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Dye-Substituted Acetylenes and Diacetylenes: Convenient Polymerization As Studied by Differential Scanning Calorimetry, FT-IR, and UV−vis Spectroscopy

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ABSTRACT: A series of phthalimide- and 1,12-benzoperylene-1′,2′-dicarboxylic imido-linked alkynes were prepared and analyzed by UV, FT-IR, optical microscopy, and differential scanning calorimetry. The possibility to convert ω-alkynes (R−(CH$_2$)$_n$−C≡CH) to diacetylenic compounds (R−(CH$_2$)$_n$C≡C−C≡C−(CH$_2$)$_n$−R) was investigated for R = phthalimide and 1,12-benzoperylene-1′,2′-dicarboxylic imide with n = 1, 3, and 9. Formation of the diacetylenic compound is usually straightforward (as checked by comparison with independently synthesized diacetylenes), and in some cases heat-induced polymerization of the thus-formed diacetylenes proceeds directly. For the perylene imide-linked materials with $n = 1$ and $n = 3$ 1,2-polymerization occurs, while for $n = 9$ 1,4-polymerization occurs. The 1,4-polymerization is also observed for the phthalimide-linked materials. For R = phthalimide and $n = 1$ this 1,4-polymerization can only be induced by further heating, while for the analogous $n = 9$ compound 1,4-polymerization is already induced by UV−vis irradiation at room temperature. This is related to the flexibility of the methylene spacer in the crystal.

Introduction

Conjugated polymers are a topic of much ongoing research in the quest to find alternatives for inorganic (semi)conductors, due to the relative ease of processing of both monomers and polymers and the interesting properties of organic polymers as in applications such as light-emitting diodes and field-effect transistors.[1] In this category polydiacetylenes (PDAs)[2,3] form a promising class of polymeric compounds with interesting photonic properties. A new application for these materials, which makes use of their high charge mobility,[4] can be found in the construction of organic solar cells. This potential use depends largely on the possibility to acquire polymers with a large conjugation length, which can function as a one-dimensional electronic conductor (molecular wire). Such a high level of conjugation can be obtained via so-called topochemical or solid-state polymerization of substituted diacetylenes (DAs).[5] This proceeds via a lattice-controlled 1,4-addition reaction, which can be induced by heat or radiation (visible, ultraviolet, X-ray, or γ) or by subjecting monomer crystals to mechanical stress. For such devices materials can be synthesized in which the polymerizable diacetylene moiety is coupled via a (flexible) spacer to an organic dye molecule. Topochemically polymerized PDAs that are coupled to organic dyes should therefore display three properties that are quintessential for photovoltaic energy conversion: (i) efficient absorption of sunlight, (ii) generation of electric charges by light-induced electron transfer, and (iii) transport of charge carriers to produce electricity.[6]

Materials that can, in principle, be used in organic solar cells are therefore obtainable by functionalization of diacetylenic compounds with large disklike dye molecules, such as phthalocyanine or perylene derivatives, connected by alkyl spacers: dye−spacer−DA. These monomeric diacetylenes are likely to have mesogenic properties as a result of the stacking of the π-systems and the flexible alkyl diacetylenic side chains,[7] which make them structurally related to triplet liquid crystals.[8] Ordering of the molecules in the solid phase via the liquid crystalline phase followed by polymerization is thus expected to give rise to polymeric structures with the polymer chain parallel to the columnar axis.

Several groups have reported on molecules containing dyes such as porphyrin[9] and phthalocyanine[10] bridged by a diacetylene group as spacer. Also, photophysical and charge transport properties of diacetylene−porphyrin conjugated polymers have been investigated.[11]

In this paper we report on the synthesis of a series of acetylenic (type A) and diacetylenic (type DA) compounds, with alkyl aromatic substitution (Scheme 1). To the best of our knowledge, this is the first report on polydiacetylenes with dye molecules linked via a flexible spacer. In this set (Scheme 1) systematic variation of the length of the alkyl spacer between the aromatic and alkyne moieties and of the size of the π-system was applied to obtain clear insight into the role of flexibility of their relative orientations in the polymerization process. Polymerization of the diacetylenic as well as acetylenic compounds was investigated because of the possible reduction in reaction steps if polydiacetylene formation would be possible straight from the acetylene. The synthesis of the resulting polymers is described, and their properties—as studied by differential scanning calorimetry (DSC), optical polarization microscopy, FT-IR, and UV−vis spectroscopy—are discussed.

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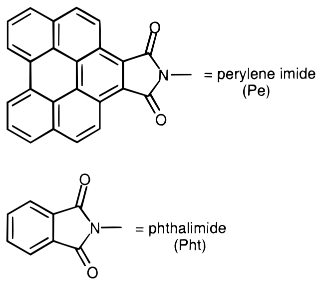
Scheme 1. Investigated Compounds



$R{-}(CH_2)_n{-}C{\equiv}CH$ (A)

$R{-}(CH_2)_n{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_n{-}R$ (DA)

Compound	Type	R	*n*
1	A	Pe	1
2	A	Pe	3
3	A	Pe	9
4	DA	Pe	9
5	A	Pht	1
6	DA	Pht	1
7	A	Pht	9
8	DA	Pht	9

Experimental Details

Sample Characterization. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired using a 200 MHz Bruker AC200 spectrometer at room temperature unless noted otherwise. All spectra measured in hot pyridine (90 °C) were collected with a 400 MHz Bruker DPX400 spectrometer. UV−vis spectra were recorded with a Perkin-Elmer Lambda 18 spectrophotometer. Fourier transform infrared (IR) measurements were performed with a Bio Rad FTS-7 spectrophotometer. Field desorption (FD) and electron impact (EI) mass spectra (MS) were recorded on a MAT95 mass spectrometer. DSC measurements were conducted using a Perkin-Elmer DSC 7 instrument. A 10 °C/min heating/cooling rate was used, and a nitrogen purge was maintained over the samples at all times. Transition temperatures were taken from the maximum points on the endo- and exotherms and the enthalpies from the integrated area under the curves. Optical microscopy studies were performed on an Olympus optical microscope equipped with crossed polarizers and a Mettler FP-80 HT hot stage. Unless mentioned otherwise, a 10 °C/min heating/cooling rate was used. Samples were prepared by placing thin films or solid powder samples onto a glass slide and adding a coverslip or a second glass slide.

Materials. Phthalic anhydride, potassium phthalimide, and perylene were purchased from Acros. Propargylamine was purchased from Aldrich. 10-Undecyn-1-ol and 5-chloro-1-pentyne were purchased from ABCR, Karlsruhe. Commercially available chemicals were used without further purification. Copper(I) chloride was prepared by reduction of copper(II) chloride with ascorbic acid.[12] Ether refers throughout the text to diethyl ether.

Syntheses. **1,12-Benzoperylene-1′,2′-dicarboxylic Anhydride.** This compound was prepared in quantitative yield from perylene (10 g, 39.6 mmol) as described.[13] Since not all spectral data are given in the literature, IR and ^{1}H NMR data are reported here.

IR (KBr) 3050 (w), 1830 (s), 1814 (s), 1784 (m), 1763 (s), 1757 (s), 1487 (m), 1328 (m), 1292 (s), 1223 (m), 1182 (s), 898 (m), 830 (s), 768 (m) cm^{-1}; ^{1}H NMR (pyridine-d_5, measured at 90 °C) δ 8.24 (t, $J = 7.6$ Hz, 2H), 8.41 (br d, $J = 7.6$ Hz, 2H), 8.43 (d, $J = 8.8$ Hz, 2H), 9.27 (d, $J = 8.8$ Hz, 2H), 9.29 (br d, $J = 7.6$ Hz, 2H). Anal. Calcd (in wt %) for $C_{24}H_{10}O_3$: C, 83.23; H, 2.91. Found: C, 83.52; H, 2.81. Due to the poor solubility in (deuterated) solvents (including hot pyridine), no ^{13}C NMR data could be obtained.

1-(1,12-Benzoperylene-1′,2′-dicarboxylic imido)-2-propyne (1). A mixture of 1,12-benzoperylene-1′,2′-dicarboxylic anhydride (3.5 g, 10 mmol), propargylamine (5.6 g, 100 mmol), and *N*-methylpyrrolidinone (100 mL) was heated at 70 °C under nitrogen for 20 h. After the mixture cooled to room temperature, benzene (150 mL) was added. The precipitate was washed with benzene and purified by Soxhlet extraction with toluene. The toluene mixture was cooled to room temperature. The crystallized material was collected by filtration and vacuum-dried to give 3.4 g (90%) yield of product.

IR (KBr) 3258 (s), 3078 (w), 3044 (w), 2961 (w), 2925 (w), 2123 (w), 1759 (s), 1703 (vs), 1418 (m), 1381 (s), 1343 (s), 1315 (m), 1285 (m), 1154 (w), 1118 (m), 1070 (w), 978 (w), 938 (w), 920 (w), 827 (s), 761 (m), 749 (m), 719 (w), 661 (m) cm^{-1}; ^{1}H NMR (pyridine-d_5, measured at 90 °C) δ 3.40 (t, $J = 2.5$ Hz, 1H), 4.88 (d, $J = 2.5$ Hz, 2H), 8.15 (dd, $J = 7.8$ Hz, $J = 7.9$ Hz, 2H), 8.29 (m, 4H), 9.22 (d, $J = 7.7$ Hz, 2H), 9.40 (d, $J = 9.1$ Hz, 2H); Nominal mass: Calcd $m/z = 383$; FD-MS $m/z = 383$. Anal. Calcd (in wt %) for $C_{27}H_{13}NO_2$: C, 84.58; H, 3.42; N, 3.65. Found: C, 84.37; H, 3.30; N, 3.70. Due to the poor solubility in (deuterated) solvents (including hot pyridine), no ^{13}C NMR data could be obtained.

5-Iodo-1-pentyne. A solution of 5-chloro-1-pentyne (25 g, 224 mmol) and sodium iodide (75 g, 500 mmol) in acetone (300 mL) was refluxed for 16 h. After cooling to room temperature, the precipitate was collected by filtration and washed with acetone. The filtrate was concentrated by evaporation and poured into water (300 mL). After extraction with ether the combined organic layers were dried ($MgSO_4$). Filtration, concentration, and subsequent vacuum-drying yielded 45.8 g (97%) of product, with spectral data as reported.[14]

3,5,7-Triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane,5-[pent-1-ynyl]-iodide. A solution of 5-iodo-1-pentyne (22.9 g, 118 mmol) and hexamethylenetetramine (18.7 g, 130 mmol) in chloroform (225 mL) was refluxed for 16 h. After the solution cooled to room temperature, the precipitate was filtered off and washed with chloroform. The filtrate was concentrated by evaporation to a volume of 100 mL and again refluxed for 6 h. After the mixture cooled to room temperature, the above-described filtration and wash procedure was repeated. The filtrate was then concentrated by evaporation to 75 mL, and the above-described reflux, cool, filtration, and wash procedure was repeated again. The three portions of thus obtained solid material had identical ^{1}H NMR spectra and were combined to give a 33.6 g (85%) yield of product.

IR (KBr) 3208 (vs), 2958 (s), 2888 (m), 2109 (w), 1468 (w), 1451 (m), 1417 (m), 1390 (m), 1364 (m), 1319 (m), 1296 (m), 1278 (s), 1219 (s), 1134 (s), 1056 (m), 1020 (m), 999 (vs), 964 (s), 927 (m), 822 (s), 798 (s), 783 (s) cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$) δ 1.77−1.92 (m, 2H), 2.25 (dt, $J = 6.8$ Hz, $J = 2.6$ Hz, 2H), 2.75−2.84 (m, 2H), 2.96 (t, $J = 2.7$ Hz, 2H), 4.45 (d, $J = 12.0$ Hz, 3H), 4.60 (d, $J = 12.5$ Hz, 3H), 5.07 (s, 6H); ^{13}C NMR ($(CD_3)_2SO$) δ 15.37, 18.55, 54.83, 69.78, 72.61, 77.87, 82.48. Anal. Calcd (in wt %) for $C_{11}H_{19}IN_4$. 0.5 H_2O: C, 38.49; H, 5.87; N, 16.33. Found: C, 38.66; H, 5.72; N, 16.56.

5-Amino-1-pentyne. To a mixture of 3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane,5-[pent-1-ynyl]-iodide (30 g, 89.8 mmol) in ethanol (200 mL) was added concentrated HCl (60 mL). The solution was stirred at room temperature for 20 h. After addition of water (50 mL) and evaporation of ethanol, Na_2CO_3 was added until pH ≈ 10. The resulting mixture was extracted with ether. The combined organic layers were dried ($MgSO_4$), concentrated, and vacuum-dried to give a 3.5 g (47%) yield of product with spectral data as reported.[15]

1-(1,12-Benzoperylene-1′,2′-dicarboxylic imido)-4-pentyne (2). This compound was synthesized in analogy to the synthesis of 1-(1,12-benzoperylene-1′,2′-dicarboxylic imido)-2-propyne. For the synthesis 1,12-benzoperylene-1′,2′-dicarboxylic anhydride (0.5 g, 1.4 mmol), 5-amino-1-pentyne (3.5 g, 42 mmol) and *N*-methylpyrrolidinone (25 mL) were used. Yield after recrystallization from toluene: 0.48 g (81%).

IR (KBr) 3250 (s), 3080 (w), 3051 (w), 2938 (m), 2864 (w), 2121 (w), 1750 (s), 1699 (vs), 1438 (m), 1395 (s), 1373 (s), 1285 (m), 1152 (m), 1117 (m), 1014 (w), 926 (w), 824 (vs), 762 (m), 750 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.00 (t, $J = 2.6$ Hz, 1H), 2.10−2.19 (m, 2H), 2.43 (dt, $J = 6.8$ Hz, $J = 2.6$ Hz, 2H), 4.02 (t, $J = 7.0$ Hz, 2H), 8.12−8.31 (m, 6H), 9.11 (d, $J = 7.7$ Hz, 2H), 9.22 (d, $J = 9.0$ Hz, 2H); Anal. Calcd (in wt %) for $C_{29}H_{17}NO_2$: C, 84.65; H, 4.16; N, 3.40. Found: C, 84.41; H, 4.08; N, 3.29. Due to the poor solubility in (deuterated) solvents (including hot pyridine), no ^{13}C NMR data could be obtained.

11-Amino-1-undecyne. 1-Phthalimido-10-undecyne (5.9 g, 20 mmol) and hydrazine monohydrate (2.2 g, 44 mmol) were dissolved in ethanol (140 mL) and stirred for 16 h at room temperature. Then, water (50 mL) was added, and the resulting mixture was acidified to pH = 3. The precipitated solid was removed, and the filtrate was concentrated, cooled to 0 °C, and treated with aqueous NaOH (10 N) to pH ≈ 10. The solution was extracted with dichloromethane, and the combined organic layers were dried ($MgSO_4$), filtered, and evaporated to give a 2.5 g (75%) yield of product with spectral data as reported.[16]

1-(1,12-Benzoperylene-1′,2′-dicarboxylic imido)-10-undecyne (3). A mixture of 1,12-benzoperylene-1′,2′-dicarboxylic anhydride (1.8 g, 5 mmol), 11-amino-1-undecyne (3.2 g, 19 mmol), and *N*-methylpyrrolidinone (50 mL) was heated at 70 °C under nitrogen for 20 h. After the solution cooled to room temperature, methanol (100 mL) was added. The precipitate was washed with benzene/methanol (1:1), vacuum-dried, and subjected to column chromatography (silica gel, 0.04−0.063 mm, dichloromethane/petroleum ether 40−60 (1:1)), followed by recrystallization from toluene/petroleum ether 60−80, to yield 1.15 g (46%) of product.

IR (KBr) 3262 (m), 3080 (w), 3041 (w), 2922 (s), 2848 (s), 2114 (w), 1755 (s), 1704 (vs), 1616 (w), 1463 (m), 1440 (m), 1400 (s), 1396 (s), 1366 (s), 1337 (m), 1285 (m), 1186 (w), 1152 (w), 1064 (m), 1008 (w), 831 (s), 769 (m), 751 (s), 660 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24−1.54 (m, 12H), 1.84 (q, $J = 6.7$ Hz, 2H), 1.92 (t, $J = 2.6$ Hz, 1H), 2.17 (dt, $J = 6.8$ Hz, $J = 2.6$ Hz, 2H), 3.81 (t, $J = 7.3$ Hz, 2H), 7.89−8.07 (m, 6H), 8.82 (d, $J = 8.9$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 18.37, 27.04, 28.45, 28.71, 29.03, 29.24, 29.40, 37.91, 68.04, 84.81, 121.40, 122.48, 123.18, 123.70, 124.08, 126.40, 127.20, 127.29, 129.75, 131.78, 169.67; Anal. Calcd (in wt %) for $C_{35}H_{29}NO_2$: C, 84.82; H, 5.90; N, 2.83. Found: C, 84.58; H, 5.77; N, 2.80.

1,22-Bis(1,12-benzoperylene-1′,2′-dicarboxylic imido)-10,12-docosadiyne (4). 1-(1,12-Benzoperylene-1′,2′-dicarboxylic imido)-10-undecyne (0.5 g, 1 mmol) was dissolved in *N*,*N*-dimethylformamide (50 mL) and benzene (25 mL) at 70 °C.[17] To this solution were added copper(I) chloride (0.1 g, 1.0 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.1 g, 0.86 mmol). Oxygen was bubbled through the reaction mixture for 3 h at 70 °C. After the mixture cooled to room temperature, methanol (100 mL) was added. The precipitate was washed with 0.6 N HCl (50 mL), water (200 mL), and methanol (50 mL) and was Soxhlet extracted with pyridine. The pyridine mixture was cooled to room temperature. The crystallized material was collected by filtration and vacuum-dried. Subsequently, the obtained solid was washed (Soxhlet extraction) with acetone to give 0.41 g of product (82%).

IR (KBr) 3076 (w), 3046 (w), 2928 (s), 2854 (s), 2153 (w), 1755 (s), 1703 (vs), 1463 (m), 1439 (m), 1400 (s), 1396 (s), 1368 (s), 1339 (m), 1285 (m), 1154 (w), 1067 (m), 1008 (w), 828 (s), 767 (m), 751 (s), 661 (m) cm^{-1}; ^1H NMR (pyridine-d_5, measured at 90 °C) δ 1.34−1.58 (m, 24H), 2.00−2.04 (m, 4H), 2.28 (t, $J = 6.8$ Hz, 4H), 4.02 (t, $J = 7.4$ Hz, 4H), 8.03 (t, $J = 7.4$ Hz, 4H), 8.14 (d, $J = 8.9$ Hz, 4H), 8.18 (d, $J = 7.2$ Hz, 4H), 8.97 (d, $J = 7.2$ Hz, 4H), 9.31 (d, $J = 9.0$ Hz, 4H). Anal. Calcd (in wt %) for $C_{70}H_{56}N_2O_4$: C, 84.99; H, 5.71; N, 2.83. Found: C, 84.70; H, 5.64; N, 2.90. Due to the poor solubility in (deuterated) solvents (including hot pyridine) no ^{13}C NMR data could be obtained.

1-Phthalimido-2-propyne (5). This compound was synthesized in analogy to the synthesis of imido phthalocyanines.[18] A mixture of phthalic anhydride (14.8 g, 100 mmol), propargylamine (12.1 g, 220 mmol), and *N*-methylpyrrolidinone (50 mL) was heated at 70 °C under nitrogen for 20 h. After cooling to room temperature, the reaction mixture was poured into cold water. The precipitated solid was obtained by filtration, washed with water, and crystallized from acetone to give 6.7 g (36%) of white needles.

IR (KBr) 3295 (s), 3048 (w), 2966 (m), 2943 (w), 2130 (w), 1771 (vs), 1717 (vs), 1470 (s), 1429 (s), 1397 (vs), 1353 (s), 1328 (s), 1189 (m), 1122 (s), 1089 (m), 951 (m), 925 (m), 841 (m), 802 (m), 728 (s), 710 (m), 691 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (t, $J = 2.6$ Hz, 1H), 4.43 (d, $J = 2.5$ Hz, 2H), 7.67−7.77 (m, 2H), 7.82−7.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.00, 71.50, 77.18, 123.59, 131.98, 134.24, 166.99; Anal. Calcd (in wt %) for $C_{11}H_7NO_2$: C, 71.34; H, 3.81; N, 7.56. Found: C, 71.08; H, 3.73; N, 7.45.

1,6-Bis(phthalimido)-2,4-hexadiyne (6). Analogous to a general procedure,[19] 1-(phthalimido)-2-propyne (1.9 g, 10 mmol) was dissolved in 2-propanol (150 mL) at 50 °C. To this solution were added copper(I) chloride (0.05 g, 0.5 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.1 mL). Oxygen was bubbled through the reaction mixture for 2 h at 50 °C and, subsequently, for 2 h at 70 °C. The resulting reaction mixture was poured into water and acidified with concentrated HCl (pH < 3). The precipitate was washed with water and vacuum-dried to yield a white crystalline solid, which was sonicated with acetone (25 mL). The solid was subsequently washed with acetone, vacuum-dried, and recrystallized from acetone to give 1.46 g (85%) of white crystals.

IR (KBr) 3058 (w), 2949 (w), 2918 (w), 1768 (s), 1725 (vs), 1612 (m), 1469 (s), 1420 (s), 1392 (vs), 1341 (s), 1323 (s), 1189 (m), 1118 (s), 1087 (m), 942 (s), 921 (w), 799 (w), 726 (s), 709 (m) cm^{-1}; ^1H NMR ($(CD_3)_2SO$) δ 5.50 (s, 4H), 7.86 (m, 8H); ^{13}C NMR ($(CD_3)_2SO$) δ 27.26, 66.11, 73.75, 123.39, 131.40, 134.74, 166.58. Anal. Calcd (in wt %) for $C_{22}H_{12}N_2O_4$: C, 71.73; H, 3.28; N, 7.61. Found: C, 71.46; H, 3.20; N, 7.55.

11-Chloro-1-undecyne. Analogous to a general procedure,[20] a solution of undecyn-1-ol (25.7 g, 153 mmol), pyridine (12.2 g, 155 mmol), and ether (25 mL) was added dropwise to a mixture of thionyl chloride (20.2 g, 170 mmol) and ether (25 mL). The reaction mixture was subsequently refluxed (2 h), poured into water, and extracted with ether. The resulting organic phase was washed with water, a Na_2CO_3 solution, and again water, dried ($MgSO_4$), concentrated, and vacuum-dried to give 28 g (98%) of product, with spectral data as reported.[21]

1-Phthalimido-10-undecyne (7). Analogous to a general procedure,[22] a solution of 11-chloro-1-undecyne (27.9 g, 150 mmol), potassium phthalimide (29.6 g, 160 mmol), and potassium iodide (26.6 g, 160 mmol) in *N*,*N*-dimethylformamide (80 mL) was heated at 100 °C for 6 h and subsequently poured into water. The precipitate was washed with water, dissolved in dichloromethane, dried over $CaCl_2$, and concentrated. Column chromatography (silica gel, 0.04−0.063 mm, dichloromethane) followed by recrystallization from ethanol furnished 23.6 g (53%) of white crystals.

IR (KBr) 3272 (s), 3090 (w), 3059 (w), 2918 (s), 2850 (s), 2111 (w), 1768 (s), 1709 (vs), 1614 (m), 1465 (s), 1439 (s), 1400 (s), 1369 (s), 1337 (m), 1284 (w), 1217 (w), 1176 (m), 1067 (s), 1039 (m), 1006 (m), 942 (m), 884 (m), 858 (w), 792 (w), 723 (s), 711 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19−1.68 (m, 14H), 1.91 (t, $J = 2.6$ Hz, 1H), 2.17 (dt, $J = 6.9$ Hz, $J = 2.6$ Hz, 2H), 3.66 (t, $J = 7.1$ Hz, 2H), 7.64−7.73 (m, 2H), 7.78−7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.38, 26.82, 28.44, 28.58, 28.67, 28.98, 29.10, 29.31, 38.05, 68.08, 84.76, 123.15, 132.18, 133.83, 168.46. Anal. Calcd (in wt %) for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.70; H, 7.93; N, 4.62.

1,22-Bis(phthalimido)-10,12-docosadiyne (8). To a solution of 1-phthalimido-10-undecyne (2.8 g, 10 mmol) in 2-propanol (100 mL) was added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.1 mL) and 0.05 g of copper(I) chloride (0.05 g, 0.5 mmol). Oxygen was bubbled through the reaction mixture for 1 h at room temperature and 5 h at 50 °C. The reaction mixture was poured into water and acidified with concentrated HCl (pH < 3). After extraction with dichloromethane the resulting organic phase was dried ($MgSO_4$), concentrated, and vacuum-dried to yield a white crystalline solid. Column chromatography (silica gel, 0.04−0.063 mm; dichloromethane) yielded 2.3 g (79%) of 1,22-bis(phthalimido)-10,12-docosadiyne, which was stored under nitrogen at −20 °C.

IR (KBr) 3099 (w), 3068 (w), 3032 (w), 2964 (m), 2935 (s), 2848 (s), 2140 (w), 1773 (s), 1724 (vs), 1615 (m), 1466 (s), 1438 (m), 1396 (s), 1363 (s), 1331 (m), 1267 (w), 1254 (w), 1220 (w), 1187 (m), 1131 (w), 1055 (s), 1006 (m), 942 (m), 884 (m), 801 (w), 721 (s), 712 (s), 624 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21−1.64 (m, 28H), 2.15 (t, $J = 6.7$ Hz, 4H), 3.60 (t, $J = 7.1$ Hz, 4H), 7.58−7.68 (m, 4H), 7.72−7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.19, 26.81, 28.31, 28.58, 28.78, 28.98, 29.11, 29.28, 38.04, 65.26, 77.51, 123.15, 132.17, 133.84, 168.47. Anal. Calcd (in

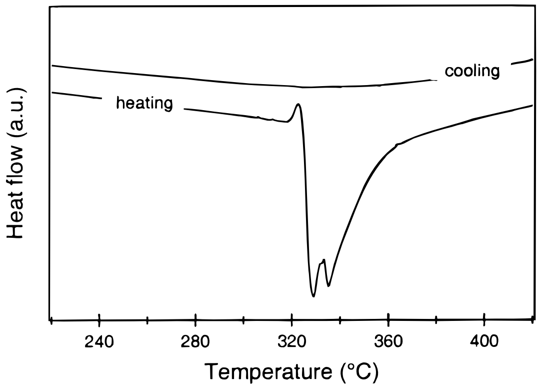


Figure 1. DSC thermograms of **1**.

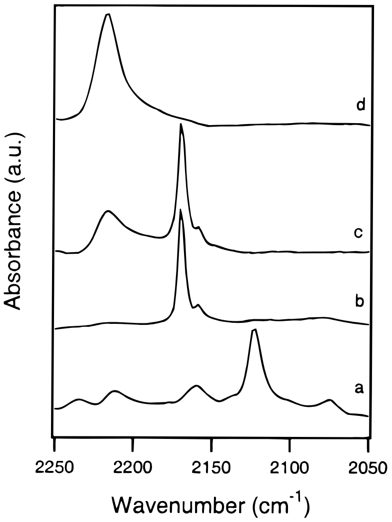


Figure 2. Changes in C≡C stretching vibrations as detected by FTIR spectra of **1** (a, bottom) **1**-420 °C/DSC (b), **1**-500 °C/1 h (c), and **1**-500 °C/2 h (d, top).

wt %) for $C_{38}H_{44}N_2O_4$: C, 76.99; H, 7.48; N, 4.73. Found: C, 76.71; H, 7.63; N, 4.50.

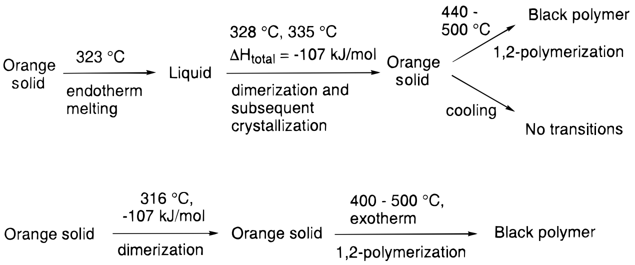
Polymerizations. Methods used for polymerization were heat treatment (in the DSC apparatus or in an oven) and UV irradiation. For UV irradiation thin films were prepared by melting a small amount of the diacetylenic compound between a glass slide and a glass coverslip. By applying a light pressure on the coverslip a film is formed, which was irradiated under a medium-pressure mercury UV lamp for varying amounts of time.

Results and Discussion

Perylene Imide-Linked Acetylenes and Diacetylenes. The perylene imide-linked acetylene compounds **1**−**3** were subjected to heat treatment via differential scanning calorimetry (DSC) to record any heat exchange due to phase transitions or reactions. Figure 1 contains the DSC thermograms of **1**, which are depicted schematically in Scheme 2 (top).

Upon slow heating (in DSC) compound **1** is stable up to a temperature of about 320 °C. Further heating yields a small endotherm (peak maximum at 323 °C), immediately followed by two strong exotherms ($\Delta H_{\text{total}} = -107$ kJ/mol) at 328 and 335 °C. This process yields an orange solid that appeared to be insoluble in many organic solvents, including hot pyridine. In addition, no transitions were detected during the subsequent cooling scan. According to optical microscopy measurements, the small endotherm at 323 °C is due to melting of **1**. If the heating is subsequently continued to 500 °C, a black solid is formed via an exothermic reaction, which shows no phase transitions upon subsequent cooling. No reaction enthalpy for this polymerization could be derived from the DSC data due to severe sublimation.

Scheme 2. Thermally Detected Phase Transitions and Reactions of Compounds 1 (top) and 2 (bottom)



IR spectra of **1** (see Figure 2) were measured before heating, directly after heating in the DSC apparatus to 420 °C (this material is abbreviated as **1**-420 °C/DSC), and after heating in an oven at 500 °C for 1 h (**1**-500 °C/1 h) and for 2 h (**1**-500 °C/2 h).

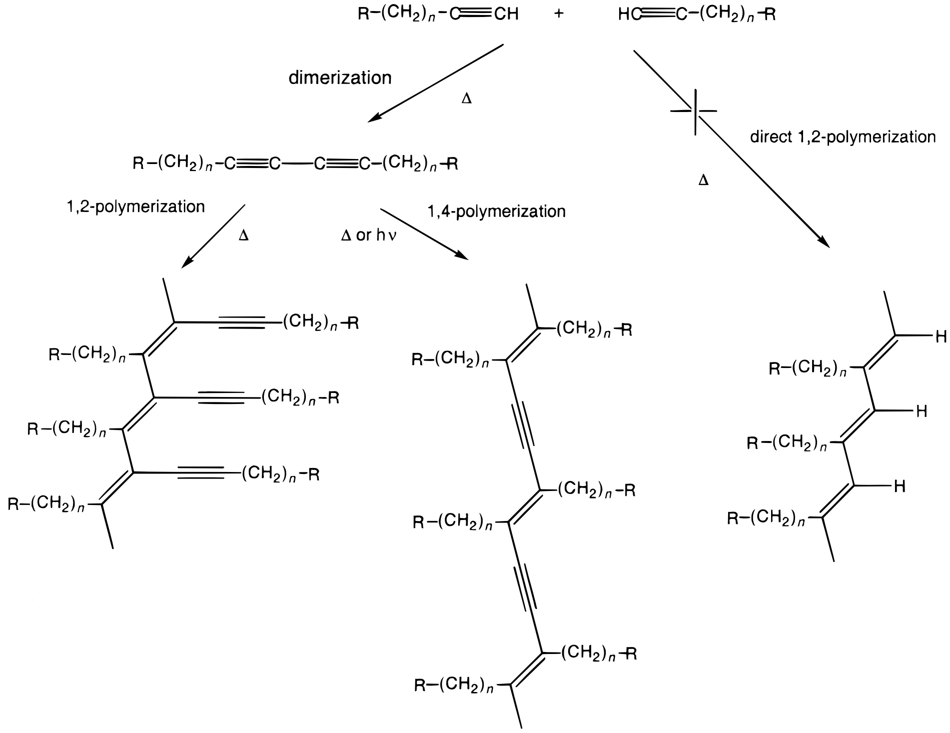
Comparison of the IR spectra (700−4000 cm^{-1}) reveals that all characteristic absorption peaks >1500 cm^{-1} in spectrum a are also present in the spectra of the heated materials, except for the weak absorption at 2123 cm^{-1} (C≡C) and the medium absorption at 3258 cm^{-1} (≡C−H). The changes that occur upon heating of **1** show most clearly via a comparison of the spectra between 2050 and 2250 cm^{-1}, in which the C≡C stretching vibration can be observed. The disappearance of the absorption at 2123 cm^{-1} suggests that immediately after melting of **1** a reaction occurs in which the acetylene group is involved. Moreover, the appearance of a new weak absorption at 2170 cm^{-1} in spectrum b suggests that the environment of the acetylene group is slightly altered.

The effect of prolonged heating at 500 °C appears most clearly from the appearance of a new strong absorption at 2219 cm^{-1} (compare parts d and b of Figure 2; see Figure 2c, for intermediate result after 1 h). The absence of weight loss during the formation of this black polymer, together with the IR results, implies that heating of **1** at 500 °C does not result in significant chemical degradation.

To explain these results, the reaction route shown in Scheme 3 is proposed. During the first heating scan **1** melts (small endotherm, Figure 1) and subsequently reacts with itself to form a centrosymmetric diacetylenic compound (first exotherm, Figure 1). The second exotherm of Figure 1 is due to crystallization of the newly formed compound. This reaction also explains the observed changes in the IR spectra (Figure 2). Extending the heat treatment to 500 °C allows an additional polymerization reaction to occur. The color change from red to black without significant weight loss points toward formation of a conjugated polymer.[23] As shown in Scheme 3, polymerization via 1,2-addition gives a polyacetylene structure with an IR-active (asymmetric) alkyne bond and 1,4-addition gives a polydiacetylene structure with an IR-inactive (symmetric) alkyne bond. The presence of the strong absorption at 2217 cm^{-1} in the IR spectrum (Figure 2d) therefore suggests that this polymer is not the result of 1,4-addition but, in contrast, of 1,2-addition.

Such thermally induced 1,2-addition of diacetylenes has also been reported for vapor-deposited polymeriza-

Scheme 3. Dimerization and Polymerization Reactions of Acetylenic Compounds



tion of butadiyne.[24] A direct formation of polyacetylene from **1**, as has been reported for aromatic acetylene compounds,[25] cannot explain all observed results: no absorption from thus-formed =C−H bonds can be detected in the 3000−3100 cm^{-1} region.

A long-term aim of our research is the construction of thin layers of dye molecules for the potential use in organic solar cells. On the basis of the abovementioned results, heating a thin film of the acetylene compound **1** should lead, via the intermediate diacetylene, in one step to the corresponding perylene-substituted polyacetylene film. Due to the very poor solubility in common organic solvents, films of **1** cannot be prepared from solution. As has been reported for other insoluble perylene derivatives,[26] a thin layer of this compound on a substrate can be obtained via chemical vapor deposition (10^{-2}−10^{-1} Torr, 250−300 °C). During subsequent heat treatment at 400 °C melting and solidification of the film is observed. In this way smooth films of, apparently diacetylenic, material could be prepared on ITO and glass substrates. For polymerization the film has to be treated at a temperature of 500 °C. Unfortunately, the large area of the film promotes significant sublimation of material under these circumstances.

To investigate to which degree both dimerization and mode of polymerization are affected by the spacer length $-(CH_2)_n-$, the phase transitions of **2** ($n = 3$; see Scheme 2, bottom) were measured. In the DSC heating and cooling thermograms of **2** (Figure 3, no peaks were present in the second heating (not shown)) only one strong exotherm is observed at 316 °C ($\Delta H = -105$ kJ/mol). Optical microscopy measurements confirmed that no melting occurred during the heating procedure. In the IR spectrum of the product after DSC heat treatment both the ≡C−H stretching vibration (at 3250 cm^{-1}) and the C≡C stretching vibration (at 2121 cm^{-1}) cannot be detected anymore, pointing to the disappearance of the alkyne and formation of the dialkyne. Further heating of the resulting material to 500 °C yields a black polymer, which was characterized by IR. In this spectrum a new peak at 2216 cm^{-1} comes up that is absent in the dialkyne spectrum. Since symmetrical diacetylenes are IR-inactive, this suggests that the polymerization at least partially occurred via 1,2-polymerization just as observed for **1**. According to these results, the same heat-induced reaction likely occurs as for **1** (with the difference that for **2** the dimerization reaction takes place in the solid state), and the proposed phase transitions can therefore be summarized as in Scheme 2.

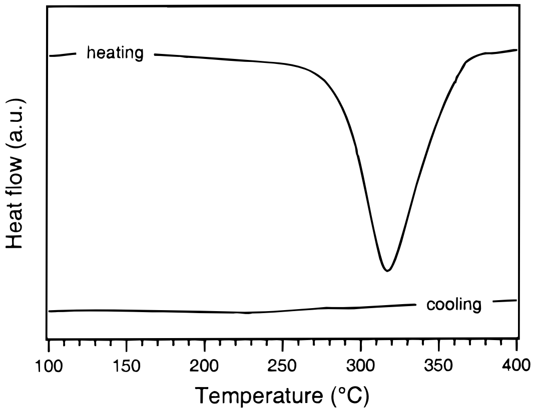


Figure 3. DSC thermograms of **2**.

The DSC results for the perylene imide-linked 1-alkyne with the longest alkyl spacer ($n = 9$; **3**) are depicted in Figure 4a and Scheme 4 (top). After the first heating a reversible crystallization at 189 °C and melting at 195 °C is observed (not shown). At temperatures above 300 °C a very strong broad exotherm is detected at 344 °C (third heating). From the new reversible crystallization and melting points of 207 and 240 °C, respectively, it can be deduced that a new compound has been formed. A likely candidate for this material is the diacetylenic species **4** (perylene−$(CH_2)_9$−C≡C−C≡C−

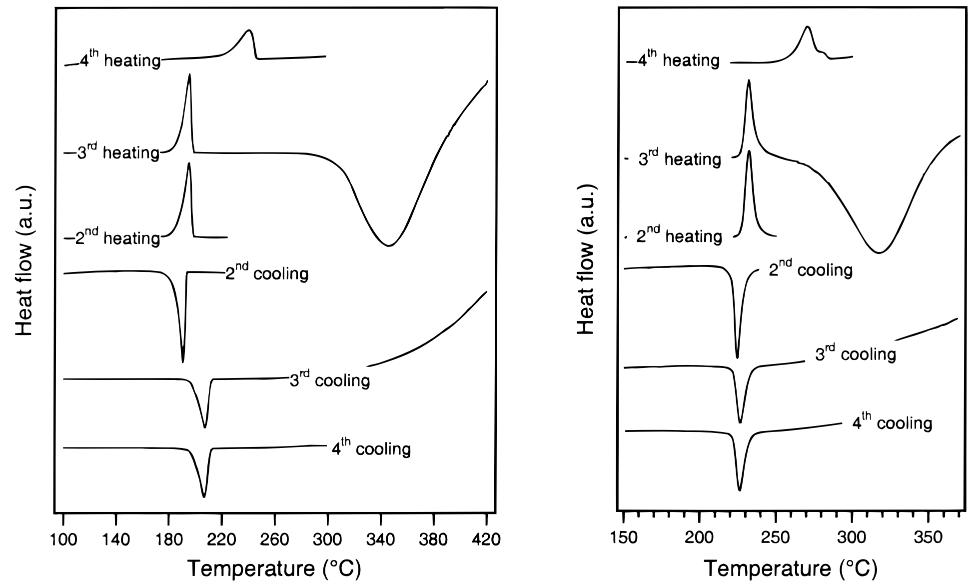
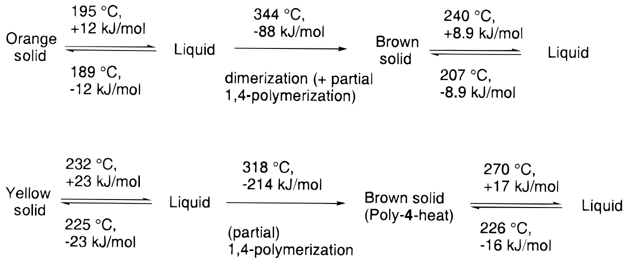


Figure 4. DSC thermograms of compounds **3** (a, left) and **4** (b, right).

Scheme 4. Thermally Detected Phase Transitions and Reactions of Compounds 3 (top) and 4 (bottom)



$(CH_2)_9$−perylene), which was independently synthesized to study the data for **3** in detail, and their chemistry will be discussed together.

The thermal behavior of compound **4** is presented in Figure 4b and Scheme 4 (bottom). After the first heating (not shown) reversible crystallization and melting are observed at 225 °C (first and second cooling scan) and 232 °C (second and third heating scan), respectively. Extension of the heating scan toward higher temperatures shows, however, that a very strong and broad exotherm at 318 °C is present (third heating scan), with $\Delta H = -214$ kJ/mol. The then resulting material crystallizes at 226 °C (third and fourth cooling scan) and melts at 270 °C (fourth heating scan). From the different crystallization and melting temperatures found after the third heating scan, it can be concluded that a new compound is formed during this heating procedure. These data are interpreted to indicate the partial polymerization of **4** to poly-**4**-heat. Heating of **4** for 3 h at ca. 340 °C yielded complete polymerization to a black solid.

To confirm these conclusions, IR spectra of **3** were measured, both before (Figure 5a) and after (Figure 5c) the DSC measurements shown in Figure 4a. Again, similar observations as for **1** and **2** are made, i.e., a strong absorption at 3262 cm^{-1} ($\equiv$C−H) and a very weak absorption at 2114 cm^{-1} (C$\equiv$C) in spectrum a have disappeared in spectrum c. Besides these changes, all spectra of Figure 5 are very much alike. In combination with the absence of detectable weight loss, this indicates that no significant chemical degradation occurs during the DSC heating procedure. The IR results imply that

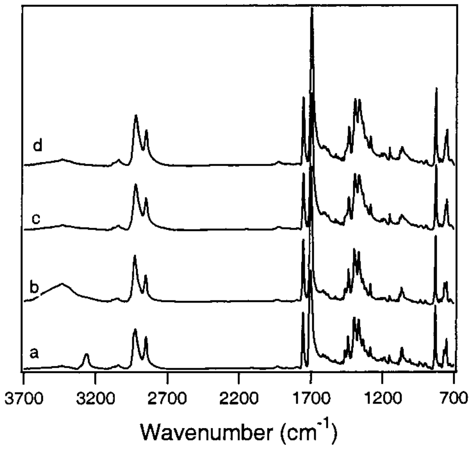


Figure 5. IR spectra of **3** and **4** and the polymers obtained from them, poly-**3**-heat and poly-**4**-heat (from bottom to top).

the acetylene group is again subject of reaction. However, from the observation that the melting and crystallization points of the first product of **3** are not identical to those of **4** (240 and 207 °C and 232 and 225 °C, respectively), it can be concluded that the centrosymmetric dialkyne **4** is not the end product of the thermal reactions of **3**. Indeed, heating of **3** for 4 h at about 340 °C yielded a black solid (besides substantial sublimation of **3**). DSC analysis of this polymer showed no transitions, and with IR no new absorptions were detected in the 3000−3100 cm^{-1} region or around 2200 cm^{-1}, corresponding to =C−H stretch and C$\equiv$C stretch vibrations, respectively. This indicates that a 1,4-polymer has been formed.

Three possible reaction routes could possibly explain the observed results: (i) **3** dimerizes to **4**, which subsequently polymerizes; (ii) **3** partially dimerizes to **4**, and polymerization of the mixture of **3** and **4** occurs; (iii) **3** polymerizes to a polyacetylene structure. However, since no new absorption was detected in the 3000−3100 cm^{-1} region of spectrum d, explanations ii and iii are unlikely: if the acetylene group polymerizes without dimerization step, an absorption from =C−H bonds would have been detected.

This explanation is also supported by the fact that the strong exotherm found for **4** (318 °C) lies below that found for **3** (344 °C), i.e., the temperature at which **4** polymerizes lies below the temperature at which **3** reacts. The similarity of the annealing products is confirmed by the strong overall resemblance between the IR spectra of the products obtained after DSC heat treatment (Figure 5, c and d, respectively). Despite this resemblance, the melt and crystallization points (207/240 and 226/270 °C, respectively) of the materials formed are not identical. These differences can be explained by a difference in molecular weight and/or molecular weight distribution (partial polymerization). Also, the UV-induced polymerization of the perylene imide **4** was investigated. IR analysis of the product showed no change in comparison with the monomer spectrum. So, it is likely that the perylene moiety anchors the diacetylene group into such a crystal packing that no polymerization occurs; polymerization induced by heat obviously is allowed because of monomer melting at higher temperatures. As suggested by a referee, this hypothesis can be tested by studying the possibility of UV-induced polymerization at slightly higher temperatures.

Finally, it is noteworthy to note the differences in behavior of **1**−**3**: a weak absorption at 2153 cm^{-1} in spectrum a (Figure 5) of **4** is observed, but in spectra c and d no absorptions are found in the 2100−2200 cm^{-1} region. This also implies that the dialkyne **4** is not the end product after heat treatment to 420 °C of **3**. For compound **1**, however, a weak absorption could be detected in the 2170 cm^{-1} region, which suggests that, in this case, the diacetylene is the end product after heating to 420 °C. The formation of polymer material, during the DSC heat treatment of **1** and **2**, might be suppressed by the immediate crystallization of the newly formed diacetylene compound. This may well be caused by the fact that for topochemical polymerization strict geometrical requirements hold.[27] Since the crystallization of both **1** and **2** will likely be dominated by the intermolecular forces between the perylene rings, this leaves very little possibilities for the linking diacetylene chains to get into a conformation that allows topochemical polymerization. In contrast, for **3** the diacetylene chain linking the perylene moieties will be somewhat more flexible, which might allow just enough conformational freedom so that the geometrical requirements for topochemical polymerization can be fulfilled.

A thin homogeneous film of **3** can readily be prepared via spin-coating from a chloroform solution. Within this film polymerization of **3** can be conveniently achieved by means of heat treatment. Thermal treatment of this film as deposited on ITO and TiO_2 destroyed it (significant droplet formation). In contrast, deposition of **3** on SnO_2 gave good homogeneous polymer films after heat treatment (15 min, 400 °C).

Phthalimide-Linked Acetylenes and Diacetylenes. Analogous DSC and IR studies have been performed on the phthalimide-coupled acetylenes and diacetylenes **5** and **6** ($n = 1$) and **7** and **8** ($n = 9$).

For alkyne **5** (see Scheme 5, top) the start of an exotherm was detected around 270 °C using DSC, but due to severe sublimation of the material, this exotherm cannot be followed accurately at temperatures >300 °C. IR of **5** shows a characteristic weak absorption at 2130 cm^{-1} (which is absent in **6**, as expected). In the product obtained after DSC heat treatment (which is fortuitously relatively pure due to abovementioned sublimation), no absorptions between 2100 and 2200 cm^{-1} and around 3300 cm^{-1} are present, strongly indicating the formation of a new material with symmetrical, and thus IR-inactive, C≡C bonds without a ≡C−H moiety. The absence of absorptions around 3000−3100 cm^{-1} excludes the presence of =C−H groups and thus polymerization to a polyacetylene structure. This suggests that dimerization of the alkyne **5** to the dialkyne **6** has taken place, which is immediately followed by 1,4-polymerization.

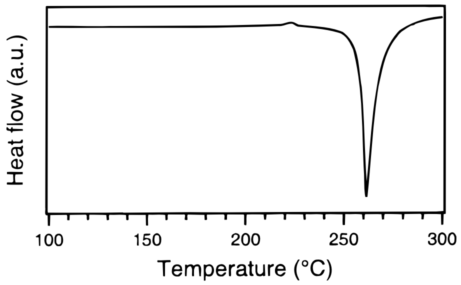


Figure 6. DSC heating thermogram of **6**.

Scheme 5. Thermally Detected Phase Transitions and Reactions of Compounds 5 (top) and 6 (bottom)

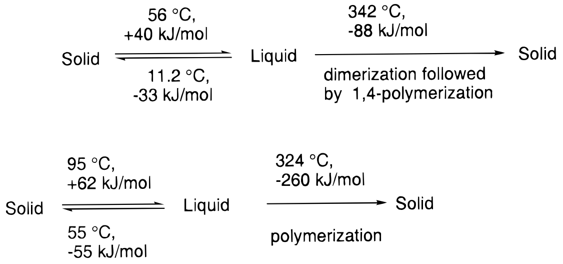
$$\text{White solid} \underset{\text{132 °C, -22 kJ/mol}}{\overset{\text{154 °C, +27 kJ/mol}}{\rightleftharpoons}} \text{Liquid} \xrightarrow[\text{exotherm, 1,4 polymerization}]{\geq 270\ \text{°C}} \text{Black polymer}$$

$$\text{White solid} \overset{\text{223 °C, +1.5 kJ/mol}}{\rightleftharpoons} \text{Liquid} \xrightarrow[\text{polymerization}]{\text{260 °C, -189 kJ/mol}} \text{Black polymer}$$

A film of independently synthesized compound **6** is stable toward UV irradiation. Similar observations were reported for structurally related compounds.[28] Therefore, the specific arrangement of the molecules in the lattice, needed for the topochemical 1,4-addition reaction,[29] is likely not present in the case of monomer **6**. In the case of monomer **8** (vide infra), the flexibility of the longer methylene spacers tremendously increases the reactivity of the monomer toward topochemical polymerization by means of UV irradiation, but for monomer **6**, however, polymerization can only be achieved by means of heat treatment.

In a DSC run of **6** from room temperature onward a small endotherm ($\Delta H = 1.5$ kJ/mol) is detected at 223 °C (see Figure 6 and Scheme 5, bottom). With optical microscopy only coloring of the crystals could be observed, suggesting that a crystal−crystal or crystal−liquid crystal phase transition occurs, which initiates the polymerization. As can be seen in Figure 6, a very strong exotherm ($\Delta H = -189$ kJ/mol) is observed at 260 °C, which is associated with thermally induced polymerization of the diacetylene groups. During the strong exotherm, the color intensifies to black, and solidification to a homogeneous film is observed. The absence of transitions in the cooling and subsequent heating scan (not shown) confirms that a new compound is formed that has no noticeable phase transitions over this temperature range. IR spectra of the formed material still show no absorptions in the 2100−2200 cm^{-1} area, which suggests that 1,4-polymerization has taken place. As can be seen in Figure 6, immediately after the small endotherm at 223 °C the DSC heating scan starts to deviate from the baseline, which also indicates that a rearrangement of the molecules in the lattice (crystal−

Scheme 6. Thermally Detected Phase Transitions and Reactions of Compounds 7 (top) and 8 (bottom)



crystal or crystal–liquid crystal transition) triggers polymerization. A dependence of the reactivity on the crystal phase of a compound has been reported for structurally related symmetric diacetylenes[30a] and asymmetric diacetylenes.[30b] Analogously, thermally induced liquid-state polymerization for structurally related symmetric diacetylenes,[7] asymmetric diacetylenes,[28,31] and disklike mesogenic diacetylenes could explain the abovementioned observations for the polymer.[32]

As for the perylene imide-linked (di)acetylenes the effect of the length on the alkyl linker was studied. Therefore, the alkyne **7** and dialkyne **8** were synthesized, and their behavior under heating and UV irradiation was investigated. For **7** similar DSC (Scheme 6, top) and IR results were obtained as for the analogous perylene-linked alkyne **3**. The phase transitions are generally similar to those of **3**: the material melts and crystallizes reversibly, just above room temperature. With continued heating at >300 °C a thermal reaction occurs (exotherm at 342 °C), which likely corresponds to dimerization to the dialkyne **8** and polymerization of this new material, as was confirmed by IR measurements: the characteristic C≡C stretching vibration at 2111 cm^{-1} and the ≡C–H stretching vibration at 3272 cm^{-1} of the alkyne **7** have both disappeared in the product after DSC heating. Since no other peaks corresponding to C–H stretching vibration appear, the occurrence of 1,2-polymerization can be excluded. In combination with the observation that in the final product no phase transitions <380 °C do occur, it is unlikely that this product is the dimer, dialkyne **8**, and most likely the dimerization of **7** is thus immediately followed by 1,4-polymerization.

To see whether the heating of **7** does indeed result in the dialkyne **8**, this material was independently synthesized and studied. Interestingly, and in contrast with all other species in this study, **8** polymerized very rapidly by UV–vis irradiation to form a blue polymer. This process was studied by measuring the UV–vis spectra of a film of **8** as a function of irradiation time (Figure 7).[33] An absorption peak at 665 nm (main $\pi \rightarrow \pi^*$ transition) and a shoulder at 601 nm are growing in over time, which is attributed to the topochemical polymerization of **8**.[34] The absorption intensity increases unto 300 min of irradiation, after which no further intensity increase is observed, which indicates that the topochemical polymerization has stopped.

Compound **8** spontaneously polymerizes in the solid state, which can easily be detected by a bluish glow. Although topochemical polymerization of **8** can be stopped by storage in a cold (–20 °C) and dark place, it could not totally be prevented during sample preparation. A very small absorption at 522 nm is already observed in the UV–vis spectrum before UV irradiation, which is characteristic for one form of thermally formed polymer (vide infra).

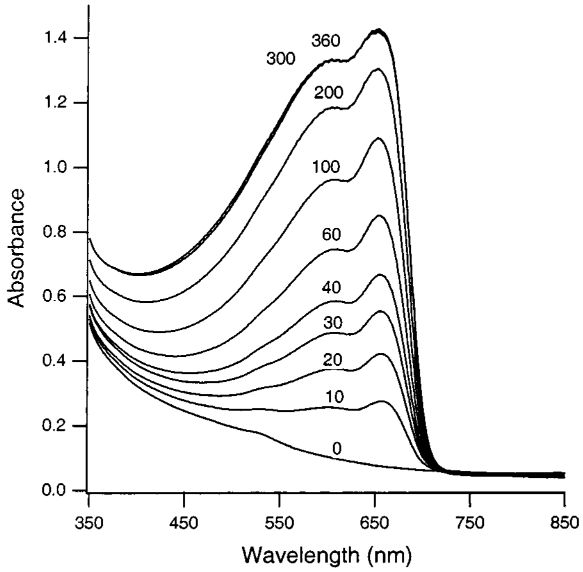


Figure 7. UV irradiation time dependence (in minutes) of the UV–vis absorption spectra of a thin film prepared from compound **8**.

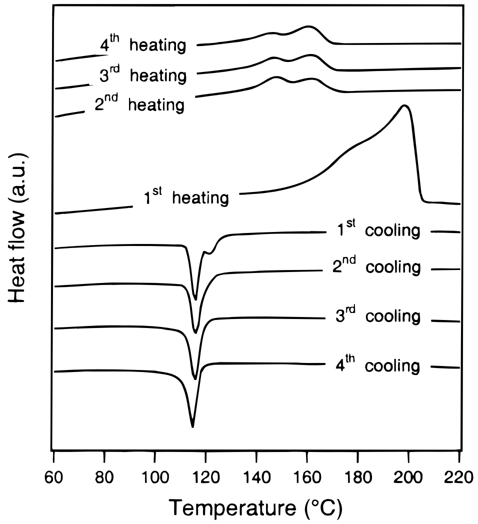


Figure 8. DSC thermograms of topochemically polymerized material of compound **8** (poly-**8**-blue).

The topochemically polymerized blue film of poly-**8**-blue can be converted to a red form (poly-**8**-red) by a heat treatment. This so-called thermochromatic transition[35] can also be observed by means of DSC (Figure 8). A sample of poly-**8**-blue was washed with acetone (Soxhlet extraction) in order to remove traces of monomer, directly after which the DSC experiment was performed. The first heating scan shows a very broad endotherm at 196 °C ($\Delta H = 52.3$ kJ/mol), which corresponds to the irreversible blue-to-red transition. The subsequent cooling scans all have an exotherm at 113 °C with $\Delta H = -6.6$ kJ/mol. According to optical microscopy measurements, this transition is due to crystallization. After the blue-to-red transition, the subsequent heating scans show two reversible endotherms at 145 and 159 °C, with ΔH_{total} of both peaks is 6.6 kJ/mol. Although the origin of both peaks is not clear at the moment, it is likely that at least the second peak is due to melting of the polymer material, as was supported by the observation of an isotropic phase after the second endotherm.

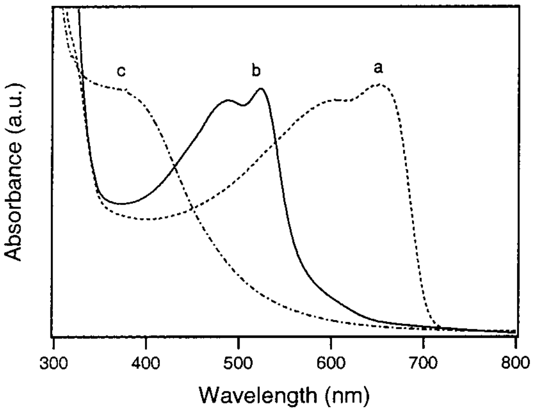


Figure 9. UV–vis spectra of films of poly-**8**-blue (a), poly-**8**-red (b), and poly-**8**-heat (c).

In addition to the DSC measurements, the thermochromic transition can, of course, be observed with UV–vis spectroscopy. Figure 9 shows that a strong blue shift is observed in going from the blue form (spectrum a) to the red form (spectrum b) and also depicts the UV–vis spectrum (spectrum c) from the material obtained after DSC heat treatment (T_{max} = 400 °C) of compound **8** (poly-**8**-heat) (vide infra). The red form has an absorption maximum at 522 nm, with a shoulder at 490 nm.

Two hypotheses have been suggested for these thermochromatic transitions of PDAs. First, they might correspond to a decrease of the effective delocalization length of the π electrons.[36] Thermal treatment might allow the polymer to find an overall more stable crystal structure, which, however, can have a shorter delocalization length. In other words, the lattice forces a structure onto the conjugated PDA backbone, which results in a disturbance of the conjugation of the π-orbitals. Second, it has been suggested that the difference in spectroscopic properties between the blue and the red forms of PDA might be attributed to their molecular packing, i.e., the stacking manner or the orientation of the chains with respect to each other.[37] In this case intermolecular interactions would be dominating this phenomenon. It is currently unclear whether these hypotheses explain our data and, if so, which of these would be the most correct one.

Polymerization of diacetylenes can also be introduced by heat treatment.[7,38] The thermal analysis of compound **8** (20–400 °C) is summarized in Scheme 6 (bottom). Normal melting (95 °C) and crystallization (55 °C) behavior is observed for **8** in the first DSC scan from 20 to 200 °C. The second DSC scan, running to higher temperatures, reveals in the isotropic phase a strong exotherm at 324 °C. This behavior is also observed for other diacetylenic compounds.[38] No transitions are observed in the second cooling scan. A red highly viscous material was obtained after this DSC heat treatment procedure. It has been suggested that in the isotropic liquid state thermally induced polymerization results in the formation of low conjugation length PDA.[7] In addition, some portion might be the result of 1,2-polymerization rather than 1,4-polymerization or other cross-linking reactions.[7]

Figure 9 also shows the UV–vis spectrum (c) of poly-**8**-heat. The maximum of the lowest energy transition that was previously observed for the blue and red forms of the polymer at 665 nm (a) and 522 nm (b), respectively, has for poly-**8**-heat shifted to a shoulder at 380 nm (c). This is in line with previous studies, in which it was suggested that, in the case of thermally polymerized DA, PDA with a lower conjugation length is formed.[38]

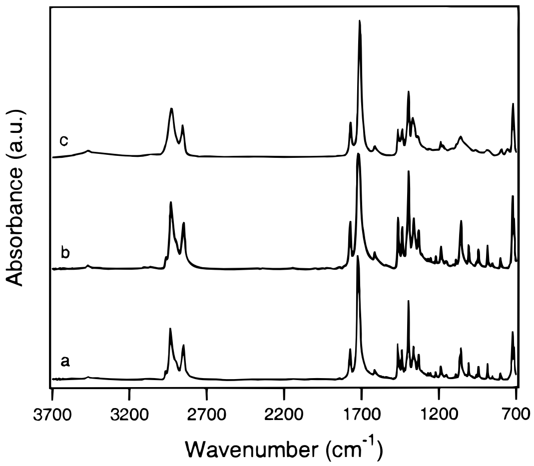


Figure 10. IR spectra of **8** (a), poly-**8**-heat (b), and poly-**8**-blue (c).

IR spectra of **8** (spectrum a), poly-**8**-heat (spectrum b), and poly-**8**-blue (spectrum c) are depicted in Figure 10. The strong resemblance between the spectra indicates that the different polymerization procedures (heating or irradiation) give structurally related polymeric materials. In combination with the absence of detectable weight loss, this suggests that no significant chemical degradation occurs during either of the polymerization procedures. Poly-**8**-blue is a pure 1,4-addition polymer with symmetric triple bonds[35a] and, therefore, has no IR absorption in the 2200 cm^{-1} region. The absence of a similar triple-bond absorption in spectrum b therefore indicates that poly-**8**-heat is also mainly formed by 1,4-addition of **8**.

For **8** conformational freedom is obtained by the two flexible alkyl spacers attached to the diacetylene moiety of the centrosymmetric molecule. As a result, the relative orientation of the dialkyne moieties in the crystal can apparently be optimized for the solid-state polymerization that is observed. Compounds **4** and **6** are, in contrast, insensitive toward polymerization induced by UV and γ irradiation. For **6** and **4**, the conformational freedom of the diacetylene group is reduced by shortening of the methylene spacer length (**6**) or enlargement of the aromatic moiety with increased intramolecular $\pi \rightarrow \pi$ stacking interactions (**4**) of the side groups. Either of these factors appears to inhibit the solid-state polymerization by not enabling the diacetylene molecules to get into the geometry required for topochemical 1,4-polymerization.[27,29]

As for compound **3**, a thin film of compound **8** can easily be prepared via spin-coating from a chloroform solution on glass or ITO. Afterward, the topochemical polymerization of **8** is performed by UV irradiation, yielding a smooth, blue polydiacetylene film. Photoelectrical characterization of such ultrathin polyacetylene and polydiacetylene films is currently under investigation.

Conclusions

Study of the phase behavior of a series of acetylenic and diacetylenic materials has shown that perylene- or phthalimide-linked acetylene compounds can easily be dimerized by a heat treatment. The thus-obtained diacetylenes are prone to polymerization to polyacetylenes and polydiacetylenes by thermal activation. This one-pot polymerization from soluble acetylenes thus opens the way to the convenient formation of thin films of highly insoluble polydiacetylenes. The presence of a large π-system (perylene) and short alkyl spacer between the π-system and the alkyne/dialkyne promotes 1,2-polymerization. A smaller π-system (phthalimide) and/or a long, flexible alkyl spacer between the π-system and the alkyne/dialkyne yield 1,4-polymerization.

1,22-Bis(phthalimido)-10,12-docosadiyne (**8**) could be polymerized by both thermal and photochemical activation, while thermal treatment of the photochemically formed polymer changes many of its properties. Polyacetylene and polydiacetylene polymers can thus be synthesized as ultrathin films (in one step via heat treatment of the acetylene or starting with the diacetylene using UV irradiation) with different optical and optoelectrical[39] properties, making them of significant interest for applications such as organic solar cell studies.

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References and Notes

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