 describing the synthesis of the ethyl-containing monomer **1**.

(3) Scheme I. The iterative divergent/convergent synthetic approach to the linear oligomers.

(4) Table 1. Characterization data for the linear oligomers.

(5) Scheme 2. Synthesis of the 3-ethylheptyl-containing monomer **2**.

(6) Figure 1. UV absorbance maxima (CH_2Cl_2) of the monomer through 16-mer, **2**, **8**, **14**, **20**, and **23**, respectively.

(7) Figure 2. UV spectrum of the 16-mer (**23**).

(8) Figure 3. M_n as determined using SEC (THF, polystyrene) versus the actual molecular weights of the monomer through 16-mer, **2**, **8**, **14**, **20**, and **23**, respectively.

Table 1. Characterization Data.

13: IR (KBr) 2965, 2872, 2151, 1590, 1503, 1401, 1246, 841 cm-1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.45 (d, J = 8.2 Hz, 1 H), 7.40 (d, J = 7.8 Hz, 1 H), 7.39 (br m, 2 H), 7.35 (d, J = 1.3 Hz, 1 H), 7.32 (dd, J = 7.9, 1.7 Hz, 1 H), 7.32 (dd, J = 7.9, 1.7 Hz, 1 H), 7.29 (d, J = 1.9, 1 H), 7.27 (dd, J = 8.2, 1.6 Hz, 1 H), 7.23 (dd, J = 8.2, 2.1 Hz, 1 H), 3.76 (q, J = 7.2 Hz, 4 H), 2.885 (q, J = 7.5 Hz, 2 H), 2.884 (q, J = 8.2 Hz, 2 H), 2.87 (q, J = 7.5 Hz, 2 H), 2.79 (q, J = 7.6 Hz, 2 H), 1.32 (t, J = 7.6 Hz, 6 H), 1.31 (t, J = 7.6 Hz, 3 H), 1.26 (t, J = 7.6 Hz, 3 H), 0.25 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.75, 147.50, 147.22, 146.69, 146.62, 133.29, 132.75, 132.54, 132.50, 131.33, 131.26, 131.21, 129.18, 129.06, 129.03, 124.45, 123.85, 123.79, 122.78, 122.68, 122.16, 120.72, 118.88, 117.96, 103.82, 100.29, 94.99, 94.80, 93.08, 90.93, 89.98, 89.73, 28.33, 28.05, 28.03, 27.99, 15.21, 15.05, 15.01, 14.80, 0.33. LRMS Calc'd for $C_{47}H_{51}N_3Si$: 685. Found: 685.

14: IR (neat) 2956, 2151, 1595, 1464, 1402, 1236, 1103 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 - 7.27 (m, 12 H), 3.76 (q, J = 7.1 Hz, 4 H), 2.98 - 2.70 (m, 8 H), 1.82 - 1.63 (m, 4 H), 1.59 - 1.05 (m, 46 H), 1.05 - 0.78 (m, 24 H), 0.27 (s, 9 H). Calc'd LRMS for $C_{75}H_{107}N_3Si$: 1077.8. Found: 1077.9. λ_{max} (CH_2Cl_2) = 372 nm. UV 10% edge value = 421 nm. M_n = 1335, M_w = 1388, M_w/M_n = 1.06.

19: Direct exposure MS statistical isotopic range calculated for $C_{87}H_{83}N_3Si$: 1198 (95%), 1199 (100%), 1200 (55%). Found: 1098.6 (signifying loss of the triazene moiety at 100 amu). λ_{max} (CH_2Cl_2) = 364 nm. UV 10% edge value = 500 nm.

20: IR (neat) 2952, 2198, 2147, 1464, 827 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 - 7.27 (m, 24 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.98 - 2.63 (m, 16 H), 1.84 - 1.58 (m, 8 H), 1.58 - 1.10 (m, 86 H), 1.10 - 0.78 (m, 48 H), 0.27 (9 H). λ_{max} (CH_2Cl_2) = 376. UV 10% edge value = 422 nm. M_n = 2800, M_w = 2960, M_w/M_n = 1.05. MALDI MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for $C_{143}H_{195}N_3Si$: 1984. Found peak maximum (M

+ 1): 1791±9 (large error due to broad signal), (loss of -$SiMe_3$ at 73 amu, -N_3Et_2 at 100 amu, -C≡C at 24 amu which a common phenyl-alkynyl cleavage route).[11]

23: IR (neat) 2956, 2927, 2360, 2340, 1506, 1458 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.24 (m, 48 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.95 - 2.65 (m, 32 H), 1.82 - 1.58 (m, 16 H), 1.58 - 1.10 (m, 166 H), 1.10 - 0.70 (m, 96 H), 0.26 (s, 9 H). λ_{max} (CH_2Cl_2) = 376 nm. UV 10% edge value = 422 nm. M_n = 6649, M_w =7114, M_w/M_n = 1.07. MALDI MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for **23** with $C_{279}H_{371}N_3Si$: 3795. Found (M + 1): 3486±14 (large error due to broad signal), (signifying loss in the MS of the -$SiMe_3$ at 73 amu, -N_3Et_2 at 100 amu, -C≡C at 24 amu which a common phenyl-alkynyl cleavage route, and a -C_8H_{17} fragment at 113 amu which represents a typical benzylic methylene-ethylene cleavage site.)[11]