Thermal and Photoinduced Polymerization of Thin Diacetylene Films. 1. Phthalimido-Substituted Diacetylenes

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ABSTRACT: A series of phthalimido-substituted (Pht) diacetylenes with the structure Pht−$(CH_2)_n$−C≡C−C≡C−$(CH_2)_m$−R was synthesized. The influence of the length of the alkyl spacer n between the phthalimido group and the diacetylene group, the length of the alkyl spacer m and an additional polar group R on the thermal and UV-induced polymerization was investigated by systematic variation of n, m, and R (for R = H and $m = 8$, $n = 1, 3, 4, 5, 8, 9$; for $n = 9$ and $m = 3$, R = H, CH_2OH, COOH). All synthesized compounds underwent thermal polymerization. The polymerization temperature increased with longer n spacer or shorter m spacer, and no effect was observed on variation of R. For UV-induced polymerization, a spacer length n of more than four carbon atoms was necessary. Introduction of a hydrogen-bond-forming hydroxyl or carboxyl group at the other side of the diacetylene yielded polymers with a significantly higher degree of conjugation and also improved film formation on quartz enormously.

Introduction

Polydiacetylenes are unique conjugated polymers, because they can be formed in a highly ordered form from diacetylene monomers by topochemical, solid-state polymerization yielding single crystals.[1] Such single crystals are known to have large third-order nonlinear optical susceptibilities due to their extended π-systems.[2] This electronic structure is crucial for the use of polydiacetylenes as solid hole conductors in organic solar cells.[3] Solid hole conductors have recently also been advocated by Grätzel and co-workers, in a related effort to replace the triiodide−iodide redox couple that requires the use of a solvent.[4] Use of 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (OMeTAD) effected the transport of holes, likely via a hopping mechanism from molecule to molecule. Such multiple hopping is not required for charge transport along the backbone of a conjugated polymer, which suggests that such charge transport should be very fast. This is in fact the case, as values for the mobility between 5 and 500 × 10^{-4} $m^2/(V\ s)$ have been measured,[5,6] suggesting that this type of charge transport is potentially fast enough not to be efficiency-limiting in organic solar cells. In addition, the mobility is highly dependent on the degree of polymerization and the detailed molecular structure of the diacetylene monomer.[6]

Thin films of amphiphilic diacetylenes can be formed via Langmuir−Blodgett deposition. In contrast with polymerization at the water−air interface polymerization of the transferred film tends to yield films with a large number of defects, such as cracks and grain boundaries.[7] Moreover, deposition of these layers on a substrate yields polymer films with the conjugated polymer backbone parallel to the substrate surface, which is of no use in the construction of solar cells in which the polymer backbone should be (more or less) perpendicular to the electrodes. Therefore, spin-coated films are being used in this study, as these films can provide the polymer backbone under a large tilting angle relative to the substrate surface.

In this study, several asymmetrical diacetylenes that are linked to a phthalimido (Pht) group have been synthesized and their thermal and light-induced polymerization was investigated. The choice of these materials was prompted by the results of a recent study from our laboratories.[3] Light-induced polymerization of a symmetrical diacetylene with a phthalimido group at either end of a C_9 alkyl spacer (Pht−$(CH_2)_9$−C≡C−C≡C−$(CH_2)_9$−Pht) gave a blue polymer. In sharp contrast, replacing both phthalimido groups with perylene imides prohibited polymer formation completely. It was hypothesized that the increased size of the π-system in the perylene derivatives and the resulting increased $\pi-\pi$ interactions provide a rigid anchor for the relative position of diacetylene groups, which hampers the atom displacements that are required[8] to take place during polymerization. Diacetylenes with reduced $\pi-\pi$ anchoring should therefore have enough flexibility for polymerization to occur. Specifically, asymmetrical diacetylenic materials with an aromatic moiety only on one side, which is still large enough to provide sufficient ordering to allow topochemical polymerization, should be useful in this regard.

To test this hypothesis, and to study the effects on polymer formation, the compounds depicted in Scheme 1 were synthesized, and their thermal behavior was investigated with differential scanning calorimetry (DSC). The influence of the alkyl spacer length n between the diacetylene and phthalimido moieties on phase transitions, polymerization, and polymer properties was investigated for these materals and the corresponding polydiacetylenes as obtained both by thermal and light-induced polymerization. In addition, the influence of polar groups with hydrogen-bonding capacity (−OH and −COOH) at the other end of the diacetylene on the polymerization and adsorption to quartz was studied.

The effects of enlargement of the aromatic unit from a phthalimido to a naphthalimido derivative and sym-

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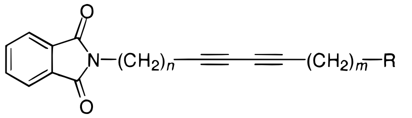
Scheme 1. Investigated Compounds



1-8-H	n=1, m=8, R=H
3-8-H	n=3, m=8, R=H
4-8-H	n=4, m=8, R=H
5-8-H	n=5, m=8, R=H
8-8-H	n=8, m=8, R=H
9-8-H	n=9, m=8, R=H
9-3-H	n=9, m=3, R=H
9-3-CH$_2$OH	n=9, m=3, R=CH$_2$OH
9-3-COOH	n=9, m=3, R=COOH

metrically substituted naphthaldiimides will be published in a separate paper.[9]

Experimental Details

Sample Characterization. ^{1}H and ^{13}C NMR spectra were acquired using a 200 MHz Bruker AC200 spectrometer at room temperature. Coupling constants (J) are given in Hz. 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 during the measurements. Phase transition and polymerization temperatures were taken from the maximum points on the endo- and exotherms, and the enthalpies were taken 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 operated at 4 °C/min temperature increase. Samples were prepared by casting thin films or placing solid powder samples onto a glass slide and adding a coverslip. Trimethylsilyl-coated glass slides (TMS-glass) were acquired by allowing the slide to stand in pure hexamethyldisilazane at room temperature overnight. Titanium dioxide was used as anatase with a surface roughness of 50−70 nm. N,N-dimethyl-3,4:9,10-perylenetetracarboxydiimide (perylene imide) was used as a 20 nm layer sublimed on indium tin oxide (ITO). Quartz was Suprasil I quality purchased from Heraeus. Irradiations were performed with a weak medium-pressure mercury UV-lamp (8W) as standardly used in UV-detection of thin-layer chromatography plates.

Materials. Phthalimide, potassium phthalimide, propargyl alcohol, 8-bromo-1-octanol, and 2-methoxyethoxymethyl chloride (MEM−Cl) were purchased from Aldrich. 1-Decyne, 1-pentyne, 4-pentyn-1-ol, and 5-hexyn-1-ol were purchased from ABCR, Karlsruhe, Germany. 10-Undecyn-1-ol was purchased from Lancaster. 6-Heptyn-1-ol was synthesized by LiAlH$_4$ reduction[10] of 6-heptynoic acid (Fluka) in 68% yield, and showed spectral data as reported.[11] Copper(I) chloride was prepared by reduction of copper(II) chloride with ascorbic acid.[12]

1-Iodoalkynes. The 1-iodoalkynes **1** and **2** were synthesized on a 20-g scale from the corresponding 1-alkynes following the procedure of Barbu and Tsibouklis.[13]

1-Iododec-1-yne (**1**). Yield: 75%. ^{1}H NMR: δ 2.34 (t, J = 7.0, 2H), 1.50 (quin, J = 7.0, 2H), 1.38−1.26 (m, 10H), 0.87 (t, J = 6.5, 3H). ^{13}C NMR: δ 94.86, 31.84, 29.17, 29.06, 28.81, 28.51, 22.68, 20.84, 14.14, −7.58.

1-Iodopent-1-yne (**2**). Yield: 63%. ^{1}H NMR: δ 2.32 (t, J = 7.0, 2H), 1.52 (sextet, J = 7.1, 2H), 0.96 (t, J = 7.3, 3H). ^{13}C NMR: δ 94.68, 22.79, 22.01, 13.45, −7.30.

Cadiot−Chodkiewicz Coupling to Diacetylene. Trideca-2,4-diyn-1-ol (**3**). Trideca-2,4-diyn-1-ol was synthesized according to the procedure of Barbu and Tsibouklis[13] from 1-iododec-1-yne and propargyl alcohol. This yielded, after silica gel chromatography (40−63 μm, chloroform), 3.8 g of product (20 mmol, 36%) with spectral data as reported.[14]

For the other diacetylenes (**4** − **8**) the Cadiot−Chodkiewicz coupling method described by Mowery and Evans[15] was used on a 14−19 mmol scale. The products were purified by silica gel chromatography (40−63 μm, 0−4% methanol in dichloromethane).

Pentadeca-4,6-diyn-1-ol (**4**). Yield: 4.1 g (19 mmol, 68%). ^{1}H NMR: δ 3.68 (m, 2H), 2.34, (t, J = 7.0, 2H), 2.20 (t, J = 6.9, 2H), 2.13 (br s, 1H), 1.79−1.66 (quin, J = 6.9, 2H), 1.55−1.15 (m, 12H), 0.84 (t, J = 6.5, 3H). ^{13}C NMR: δ 77.82, 76.44, 65.77, 65.08, 61.25, 31.81, 30.98, 29.14, 29.05, 28.85, 28.31, 22.64, 19.15, 15.69, 14.07.

Hexadeca-5,7-diyn-1-ol (**5**). Yield: 3.9 g (17 mmol, 56%). ^{1}H NMR: δ 3.64 (t, J = 6.0, 2H), 2.28 (t, J = 6.7, 2H), 2.22 (t, J = 6.9, 2H), 1.71−1.24 (m, 17H), 0.85 (t, J = 6.5, 3H). ^{13}C NMR: δ 77.77, 76.85, 65.65, 65.08, 62.25, 31.78, 31.69, 30.30, 29.10, 29.03, 28.81, 28.28, 24.57, 22.60, 19.14, 18.95.

Heptadeca-6,8-diyn-1-ol (**6**). Yield: 3.4 g (14 mmol, 51%). ^{1}H NMR: δ 3.61 (t, J = 6.1, 2H), 2.24 (t, J = 6.1, 2H), 2.21 (t, J = 6.8, 2H), 1.61−1.24 (m, 18H), 0.85 (t, J = 6.5, 3H). ^{13}C NMR: δ 77.70, 77.09, 65.49, 65.16, 62.71, 32.19, 31.82, 29.15, 29.06, 28.86, 28.33, 28.11, 28.00, 22.65, 19.19, 14.10. EI: calculated mass for $C_{17}H_{28}O$, 248.2140; measured, 248.2136.

Heneicosa-10,12-diyn-1-ol (**7**). Yield: 5.3 g (17 mmol, 58%). ^{1}H NMR: δ 3.63 (t, J = 6.5, 2H), 2.23 (t, J = 6.8, 4H), 1.55−1.20 (m, 26H), 0.87 (t, J = 6.5, 3H). ^{13}C NMR δ 77.57, 77.48, 65.27, 65.22, 63.04, 32.77, 31.83, 29.41, 29.36, 29.15, 29.07, 29.01, 28.86, 28.80, 28.35, 28.32, 25.71, 22.65, 19.20, 14.10. EI: calculated mass for $C_{21}H_{36}O$, 304.2766; measured, 304.2763.

Hexadeca-10,12-diyn-1-ol (**8**). Yield: 4.5 g (19 mmol, 67%). ^{1}H NMR: δ 3.59 (t, J = 6.5, 2H), 2.28−2.14 (m, 4H), 1.70−1.26 (m, 16H), 0.95 (t, J = 7.3, 3H). ^{13}C NMR δ 77.49, 77.35, 65.37, 65.24, 62.98, 32.75, 29.40, 29.35, 29.00, 28.79, 28.30, 25.70, 21.84, 21.16, 19.17, 13.47. EI: calculated mass for $C_{16}H_{26}O$, 234.1984; measured, 234.1979.

Phthalimido Diacetylenes. For **1-8-H**, **3-8-H**, **4-8-H**, and **9-8-H** the corresponding alcohols **3**, **4**, **5**, and **7**, respectively, were converted to the chloro derivatives[16] followed by substitution with potassium phthalimide.[17] The chloro derivatives were purified by silica gel chromatography (40−63 μm, dichloromethane/petroleum ether 40−60 (1:1)), except for **9-8-H**, which required no further purification. Compounds **5-8-H** and **9-3-H** were synthesized directly from the alcohol (**6** or **8**) using the Mitsunobu reaction.[18] The phthalimido diacetylenes were purified by silica gel chromatography (40−63 μm, dichloromethane) to yield white solids in all cases.

1-Chloro-trideca-2,4-diyne (**9**). Yield: 2.9 g (14 mmol, 46%). ^{1}H NMR: δ 4.12 (t, J = 1.1, 2H), 2.21 (t, J = 6.9, 2H), 1.54−1.20 (m, 12 H), 0.82 (t, J = 6.5, 3H). ^{13}C NMR: δ 82.99, 71.58, 69.58, 64.22, 31.82, 30.93, 29.14, 29.04, 28.84, 28.06, 22.66, 19.29, 14.10.

1-Chloro-pentadeca-4,6-diyne (**10**). Yield: 1.9 g (8.0 mmol, 44%). ^{1}H NMR: δ 3.63 (t, J = 6.3, 2H), 2.45 (t, J = 6.8, 2H), 2.23 (t, J = 6.8, 2H), 1.96 (dt, J = 6.8, 6.3, 2H), 1.58−1.17 (m, 12H), 0.86 (t, J = 6.5, 3H). ^{13}C NMR: δ 78.18, 75.14, 66.33, 64.97, 43.50, 31.84, 31.08, 29.16, 29.07, 28.86, 28.29, 22.67, 19.18, 16.68, 14.12.

1-Chloro-hexadeca-5,7-diyne (**11**). Yield: 1.6 g (6.3 mmol, 39%). ^{1}H NMR: δ 3.48 (t, J = 6.6, 2H), 2.24 (t, J = 6.6, 2H), 2.18 (t, J = 6.9, 2H), 1.90−1.78 (m, 2H), 1.68−1.57 (m, 2H), 1.49−1.20 (m, 12H), 0.81 (t, J = 6.4, 3H). ^{13}C NMR: δ 77.97, 76.26, 66.00, 65.07, 44.39, 31.83, 31.44, 29.16, 29.07, 28.86, 28.32, 25.51, 22.66, 19.19, 18.52, 14.10.

1-Chloro-heneicosa-10,12-diyne (**12**). Yield: 4.2 g (13 mmol, 75%). ^{1}H NMR: δ 3.51 (t, J = 6.8, 2H), 2.22 (t, J = 6.8, 4H), 1.81−1.18 (m, 26H), 0.85 (t, J = 6.5, 3H). ^{13}C NMR: δ 77.47, 77.31, 65.28, 65.20, 45.06, 32.59, 31.79, 29.45, 29.24, 29.12, 29.03, 28.92, 28.81, 28.72, 28.31, 28.27, 26.81, 25.69, 22.62, 19.15, 14.06.

2-(Trideca-2,4-diynyl)-isoindole-1,3-dione (1-8-H). Yield: 1.0 g (3.1 mmol, 17%) (yield was not optimized). ^{1}H NMR: δ 7.88−7.79 (m, 2H), 7.75−7.66 (m, 2H), 4.47 (t, J = 1.0, 2H), 2.19 (t, J = 6.8, 2H), 1.53−1.21 (m, 12H), 0.83 (t, J = 6.5, 3H). ^{13}C NMR: δ 166.86, 134.23, 131.99, 123.59, 80.80, 68.94, 68.35, 64.42, 31.80, 29.12, 29.02, 28.80, 28.06, 27.70, 22.64, 19.17, 14.10; IR (KBr): 2954 (m), 2923 (m), 2852 (m), 2258 (m), 1780 (m), 1770 (m), 1728 (s), 1469 (m), 1419 (m), 1390 (m), 1344 (m), 1319 (m), 1118 (m), 942 (m), 724 (m), 708 (m) cm^{-1}. EI: calculated mass for $C_{21}H_{23}NO_2$, 321.1729; measured, 321.1730.

2-(Pentadeca-4,6-diynyl)-isoindole-1,3-dione (3-8-H). Yield: 2.6 g (7.4 mmol, 92%). ^{1}H NMR: δ 7.88−7.79 (m, 2H), 7.74−7.65 (m, 2H), 2.77 (t, J = 6.9, 2H), 2.33 (t, J = 7.0, 2H), 2.17 (t, J = 6.7, 2H), 1.91 (quin, J = 6.9, 2H), 1.49−1.25 (m, 12H), 0.86 (t, J = 6.4, 3H). ^{13}C NMR: δ 168.21, 133.79, 132.00, 123.16, 77.85, 75.44, 65.94, 64.82, 37.12, 31.72, 29.03, 28.95, 28.74, 28.16, 27.02, 22.54, 19.05, 17.05, 14.00. IR (KBr): 2929 (m), 2856 (m), 2255 (w), 2160 (w), 1774 (m), 1714 (s), 1616 (w), 1467 (m), 1437 (m), 1395 (s), 1372 (m), 1188 (m), 1115 (m), 1089 (m), 1025 (m), 884 (m), 719 (s) cm^{-1}. EI: calculated mass for $C_{23}H_{27}NO_2$, 349.2042; measured, 349.2036.

2-(Hexadeca-5,7-diynyl)-isoindole-1,3-dione (4-8-H). Yield: 1.9 g (5.2 mmol, 81%). ^{1}H NMR: δ 7.85−7.76 (m, 2H), 7.73−7.64 (m, 2H), 3.67 (t, J = 6.9, 2H), 2.28 (t, J = 6.9, 2H), 2.20 (t, J = 6.9, 2H), 1.81−1.23 (m, 16H), 0.85 (t, J = 6.4, 3H). ^{13}C NMR δ 168.32, 133.87, 132.03, 123.15, 77.81, 76.39, 65.82, 65.08, 37.28, 31.77, 29.09, 29.01, 28.80, 28.25, 27.72, 25.51, 22.60, 19.14, 18.75, 14.05. IR (KBr): 2928 (m), 2851 (m), 2257 (vw), 2159 (vw), 1775 (m), 1720 (s), 1464 (m), 1438 (m), 1398 (m), 1371 (m), 1361 (m), 1338 (m), 1218 (m), 1188 (m), 1116 (m), 1041 (m), 910 (m), 858 (m), 797 (m), 723 (m), 713 (m) cm^{-1}. EI: calculated mass for $C_{24}H_{29}NO_2$, 363.2198; measured, 363.2199.

2-(Heptadeca-6,8-diynyl)-isoindole-1,3-dione (5-8-H). Yield: 3.9 g (10 mmol, 86%). ^{1}H NMR: δ 7.87−7.78 (m, 2H), 7.73−7.64 (m, 2H), 3.66 (t, J = 7.2, 2H), 2.27−2.18 (m, 4H), 1.73−1.24 (m, 18H), 0.85 (t, J = 6.5, 3H). ^{13}C NMR: δ 168.41, 133.87, 132.14, 123.19, 77.75, 76.93, 65.57, 65.15, 37.76, 31.83, 29.14, 29.07, 28.86, 28.33, 28.09, 27.88, 26.01, 22.66, 19.20, 19.10, 14.11. IR (tetra): 2930 (s), 2858 (m), 2235 (w), 2145 (w), 1774 (m), 1716 (s), 1467 (m), 1438 (m), 1396 (s), 1367 (m), 1337 (m), 1216 (m), 1188 (m), 1118 (m), 1045 (m), 772 (m), 719 (s) cm^{-1}. EI: calculated mass for $C_{25}H_{31}NO_2$, 377.2355; measured, 377.2349.

2-(Heneicosa-10,12-diynyl)-isoindole-1,3-dione (9-8-H). Yield: 4.2 g (9.7 mmol, 76%). ^{1}H NMR: δ 7.86−7.77 (m, 2H), 7.72−7.63 (m, 2H), 3.65 (t, J = 7.3, 2H), 2.21 (t, J = 6.6, 4H), 1.68−1.23 (m, 26H), 0.85 (t, J = 6.5, 3H). ^{13}C NMR: δ 168.41, 133.79, 132.12, 123.09, 77.51, 77.45, 65.20, 37.98, 31.78, 29.24, 29.08, 28.94, 28.81, 28.74, 28.53, 28.29, 26.76, 22.60, 19.15, 14.06. IR (KBr): 3455 (m), 2923 (s), 2853 (m), 2138 (vw), 1773 (m), 1702 (s), 1467 (m), 1400 (s), 1364 (m), 1072 (m), 1025 (m), 886 (m), 717 (s) cm^{-1}. EI: calculated mass for $C_{29}H_{39}NO_2$, 433.2975; measured, 433.2976.

2-(Hexadeca-10,12-diynyl)-isoindole-1,3-dione (9-3-H). Yield: 6.7 g (18 mmol, 97%). ^{1}H NMR: δ 7.87−7.78 (m, 2H), 7.73−7.64 (m, 2H), 3.65 (t, J = 7.3, 2H), 2.21 (t, J = 6.7, 4H), 1.68−1.27 (m, 16H), 0.96 (t, J = 7.3, 3H). ^{13}C NMR: δ 168.42, 133.79, 132.12, 123.10, 77.48, 77.30, 65.32, 65.20, 38.00, 29.24, 29.06, 28.94, 28.73, 28.53, 28.25, 26.76, 21.79, 21.14, 19.14, 13.44. IR (KBr): 3457 (m), 2927 (m), 2851 (m), 1771 (m), 1711 (s), 1464 (m), 1429 (m), 1395 (m), 1366 (m), 1065 (m), 714 (m) cm^{-1}. EI: calculated mass for $C_{24}H_{29}NO_2$, 363.2198; measured, 363.2193.

2-(Eicosa-9,11-diynyl)-isoindole-1,3-dione (8−8-H). Compound **8-8-H** was synthesized via the following five steps.

1-Bromo-8-[(2-methoxyethoxy)methoxy]octane (**13**). 1-Bromo-8-[(2-methoxyethoxy)methoxy]octane was synthesized according to the procedure of Corey et al.[19] from 8-bromo-1-octanol. Purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (4:1)) yielded 5.8 g (20 mmol, 71%) of 1-bromo-8-[(2-methoxyethoxy)methoxy]-octane with spectral data as reported.[20]

8-[(2-Methoxyethoxy)methoxy]-1-trimethylsilyl-1-octyne (**14**). The resulting bromide **13** was converted to **14** with 1 equiv of trimethylsilylacetylene and butyllithium[21] in 2.8 g yield (9.0 mmol, 47%) after purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (4:1). ^{1}H NMR: δ 4.69 (s, 2H), 3.67−3.63 (m, 2H), 3.57−3.48 (m, 4H), 3.37 (s, 3H), 2.18 (t, J = 7.0, 2H), 1.65−1.20 (m, 12H), 0,12 (s, 9H). ^{13}C NMR: δ 107.69, 95.44, 84.17, 71.80, 67.92, 66.63, 59.02, 29.66, 29.26, 29.01, 28.72, 28.58, 26.12, 19.82, 0.17. EI: calculated mass for $C_{17}H_{34}O_3Si$, 314.2277; measured, 314.2278.

1-[(2-Methoxyethoxy)methoxy]eicosa-9,11-diyne (**15**). The trimethylsilyl group was removed with potassium fluoride over 2 days following Xu et al., to yield 1.87 g (7.6 mmol, 96%) of 8-[(2-methoxyethoxy)methoxy]-1-octyne with spectral data as reported.[20] The product was directly used in a Cadiot−Chodkiewicz coupling[15] with 1-iododec-1-yne without potassium hydroxide. Purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (3:1) yielded 1.0 g (2.7 mmol, 36%) of **15**. ^{1}H NMR: δ 4.58 (s, 2H), 3.58−3.52 (m, 2H), 3.45−3.36 (m, 4H), 3.26 (s, 3H), 2.10 (t, J = 6.8, 4H), 1.47−1.08 (m, 24H), 0.74 (t, J = 6.5, 3H). ^{13}C NMR: δ 95.40, 77.52, 77.39, 71.77, 67.85, 66.60, 65.22, 58.99, 31.78, 29.61, 29.21, 29.11, 29.01, 28.81, 28.73, 28.29, 26.11, 22.61, 19.15, 14.07. EI: calculated mass for $C_{24}H_{42}O_3$, 378.3134; measured, 378.3129.

Eicosa-9,11-diyn-1-ol (**16**). The MEM group was removed using trimethylsilyl chloride and sodium iodide,[22] yielding 0.78 g (99%) of eicosa-9,11-diyn-1-ol. ^{1}H NMR: δ 3.57 (t, J = 6.5, 2H), 2.18 (t, J = 6.8, 4H), 1.49−1.19 (m, 24H), 0.81 (t, J = 6.5, 3H). ^{13}C NMR: δ 77.56, 77.42, 65.24, 65.16, 62.99, 32.70, 31.79, 29.20, 29.11, 29.02, 28.82, 28.70, 28.30, 28.26, 25.63, 22.62, 19.16, 14.07.

2-(Eicosa-9,11-diynyl)-isoindole-1,3-dione (8-8-H). A 0.70 g (2.4 mmol) sample of **16** was converted to the phthalimido product **8-8-H** using the Mitsunobu reaction.[18] Purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (4:1)) yielded 0.53 g (56%) of **8-8-H**. ^{1}H NMR: δ 7.83−7.76 (m, 2H), 7.72−7.65 (m, 2H), 3.64 (t, J = 7.3, 2H), 2.20 (t, J = 6.6, 4H), 1.66−1.22 (m, 24H), 0.84 (t, J = 6.5, 3H). ^{13}C NMR: δ 168.80, 133.80, 132.12, 123.11, 77.54, 77.39, 65.23, 37.97, 31.79, 29.10, 29.02, 28.97, 28.91, 28.82, 28.70, 28.52, 28.30, 28.24, 26.76, 22.61, 19.15, 14.07. IR (KBr): 2931 (s), 2858 (m), 1774 (m), 1718 (vs), 1467 (m), 1438 (m), 1395 (m), 1369 (m), 1188 (m), 1060 (m), 796 (m), 719 (m) cm^{-1}. EI: calculated mass for $C_{28}H_{37}NO_2$, 419.2824; measured, 419.2821.

2-(17-Hydroxyheptadeca-10,12-diynyl)isoindole-1,3-dione (9-3-CH$_2$OH) and Derivative 9-3-COOH. 9-3-CH$_2$OH was synthesized via the following five steps. **9-3-COOH** was synthesized by oxidation of **9-3-CH$_2$OH**.

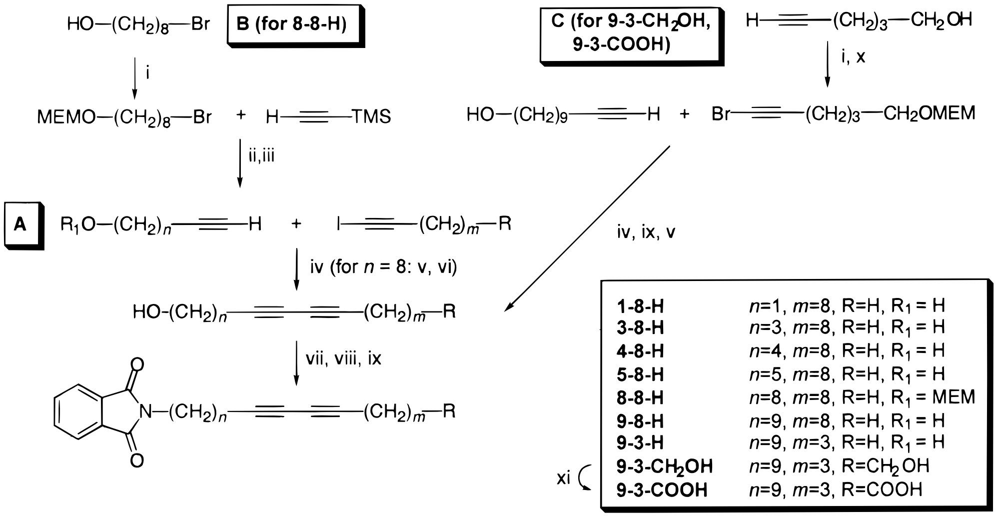
6-[(2-Methoxyethoxy)methoxy]hexyne (**17**). 5-Hexyn-1-ol (14.7 g, 0.15 mol) was reacted for 24 h with 1.5 equiv of MEM-Cl following Corey et al.[19] to yield quantitatively 6-[(2-methoxyethoxy)methoxy]hexyne. ^{1}H NMR: δ 4.56 (s, 2H), 3.58−3.53 (m, 2H), 3.47−3.40 (m, 4H), 3.25 (s, 3H), 2.10 (dt, J = 6.7, 2.7, 2H), 1.85 (t, J = 2.7, 1H), 1.63−1.48 (m, 4H). ^{13}C NMR: δ 95.31, 84.05, 71.70, 68.48, 67.08, 66.60, 58.86, 28.60, 25.12, 18.05. EI: calculated mass for $C_{21}H_{36}O_4$, 155.1072; measured, 155.1075.

1-Bromo-6-[(2-methoxyethoxy)methoxy]hexyne (**18**). 6-[(2-Methoxyethoxy)methoxy]hexyne (27.9 g, 0.15 mol) was converted into the bromo alkyne with silver nitrate and *N*-bromosuccinimide following the procedure of Boden et al.[23] Yield: 38.7 g (0.15 mol, 97%). ^{1}H NMR: δ 4.63 (s, 2H), 3.67−3.57 (m, 2H), 3.52−3.45 (m, 4H), 3.32 (s, 3H), 2.17 (t, J = 6.7, 2H), 1.66−1.46 (m, 4H); ^{13}C NMR: δ 95.46, 79.97, 71.80, 67.20, 66.73, 59.02, 37.96, 28.75, 25.04, 19.46.

17-[(2-Methoxyethoxy)methoxy]heptadeca-10,12-diyn-1-ol (**19**). Cadiot−Chodkiewicz coupling was performed according to the method of Mowery and Evans.[15] The product was purified using column chromatography (63−200 μm silica gel, petroleum ether 40−60/ethyl acetate (3:1)) yielding 33.4 g (95 mmol, 65%). ^{1}H NMR: δ 4.64 (s, 2H), 3.68−3.46 (m, 8H), 3.33 (s, 3H), 2.23 (t, J = 6.6, 2H), 2.18 (t, J = 6.7, 4H), 1.66−1.20 (m, 19H). ^{13}C NMR: δ 95.42, 77.56, 76.83, 71.78, 67.17, 66.71, 65.62, 65.21, 62.92, 58.99, 32.74, 29.38, 29.33, 28.97, 28.81, 28.76, 28.27, 25.70, 25.09, 19.15, 18.96. FD−MS: m/z = 352.

2-(17-[(2-Methoxyethoxy)methoxy]heptadeca-10,12-diynyl)isoindole-1,3-dione (**20**). Using the Mitsunobu reaction,[18] 33.1 g (94 mmol) of the alcohol was converted into the

Scheme 2. Synthesis of Investigated Diacetylenes[a,b]



[a] Note: All syntheses start from point **A**, apart from **8-8-H** which starts from **B**, and **9-3-CH$_2$OH/9-3-COOH**, which start from **C**. [b] Reactions used: (i) MEM-Cl, diisopropylethylamine, CH_2Cl_2, room temperature; (ii) 1 Eq. BuLi, HMPA, THF, 0 °C; (iii) KF, DMF, room temperature; (iv) CuCl, $EtNH_2$, $NH_2OH.HCl$, KOH, MeOH, THF, −20 °C → room temperature; (v) CuCl, $EtNH_2$, $NH_2OH.HCl$, MeOH, THF, −20 °C → room temperature; (vi) TMSCl, NaI, CH_3CN, −20 °C; (vii) for **1-8-H**, **3-8-H**, **4-8-H**, and **9-8-H**, $SOCl_2$, pyridine, ether, reflux, (viii) For **1-8-H**, **3-8-H**, **4-8-H**, and **9-8-H**, K-phthalimide, KI, DMF, 100 °C; (ix) for **5-8-H**, **8-8-H**, and **9-3-R**, phthalimide, diethylazodicarboxylate, PPh_3, THF, 0 °C; (x) *N*-bromosuccinimide, $AgNO_3$, acetone, room temperature; (xi) pyridinium dichromate, DMF, room temperature.

phthalimido product. Purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate) using an eluent ratio of 1:1 and, subsequently, two times with a ratio of 2:1 yielded 37.1 g (77 mmol, 82%) of product. ^{1}H NMR: δ 7.87−7.75 (m, 2H), 7.70−7.63 (m, 2H), 4.68 (s, 2H), 3.68−3.61 (m, 4H), 3.57−3.50 (m, 4H), 3.37 (s, 3H), 2.26 (t, J = 6.3, 2H), 2.20 (t, J = 6.7, 2H), 1.73−1.26 (m, 18H). ^{13}C NMR: δ 168.46, 133.84, 132.17, 123.14, 95.45, 76.93, 71.80, 67.18, 66.72, 65.62, 65.19, 59.03, 38.03, 29.29, 29.11, 28.98, 28.78, 28.57, 28.29, 26.81, 25.11, 19.17, 18.99. FD−MS: m/z = 481.

2-(17-Hydroxyheptadeca-10,12-diynyl)isoindole-1,3-dione (9-3-CH$_2$OH). Removal of the MEM group was accomplished using trimethylsilyl chloride and sodium iodide[22] ($ZnBr_2$[19] had no effect). Purification with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (1:1)) yielded 13.8 g (35 mmol, 90%) of product. ^{1}H NMR: δ 7.82−7.72 (m, 2H), 7.68−7.59 (m, 2H), 3.63−3.56 (t, J = 6.2, 4H), 2.23 (t, J = 6.8, 2H), 2.16 (t, J = 7.3, 2H), 1.69−1.21 (m, 18H). ^{13}C NMR: δ 168.50, 133.87, 132.10, 123.14, 77.71, 76.96, 65.67, 65.19, 62.17, 38.02, 31.72, 29.26, 29.07, 28.94, 28.74, 28.54, 28.25, 26.79, 24.64, 19.14, 18.98; IR (KBr) 3465 (m), 2933 (m), 2859 (m), 2253 (w), 2159 (w), 1769 (s), 1709 (s), 1617 (m), 1464 (m), 1399 (m), 1366 (m), 1167 (m), 1059 (m), 1011 (m), 951 (m), 887 (m) cm^{-1}. EI: calculated mass for $C_{25}H_{31}NO_3$, 393.2304; measured, 393.2304.

1-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)heptadeca-5,7-diynoic acid (9-3-COOH). Alcohol **9-3-CH$_2$OH** (4.26 g, 10.5 mmol) was oxidized following the method of Xu et al.[24] The product was purified with silica gel chromatography (63−200 μm, petroleum ether 40−60/ethyl acetate (1:1)) yielding 2.6 g (6.4 mmol, 61%) of the acid. ^{1}H NMR: δ 9.64 (very br s, 1H), 7.81−7.72 (m, 2H), 7.68−7.59 (m, 2H), 3.59 (t, J = 7.2, 2H), 2.43 (t, J = 7.3, 2H), 2.28 (t, J = 6.8, 2H), 2.15 (t, J = 6.8, 2H), 1.77 (br quin, J = 6.9, 2H), 1.62−1.10 (m, 14H). ^{13}C NMR: δ 178.91, 168.44, 133.79, 132.04, 123.09, 78.00, 75.62, 66.30, 64.97, 37.96, 32.54, 29.19, 29.01, 28.88, 28.68, 28.48, 28.15, 26.72, 23.15, 19.07, 18.49. IR (KBr): 3465 (m), 3058 (w), 2932 (m), 2848 (m), 2261 (vw), 2151 (vw), 1772 (m), 1718 (s), 1466 (m), 1438 (m), 1397 (s), 1365 (m), 1332 (m), 1277 (w), 1296 (m), 1059 (m), 1007 (w), 942 (m), 885 (m), 721 (m), 712 (m) cm^{-1}. EI: calculated mass for $C_{25}H_{29}NO_4$, 407.2097; measured, 407.2094.

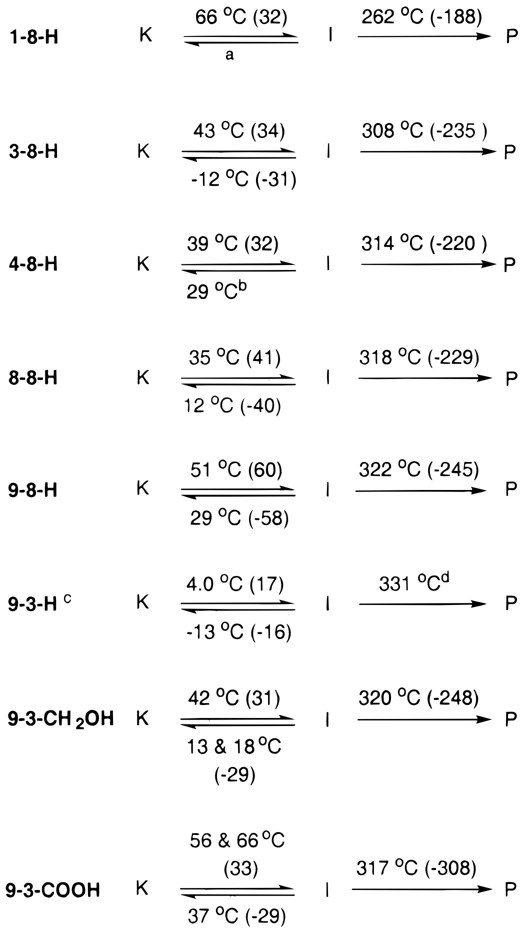
Results and Discussion

Synthesis. The asymmetrical diacetylenes were synthesized as depicted in Scheme 2. Coupling of an ω-alcohol-substituted 1-alkyne and a Br− or I−alkyne using the Cadiot−Chodkiewicz reaction with CuCl[15] yielded the diacetylene, in which the alcohol group could be substituted with a phthalimido group.[18] For **8-8-H** the alcohol-substituted alkyne was not commercially available. Therefore, the alkyne was synthesized from 8-bromo-1-octanol and trimethylsilylacetylene using the MEM−ether as a protective group. For **9-3-CH$_2$OH** and **9-3-COOH**, 5-hexyn-1-ol was protected using the MEM−ether to differentiate between both alcohol substituents in the diacetylene and selectively introduce a phthalimido group.

Thermal Polymerization. The synthesized diacetylenes were subjected to DSC measurement. For all compounds a brown polymer product was formed above 200 °C with a broad absorption between 300 and 500 nm. Comparison of the IR spectra before and after polymerization shows that the asymmetrical C≡C stretch band(s) between 2130 and 2270 cm^{-1} has/have disappeared in the brown polymer product. This means predominantly 1,4-polymerization has taken place, yielding a rather symmetrically substituted C≡C bond, as 1,2-polymerization would have yielded an asymmetrically substituted and, thus, IR-active alkyne bond.[3] For all monomers in this report, the corresponding IR bands are given in the Experimental Details section. 1,4-Polymerization in the liquid state has been observed by other authors.[25]

DSC measurement of the compound with the shortest n spacer under study, **1-8-H**, displays a melting point at 66 °C (also confirmed by polarization microscopy) with an endothermic peak of 32 kJ/mol (Scheme 3). Cooling down rapidly (in DSC, 10 °C/min) reveals no crystallization, in line with polarization microscopy measurements that only showed crystallization on prolonged standing (>8 h). Heating with DSC toward

Scheme 3. Phase Transitions of the Compounds under Study As Observed with DSC (*K* = Crystal; I = Isotropic Liquid; P = Polymer; Enthalpies of the Corresponding Phase Transition Given in Parentheses (kJ/mol))



[a] Very slow crystallization. [b] Only partial crystallization. [c] In first heating scan melting at 37 °C (30 kJ/mol). [d] No exact measurement of enthalpy of polymerization possible due to sublimation.

300 °C shows a large exotherm at 262 °C, which is interpreted to be polymer formation on the basis of IR data.

Compound **3-8-H** crystallizes very slowly and is waxy at room temperature. Like **1-8-H** and **3-8-H**, **4-8-H** crystallizes very slowly, and with DSC only partial crystallization could be observed (Scheme 3). Both compounds do polymerize above 300 °C.

DSC measurement of **5-8-H** (no phase transition scheme given) showed no endothermal peaks by heating from −40 °C onward. The compound did not crystallize when left at −40 °C for 1 h and if stored at −20 °C it remains an oil, so the melting point is at least beneath −20 °C, which is suprisingly low compared to those of the other compounds. At about 200 °C a very broad exothermal peak started, which goes on until 400 °C. Unfortunately, substantial sublimation hampers an adequate measurement of the heat of formation for polymerization of **5-8-H**.

Compounds **8-8-H** and **9-8-H** show a completely reversible melting and crystallization with DSC (Scheme 3), which could be confirmed with polarization microscopy. **8-8-H** shows no IR bands around 2200 cm^{-1} in the monomer, while **9-8-H** does show a small band. Most likely, **8-8-H** has a different crystal structure from **9-8-H**, due to the small difference in alkyl substitution. Both **8-8-H** and **9-8-H** form the 1,4-polymer above 300 °C.

The thermal reactivity of the C_1 spacer derivative differs significantly from that of the longer analogues: **3-8-H**, **4-8-H**, **8-8-H**, and **9-8-H**. **1-8-H** already polymerizes at 262 °C, while the other compounds polymerize only above 300 °C. In line with observations by Schen et al.[26] for related species this can be rationalized by the idea that **1-8-H** has a greater rigid-rod character due to the nonflexible link between the phthalimido and diacetylene moieties. Therefore, it tends to maintain the intermolecular $\pi-\pi$ interactions in the liquid state. As a result the diacetylene groups are on average better in position for polymerization and this consequently lowers the activation barrier for this reaction. In line with this idea, the polymerization temperature of the series of compounds ($n = 3-9$) increases slightly as the length of the spacer n increases: for polymerization the van der Waals forces between the spacers of adjacent molecules must partly be overridden to enable the molecules to slip into the right position for polymerization.[8] When the number of methylene groups n increases stronger van der Waals forces must be overcome by addition of more thermal energy to the system, and therefore, polymerization takes place at higher temperatures. A surprising effect was observed with the entropy changes obtained from $\Delta H = T\Delta S$ at the melting point. ΔS values for melting increases from 94 to 185 J mol^{-1} K^{-1} on going from **1-8-H** to **9-8-H**.

A second item of investigation concerned the influence of the length m of the alkyl group at the other (free) side of the diacetylene. To this aim **9-3-H** was synthesized and compared specifically with **9-8-H**. In the first DSC heating scan of **9-3-H** reproducible melting at 37 °C is observed and in subsequent heating scans at 4.0 °C after partial crystallization at −12 °C (Scheme 3). The melting point at 37 °C from the melt could be confirmed with polarization microscopy. Compound **9-3-H** shows no IR bands around 2200 cm^{-1} in the monomer as well as in the polymer (similar to observation for **8-8-H**). It is noteworthy that the polymerization temperature is still increasing from 322 °C for **9-8-H** to 331 °C for **9-3-H**, while the number of methylene groups, and thus the overall strength of van der Waals forces in the outer alkyl spacer, decreases.

To study the effects of additional polar groups in **9-3-H**, compounds **9-3-CH$_2$OH** and **9-3-COOH** have been synthesized containing a hydroxyl and carboxylic acid group, respectively, in the m spacer. Compound **9-3-CH$_2$OH** melts and crystallizes reversibly. Interestingly, a double crystallization peak at 13 and 18 °C is observed during DSC (see Scheme 3). This can tentatively be explained by assuming that on cooling first a less ordered/stable crystal structure is formed, which on further cooling reorganizes into a slightly more stable crystal structure. The corresponding endothermic peak is not split, although a broadening of the melting peak is observed. With optical microscopy two melting points at 42.5 and 46.4 °C could be observed at a heating rate of 4 °C/min for **9-3-CH$_2$OH** when this had been crystallized at 4 °C overnight. **9-3-CH$_2$OH** polymerizes at 320 °C.

For **9-3-COOH** the melting point was observed at 71 °C during the first heating scan (Scheme 3 and Figure 1) in DSC, while in subsequent DSC heating scans a double peak at 56 and 66 °C was observed. With polarization microscopy the initial melting point at 71

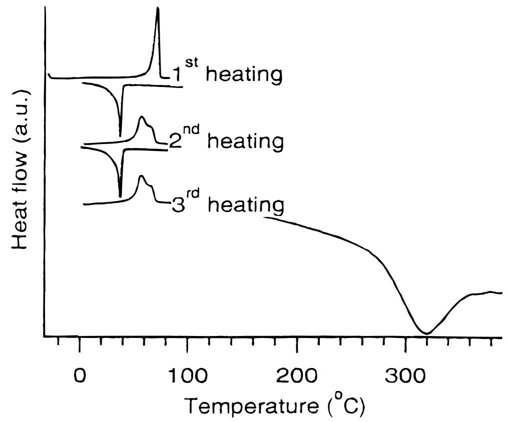


Figure 1. DSC thermograms of compound **9-3-COOH**.

°C could be confirmed, while after crystallization at 4 °C a double peak at 68.5 °C (fanlike structures) and 74 °C (small needles) was present. The small needles are the only crystal structure when the compound is allowed to slowly crystallize at room temperature, and these melt at 74 °C. Polymerization is observed at 317 °C for **9-3-COOH**.

The melting points of **9-3-CH$_2$OH** (42 °C) and **9-3-COOH** (56 and 66 °C) are higher than that of the alkyl analogue **9-3-H** (4 °C). Obviously, hydrogen bonds can be formed, which have to be broken upon isotropization of the crystal. The polymerization temperature of these two polar compounds is slightly lower than that of **9-3-H**. Because of sublimation of **9-3-H** one cannot compare the enthalpy of polymerization of these three compounds with $m = 3$, but it is for **9-3-CH$_2$OH** and **9-3-COOH** close to the value of **9-8-H**, indicating that a long alkyl chain has the same effect on polymerization as an $-$OH or $-$COOH group.

Film Adsorption. For use of the polydiacetylenes in organic solar cells, it is necessary that a smooth, homogeneous organic film is formed on hydroxylic surfaces. This film should cover the whole surface and should be pinhole-free to prevent short-circuiting that would annihilate the yield of such a solar cell. To investigate film formation, the attempt was made to make monomer films by spin-coating on three different substrates: quartz, covalently bonded trimethylsilyl-coating on glass (TMS-glass; see Experimental Details), or perylene imide (20 nm) sublimed on ITO. For **1-8-H**, **3-8-H**, and **4-8-H** only droplets were formed on quartz. Moreover, **3-8-H** and **4-8-H** did not solidify but stayed waxy even after cooling to 4 °C overnight. **5-8-H** is an oil at room temperature, and film formation at room temperature could not be investigated as such.[27] Compounds **8-8-H** and **9-8-H** display crystallization on quartz in patches; the surface is not completely covered. **9-3-H** gave on quartz only droplets, but on TiO$_2$ small patches of film could be formed. Because these compounds are quite apolar, film formation (and subsequent polymerization) was studied on more apolar materials such as TMS-glass and perylene imide on ITO. Compound **3-8-H** showed no improvement on either material. **4-8-H** was spin-coated on TMS-glass and yielded many small spots of compound present on the surface. Compound **4-8-H** showed the same small spots on a perylene imide layer as on TMS-glass. Spin-coating of **9-8-H** on TMS-glass or on perylene imide on ITO followed by irradiation showed a complete coverage of the surface, which was characterized by absorption maxima at 510 and 554 nm and 508 and 557 nm, respectively, comparable to the data obtained on quartz: 526 and 558 nm (Table 1). Apparently, this compound crystallizes on all three substrates in a similar crystal structure, yielding similar polymer lengths. Obviously, the substrate on which the sample is spin-coated has only a small influence—but just enough for **4-8-H**—on the crystallization of the compound: the bulk material crystallizes in a way that is inherent to that compound. However, film formation can be influenced by the nature of the substrate.

Table 1. UV−Vis Absorption Maxima of the Polymers Formed upon Irradiation of Films on Quartz

compound	absorption maxima (nm)
8-8-H	562
9-8-H	526, 558
9-3-H	494, 542[a]
9-3-CH$_2$OH	540, 586
9-3-COOH	576, 615

[a] Film on TiO$_2$.

Finally, the apolar diacetylenes were compared with the more polar compounds **9-3-CH$_2$OH** and **9-3-COOH**, which were expected to give a better film formation onto the polar substrate. **9-3-CH$_2$OH** formed numerous little crystallites, yielding a completely covered quartz surface and a filmlike layer. Compound **9-3-COOH** formed fanlike structured crystallites as well as crystallites consisting of very small needles. This compound also forms a film, suggesting that the introduction of a polar group generally yields better films on the investigated surfaces.

Light-Induced Polymerization. To investigate the light-induced formation of polymer in the spin-coated films, the monomer films were irradiated with UV light. **1-8-H**, **3-8-H**, and **4-8-H** showed no measurable polymer formation on quartz in line with their lack of film formation. Likewise **1-8-H** and **3-8-H** did not give any polymer formation on TMS−glass, but **4-8-H** does give a measurable amount of polymer on TMS−glass: a small band around 530 nm could be observed. In contrast, UV irradiation of **8-8-H** gave a purple polymer at room temperature with a broad maximum at 562 nm, while UV irradiation of **9-8-H** yielded a red polymer characterized by a broad absorption band with two maxima at 526 and 558 nm (see Table 1). The observation that **8-8-H** has only one absorption maximum, while **9-8-H** displays two, might be an effect of a different crystal packing.

There seems to be an interesting contrast in the factors that facilitate thermal and UV-induced polymerization. UV-induced polymerization is easier if enough flexibility exists between the aromatic moiety and the diacetylene group, while thermal polymerization is faster (takes place from lower temperatures onward) for shorter aromatic group−diacetylene linkages. A similar difference in thermal and UV-induced reactivity was observed by Hammond and Rubner:[28] their diacetylenes having a C$_4$−O− spacer are in the liquid state much more reactive than analogues with a C$_9$−O− spacer. In the solid state the reactivity is reversed: the C$_9$−O− derivative is the more reactive one. This is in agreement with our finding that only from C$_5$ spacers onward does polymerization in the solid state occur. A flexible spacer between the diacetylene group and the aromatic group is thus necessary for this reaction.[8]

Variation of the *m* spacer of the diacetylene group also displays interesting trends. **9-3-H** could be crystallized

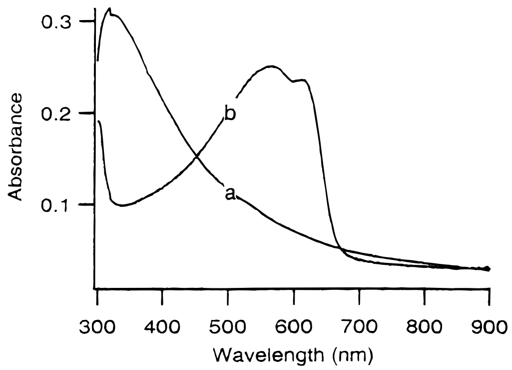


Figure 2. UV−vis absorption spectra of a cast thin film of a thermal partially polymerized sample of **9-3-COOH** (formed by heating in DSC) from chloroform (a) and UV-polymer formed by irradiation of spin-coated **9-3-COOH** monomer (b; irradiated for 40 min in air atmosphere).

on TiO_2 and the UV-polymer showed a pattern similar to **9-8-H**, with absorption maxima at 494 and 542 nm for **9-3-H** and at 506 and 553 nm for **9-8-H** on TiO_2, respectively. The polar compounds **9-3-CH$_2$OH** and **9-3-COOH** show absorption maxima at longer wavelengths (Table 1) and therefore have a higher degree of conjugation.

For these phthalimido-derivatized diacetylenes, the UV-polymerized compounds appear to absorb at longer wavelengths and, thus, have a higher degree of conjugation than the partially polymerized sample formed in the DSC experiment (see Figure 2). This is as expected, since the thermal polymer is formed in the disordered isotropic phase of the compound, whereas the UV-polymer is formed in the crystal phase, which has a very ordered monomer stacking yielding higher conjugation lengths upon UV-polymerization.

The fact that the compounds with a phthalimido group at one end of the molecule and at the other end a polar group yield polymers with a higher degree of conjugation (higher λ_{max}) than **9-8-H** suggests the diacetylene groups stack better in the crystal structure for polymerization. This can be explained by having two different anchors ($\pi-\pi$ interacting phthalimido group and the polar hydrogen bond-forming −OH or −COOH) at each side of the diacetylene group that each preferentially interact with moieties of the same type. This leads to preferential unidirectional stacking: head-to-head and tail-to-tail as was visualized with molecular mechanics calculations (Figure 3).[29] In contrast, the apolar compound with only one anchor—the phthalimido group—yields $\pi-\pi$ stacks with less preferred orientation of the hydrocarbon moiety, which reduces the degree of ordering; e.g., head-to-tail stacking becomes possible. Therefore, the compounds with two different anchors, a phthalimido group with $\pi-\pi$ interactions and a polar group able to form a hydrogen bond, yield a better crystal geometry for the diacetylene groups to polymerize. Post-polymerization reorganization of the hydroxyl group does not explain the formation of longer polymers compared to **9-3-H**, because the absorption maximum would in that case change with time, which it does not.

The fact that **9-3-COOH** yields a higher λ_{max} than **9-3-CH$_2$OH** is, presumably, due to the stronger hydrogen bonds in the acid derivative. These force the occurrence of increased order in the crystal structure for the polymerization of the diacetylene groups, yielding more diacetylene units in an appropriately ordered stack for polymerization. This is currently being investigated by molecular mechanics.[29]

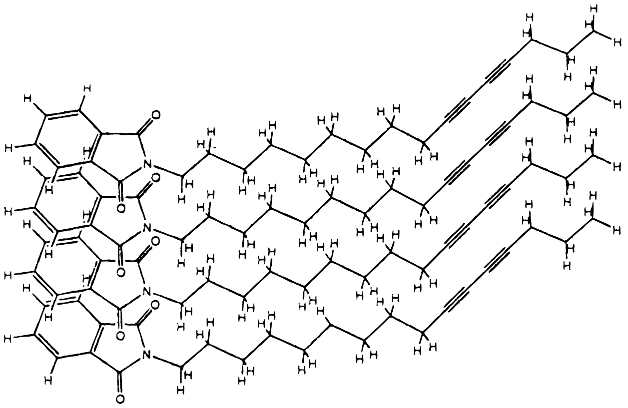


Figure 3. Schematic representation of the head-to-head/tail-to-tail stacking of phthalimido(head)-substituted diacetylenes as calculated with molecular mechanics.

An approximate determination of the polymer conversion in these spin-coated films was performed from the absorption spectra of the polymer using the phthalimide unit as a reference.[6] Surprisingly, only a small difference was found for the polar compounds **9-3-CH$_2$OH** and **9-3-COOH** and the apolar compound **9-8-H**, namely polymer conversions of 32%, 37%, and 38% (each value ±5%), respectively. Apparently, the introduction of a hydrogen-bonding group and of a long alkyl chain overall have a similar effect on polymerization. Shortening the *m* chain of **9-8-H** to three C atoms in **9-3-H** gives a much lower polymer conversion of only 9%. Moreover, **8-8-H** gives a polymer yield of 51 ± 5%. This indicates that the molecules with on one side of the diacetylene moiety a long alkyl chain attached to a phthalimide group and on the other side a crystal order-inducing group (polar: −OH or $-CO_2H$; apolar: long *n*-alkyl chain) arrange in a crystal structure that is well-suited for polymerization.

So a certain spacer length between the aromatic group and the diacetylene is necessary for polymerization: at least a C_5 spacer if the aromatic group is a phthalimido group. Removing one of the aromatic groups as mentioned in the Introduction seems to introduce too much flexibility, probably because a head-to-tail stacking becomes important, yielding a poorer crystal structure for polymerization. Introduction of a second anchor next to the phthalimido group on the other side of the diacetylene group improves the crystal stacking for polymerization, yielding polymers with higher absorption maxima. Alternatively, molecules with two symmetrically placed diacetylene moieties might be useful, and these will be published in a separate paper.[9]

For all compounds investigated irradiation for longer times resulted in a gradual decay of the UV−vis absorption bands originally present.[30] For **9-3-COOH** the degradation was investigated in more detail. Under argon (glovebox) the photoinduced degradation of the formed polymer is slowed compared to the decay in air, while the initial polymer bands have the same absorption maxima. The intensity of the polymer bands increases until 40 min in air, after which the intensity as well as the absorption maxima start to decrease and after 4 h of UV irradiation in air the polymer has fully degraded (Figure 4). However, under argon even after 12 h of UV-irradiation the same absorption maxima as well as the maximum intensity (reached after 4 h) are

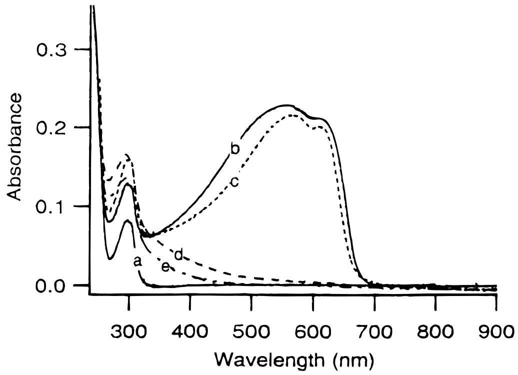


Figure 4. UV−vis absorption spectra of a thin film prepared from monomer **9-3-COOH** at $t = 0$ (a), irradiated in argon atmosphere at $t = 12$ h (b) or in air atmosphere at t = 40 min (c) and at $t = 4$ h (d) or $t = 7$ h (e).

still present. During this bleaching process in air the maximum of the UV−vis absorption gradually shifts from 576 and 615 nm toward shorter wavelengths, and eventually disappears under the aromatic absorption (Figure 4, traces a, d, and e). Given the difference in photochemistry in air or in argon atmosphere, this shift is likely caused by oxidation processes. These diminish the conjugation in the sample, and thus cause the gradual shift of absorption.

Conclusions

Thin films of phthalimido substituted diacetylenes with the overall structure Pht−$(CH_2)_n$-C≡C−C≡C−$(CH_2)_m$−R can be formed with a variety of spacer lengths n and m and variation of R. High-quality film formation is required for the light-induced 1,4-polymerization, and this can be affected by materials with $n > 4$, while polar R groups (−OH and −COOH) further improve this. The thus formed polydiacetylenes display UV−vis absorption maxima around 500−615 nm.

This contrasts in two ways with the data observed for thermally obtained polymers. First, for thermally induced polymerization, the smaller values of n are preferred. Second, the thus formed polymers display significantly blue-shifted absorption maxima. The best film formation and the highest degree of conjugation are obtained for those materials that form a stack of diacetylene moieties placed in a flexible manner (via long alkyl spacers) between two different anchors, e.g., an aromatic and a polar group as the phthalimido and carboxylic acid group, respectively. Such materials have the appropriate ordering with respect to the substrate surface normal and can play an important role in the development of photonic devices such as organic solar cells.

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