

Polydiacetylenes with Long Wavelength Absorption

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A series of 1,6-disubstituted-2,4-hexadiynes, where the substituents are *para*-substituted benzene rings that have either a dicyanovinyl or tricyanovinyl group as one substituent and have either an oxygen or N-alkyl group connecting to the hexadiyne chain, was designed to lead to polydiacetylenes (PDAs) with long wavelength absorption, and these PDAs were synthesized. These new compounds, in contrast to other diacetylene monomers, are relatively insensitive to ultraviolet light and ionizing radiation under ambient temperature and require heating above 100 °C to bring about preparatively useful conversion to polymer. The new PDAs have the usual en-yne backbone structure as shown by Raman spectroscopy. Three of the new PDAs exhibit maxima in diffuse reflectance at wavelengths as long as or longer than the PDA of 1,6-di-*N*-carbazolyl-2,4-hexadiyne.

Introduction

As a consequence of their synthesis by topochemical and topotactic solid-state polymerization, polydiacetylenes (PDAs, **1**) provide several examples of conjugated polymers available in the form of macroscopic single crystals.¹ Hence PDAs are examples of the best defined polymers, and they have received considerable attention in recent years for potential applications deriving from both their linear and nonlinear optical properties.¹ Among PDAs that are defined by both a complete crystal structure and an electronic spectrum recorded on a single-crystal specimen, the PDA of 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH, **2**) has the longest wavelength absorption,² with its spectrum reaching maximum intensity at 656 nm. In the initial study^{2b} of the spectrum of PDA-DCH, it was suggested that the effect of the carbazolyl group was its contribution to increasing the polarizability of the environment surrounding the conjugated chain.

At present, there is broad consensus^{2a,3} that electronic spectra of PDAs should be discussed in the molecular exciton framework, namely

$$E(k) = E_0 + D + I(k) \quad (1)$$

In eq 1, E_0 is the excitation energy for an isolated chain in the gas phase, D summarizes the energetics of the gas-to-crystal band shift, and $I(k)$ summarizes the exciton transfer interaction between translationally equivalent and nonequivalent moieties. Because the studies of Sixl⁴ have shown that the spectrum of an "infinite" PDA chain is achieved with about 8 repeat units, it follows that attempts to shift the spectrum of a PDA to lower energy should focus on enhancing D . A typical approach^{2a,3} to D follows from consideration of the side groups as a polarizable medium for the conjugated chain. Therefore, side-group polarizability appears to be a major contributor to D .

In the interest of obtaining new PDAs that absorb at wavelengths as long or longer than PDA-DCH, design criteria should emphasize groups that are planar conjugated molecules comparable in size to carbazole and with electronic spectra having intense absorption maxima at wavelengths comparable to or longer than that of carbazole.

It is appropriate to note that there are several examples of PDAs reported^{11,5} to have absorption maxima

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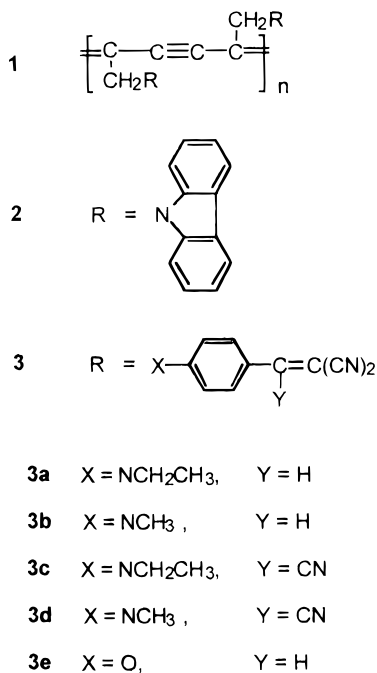
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Scheme 1



near or longer than 700 nm. However, for these systems, in the absence of additional characterization, it is not possible to assess the role of interactions such as aromatic conjugation⁶ or mechanical strains.⁷

We have designed and synthesized a series of derivatives of 2,4-hexadiyne that have *para*-substituted aromatic rings at the 1 and 6 positions. One substituent is either a dicyanovinyl or tricyanovinyl group, and the other, which connects to the hexadiyne, is either an ether oxygen or an alkylamine nitrogen. The molecular structures of these monomers are given in Scheme 1. These aromatic rings have their low energy intense electronic transition at wavelengths longer than carbazole, as indicated in the *Experimental Section*.

Experimental Section

General. Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory or Robertson Microlit. Ultraviolet-visible (UV-vis) solution spectra of the monomers were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer 1720 FT-IR spectrometer. The Raman spectra of the monomers and polymers were recorded in the solid state on polycrystalline samples with the Perkin-Elmer FT-IR spectrometer with Raman accessory using 1064 nm excitation. Diffuse reflectance was recorded on a Varian Cary 17 spectrophotometer. Samples for diffuse reflectance were measured against NaCl as the transparent reference material. The NaCl used in these experiments was ground to a fine powder that lacked specular components. Samples for diffuse reflectance were dispersed in this powdered NaCl as monomers and polymerized as described later. Examination of these samples by optical microscopy revealed that they lacked visible specular characteristics. X-ray powder diffraction of the monomers and polymers was recorded from $2\theta = 2$ to 60° using a CuK α source on either a Rigaku RU-300 Rotaflex or Phillips diffractometer.

Thermal decomposition temperatures of the monomers were determined using a TA Instruments TGA 2950 thermal gravimetric analyzer. Exothermic-heat-initiated polymerization was detected with the aid of a TA Instruments DSC2910 differential scanning calorimeter. The ¹H and ¹³C NMR spectra were recorded on either 200 or 250 MHz Bruker spectrometers. The ¹³C spectra are in agreement with spectra calculated by ACD/CNMR from Advanced Chemistry Development Inc.

1,6-Bis(*N*-ethyl-*N*-phenylamino)-2,4-hexadiyne. The procedure follows that of Schleier.⁸ To a stirred mixture of CuCl (4.90 g, 0.0495 mol) in 300 mL of dimethylformamide (DMF) at room temperature in a bubbler was added *N,N,N,N*-tetramethylethylenediamine (5.54 g, 0.0478 mol). To this mixture was added via dropping funnel over 45 min *N*-ethyl-*N*-propargylaniline (9.24 g, 0.0581 mol) in 150 mL of DMF. Oxygen was then allowed to bubble through the mixture while the mixture was magnetically stirred. After 21 h, water (100 mL) to which concentrated HCl (5 mL) had been added was added to the reaction mixture in a dropwise manner. Then, water (500 mL) was added in the same way. This mixture was filtered by suction and washed with a little HCl of the same dilution as already mentioned and dried in a vacuum dissector to yield 5.67 g (62%) of light plates. Separation on a silica gel column eluted with a 4:1 hexane/ethyl acetate mixture and evaporation to a small volume yielded a product of higher purity, mp 109.3–111.4 °C. IR (KBr): 3064, 3029, 2975, 2878, 1599, 1505, 1427, 1385, 1327, 1248, 1185, 749, 693 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, δ): 1.25 (t, $J = 7$ Hz, 6 H, CH₃), 3.46 (q, $J = 7$ Hz, 4 H, -CH₂CH₃), 4.11 (s, 4 H, CCH₂-), 7.05 (m, 6 H, Ar H), 7.31 (m, 4 H, Ar H). ¹³C NMR (200 MHz, CDCl₃, δ): 13.0 (-CH₃), 40.1 (-CH₂CH₃), 46.0 (≡CCH₂-), 68.5 (≡C-C≡), 75.4 (≡CCH₂-), 114.3 (Ar), 118.3 (Ar), 129.7 (Ar), 148.2 (Ar).

Anal. Calcd for C₂₂H₂₂N₂: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.30; H, 7.17; N, 8.83.

1,6-Bis(*N*-[*p*-formylphenyl]-*N*-methylamino)-2,4-hexadiyne. First, POCl₃/3.20 g, 20.8 mM) was added to DMF, that had been dried over sieves (5.55 mL, 80.3 mM), in a 50-mL three-necked flask that was chilled in an ice bath. This addition was made under argon in a dropwise manner with a syringe. The solution was stirred during the addition. Then, in the same manner, 1,6-bis(*N*-methyl-*N*-phenylamino)-2,4-hexadiyne⁸ (3.00 g, 10.4 mmol) dissolved in DMF (6 mL) was added.⁹ The reaction mixture was heated, with stirring on a steam bath for 2 h. This heating/stirring was interrupted by manually breaking up the thick brown muddy mass that separated. The mixture was poured over crushed ice (35 g). The material remaining in the flask was washed out with a little ice water and added to the mixture, which was then neutralized with saturated sodium acetate. Refrigeration overnight, suction filtration, washing with water, and drying under vacuum resulted in 2.92 g of brown cake. This material was stirred in 200 mL of acetone for 2 h and filtered. The procedure was repeated and resulted in a yield of 1.79 g of gray cake, mp 190.7–191.7 °C. The filtrates were evaporated and then worked with about 15 mL acetone and filtered. The resulting solid material was washed with a little acetone to yield 0.59 g of small orange brown crystals, mp 186–189 °C, that were shown by IR to be the same compound (total yield, 2.37 g, 66%). IR (KBr): 2957, 2914, 2824, 2745, 1664, 1603, 1558, 1524, 1482, 1440, 1371, 1316, 1243, 1205, 1170, 1111, 989, 924, 805, 734, 598, 504 cm⁻¹. ¹H NMR (250 MHz, DMSO-*d*₆, δ): 3.11 (s, 6 H, -CH₃), 4.49 (s, 4 H, ≡CCH₂-), 7.00 (d, $J = 13$ Hz, 4 H, Ar H), 7.77 (d, $J = 13$ Hz, 4 H, Ar H), 9.80 (s, 2H, CHO). ¹³C NMR (250 MHz, DMF-*d*₇, δ): 38.4 (-CH₃), 42.3 (≡CCH₂-), 67.9 (≡C-C≡), 75.5 (-CH₂C≡), 113.1 (Ar), 127.4 (Ar), 131.9 (Ar), 153.8 (Ar), 190.6 (-CHO).

Anal. Calcd for C₂₂H₂₀N₂O₂: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.60; H, 5.94; N, 8.06.

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4-(*N*-Methyl-*N*-propargylamino)benzaldehyde. First POCl₃ (5.00 g, 32.6 mmol) was added in a dropwise manner to DMF (9 g, 123 mmol) in a 50-mL three-necked flask at 0 °C with magnetic stirring. In the same manner, *N*-methyl-*N*-propargylaniline (4.73 g, 32.6 mmol) in DMF (2 mL) was added. The reaction was then heated to between 67 and 105 °C for 3 h in an oil bath before being poured onto crushed ice (30 g) and neutralized to pH 6–8 with saturated sodium acetate (30 mL). This mixture was kept for 2 days at 0 °C. The mass of white crystals and red gum was then treated in an ice bath with 2 N HCl (32 mL) and then with concentrated NaOH solution until just a little acid remained before being neutralized with sodium acetate solution. Next, the mixture was suction filtered and dried in a vacuum desiccator to yield 3.96 g (70%) of salmon pink crystals, mp 66.2–69.5 °C. IR (KBr): 3247, 2914, 2824, 2750, 2114, 1653, 1598, 1532, 1449, 1386, 1336, 1241, 1212, 1169, 998, 817, 741, 683 cm⁻¹. ¹H NMR (250 MHz, CDCl₃, δ): 2.27 (t, *J* = 2.5 Hz, 1 H, ≡C–H), 3.15 (s, 3 H, –CH₃), 4.18 (d, *J* = 2.5 Hz, 2 H, –CH₂–), 6.86 (d, *J* = 7.5 Hz, 2 H, Ar H); 7.81 (d, *J* = 7.5, 2 H z, Ar H), 9.82 (s, 1 H, –CHO). ¹³C NMR (200 MHz, CDCl₃, δ): 38.2 (–CH₃), 41.6 (–CH₂–), 72.4 (≡C–H), 78.1 (–CH₂C≡), 112.2 (Ar), 126.3 (Ar), 131.7(Ar), 152.9 (Ar), 190.3 (–CHO).

Anal. Calcd for C₁₁H₁₁NO: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.20; H, 6.61; N, 8.08.

***p*-Dicyanovinyl-*N*-methyl-*N*-propargylaniline.** In methanol (50 mL) that contains dissolved (by warming) 4-(*N*-methyl-*N*-propargylamino)benzaldehyde (3.82 g, 22.1 mmol) is dissolved malononitrile (2.99 g, 45.3 mmol). This solution is transferred to a three-necked flask, and 0.6 mL of morpholine is added, and the solution is heated to reflux.¹⁰ At this point, bright yellow crystals in the original flask showed that the reaction had started without catalyst. These crystals were added to the cooled reaction in which yellow crystals had also formed and the whole thing was heated to reflux again for a total of 1 h before being cooled to room temperature. The crystals were separated by suction and washed with methanol to yield 3.96 g (81%), mp 144.1–146.4 °C. Visible spectrum (acetone) λ_{max} (log ε): 417 nm (4.61). IR (KBr): 3272, 3090, 2921, 2214, 1605, 1564, 1516, 1380, 1338, 1250, 1190, 1213, 992, 930, 818, 740, 685, 661, 602 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, δ): 2.25 (t, *J* = 2.5 Hz, 1 H, ≡C–H), 3.14 (s, 3 H, –CH₃), 4.14 (d, *J* = 2.5 Hz, 2 H, –CH₂–), 6.80 (d, *J* = 10 Hz, 2 H, Ar), 7.49 (s, 1 H, =CHAr), 7.83 (d, *J* = 10 Hz, 2 H, Ar). ¹³C NMR (250 MHz, DMSO-*d*₆, δ): 38.2 (–CH₃), 41.2 (–CH₂–), 71.1 (≡C–H), 75.2 (–CH₂C≡), 79.3 (=C(CN)₂), 113.2 (Ar), 115.4 (CN), 116.2 (CN), 120.2 (Ar), 133.6 (Ar), 153.5 (Ar), 159.6 (=C(H)Ph).

Anal. Calcd for C₁₄H₁₁N₃: C, 76.00; H, 5.01; N, 18.99. Found: C, 76.13; H, 5.29; N, 19.06.

1,6-Bis(*N*-methyl-*N*-[*p*-dicyanovinylphenyl]amino)-2,4-hexadiyne (mono-3b). In DMF (60 mL) in a dried 250-mL three-necked flask at 60 °C was dissolved 1,6-bis(*N*-methyl-*p*-formylphenyl)amino)-2,4-hexadiyne (2.20 g, 6.40 mmol). To this solution cooled to room temperature was added by pipet melted malononitrile (1.69 g [1.61 mL], 25.6 mmol) and 0.4 mL of morpholine and the solution was heated to 40 °C for 17 h and then cooled in the refrigerator. Finally the solid material was suction filtered and washed with water and then methanol and the air-dried to yield 0.472 g of fine yellow crystals. Gradually diluting the filtrate with water (90 mL) while stirring, suction filtering and washing with water and then methanol (20 mL) and air-drying produced 2.18 g more of fine crystals colored brown by impurities, for a total of 2.65 g (94% crude yield). Both yellow and brown crystals were dried in a vacuum desiccator over P₂O₅. The yellow crystals melted at about 225 °C, and turned red at around 230 °C. Recrystallization of brown and yellow crystals from chlorobenzene yielded small yellow needles that melted with decomposition at about 250 °C, when the melting point was taken quickly, but started decomposing in the high 100s °C and did

not melt when the melting point was taken slowly. The compound was shown to decompose sharply at 250 °C with loss of 29% of its weight by thermogravimetric analysis (TGA), 10 °C/min. A differential scanning calorimetry (DSC) exotherm was observed at 232 °C, 2 °C/min ambient to 250 °C, but no endotherm was semi. The density was determined by neutral buoyancy in hexane-carbon tetrachloride to be 1.25–(1) g/cm³. Visible spectrum (acetone) λ_{max} (log ε): 416 nm (4.97). IR (KBr) 2220, 1608, 1573, 1521, 1452, 1391, 1340, 1252, 1199, 1112, 994, 933, 817, 739, 608, 536, 476, 420 cm⁻¹. FT-Raman 1117, 1164, 1189, 1330, 1368, 1426, 1453, 1520, 1559, 2220, 2254 (C≡C) cm⁻¹. ¹H NMR (250 MHz, DMSO-*d*₆, δ): 3.07 (s, 6 H, –CH₃), 4.46 (s, 4 H, ≡CCH₂–), 6.94 (d, *J* = 9 Hz, 4 H, Ar H), 7.86 (d, *J* = 9 Hz, 4 H, Ar H), 8.11 (s, 2 H, CHO). ¹³C NMR (200 MHz, DMSO-*d*₆, δ): 38.1 (–CH₃), 41.5 (–CH₂–), 67.3 (≡C–C≡), 71.3 (–CH₂C≡), 74.9 (=C(CN)₂), 112.8 (Ar), 115.0 (CN), 115.8 (CN), 120.2 (Ar), 133.3 (Ar), 153.0 (Ar), 159.4 (=C(H)Ph). Powder X-ray *d* spacings: 13, 6.45, 6.03(s), 5.82(s), 4.77, 4.08, 3.83, 3.67, 3.52(s), 3.45(s), 3.22, 3.07, 2.83, 2.51 Å.

Anal. Calcd for C₂₈H₂₀N₆: C, 76.35; H, 4.48; N, 19.08. Found: C, 75.86; H, 4.56; N, 18.61.

An alternate procedure uses symmetric acetylene coupling in the manner of Schleier.⁸ CuCl (0.0525 g, 0.530 mM), *N,N,N,N*-tetramethylethylenediamine (TMEDA, 0.0860 g, 0.741 mmol), and DMF (4 mL) were stirred magnetically in a 20-mL flask until the mixture turned an intense dark blue. To this mixture, at 0 °C, was added dicyanovinylmethylpropargylaniline (1.131 g, 5.14 mM) in DMF (6–7 mL) in a dropwise manner over a period of 20 min. The reaction continued for 40 h at the same temperature. The mixture was suction filtered, and the yellow solid material was washed with 1 N HCl, then water, then methanol, and then a little CH₂Cl₂. After being air-dried, a yield of 0.383 g (34%) was obtained. The compound would irreversibly melt at 250 °C, when the melting point was taken with a rapid heating rate.

1,6-Bis(*N*-ethyl-*N*-[*p*-tricyanovinylphenyl]amino)-2,4-hexadiyne (mono-3c). The procedure follows that of McKusick and Melby.¹¹ To a stirred solution of 1,6-bis(*N*-ethyl-*N*-phenylamino)-2,4-hexadiyne (1.008 g, 3.50 mmol) in DMF (5 mL) at 40 °C was added, over a period of 1–3 min, tetracyanoethylene (TCNE, 0.967 g, 7.55 mmol), and the mixture was stirred magnetically for 5 h at 40–51 °C under reduced pressure (aspirator). Cooling to 0 °C overnight, suction filtering and washing with methanol and ether, and drying under vacuum yielded 0.502 g of red material (0.969 M, 31.5% yield), which did not melt but began to turn a very dark purple above 155 °C (dec 260–370 °C, weight loss of 30% by TGA, 10 °C/min). A DSC exotherm was observed at 222 °C (5 °C/min, room temperature to 240 °C). The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.20–(1) g/cm³. Visible spectrum (acetone) λ_{max} (log ε): 499 nm (4.85). Diffuse reflectance, 1.7% in NaCl: 540 nm. IR (KBr): 3118, 2966, 2219, 1605, 1500, 1456, 1412, 1340, 1224, 1197, 1121, 1007, 833, 800, 749 cm⁻¹. FT-Raman: 1183, 1217, 1337, 1452, 1482, 1536, 2216, 2254 (C≡C) cm⁻¹. ¹H NMR (250 MHz, DMSO-*d*₆, δ) 1.18 (t, *J* = 7 Hz, 6 H, –CH₃), 3.63 (q, *J* = 7 Hz, 4 H, –CH₂CH₃), 4.54 (s, 4 H, ≡CCH₂–), 7.05 (d, *J* = 9 Hz, 4 H, Ar H), 7.95 (d, *J* = 9 Hz, 4 H, Ar H). ¹³C NMR (250 MHz, DMSO-*d*₆, δ): 13.2 (–CH₃), 40.1 (–CH₂CH₃), 47.0 (≡CCH₂–), 68.3 (≡C–C≡), 76.2 (–CH₂C≡), 79.8 (=C(CN)₂), 114.2 (Ar), 114.8 (CN), 115.0 (CN), 115.6 (CN), 118.2 (Ar), 133.3 (Ar), 138.2 (=C(CN)Ph), 153.7 (Ar). Powder X-ray *d* spacings 14, 9.4, 7.8, 7.10, 6.70, 6.23, 5.25, 4.74, 4.30, 4.05, 3.96, 3.92, 3.85, 3.75, 3.64, 3.57, 3.46, 3.42, 3.24, 2.81, 2.67, 2.63, 2.58 Å.

Anal. Calcd for C₃₂H₂₂N₈: C, 74.12; H, 4.28; N, 21.61. Found: C, 74.21; H, 4.64; N, 21.00.

1,6-Bis(*N*-ethyl-*N*-[*p*-tricyanovinylphenyl]amino)-2,4-hexadiyne polymer (3c). The monomer was recrystallized from 80% toluene–20% methylethyl ketone and, after being heated for 230 h at 130 °C in a sealed ampule, appeared purple when ground with NaCl, but looked black in crystalline form.

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The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.26(1) g/cm³. A sample for visible-IR diffuse reflectance was prepared by grinding 10 mg of monomer into 4 g of NaCl and heating for 2 weeks at 140 °C in an evacuated ampule: 507, 540 (shoulder), 665 nm, and tailing out to 1110 nm. IR (KBr): 2216, 1603, 1494, 1456, 1417, 1342, 1222, 1192, 824 cm⁻¹. FT-Raman: 1222, 1444 (C=C), 1490, 1519, 1537, 2075 (C≡C), 2122 cm⁻¹. Powder X-ray *d* spacings: 14, 12, 10, 9.7, 6.70, 5.86, 5.02, 4.88, 4.57, 4.48, 4.04, 3.81, 3.45, 3.26, 3.15, 3.03, 3.05, 3.02, 2.82 Å.

***p*-Tricyanovinyl-*N*-methyl-*N*-propargylaniline.** To a solution of (7.84 g, 0.0543 mol) of *N*-methyl-*N*-propargylaniline in DMF (16 mL), TCNE (6.0303g, 0.04567 mol) was added slowly over 10 min, maintaining a temperature of 45–50 °C (cooling in an ice bath was necessary). The reaction was held at this temperature for another 15 min. The purple syrup was taken up in 80–90 mL of ether and washed twice with water, and the ether was evaporated. The semisolid purple mass was mixed with 5 mL of iced methanol and 10 mL of iced ether and suction filtered to yield 9.030 g of crude product. Recrystallization from 40 mL of hot acetic acid yielded 4.191 g (37%) of red-violet crystals, mp 159.4–160.1 °C. Visible spectrum (acetone) λ_{max} (log ε): 494 nm (4.60). IR (KBr): 3326, 2217, 1605, 1495, 1397, 1342, 1224, 1195, 825, 760, 666, 620 cm⁻¹. ¹H NMR (250 MHz, CDCl₃, δ): 2.33 (t, *J* = 2 Hz, 1 H, ≡C–H), 3.23 (s, 3 H, –CH₃), 4.23 (d, *J* = 2 Hz, 2 H, –CH₂–), 6.88 (d, *J* = 10 Hz, 2 H, Ar H), 8.14 (d, *J* = 10 Hz, 2 H, Ar H). ¹³C NMR (250 MHz, DMSO-*d*₆, δ): 39.1 (–CH₃), 42.1 (–CH₂–), 76.2 (≡C–H), 79.4 (–CH₂–C≡), 79.9 (=C(CN)₂), 114.3 (Ar), 114.9 (CN), 115 (CN), 115.6 (CN), 118.4 (Ar), 133.1 (Ar), 138.2 (=C(CN)Ph), 154.9 (Ar).

1,6-Bis(*N*-methyl-*N*-[*p*-tricyanovinylphenyl]amino)-2,4-hexadiyne (mono-3d). To a stirred solution of 1,6-bis-(*N*-methyl-*N*-phenylamino)-2,4-hexadiyne (0.615 g, 2.33 mmol) in DMF (3 mL) at 40 °C was added TCNE (0.664g, 5.18 mmol) over 5 min. The mixture was stirred under static argon for 2 h at 45–50 °C. After cooling to 0 °C, suction filtering and washing with iced methanol and ether yielded 0.137 g of red material. The filtrate, after removal of the ether and methanol under reduced pressure and dilution with DMF (3 mL), was stirred in a 50-mL flask at 45–50 °C under a stream of nitrogen for another few hours until it became almost solid. The filtrate was then heated briefly to 100 °C to dissolve precipitated matter, cooled to 0 °C, suction filtered, washed with iced methanol and ether, and vacuum-dried to yield 0.505 g (56% yield total) of fine red crystals, which did not melt but began to turn a very dark purple above 130 °C (dec 211–345 °C, weight loss of 31.5% by TGA). A DSC exotherm was observed at 207 °C (5 °C/min, ambient to 210 °C). The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.23(1) g/cm³. Visible spectrum (acetone) λ_{max} (log ε): 494 nm (4.73). Diffuse reflectance, 1% in NaCl: 525 nm. IR (KBr): 2218, 1604, 1494, 1393, 1342, 1220, 1191, 824 cm⁻¹. FT-Raman: 1442, 1490, 1544, 2217 cm⁻¹. ¹H NMR (250 MHz, DMSO-*d*₆, δ): 2.97 (s, 6 H, –CH₃), 4.57 (s, 4 H, –CH₂–), 7.05 (d, *J* = 12 Hz, 4 H, Ar H), 7.94 (d, *J* = 12 Hz, 4 H, Ar H). ¹³C NMR (250 MHz, DMSO-*d*₆, δ): 39.3 (–CH₃), 42.7 (–CH₂–), 68.5 (≡C–C≡), 75.6 (–CH₂C≡), 80.7 (=C(CN)₂), 114.4 (Ar), 114.7 (CN), 114.9 (CN), 115.6 (CN), 118.6 (Ar), 133.1 (Ar), 138.5 (=C(CN)Ph), 154.7 (Ar). Powder X-ray *d* spacings (rec. from acetonitrile): 14(s), 10.3(s), 8.6(s), 8.10(s), 7.03(s), 6.00, 5.64, 5.15, 4.92, 4.76, 4.66, 4.41, 4.22, 4.14, 4.22, 4.14, 4.02, 3.91, 3.81, 3.71, 3.52(s), 3.36(s), 3.28, 3.21, 3.14, 2.99, 2.83 Å.

Anal. Calcd for C₃₀H₁₈N₈: C, 73.47; H, 3.67; N, 22.85. Found: C, 73.08; H, 3.76; N, 22.75.

An alternate procedure uses symmetric acetylene coupling.⁸ A mixture of CuCl (0.0853 g, 0.862 mM), TMEDA (0.1006 g, 0.867 mM) and 4 mL of DMF was magnetically stirred in a 20-mL flask until the mixture turned an intense dark blue. To this mixture, at 0 °C, was added tricyanovinylmethylpropargylaniline (0.999 g, 4.06 mM) in DMF (6 to 7 mL) in a dropwise manner over 20 min, and the reaction continued with magnetic stirring for 40 h at the same temperature. The mixture was suction filtered and the red solid material was

washed with 0.5 N HCl, water, and a little acetone to yield 0.503 g (51%).

1,6-Bis(*N*-methyl-*N*-[*p*-tricyanovinylphenyl]amino)-2,4-hexadiyne polymer (3d). The monomer was recrystallized from acetonitrile and became very dark after being heated 230 h at 130 °C in a vacuum oven. The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.32(1) g/cm³. A sample for visible-IR diffuse reflectance was prepared by grinding 10 mg of monomer into 4 g of NaCl and heating for 2 weeks at 140 °C in a sealed vial: 540 and 660 nm, and a tail going out to 1060 nm. IR (KBr): 2215, 1605, 1494, 1397, 1343, 1191, 824 cm⁻¹. FT-Raman: 1218, 1331, 1445 (C=C), 1487, 2076, (C≡C) cm⁻¹. Powder X-ray *d* spacings: 13, 11.6(s), 10.8(s), 9.5(s) 6.88, 6.48, 5.87, 5.36, 4.72, 4.40, 4.03, 3.86, 3.70, 3.57, 3.44, 3.22, 3.04, 2.90, 2.77, 2.62, 2.60 Å.

Anal. Calcd for C₃₀H₁₈N₈: C, 73.47; H, 3.62; N, 22.50. Found: C, 70.40; H, 3.57; N, 21.34.

1,6-Bis(*p*-oxybenzaldehyde)-2,4-hexadiyne.¹² To a solution of KOH (1.68 g, 0.030 mol) and *p*-hydroxybenzaldehyde (3.51, 0.029 mol) in 46 mL methanol was added 1,6-bis(*p*-toluenesulfonate) of 2,4-hexadiyne¹³ (5.51 g, 0.013 mol), and the mixture refluxed for 14.5 h before being cooled to room temperature. Suction filtration left a brown mass that was washed with 14 mL of water and a little methanol to yield 2.90 g of a dark tan material. Crystallization from hot toluene yielded 1.20 g of brown crystals, mp 164–172 °C. Further concentrations of the mother liquor yielded three fractions of slightly lower mp, bringing the total to 1.94 g (46%) IR (KBr): 3076, 2927, 2837, 2737, 1691, 1602, 1577, 1508, 1426, 1370, 1304, 1247, 1161, 1020, 838, 653, 666, 623, 512 cm⁻¹. ¹H NMR (250 MHz, CDCl₃, δ): 4.87 (s, 4 H, –CH₂–), 7.07 (d, *J* = 8 Hz, 4 H, Ar H), 7.87 (d, *J* = 8 Hz, 4 H, Ar H), 9.94 (s, 2 H, CHO). ¹³C NMR (250 MHz, CDCl₃, δ): 56.7 (–CH₂–), 71.9 (≡C–C≡), 74.4 (–CH₂C≡), 115.6 (Ar), 131.3 (Ar), 132.3 (Ar), 162.5 (Ar), 190.9 (CHO).

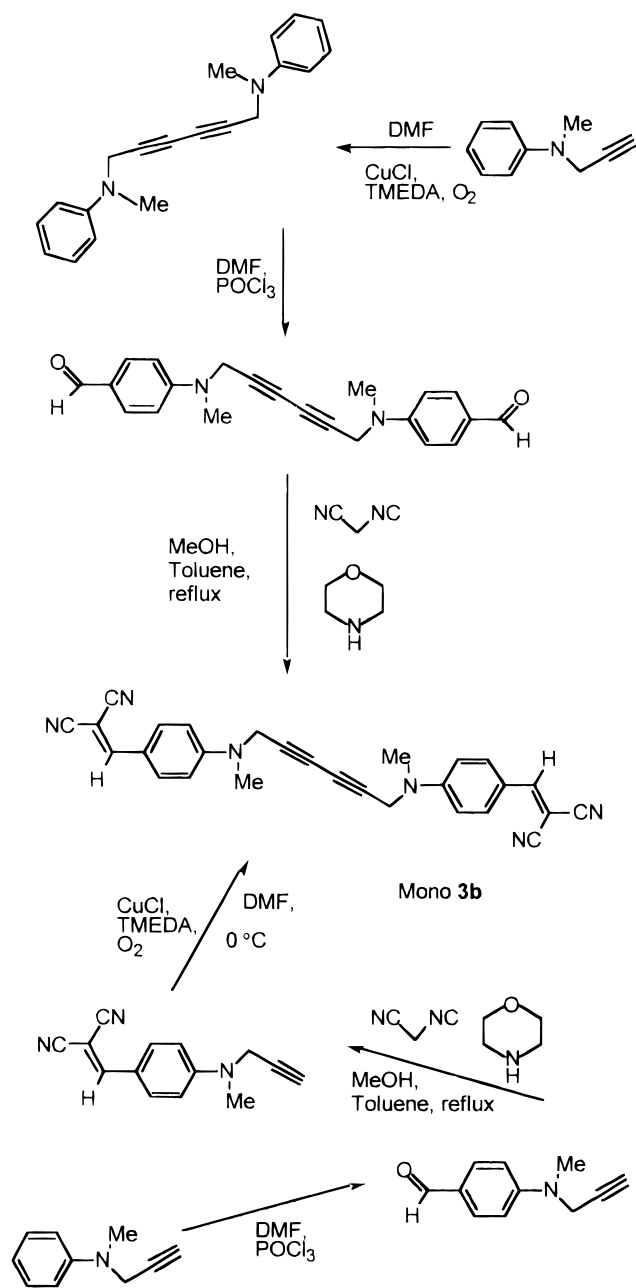
Anal. Calcd for C₂₀H₁₄O₄: C, 75.46; H, 4.43. Found: C, 74.96; H, 4.50.

1,6-Bis(*p*-oxybenzylidenemalononitrile)-2,4-hexadiyne (mono-3e).¹² A mixture of 1,6-bis(*p*-oxybenzaldehyde)-2,4-hexadiyne (3.80 g, 0.0119 mol), malononitrile (3.08 g, 0.0467 mol), and morpholine (40 drops) in methanol (175 mL) and toluene (175 mL) were refluxed for 8 h and allowed to cool to ambient temperature. Suction filtration yielded 2.80 g of dark green crystals. Concentration of the filtrate to one-half volume yielded 0.1498 g of yellow-green flakes. Addition of water to the filtrate precipitated 0.211 g of a yellow green solid that was easily separated, and filtration of the water layer overnight yielded another 1.01 g of similar material. All recovered material was dissolved in 200 mL of boiling acetic acid, filtered, and kept in the dark. On cooling, yellow crystals had formed on the sides of the flask (1.02 g) that turned green on filtration and washing with water and methanol. Addition of water to the mother liquor produced another 3.21 g of fine yellow crystals, which also turned green upon filtration and washing, to yield a total of 4.23 g (86%) that does not melt but slowly turns brick red between 102 and 138 °C after recrystallization from acetonitrile. The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.26(1) g/cm³. UV-vis (acetonitrile) λ_{max} (log ε): 341 nm (4.78). IR (KBr): 3027, 2230, 2223, 1602, 1588, 1562, 1510, 1430, 1397, 1317, 1269, 1230, 1018, 831, 613, 531 cm⁻¹. FT-Raman: 1010, 1159, 1184, 1236, 1274, 1320, 1375, 1435, 1563, 1586, 1603, 2229, 2259 (C≡C) cm⁻¹. ¹H NMR (250 MHz, acetone-*d*₆, δ): 5.14 (s, 4 H, –CH₂–), 7.27 (d, *J* = 10 Hz, 4 H, Ar H), 8.10 (d, *J* = 10 Hz, 4 H, Ar H), 8.21 (s, 2 H, =CHAr). ¹³C NMR (250 MHz, DMF-*d*₇, δ): 57.0 (–CH₂–), 70.9 (≡C–C≡), 75.8 (–CH₂C≡), 78.9 (=C(CN)₂), 114.3 (CN), 115.2 (CN), 116.4 (Ar), 125.9 (Ar), 133.8 (Ar), 160.7 (=C(H)Ar), 162.0 (Ar). Powder X-ray *d*

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Scheme 2



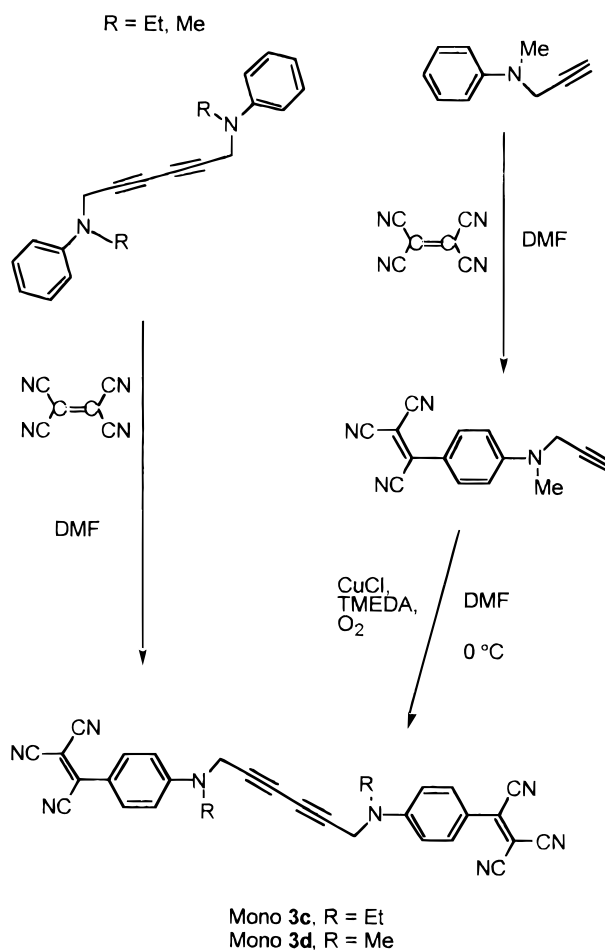
spacings (from acetone): 14, 9.8, 7.7, 6.9, 6.71, 6.55, 5.94, 5.30, 4.98, 4.80, 4.74, 4.69, 4.14, 3.81, 3.67, 3.63, 3.53, 3.26 Å.

Anal. Calcd for $C_{26}H_{14}N_4O_2$: C, 75.35; H, 3.41; N, 13.52. Found: C, 75.29; H, 3.59; N, 13.29.

1,6-Bis(*p*-oxybenzylidene malononitrile)-2,4-hexadiyne polymer (3e). The monomer became very dark after being heated for 230 h at 130 °C in a vacuum oven. Larger crystals (from acetone) had a metallic green gold luster, similar to PDA-DCH. The density was determined by neutral buoyancy in bromobenzene-chloroform to be 1.32(1) g/cm³. A sample for visible-IR diffuse reflectance was prepared by grinding monomer into NaCl to a concentration of 1%, and heating for 2 weeks at 140 °C in an evacuated ampule: 340 and 640 nm, and tail going out to beyond 1100 nm. IR (KBr): 2225, 1603, 1586, 1562, 1510, 1428, 1316, 1277, 1234, 1101, 1010, 830, 614 cm⁻¹. FT-Raman 1236, 1360, 1441, 1465 (C=C) 2080, (C≡C) cm⁻¹. Powder X-ray *d* spacings: 16, 14, 7.7, 7.0, 6.45, 5.62, 5.51, 4.63, 4.27, 4.05, 3.90, 3.76, 3.67, 3.29, 3.14 Å.

Anal. Calcd for $C_{26}H_{14}N_4O_2$: C, 75.35; H, 3.41; N, 13.52. Found: C, 74.84; H, 3.65; N, 13.37.

Scheme 3



Results

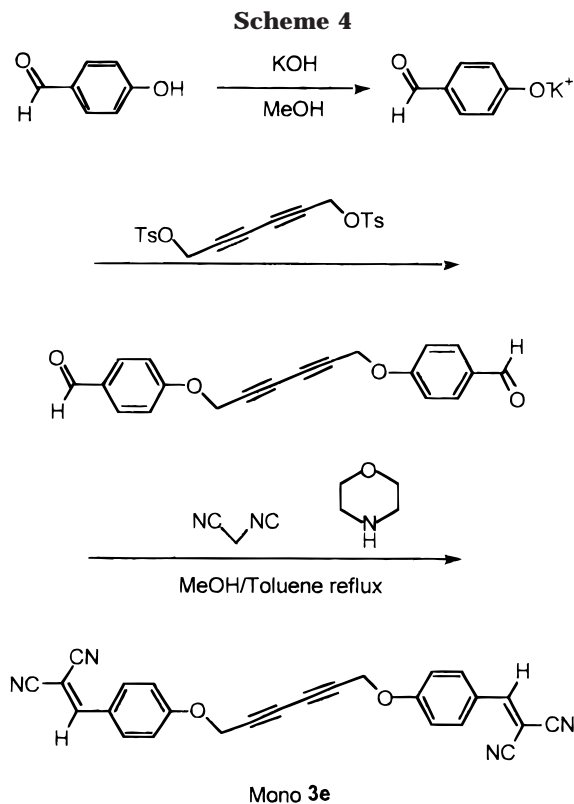
Synthesis. Compound **3b** and the monomer for **3a** are made according to Scheme 2. The appropriate propargylaniline is Hay coupled^{14,8} to form the diacetylene. The ring is then formylated at the *para* position⁹ and this moiety is converted to dicyanovinyl by a Knoevenagel reaction, with malononitrile as the active hydrogen compound, under mildly alkaline conditions.¹⁰ Alternatively, oxidative coupling of a monoacetylene at 0 °C can follow dicyanovinylation, with the slightly soluble product precipitating. Details of the synthesis of **3a**, its polymerization, the crystallographic study of the monomer and polymer, and electronic spectroscopy on single-crystal specimens will be separately reported.¹⁵ Diffuse reflectance of the PDA from **3a** reveals a maximum at 540 nm.

For the monomeric units of **3c** and **3d**, Scheme 3 shows that 1,6-bis(*N*-alkyl-*N*-phenylamino)-2,4-hexadiyne is tricyanovinylated on the *para* positions of both rings following McKusick and Melby.¹¹ Oxidative coupling can follow tricyanovinylation in the same manner as for monomeric **3b**.

The synthesis of monomer for **3e** is shown in Scheme 4. Heating the potassium salt of *p*-hydroxybenzaldehyde with 1,6-bis(*p*-toluenesulfonate)-2,4-hexadiyne¹³ in

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methanol gives the dialdehyde that is then refluxed with malononitrile in methanol/toluene with a morpholine catalyst.¹²

Solid-State Polymerization. Exposure of these monomers to UV light or 50 Mrad of ⁶⁰Co γ radiation did not lead to a preparatively useful reaction. Exposure of crystals of **3a** to 254 nm UV light resulted in cracking of the crystals. Exposure of solid **3e** to UV light slowly turns the material pink, but this is only surface reaction. Macroscopic crystals of **3e** (monomer) turn a dark maroon color on exposure to room light for several hours, but do not progress much beyond that under the same conditions for longer periods. This behavior of **3e** is somewhat reminiscent of the DCH monomer.¹⁶ Monomer **3b** decomposes before polymerization. Polymerization of **3a**, **c**, **d**, and **e** occurred on heating at 130 °C for 9 days as confirmed by disappearance of the diacetylene shift at 2254–2259 cm^{-1} (not detected in **mono-3d**) and the appearance of the normal modes associated with double bond stretching at 1444–1502 cm^{-1} and the triple bond stretch at 2075–2110 cm^{-1} in their FT-Raman spectra, and as exemplified by the spectrum of **3e** in Figure 1. For PDAs where a complete crystal structure is not available, such as those prepared herein, the observation of the normal modes associated with double- and triple-bond stretching constitutes a proof of the en-yne structure for the backbone.¹⁷

Raman data for the four polymers and DCH are summarized in Table 1.

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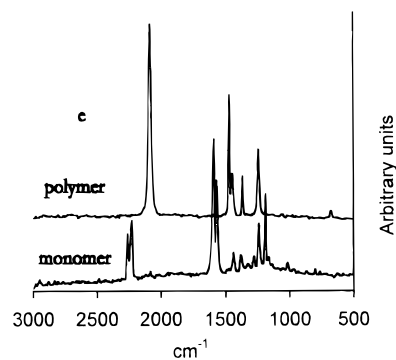


Figure 1. Raman spectra of monomer and polymer of **3e**.

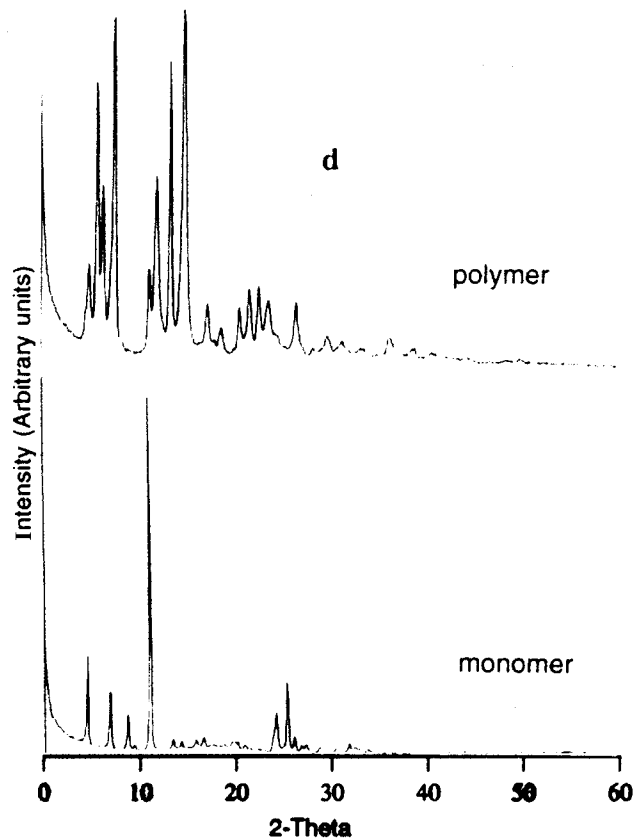


Figure 2. Powder XRD scan of monomer (lower) and polymer (upper) of **3d**.

Table 1. Raman Data for 3a, 3c–3e, and DCH

compound	monomer yne, cm^{-1}	PDA yne, cm^{-1}	PDA ene, cm^{-1}
3a	2259	2110	1502
3c	2254	2075	1444
3d	not observed	2076	1445
3e	2259	2081	1465
DCH	-----	2081 ¹⁷	1491, 1466, 1450, 1420 ¹⁷

Monomer crystals retain their shapes and luster when polymerized, undergo a color change to longer wavelengths, and acquire a metallic sheen. Powder XRD of the polymers shows them to be crystalline, but with no obvious relation to the powder pattern of their monomers, as seen in the example of **3d** in Figure 2.

Diffuse Reflectance. Because of their insolubility and our present lack of suitable single-crystal specimens, we obtained information about electronic excitations in the new PDAs from **3c–e** by diffuse reflectance. Diffuse reflectance provides information about electronic

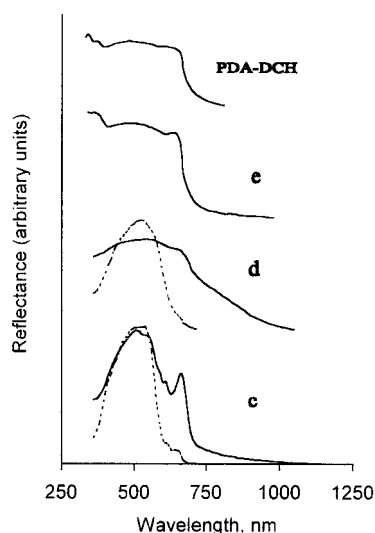


Figure 3. Comparison of diffuse reflectance of the three polymerizable compounds and DCH. Key: (-----) monomer; (—) polymer.

excitations of solids from the remission function, $f(R_\infty)$,¹⁸ which is given in eq 2.

$$f(R_\infty) = 1 - (R_\infty)^2/2(R_\infty) = k/s \quad (2)$$

where R_∞ is the reflectance of an "infinitely thick" sample, k is the absorption coefficient, and s is the scattering coefficient. The difficulty of estimating s usually precludes the obtaining of quantitative information from diffuse reflectance. Diffuse reflectance has been previously used to study PDAs and related materials,^{8,19,20} and the data obtained is in satisfactory agreement with that obtained from single-crystal specimens. In the present work, by working with samples diluted in finely ground NaCl and taking care that there is no indication of a specular component (by optical microscopic examination), we have obtained useful diffuse reflectance.

Figure 3 shows the diffuse reflectance of the PDAs of **3c–e** along with that of PDA-DCH. We note that although PDA-DCH has a maximum at 635 nm in diffuse reflectance, its maximum in single-crystal experiments is at 656 nm.² The maxima at 300–350 nm in the diffuse reflectance of PDA-DCH are those of the carbazole groups.^{2b} Because crystals of **3e** have a color very similar to those PDA-DCH, it is not surprising that its maximum is at 640 nm. The feature at 360 nm in **3e** is the side group maximum. The long wavelength peak in monomer **3c** is likely due to polymer formed during sample preparation. Both **3c** and **3d** exhibit long

wavelength reflection maxima near 665 nm, at significantly lower energy compared with PDA-DCH and **3e**.

Discussion

The requirement for thermal polymerization of these new monomers to obtain useful conversions to polymer merits comment. The bis-alkylurethanes of 5,7-dodecadiyn-1,12-diol are melt-stable and require either UV light or ionizing radiation for polymerization.²¹ This situation contrasts with other derivatives of 2,4-hexadiyne, such as the bis-*p*-toluenesulfonate or the bis-diphenylamino derivative, that are topotactically polymerized by either thermal or radiative methods.²¹ 1,6-Bis(3',6'-dibromo-*N*-carbazolyl)-2,4-hexadiyne is relatively inert to UV and ⁶⁰Co γ radiation at ambient temperature and undergoes solid-state polymerization accompanied by decomposition at >200 °C.²² Hence, the new monomers under discussion herein have a distinct reactivity pattern. Although 50 Mrad of γ radiation is sufficient to completely polymerize DCH,²³ its decreased sensitivity to radiation is thought to be due to the presence of the aromatic carbazole group. It is known that polymers with aromatic groups are less readily decomposed by ionizing radiation than aliphatic polymers, such as polyethylene.²⁴ Additionally, the bis-alkylurethanes of 5,7-dodecadiyn-1,12-diol have very large G values for radiation-initiated polymerization.²⁵ In radiation chemistry, the G value denotes the number of molecules changed for each 100 eV of energy absorbed.²⁴ By this reasoning, the new diacetylenes prepared herein, with aromatic chromophores of lower excitation energy than the carbazolyl group, appear less radiation sensitive.

The PDA-**3c**, **d**, and **e**, that possess side groups with lower energy electronic transitions than the carbazolyl group of PDA-DCH, are shown in Figure 3 to have diffuse reflectance maxima at wavelengths as long or longer than the PDA-DCH maximum at 635 nm. This result is consistent with our design strategy that the position of the spectral maximum of the PDA backbone is sensitive to the detailed nature of the interactions with the side group. Further discussion of the interactions of side groups and backbone must await the availability of single-crystal specimens of these new PDAs that are suitable for both crystallography and spectroscopy. The preparation of such specimens has been initiated.

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