A Diacetylene-Containing Wedge-Shaped Compound: Synthesis, Morphology, and Photopolymerization

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Abstract: A novel wedge-shaped compound containing two diacetylene tails, namely, methyl 3,5-bis(trideca-2,4-diynlyloxyl)benzoate (DDABM), was synthesized. As shown by UV/Vis spectroscopy this compound can be polymerized under UV irradiation. The crystalline structure of DDABM was investigated by grazing-incidence wide-angle X-ray diffraction on oriented crystalline films deposited on PTFE-rubbed silicon wafer substrates. Furthermore, the spherulites formed in thicker films were analyzed by wide-angle X-ray diffraction. A molecular packing model of

Keywords: alkynes • photochemistry • polymerization • topochemistry • X-ray diffraction DDABM based on the X-ray diffraction data is proposed. The diacetylene units are oriented along a defined lattice direction with a reticular distance of 4.85 Å, which fulfills the requirements for topochemical polymerization. It was observed that UV polymerization does not affect the phase behavior of the compound, but mainly alters its optical properties.

Introduction

As first demonstrated by Wegner,^[1] the solid-state polymerization of crystalline diacetylene follows the so-called topochemical principles.^[2] A unique feature of this reaction is that polymerization advances with only minimal structural rearrangements. Therefore, its occurrence and the stereochemistry of the polymer products are determined by the crystal structure of the monomer. As shown in Scheme 1, the necessary conditions for topochemical polymerization of diacetylene were identified as follows. The diacetylene units should be oriented along a defined lattice direction with a translational period *d* in the range of 4.7–5.2 Å, R_v must be smaller than 4 Å, with a lower limit of 3.4 Å corresponding to the van der Waals contact between the reacting carbon atoms, and the angle γ between the diacetylene rod and the translational vector must be close to 45° .^[3] This route pro-

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4300



Scheme 1. Schematic representation of topochemical polymerization of diacetylenes.

vides a unique approach toward fabrication of well-defined highly stereoregular polymers that cannot be synthesized by any alternative means.

Since the diacetylene unit was first used for topochemical polymerization, the molecular design of diacetylene derivatives has been attracting considerable interest for several decades.^[4] It is well established that diacetylene substituted with various side groups such as amide,^[5] carboxyl,^[6] and perfluorophenyl^[7] can undergo photopolymerization on UV irradiation in a wide range of ordered structures such as crystals,^[1,4b,8] liquid crystals,^[9] Langmuir–Blodgett films,^[10] self-assembled monolayers,^[6,11] lipid bilayers,^[12] vesicles,^[4c,13] and even gels.^[14] Importantly, the resulting long π -conjugated molecular structure has two spectroscopically distinct phases, that is, the so-called blue and red forms that got their names from the exciton absorption peaks at about 640 and 540 nm. The presence of these two forms in polydiacety-lenes makes them suitable for numerous promising applica-

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tions ranging from $biosensors^{[4c,15]}$ and nonlinear $optics^{[16]}$ to electron-transport materials.^[17]

Most of the diacetylene derivatives studied so far contain only one diacetylene fragment, so the conditions of their topochemical polymerization can be fulfilled by a judicious choice of side groups (R^1 and R^2 in Scheme 1). Much less studied are compounds substituted with two or more diacetylene units, which, however, form different interesting supramolecular assemblies such as rods^[18] and tubules^[19] that can be arrested by diacetylene polymerization. Furthermore, these molecules can be linked by an intermolecular reaction even at a rather low degree of diacetylene polymerization. However, it is also clear that an intramolecular reaction can result in cyclization without a significant increase of the molecular weight. Since single-crystal X-ray diffraction (XRD) data are usually not available for such systems, the relation between the molecular packing and polymerizability of these diacetylene derivatives is not fully understood so far.

Here we report on the structure–property relationship for a newly synthesized wedge-shaped molecule containing two polymerizable diacetylene tails: methyl 3,5-bis(trideca-2,4diyn-1yloxyl)benzoate (DDABM). To address the crystalline structure of DDABM before and after photopolymerization, silicon wafers rubbed with polytetrafluoroethylene (PTFE) were used as substrate to prepare oriented crystalline thin films, which were analyzed by grazing-incidence wide-angle X-ray diffraction (GIWAXD). In addition spherulites formed by DDABM in thicker films were studied by means of WAXD with a small beam size.

Results and Discussion

The synthesis of wedge-shaped DDABM is schematically depicted in Scheme 2. Firstly, 1-bromo-1-decyne (1) was obtained by bromination of 1-decyne with *N*-bromosuccinimide (NBS) and AgNO₃ as catalyst. Reacting 1 with propargyl alcohol under catalysis by CuCl gave trideca-2,4-diyn-1-ol (2), which was subsequently transformed into 1-bromotrideca-2,4-diyne (3) with triphenylphosphine dibromide (PPh₃Br₂). DDABM was synthesized from methyl 3,5-dihydroxybenzoate by etherification with 3 in acetone in the presence of K_2CO_3 .



Scheme 2. Synthetic route for the preparation of methyl 3,5-bis (trideca-2,4-diyn-1yloxyl)benzoate (DDABM). i) NBS, AgNO₃, acetone, RT, 2 h; ii) NH₂OH·HCl, CuCl, ethylamine, methanol, 35 °C 24 h; iii) PPh₃Br₂, dichloromethane, 0 °C to RT, 24 h; iv) 18-crown-6, K₂CO₃, acetone, reflux, 24 h.

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Figure 1. Polarizing optical micrographs of DDABM crystallized on cooling from the isotropic melt to room temperature before (top) and after (bottom) UV irradiation.

Wedge-shaped compound DDABM was obtained as a white crystalline powder. It forms large spherulites on cooling the isotropic melt to room temperature (see Figure 1). On irradiation with 254 nm UV light, the compound changes color from white to red and then to blue and purple. The gradual color change can be attributed to continuous formation of conjugated backbones and is observed because the electronic transition of the π electrons of the backbone occurs in the wavelength region of visible light. The polymerized compound reveals a clearly visible Maltese cross in polarizing optical micrographs (Figure 1 bottom)

when crystallized at room temperature; this feature is absent for non-irradiated samples. It is noteworthy that the melt viscosity has increased after photopolymerization.

The conversion of diacetylene groups to polydiacetylene in DDABM was monitored by UV/Vis and Raman spectroscopy. The non-irradiated sample shows no absorption in the range of 400-700 nm. After exposure to 254 nm UV irradia-

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Figure 2. UV/Vis spectra of a crystalline thin film of DDABM after exposure to 254 nm UV light for 0–60 min (film thickness is (200 ± 5) nm).

tion for 1 min, two absorption bands at $\lambda_{max} = 593$ and 540 nm appear (Figure 2). A sharp absorption band at 593 nm is assigned to the excitonic transition of the conjugated polydiacetylene chains; the position of this peak depends on the effective conjugation length of the polymer. The presence of a second band at 540 nm can be attributed to a broad distribution of the conjugation lengths present in the polymers overlaid on the vibronic side bands of the polydiacetylene due to the stretching frequency associated with the carbon–carbon double and triple bonds.^[20] On further irradiation up to 1 h, a slight blueshift of the absorption band and an increase of the absorbance are observed, after which the UV/Vis spectrum of DDABM does not change anymore. The modification of the chemical structure can be also evidenced by Raman spectroscopy (Figure 3). Thus, after UV



Figure 3. Raman spectra of DDABM during exposure to 254 nm UV light.

irradiation, a new band appears at 2124 cm^{-1} , which corresponds to polydiacetylene.^[21] Moreover, the frequency shift and intensity increase of the C=C stretching bands at about 1500 cm^{-1} in the Raman spectrum also indicate conversion of diacetylene to polydiacetylene.^[22] The DDABM sample irradiated for 1 h is still soluble in THF, chloroform, and some other organic solvents. Interestingly, size-exclusion



Figure 4. DSC curves of DDABM before and after UV irradiation for 1 h.

chromatography did not show any difference between the initial sample and the sample irradiated for 1 h, likely due to largely intramolecular cyclization. Importantly, after 2 h of irradiation the sample becomes partly insoluble in organic solvents, most probably due to the onset of intermolecular polymerization.

Differential scanning calorimetry (DSC) shows no significant differences in the thermal behavior of the irradiated and non-irradiated DDABM samples (Figure 4). Thus, on heating at a rate of 5.0 Kmin^{-1} , samples annealed at room temperature for 24 h reveal a similar thermal behavior with only one melting event, at $T_m = 47.0$ and $45.8 \,^{\circ}\text{C}$ for the UVirradiated and non-irradiated compounds, respectively. The melting enthalpies also differ only slightly: 93.2 Jg^{-1} for the non-irradiated and 93.9 Jg^{-1} for the irradiated sample. Although the sample irradiated for 2 h is partly insoluble in organic solvents, its thermal behavior is not significantly different from that of the initial sample.

By quenching DDABM from the isotropic melt to -20 °C at a cooling rate of 40 K min⁻¹, crystallization is bypassed. On heating, cold crystallization takes place with T_c at -2.8and -3.9°C for the irradiated and non-irradiated DDABM samples, respectively. The melting transition of the polymerized sample is characterized by a $T_{\rm m}$ value of 43.2 °C and a melting enthalpy of 85.0 J g⁻¹, while for the non-irradiated material the melting enthalpy and temperature are 91.0 Jg^{-1} and 44.1 °C, respectively. The minor differences in thermal behavior of irradiated and non-irradiated samples suggest that the diacetylene polymerization does not have a significant effect on the crystalline structure. This assumption is supported by WAXD measurements performed on DDABM powders annealed at room temperature before and after UV irradiation (Figure 5). The curves reveal only marginal differences in relative peak intensities, while the positions of all reflections are invariant to UV treatment.

To address the crystalline structure of DDABM, silicon wafer rubbed with PTFE was used as substrate to fabricate oriented crystalline thin films by drop casting. This substrate treatment is based on the original method of Wittmann and Smith,^[23] which is widely used to induce epitaxial or graphoepitaxial interactions with deposited organic films resulting in their pronounced orientation. On annealing the spin-

$\begin{array}{c} \begin{array}{c} 200 & \text{annealed @RT, 24h} \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$

Figure 5. One-dimensional WAXD curves corresponding to isotropic powder samples of DDABM recorded before and after 1 h UV-irradiation. The curves reveal only slight differences in the relative peak intensities.



Figure 6. Polarizing optical micrograph of a crystalline thin film of DDABM deposited on a silicon wafer rubbed with PTFE.

coated films at room temperature for 24 h, DDABM forms crystalline stripes which are oriented along the rubbing direction (Figure 6).

Two-dimensional GIWAXD patterns obtained from oriented crystalline films of DDABM are shown in Figure 7. Patterns were recorded with the X-ray beam perpendicular and parallel to the rubbing direction. The strong h00 reflections located strictly on the meridian of the patterns indicate smectic-like stacking of layers parallel to the PTFE-rubbed substrate. Furthermore, the material shows a single-crystallike orientation, as can be seen from the absence of *hkl* reflections with *l* different from 0 when viewed along the rubbing direction.

The lattice of DDABM is identified to be monoclinic with respect to β , with four molecules per unit cell, as derived from density considerations. The lattice parameters are a = 39.77, b = 16.26, c = 4.85 Å, and $\beta = 88.8^{\circ}$. The slight monoclinicity of the unit cell can be deduced from a small split of the *hkl* and *hkl* peaks, but is more clearly revealed by the fact that the *h0l* and *hkl* peaks are not positioned on the same vertical lines, as would be expected for an orthorhom-



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Figure 7. 2D grazing-incidence X-ray diffraction patterns corresponding to an oriented film of DDABM deposited on a PTFE-rubbed silicon wafer. The sample was annealed for 24 h at room temperature prior to measurements. The incident X-ray beam was oriented perpendicular (top) and parallel (bottom) to the rubbing direction. The GIWAXD patterns are recalculated into the planar *s* space.

bic unit cell (Figure 7, top). The strong orientation of the layers on PTFE, which is evident from the GIWAXD patterns in Figure 7, can be explained by the interaction between the film and the substrate. In particular, the *b* parameter of the DDABM unit cell is oriented parallel to the *a* parameter of the PTFE crystal, that is, perpendicular to the PTFE backbones. The *c* parameter of the DDABM crystal is parallel to the PTFE rubbing, so that the contact plane of the DDABM unit cell is 100. Although in principle the nature of the film–substrate interaction can be epitaxial or grapho-epitaxial, that is, due to the substrate topography, the close match of the *b* parameter of DDABM with the *a* parameter of the PTFE crystal (3.2% mismatch) prompts us to suggest that in this case one can talk about a truly epitaxial growth mechanism.

The absence of first-order diffraction peaks along \mathbf{a}^* and \mathbf{b}^* directions from the patterns indicates that the unit cell is centered in the **ab** projection. The observed reflections together with the experimental and calculated *d* spacings are given in Table 1.

The fast growth axis of DDABM can be identified from the crystal orientation in large spherulites such as those grown in films of several tens of micrometers thickness for 24 h at room temperature (cf. Figure 1). By using a rather small X-ray beam size $(200 \times 200 \ \mu\text{m}^2)$ compared to the lateral dimensions of the spherulites (see Figure 1), oriented Xray patterns can be obtained (Figure 8). This situation is similar to what was observed previously in microfocus X-ray experiments on polymer spherulites.^[24] From the presented pattern, the fast growth axis, that is, the radial direction of the spherulitic crystals, can be assigned to the crystallographic *c* axis. The absence of the higher order smectic *h*00 reflections indicates that, even in a reasonably thick film,

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Table 1. Experimental (d_{exptl}) and calculated $(d_{caled}) d$ spacings of DDABM annealed at room temperature. The values of d_{exptl} are derived from the GIWAXD patterns given in Figure 7.

h	k	1	d_{exptl} [Å]	$d_{ ext{calcd}} \left[extsf{A} ight]$	Sublattice indexes (hkl)
2	0	0	19.90	19.88	
4	0	0	9.92	9.94	
6	0	0	6.62	6.63	
10	0	0	3.97	3.98	
2	1	0	12.61	12.59	
6	1	0	6.14	6.14	
7	1	0	5.36	5.36	
8	1	0	4.75	4.75	
9	1	0	4.25	4.2	
1	2	0	8.00	7.97	
4	2	0	6.28	6.29	
6	2	0	5.12	5.14	
7	2	0	4.64	4.66	
1	3	0	5.36	5.37	
2	3	0	5.21	5.23	
3	3	0	5.01	5.02	
5	3	0	4.47	4.48	
7	3	0	3.91	3.92	
1	4	0	4.03	4.05	100
2	4	0	3.99	3.98	101
3	4	0	3.88	3.89	$10\overline{1}$
4	4	0	3.76	3.76	102
2	0	1	4.73	4.74	
2	0	-1	4.69	4.69	
6	0	1	3.97	3.95	
6	0	-1		3.88	
8	0	1	3.52	3.51	
8	0	-1		3.44	
1	1	1	4.63	4.63	010
1	1	-1		4.61	
2	1	1	4.56	4.55	$01\overline{1}$
2	1	-1		4.51	
3	1	1	4.40	4.41	011
3	1	-1		4.36	
1	2	1	4.14	4.15	
1	2	-1	4.11	4.14	
1	3	1	3.61	3.61	
1	3	$^{-1}$		3.60	
2	3	1	3.57	3.57	
2	3	-1		3.55	
3	3	1	3.48	3.50	
3	3	-1		3.48	

the smectic layers are oriented parallel to the substrate. However, since several diffraction zones are present in the pattern, a significant distribution of the crystal orientation can be assumed. This is also supported by the fact that the smectic layers are characterized by azimuthally broad reflections.

A characteristic feature of the discussed pattern is the high intensity of far wide-angle peaks located on the first and second layer lines, for example, the h40 and h11 reflections. This fact can be accounted for by the existence of a sublattice formed by the octyl groups positioned in the tails. The sublattice of the alkyl groups is a subunit of the main



Figure 8. 2D WAXD pattern recorded in transmission geometry on large spherulites of DDABM grown in thick films after annealing them for 24 h at room temperature. The pattern is recalculated into the planar *s* space.



Figure 9. Sublattice formed by octyl chains in the crystalline phase of DDABM at 25°C. The shown unit cell resembles the lattice of *n*-octane, apart from its increased c parameter.



Scheme 3. Proposed molecular packing of DDABM in the crystalline structure. From left to right: schematic view of an individual molecule, a unit cell, and a larger molecular aggregate emphasizing the smectic superstructure of DDABM. The orientation of the alkyl chains was deduced from the characteristic peaks of the alkyl sub-lattice.

lattice that shares reflections with it,^[25] even if their symmetries are different. In this case, the sublattice (Figure 9) is identified as a triclinic unit cell and is close to the lattice of *n*-octane, apart from its *c* parameter.^[26]

The indices of the sublattice and the corresponding main lattice reflections are given in Table 1. Based on the WAXD data, a sketch of a possible molecular packing in the crystalline phase of DDABM is proposed (Scheme 3). It is noteworthy that the structure in Figure 9 highlights only the alkyl part of the global unit cell such as sketched in Scheme 3. The alkyl tails in Scheme 3 are shown as thick cylinders. The **b** vector of the sublattice corresponds to the **c** axis of the main lattice, while the **ab** plane of the sublattice is parallel to the **bc** plane of the main lattice.

The projection of the sublattice **a** vector on the main lattice **ac** plane corresponds to one-fourth of the main lattice **b** vector. The *c* parameter of the sublattice is equal to approximately one-half of the *a* parameter of the main lattice. From this fact, one can assume that the main lattice contains two layers of quasi 2D "lamellar" arrays of the alkyl sublattice along its *a* direction. The lattice parameters of the triclinic sublattice are calculated to be a=4.23, b=4.85, c=19.71 Å and a=94.8, $\beta=86.1$, $\gamma=107.8^{\circ}$. According to the proposed model, the alkyl groups have a setting angle of about 60° in the **ab** plane of the main lattice, while they are inclined by about 15° toward the fast growth axis direction.

From the model depicted in Scheme 3, the inclination angle of the straight diacetylene units can be estimated. Thus, if one approximates the diameter of a diacetylene unit by 2.3 Å, it will be inclined by about 30° both towards the fast growth axis and toward the **b** vector of the main lattice. Therefore, the repeating distance of the diacetylene units (i.e., *d* in Scheme 1) should correspond to the *c* parameter of the main lattice of 4.85 Å, which fulfills the requirements for topochemical polymerization.

The thermal behavior in the temperature range of -15°C to 60°C does not reveal any significant differences between the polymerized and the unpolymerized materials, except for a small variation in the transition temperatures, as shown by temperature-dependent WAXD (Figure 10). On heating DDABM samples which were previously annealed at room temperature from -15°C, both UV irradiated and non-irradiated materials show a solid-state phase transition at around 0°C. The transition is characterized by a slight change of the relative peak intensities of the sublattice reflections. Such a change in the relative intensities likely corresponds to a modification in the conformation of the alkyl segments such as a change in the setting angles. Remarkably, this transition is not accompanied by a thermal effect. Moreover, it coincides with the main exothermic event for the quenched compound, as measured by DSC (Figure 4). The observed low-temperature phase forms only on relatively slow cooling from room temperature, whereas it does not appear on fast cooling, as seen from Figure 10 (bottom).

Conclusion

A novel wedge-shaped compound containing two diacetylene tails, namely, methyl 3,5-bis(trideca-2,4-diyn-1yloxyl)benzoate (DDABM), was synthesized. As shown by UV/Vis

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60

45

Figure 10. Scattering intensity as a function of the modulus of the scattering vector s and temperature for DDABM measured during heating from -15 °C to 60 °C at a rate of 5.0 K min⁻¹. The results for samples annealed at room temperature for 24 h before and after UV irradiation are given in the top and middle panels, respectively. The bottom panel shows the temperature-dependent structure evolution for a UV-irradiated sample quenched from the isotropic melt to -20 °C.

spectroscopy, it can be polymerized under UV irradiation. An oriented crystalline thin film of DDABM was obtained on a silicon wafer substrate rubbed with polytetrafluoroethylene and analyzed by grazing-incidence wide-angle Xray diffraction. Furthermore, the spherulites formed by DDABM in thick films were investigated by wide-angle Xray diffraction measurements with a small X-ray beam. DDABM was found to form a monoclinic crystalline lattice. The main lattice contains two layers of quasi-2D arrays of alkyl sublattice, which can be indexed to a triclinic unit cell, close to the lattice of *n*-octane apart from its increased *c* parameter. A molecular packing model in the crystalline structure of DDABM was proposed on the basis of the X-ray diffraction data, and it was found that the diacetylene units are oriented along a defined lattice direction with a reticular distance of 4.85 Å, which fulfills the requirements for the topochemical polymerization. UV polymerization does not affect the phase behavior of the compound, but mainly alters its optical properties.

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Experimental Section

Materials: Decyne (98%, Aldrich), *N*-bromosuccinimide (99%, Aldrich), propargyl alcohol (99%, Aldrich), diethylamine, NH₂OH-HCl, silver nitrate (ACS reagent, \geq 99.0%, Aldrich), copper(I) chloride (ACS reagent, \geq 90%, Sigma-Aldrich), triphenylphosphine dibromide (96%, Aldrich), methyl 3,5-dihydroxybenzoate (98%, Aldrich), potassium carbonate (ACS reagent, \geq 99.0%, Sigma-Aldrich), and 18-crown-6 (\geq 99.0%, Aldrich) were used as received. Acetone, dichloromethane, methanol, ethanol, ethyl acetate, *n*-hexane, sodium sulfate, sodium thiosulfate, sodium chloride, and hydrochloric acid were purchased from VWR. The solvents were purified by standard procedures.

1-Bromo-1-decyne (1): A solution of decyne (10 g, 72.5 mmol), *N*-bromosuccinimide (25.81 g, 145 mmol), and silver nitrate (3.815 g, 22.89 mmol) in acetone (200 mL) was stirred at room temperature for 2 h. Acetone was removed in vacuo, and the resulting product dissolved in CH₂Cl₂ and passed through a short silica gel column. The solvent was removed on a rotary evaporator to leave 1-bromo-1-decyne as a slightly yellow liquid. Yield: 14.86 g (94.5%), purity >98% by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃): δ =0.815 (t, 3H, CH₃), 1.21 (m, 10H, CH₃CH₂), 1.44 (m, 2H, CH₂), 2.12 ppm (t, 2H, CH₂C=C); ¹³C NMR: 14.1 (CH₃), 19.6 (CH₂C=), 22.6 (CH₃CH₂), 28.3, 28.8, 29.1, 29.2, 31.9 (CH₂), 37.4 (*C*= CBr), 80.4 ppm (C=CBr).

Trideca-2,4-diyn-1-ol (2): 1-Bromo-1-decyne 1 (23 g, 0.106 mol) in MeOH (20 mL) was added dropwise to a stirred mixture of propargyl alcohol (11.872 g, 0.212 mol), ethylamine (40 mL, aqueous solution, 70 wt%), $NH_2OH\text{-}HCl~(2\mbox{ g}),\ powdered\ CuCl~(0.5\mbox{ g}),\ H_2O~(40\mbox{ mL}),\ and\ MeOH$ (100 mL). Stirring was continued at 35 °C for 1 day. Afterwards, the reaction mixture was filtered, and methanol was removed from the filtrate on a rotary evaporator. The residue was extracted with diethyl ether. The organic layer was washed with water (3×30 mL) and then dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator to furnish the crude product. After column chromatography on silica gel (eluent: ethyl acetate/n-hexane 1/5), 2 was obtained as a colorless crystal. Yield: 9.38 g (86%), purity > 98% by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.815$ (t, 3H; CH₃), 1.21 (m, 10H, CH₃CH₂), 1.44 (m, 2H, CH₂), 2.12 (t, 2H, CH₂C=C), 4.25 ppm (C=CC=CCH₂OH); ¹³C NMR: 14.1 (CH₃), 19.2 (CH₂C=), 22.6 (CH₃CH₂), 28.3, 28.8, 29.1, 29.2, 31.9 (CH₂), 49.9 (CH₂OH), 64.3 (CH₂C=CC=C), 70.9 (CH₂C=CC= C), 73.4 (CH₂C=CC=C), 81.9 ppm (CH₂C=CC=C).

1-Bromotrideca-2,4-diyne (3): Compound 2 (1.75 g, 9.1 mmol) in dry dichloromethane (6 mL) was added dropwise to an ice-cooled stirred solution of PPh₃Br₂ (4.58 g, 10.5 mmol) in dry dichloromethane (40 mL). After stirring at the same temperature for 10 min, the reaction mixture was warmed to room temperature and stirring continued for 1 day. Afterwards dichloromethane was removed and the reaction mixture was diluted with ethyl acetate. The organic layer was washed with sodium thiosulfate (10% solution, 2×30 mL), water (3×30 mL), and dried over anhydrous Na2SO4. The solvent was removed on a rotary evaporator. The crude product thus obtained was purified by column chromatography on silica gel (eluent: ethyl acetate/n-hexane 2/1) to yield 1.86 g (82%) of **3** as a white power, purity > 98% by ¹H NMR spectroscopy. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 0.815$ (t, 3H, CH₃), 1.21 (m, 10H, CH₃CH₂), 1.44 (m, 2H, CH₂), 2.12 (t, 2H, CH₂C=C), 3.89 ppm (s, 2H, C=CC=CCH₂Br); ^{13}C NMR: 14.1 (CH₃), 19.2 (CH₂C=), 22.6 (CH₃CH₂), 28.3, 28.8, 29.1, 29.2, 31.9 (CH₂), 14.8 (CH₂Br), 64.4 (CH₂C=CC=C), 69.9 (CH₂C=CC=C), 71.9 (CH₂C=CC=C), 83.4 ppm (CH₂C=CC=C).

Methyl 3,5-bis (trideca-2,4-diyn-1yloxyl)benzoate (DDABM): K_2CO_3 (1.08 g, 1 mmol) and 18-crown-6 (2.6 mg, 0.01 mmol) were added to a stirred solution of methyl 3,5-dihydroxybenzoate (0.5 g, 2.5 mmol) and 3 (2.55 g, 6.25 mmol) in acetone (40 mL). The reaction mixture was heated to reflux for 24 h, and then filtered and evaporated to dryness. Water (50 mL) was added and the mixture was extracted with CH₂Cl₂ (3× 30 mL). The organic phases were combined, dried over Na₂SO₄, and the solvent evaporated in vacuo. The crude product thus obtained was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*hexane 3/1) to afford DDABM as a white powder. Yield: 0.88 g (68%), purity >98% by ¹H NMR spectroscopy. Elemental analysis (%) calcd for C₃₄H₄₄O₄ (516.32 g mol⁻¹): C 78.08, H 8.60; calcd: C 79.03 , H, 8.58; ¹H NMR (400 MHz, CDCl3): δ =0.815 (t, 9H; CH₃), 1.21 (m, 30H, CH₃CH₂), 1.44 (m, 9H, CH₂), 2.12 (t, 6H, CH₂C≡C), 4.25 (m, 2H, COOCH₂CH₃) 4.72 (s, 6H, C≡CCH₂O), 7.37 ppm (s, 2H, ArH *ortho* to CO group); ¹³C NMR: 14.1 (CH₃), 19.2 (CH₂C≡), 22.6 (CH₃CH₂), 28.3, 28.8, 29.1, 29.2, 31.9 (CH₂), 57.8 (CH₂O), 61.1 (CH₂O), 61.2 (COOCH₂CH₃), 64.4 (CH₂C≡CC≡C), 69.9 (CH₂C≡CC≡C), 71.9 (CH₂C≡ CC≡C), 83.4 (CH₂C≡CC≡C), 109 (ArC *ortho* to CO group), 126 (ArC *ipso* to CO group), 141 (ArC in 4'-position relative to CO group), 151.4 (ArC in 3',5'-positions relative to CO group), 165.8 ppm (COOCH₂CH₃).

Polymerization of DDABM: Quartz was cleaned by sonication in acetone, water, and propan-2-ol for 2 min each, followed by drying in a stream of nitrogen. A 10 gL⁻¹ solution of DDABM was prepared in chloroform. Films (200 ± 5) nm thick were obtained by drop casting. Photopolymerization was carried out by irradiation with a 6 W UV lamp at 254 nm at room temperature.

Techniques: ¹H NMR and ¹³C NMR spectra were recorded on a Varian VXR 300 instrument at 300 MHz with TMS as internal standard in $CDCl_3$ solutions with concentrations of $15-30 \text{ mgmL}^{-1}$.

Polarized optical microscopy (POM) for thermo-optical analysis was performed on a Carl Zeiss Axioplan 2 imaging polarizing microscope equipped with a Mettler Toledo FP 82HT hot stage connected to a Mettler Toledo FP 90 processor. The micrographs were recorded with a Carl Zeiss AxioCam MRc digital camera.

Raman spectra were measured on a Bruker RFS 100/S with Nd:YAG laser (λ = 1064 nm) and 500 scans.

Size exclusion chromatography (SEC) was carried out with a high-pressure liquid chromatography pump (ERC HPLC 6420) and a refractiveindex detector (Jasco RI-2031 plus) at 25 °C. The eluting solvent was THF, and a flow rate of 1.0 mL·min⁻¹ was used. Four columns with SDplus gel were employed. The length of each column was 300 mm, and the diameter was 8 mm. The diameter of the gel particles was 5 µm, and the nominal pore widths were 50, 100, 1000 and 10000 Å. Calibration with polystyrene standards was used to determine the molecular weights.

Differential scanning calorimetry (DSC) measurements were performed with a Netzsch DSC 204 unit. Samples (typical weight: 5 mg) were enclosed in standard Netzsch 25 μ L aluminum crucibles. Indium and palmitic acid were used as temperature calibration standards. The employed heating and cooling rates were 5.0 K min⁻¹. For quenching, a cooling rate of 40 K min⁻¹ was used.

UV/Vis spectra were recorded on the films of the samples at room temperature on a JASCO V-630 spectrophotometer at a scan rate of 100 nm min⁻¹. The slit width was 2 nm. Prior to drop casting of the quartz substrates, the stock 10 gL^{-1} chloroform solutions of the compounds were filtered through 0.2 µm PTFE syringe filters. UV irradiation was carried out with a 6 W UV lamp (Netz-Handlampe UVA/C, Dr. Gröbel UV-Elektronik GmbH) at 254 nm placed at a distance of 5 cm from the films.

Wide-angle X-ray diffraction (WAXD) experiments at variable temperatures were conducted at the BM26 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, by using X-ray photons with energy of 12 keV. A small amount of DDABM was enveloped in a polished aluminum foil for good heat contact and annealed for 24 h at room temperature. The temperature of the sample was controlled by using a Linkam heating stage adapted for X-ray experimentation. The 2D X-ray patterns were collected in transmission geometry by a 2D Frelon CCD with 2×2 binning giving a pixel resolution of 100 µm in both lateral directions.

Grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements were performed at the X6B beamline of the National Synchrotron Light Source (NSLS) at the BNL, Brookhaven. The used X-ray photons had an energy of 18 keV. The compounds were dissolved in chloroform to give 0.01 wt% solutions and drop cast on the PTFE-rubbed silicon wafer substrate followed by an annealing process at 25 °C for 24 h. The drop-cast samples were placed in a six-circle Huber 5020 diffractometer with vertical scattering geometry. The samples were oriented with the rubbing direction parallel and perpendicular to the incident X-ray beam.

4306 -

The 2D diffraction patterns were collected by using a Princeton Instruments CCD area detector, 8 cm 640-element Si strip detector.

X-ray data reduction and analysis: The modulus of the scattering vector $s=2\sin\theta/\lambda$, where θ is the Bragg angle and λ the wavelength, was calibrated by using several diffraction orders of silver behenate. The data reduction and analysis including geometrical and background correction, visualization and resampling into polar coordinates of the 2D diffractograms were performed by using home-built routines written in the Igor Pro software package from WaveMetrics.

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