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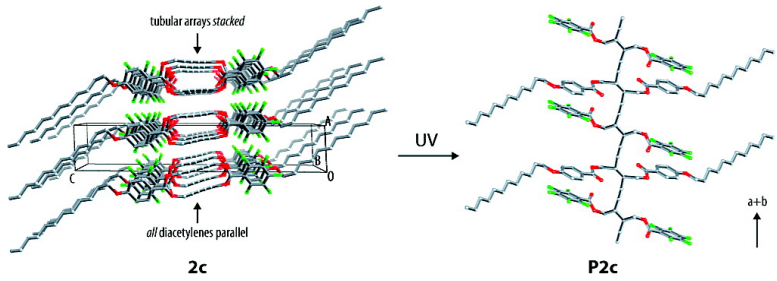

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Soluble Poly(diacetylene)s Using the Perfluorophenyl−Phenyl Motif as a Supramolecular Synthon

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Abstract: A series of diacetylene monomers with benzoyl, 4-hexylbenzoyl, 4-dodecylbenzoyl, and perfluorobenzoyl substituents were synthesized and investigated with respect to their crystal structures and polymerizability. In the absence of perfluorophenyl−phenyl interactions, the crystal structures of related alkylated and nonalkylated derivatives were substantially different and dominated by the phase segregation between the alkylated side chains and the diaryl-substituted diacetylene cores. By contrast, the perfluorophenyl−phenyl interactions served as a reliable supramolecular synthon in that they persisted in the crystal structures of different alkylated and nonalkylated derivatives. The packing of the diacetylene functions was appropriate for a topochemical polymerization in these cases, and the perfluorophenyl−phenyl interaction determined the polymerization direction. As a result, soluble alternating diacetylene copolymers were obtained which were further characterized with solution phase methods.

Introduction

Noncovalent interactions between aromatic residues are an important factor controlling the structures and properties of molecular assemblies in biological systems and have, therefore, attracted increasing interest in recent years as design elements in drug design, solution phase supramolecular chemistry, and crystal engineering, as well as materials science.[1,2] In most cases, the interacting arene residues avoid $\pi-\pi$ stacking in favor of edge-to-face interactions, or they prefer a parallel-displaced $\pi-\pi$ stacking. The latter appears to be a viable compromise between a maximum surface contact and a favorable arrangement of the residues' quadrupolar moments and, hence, the energetic optimum in terms of dispersive and electrostatic contributions. With an interplanar distance of about 3.6 Å and a parallel displacement of up to 1.8 Å, centroid distances significantly larger than 4 Å are typically observed. By contrast, arene−perfluoroarene interactions most often result in an eclipsed or staggered face-to-face $\pi-\pi$ stacking with only minimal parallel displacement, an interplanar distance of 3.4 Å, a centroid distance of around 3.7 Å, and only little deviation from a parallel packing of the interacting residues.[2,3] Experimental and calculated binding energies in the range 15 to 30 kJ mol^{-1} have been reported,[4–7] and arene−perfluoroarene interactions may be favored by up to 10 kJ mol^{-1} per phenyl ring compared to conventional arene−arene interactions.[8] The exact origin of the comparably strong interaction and the peculiar geometric features, however, is still a matter of debate. While it has been attributed to the quadrupolar moments of arene and perfluoroarene residues[9–12] which are similar in magnitude but opposite in sign,[13] recent investigations indicate that dispersive interactions may still be the most important contribution.[14–16] Equally controversial is the actual relevance of the C−H···F short contacts observed in many crystal structures as an additional stabilizing element.[3,14,17,18] Nevertheless, it is probably safe to say that the electrostatic contribution makes the difference in comparison to normal arene interactions, in particular, with respect to the reliable and peculiar packing properties.[8,15,16] It is this feature that make arene−perfluoroarene interactions an interesting "supramolecular synthon"[19] both in crystal engineering and solution phase supramolecular chemistry. They were,

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(1) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651–669.
(2) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210–1250.
(3) Reichenbächer, K.; Süss, H. I.; Hulliger, J. *Chem. Soc. Rev.* **2005**, *34*, 22–30.
(4) Gdaniec, M.; Jankowski, W.; Milewska, M. J.; Polonski, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3903–3906.
(5) Hernandez-Trujillo, J.; Colmenares, F.; Cuevas, G.; Costas, M. *Chem. Phys. Lett.* **1997**, *265*, 503–507.
(6) West, A. P., Jr.; Mecozzi, S.; Dougherty, D. A. *J. Phys. Org. Chem.* **1997**, *10*, 347–350.
(7) Lorenzo, S.; Lewis, G. R.; Dance, I. *New J. Chem.* **2000**, *24*, 295–304.
(8) Bacchi, S.; Benaglia, M.; Cozzi, F.; Demartin, F.; Filippini, G.; Gavezzotti, A. *Chem.−Eur. J.* **2006**, *12*, 3538–3546.
(9) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593–598.
(10) Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1655–1657.
(11) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
(12) Carver, F. J.; Hunter, C. A.; Seward, E. M. *Chem. Commun.* **1998**, 775–776.
(13) Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. *Chem. Phys. Lett.* **1981**, *78*, 421–423.
(14) Dunitz, J. D.; Schweizer, W. B. *Chem.−Eur. J.* **2006**, *12*, 6804–6815.
(15) Dunitz, J. D.; Gavezzotti, A.; Schweizer, W. B. *Helv. Chim. Acta* **2003**, *86*, 4073–4092.
(16) Dunitz, J. D. *ChemBioChem* **2004**, *5*, 614–621.
(17) Thalladi, V. R.; Weiss, H. C.; Blaser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702–8710.
(18) Dunitz, J. D.; Gavezzotti, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1766–1787.
(19) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327.

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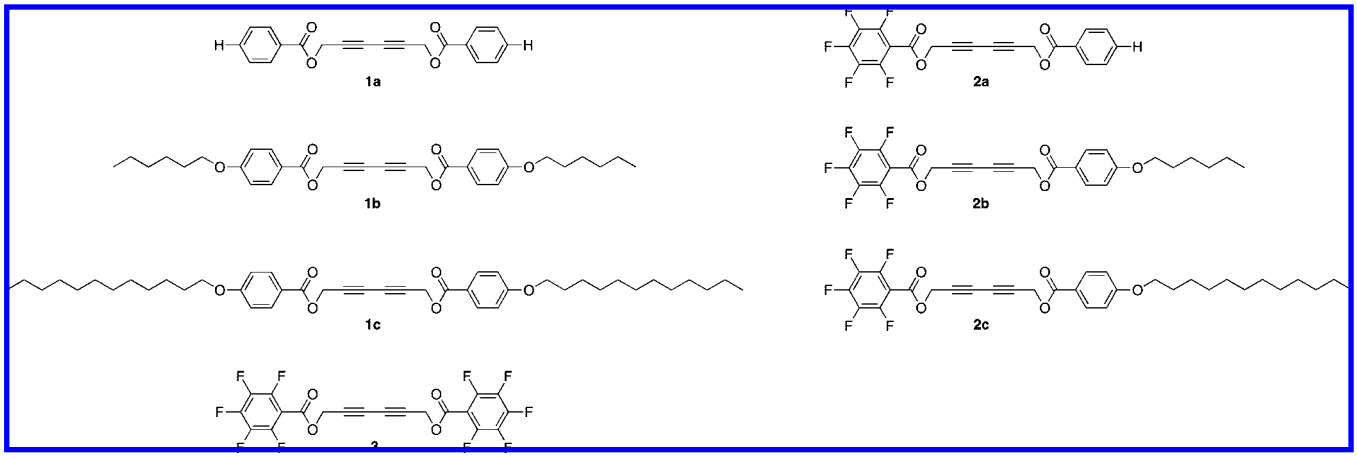
Chart 1. Diacetylene Monomers with 4-Alkylbenzoyl, Benzoyl, and Perfluorobenzoyl Substituents



for example, utilized in 2 + 2 cycloadditions of cinnamic acid or stilbene derivatives,[20] in an attempted topochemical diacetylene polymerization of diarylbutadiyne derivatives,[21] in crystal engineering investigations on (arylethynyl)benzene, 1,4-bis(arylethynyl)benzene, as well as 1,3,5-tris(arylethynyl)benzene derivatives,[22–25] and in the stacking of diaryl-β-diketonate complexes.[26] Furthermore, the role of perfluoroarene−arene interactions on the formation of thermotropic LC phases,[27,28] the gelation of octafluoronaphthalene and pyrene-endcapped PEG in aqueous solution,[29] or the conformational stability of oligopeptides containing perfluorophenylalanine residues was investigated.[30,31]

We recently reported the utilization of perfluorophenyl−phenyl interactions in the topochemical diacetylene polymerization[32,33] which led to the first unambiguously proven example of a strictly alternating diacetylene copolymer.[34] Unfortunately, the obtained copolymer turned out to be only poorly soluble in organic solvents, which hampered its characterization and limited its potential applications. This problem would be conveniently addressed with alkyl decoration, as it has been done in other examples of soluble poly(diacetylene)s.[35] However, the preparation of a corresponding alkylated alternating copolymer would require that the stacking motif established by the perfluorophenyl−phenyl interactions persisted in spite of alkylation. Only few investigations to date have dealt with functional molecules where the perfluoroarene−arene interaction competed with other types of supramolecular interactions such as hydrogen bonding[4,36–38] or van der Waals interactions between alkyl residues.[23] In the latter example, the perfluoroarene−arene interactions were shown to become less of a determining factor with increasing steric demand of the alkyl substituent.

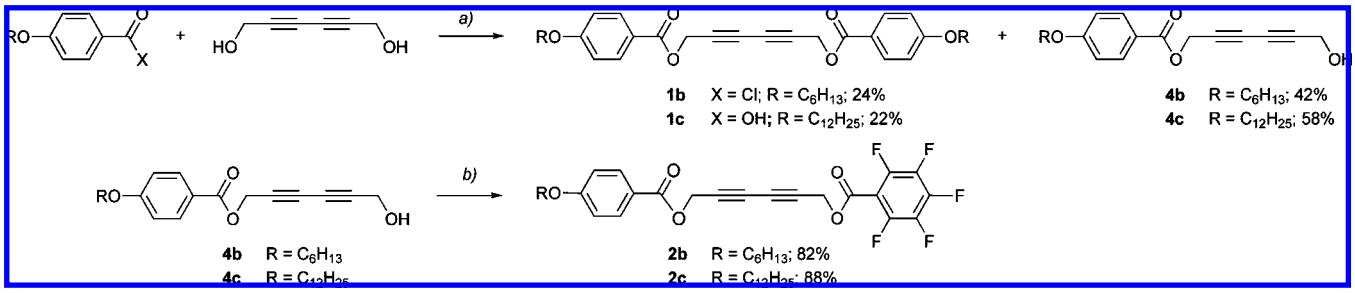
In the present paper, we prepared and investigated a series of 2,4-hexadiyne-1,6-diol derivatives with benzoyl, 4-hexylbenzoyl, 4-dodecylbenzoyl, and perfluorobenzoyl substituents (Chart 1) with respect to their crystal structures and polymerizability. We wish to demonstrate that perfluorophenyl−phenyl interactions indeed deserve to be regarded as a reliable supramolecular synthon because they persist when combined with another type of supramolecular interaction. Thus, the crystal structures of related alkylated and nonalkylated derivatives were substantially different in the absence of perfluorophenyl−phenyl interactions, and the phase segregation between the alkylated side chains and the diacetylene cores appeared to be the dominating factor in this case. By contrast, the crystal structures of different alkylated and nonalkylated diacetylene monomers which exhibited perfluorophenyl−phenyl interactions were strikingly similar and appeared to complement the requirements of both the aromatic interactions and the packing of the alkyl substituents. Moreover, the packing of the diacetylene functions was found to be appropriate for a topochemical polymerization in these cases, and the perfluorophenyl−phenyl interaction

(20) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641–3649.
(21) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248–251.
(22) Ponzini, F.; Zagha, R.; Hardcastle, K.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2323–2325.
(23) Smith, C. E.; Smith, P. S.; Thomas, R. L.; Robins, E. G.; Collings, J. C.; Dai, C.; Scott, A. J.; Borwick, S.; Batsanov, A. S.; Watt, S. W.; Clark, S. J.; Viney, C.; Howard, J. A. K.; Clegg, W.; Marder, T. B. *J. Mater. Chem.* **2004**, *14*, 413–420.
(24) Dai, C.; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W.; Viney, C. *Chem. Commun.* **1999**, 2493–2494.
(25) Watt, S. W.; Dai, C.; Scott, A. J.; Burke, J. M.; Thomas, R. L.; Collings, J. C.; Viney, C.; Clegg, W.; Marder, T. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 3061–3063.
(26) Hori, A.; Shinohe, A.; Yamasaki, M.; Nishibori, E.; Aoyagi, S.; Sakata, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7617–7620.
(27) Weck, M.; Dunn, A. R.; Matsumoto, K.; Coates, G. W.; Lobkovsky, E. B.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2741–2745.
(28) Kishikawa, K.; Oda, K.; Aikyo, S.; Kohmoto, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 764–768.
(29) Kilbinger, A. F. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1563–1566.
(30) Butterfield, S. M.; Patel, P. R.; Waters, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 9751–9755.
(31) Gorske, B. C.; Blackwell, H. E. *J. Am. Chem. Soc.* **2006**, *128*, 14378–14387.
(32) Wegner, G. *Z. Naturforsch., B* **1969**, *24*, 824–832.
(33) Zuilhof, H.; Barentsen, H. M.; van Dijk, M.; Sudhölter, E. J. R.; Hoofman, R. J. O. M.; Siebbeles, L. D. A.; de Haas, M. P.; Warman, J. M. In *Supramolecular and Photosensitive Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: San Diego, CA, 2001; pp 339−437.
(34) Xu, R.; Gramlich, V.; Frauenrath, H. *J. Am. Chem. Soc.* **2006**, *128*, 5541–5547.

(35) Most investigations on soluble poly(diacetylene)s to date have been carried out with dodeca-5,7-diyne bis(toluenesulfonate) (PTS-12), dodeca-5,7-diyne bis(butylcarboxymethyl carbamate) (P4BCMU), or closely related monomers; for the original investigations, see: Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837. Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 607. Chance, R. R. *Macromolecules* **1980**, *13*, 396.

(36) Reddy, L. S.; Nangia, A.; Lynch, V. M. *Cryst. Growth Des.* **2004**, *4*, 89–94.
(37) Meejoo, S.; Kariuki, B. M.; Harris, K. D. M. *ChemPhysChem* **2003**, *4*, 766–769.
(38) Wojciech, J.; Gdaniec, M.; Polonski, T. *Acta Crystallogr., Sect. C* **2006**, *C62*, o492–o494.

Scheme 1. Synthesis of the Monomers **1b**, **1c**, **2b**, and **2c**[a]



[a] Reaction conditions: (a) for **1b**: NEt_3, DCM; for **1c**: EDCI, DPTS, DCM; (b) C_6F_5COCl, NEt_3, DCM.

Table 1. Crystallographic Data of the Novel Monomers **1b**, **1c**, **2b**, and **2c**, as well as the Cocrystal **1b·3** in Comparison to the Previously Determined Crystal Structures of **1a**, **2a**, and the Cocrystal **1a·3**[34,40]

	1a	1b	1c	1a·3	1b·3	2a	2b	2c
formula	$C_{20}H_{14}O_4$	$C_{32}H_{38}O_6$	$C_{44}H_{62}O_6$	$C_{20}H_4F_{10}O_4$·$C_{20}H_{14}O_4$	$C_{20}H_4F_{10}O_4$·$C_{32}H_{38}O_6$	$C_{20}H_9F_5O_4$	$C_{26}H_{21}F_5O_5$	$C_{32}H_{33}F_5O_5$
mw	318.31	518.64	686.96	866.35	508.43	408.27	508.44	592.59
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
color	colorless	colorless	colorless	colorless	light orange	colorless	colorless	light orange
a (Å)	14.038(2)	25.279(5)	27.6013(7)	5.9825(7)	5.9343(1)	16.822(2)	8.5473(2)	5.9780(1)
b (Å)	4.353(1)	7.7559(14)	7.6701(2)	7.576(1)	7.4644(1)	7.1205(7)	33.5122(7)	7.3408(2)
c (Å)	14.864(2)	19.608(3)	19.6075(4)	19.295(2)	27.3032(5)	15.706(2)	8.5937(2)	32.998(1)
α (deg)	90.00	90.00	90.00	96.91(1)	97.839(1)	90.0	90.0	87.6
β (deg)	117.06(2)	129.618(10)	102.3582(8)	91.74(1)	90.534(1)	107.423(8)	98.590(1)	87.610(1)
γ (deg)	90.00	90.00	90.00	93.07(1)	93.184(1)	90.0	90.0	85.8
V (Å^3)	808.8(3)	2961.37	4054.8(2)	866.4(2)	1196.10(3)	1795.0(3)	2434.0(1)	1442.18(6)
radiation	Cu Kα	Mo Kα	Mo Kα	Cu Kα	Mo Kα	Cu Kα	Mo Kα	Mo Kα
D_{calcd} (g cm^{-3})	1.31	1.16	1.125	1.56	1.412	1.51	1.39	1.365
m_{calcd} (mm^{-1})	0.091	0.08	0.073	0.144	0.122	0.139	0.12	0.112
F_{000}	332	1112	1496	412	524	824	1048	620
T	295	295	223	295	220(2)	295	223	153
Z	2	4	4	1	1	4	4	2
R, R_w^2	0.067, 0.210	0.0545, 0.124	0.085, 0.234	0.0745, 0.243	0.0732, 0.2069	0.0593, 0.194	0.066, 0.175	0.064, 0.189
GOF	0.94	0.68	1.33	0.948	1.029	0.940	1.28	1.036

appeared to determine the direction of polymerization. Hence, soluble perfluorophenyl-substituted poly(diacetylene)s were obtained which could be characterized with solution phase methods and may, furthermore, be subjected to solution phase processing into optoelectronically active materials.

Results and Discussion

Monomer Synthesis. The nonalkylated monomers **1a**, **2a**, and **3** were prepared as described previously.[34] For the synthesis of monomer **1b** and **2b**, 4-(hexyloxy)benzoyl chloride was reacted with an approximately stoichiometric amount of hexa-2,4-diyne-1,6-diol, affording a mixture of the monosubstituted intermediate **4b** and the disubstituted diacetylene **1b** (Scheme 1). The two compounds were separated by column chromatography, and **4b** was subsequently esterified with perfluorobenzoic chloride, yielding the unsymmetrically substituted diacetylene monomer **2b**. Similarly, the dodecylated monomers **1c** and **2c** were prepared by reacting roughly equimolar amounts of 4-(dodecyloxy)benzoic acid and hexa-2,4-diyne-1,6-diol, using 4-(*N*,*N*-dimethylamino)-pyridinium 4-toluenesulfonate (DPTS) and *N*-ethyl-(*N*′-dimethylaminopropyl)-carbodiimide hydrochloride (EDCI·HCl) as the catalyst system,[39] followed by esterification of the monosubstituted compound **4c** with perfluorobenozic chloride.

Comparison of the Monomer Crystal Structures. Single-crystalline samples of **1a**−**c**, **2b**, and **2c** as well as a cocrystal **1b·3** were obtained by recrystallization from DCM/hexanes. The crystal structure observed in the case of the 2,4-hexadiyne-1,6-diyl dibenzoate **1a** (Table 1) corresponded to one of the two known polymorphs.[34,40] While, in this particular case, the geometric parameters are not appropriate for a topochemical diacetylene polymerization, the typical parallel-displaced $\pi-\pi$ stacking of the aryl substituents in **1a** is representative for various literature examples of polymerizable and nonpolymerizable diacetylene derivatives.[41–44] By contrast, the crystal structures of both the bis(*p*-hexyloxybenzoate) **1b** and the bis(4-dodecyloxybenzoate) **1c** were remarkably different from **1a** (Figure 1).

In contrast to the centrosymmetric arrangement of **1a**, the molecules in crystals of **1b** and **1c** adopted an approximate, noncrystallographic twofold axis. The two dodecyloxybenzoate substituents showed a dihedral angle of 110°, forming a "twisted U-shape" packed into layers with a mean plane distance of 6.5 Å by lattice translation along the [0 1 0] axis. For both **1b** and **1c**, two diacetylenes from layers across an inversion center exhibited C···C short contacts,[45] but the closest packing of two

(39) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65–70.

(40) Hanson, A. W. *Acta Crystallogr., Sect. B* **1975**, *B31*, 831–834.
(41) Enkelmann, V.; Wegner, G. *Angew. Chem., Int. Ed.* **1977**, *89*, 416.
(42) Enkelmann, V.; Leyrer, R. J.; Wegner, G. *Makromol. Chem.* **1979**, *180*, 1787–1795.
(43) Patel, G. N.; Duesler, E. N.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1980**, *102*, 461–466.
(44) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91–136.

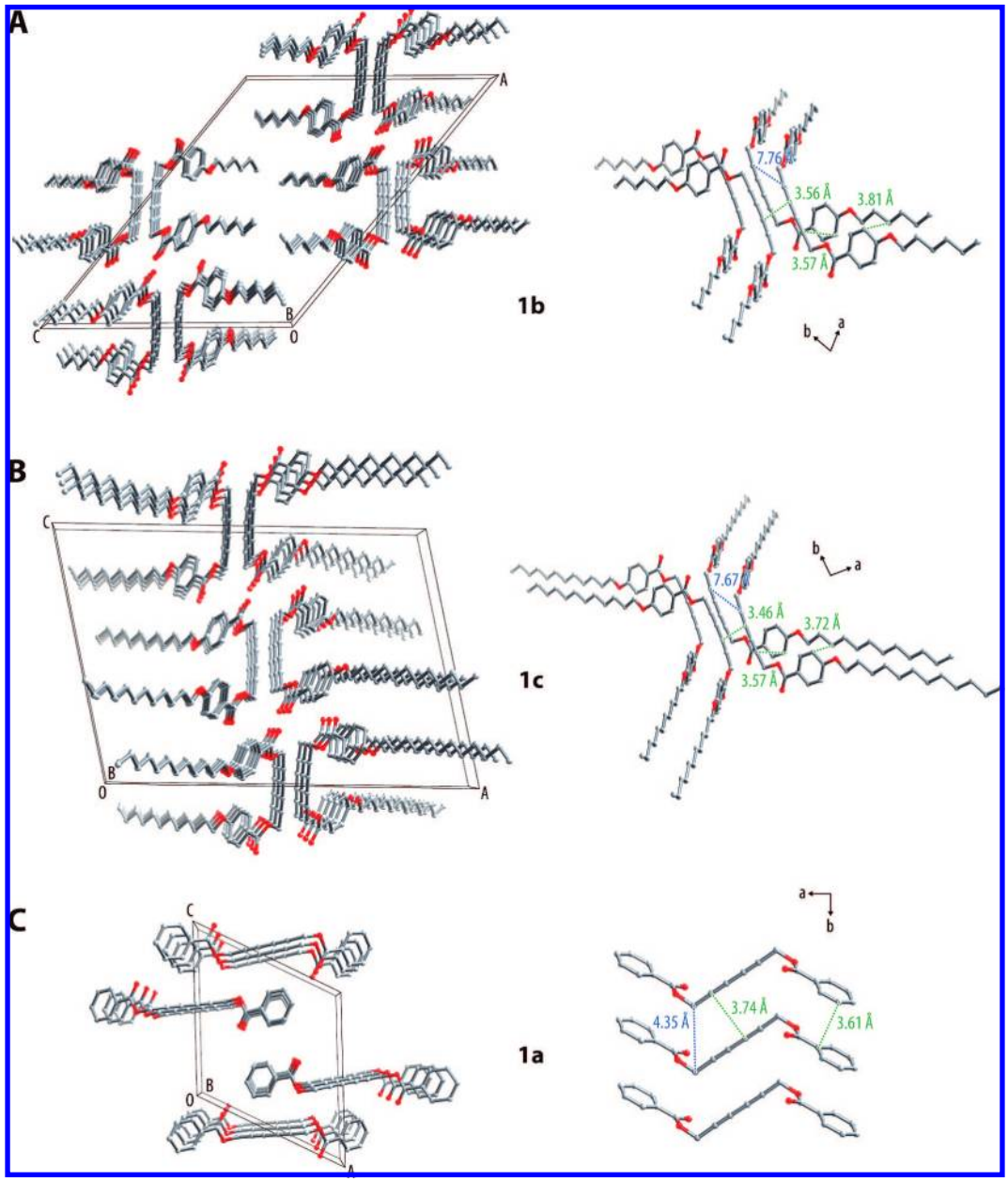


Figure 1. A comparison of the crystal structures of (A) the hexyloxy-substituted monomer **1b** and (B) the dodecyloxy-substituted monomer **1c** with (C) the previously determined crystal structure of the unsubstituted derivative **1a**[34,40] revealed that the alkyl substituents exerted a major influence. Whereas **1a** exhibited the typical parallel-displaced $\pi-\pi$ stacking of the phenyl groups, no aromatic interaction was observed in **1b** and **1c** at all which, instead, were packed in "bilayer"-like arrangements of the "twisted U-shaped" molecules.

diacetylenes within one layer occurred along the [0 1 0] direction with lattice periods of 7.756 Å (**1b**) and 7.670 Å (**1c**), respectively, which is incompatible with the requirements for a topochemical polymerization. The same distances were observed between the phenyl groups, which is obviously too large to be considered as a $\pi-\pi$ stacking interaction.[45] Instead, the molecules were arranged such that the phenyl groups gave rise to a C−H···π short contact with the alkyl residue of one neighboring molecule and a $\pi-\pi$ interaction with the diacetylene group of the other neighbor. Hence, the introduction of the alkoxy substituents significantly altered the molecular symmetry and the crystal structures of **1b** and **1c** as compared to **1a**. Looking at these differences with the eyes of a polymer chemist, one might say that, by analogy with ABA triblock copolymers, phase segregation occurred between the aliphatic side chains and the diacetylene cores of the molecules, leading to a "lamellar bilayer packing" of the "U-shaped" molecules.[45] The dense packing of the alkoxy substituents appeared to be the dominating factor in the crystal structure and outperformed $\pi-\pi$ stacking interaction of the phenyl groups which, in this sense, cannot be regarded as a reliable supramolecular synthon.

The situation was fundamentally different in the case of the cocrystals **1a·3** and **1b·3** as well as the crystals of **2a** and **2c** (Figures 2 and 3).[34,46] The remarkably similar crystal structures proved that the perfluorophenyl−phenyl interactions remained the dominating factor despite the presence of the alkyloxy

(45) See Supporting Information for additional figures and detailed discussion.

(46) It should be acknowledged that the hexyl-substituted **2b** constituted a notable exception; see Supporting Information.

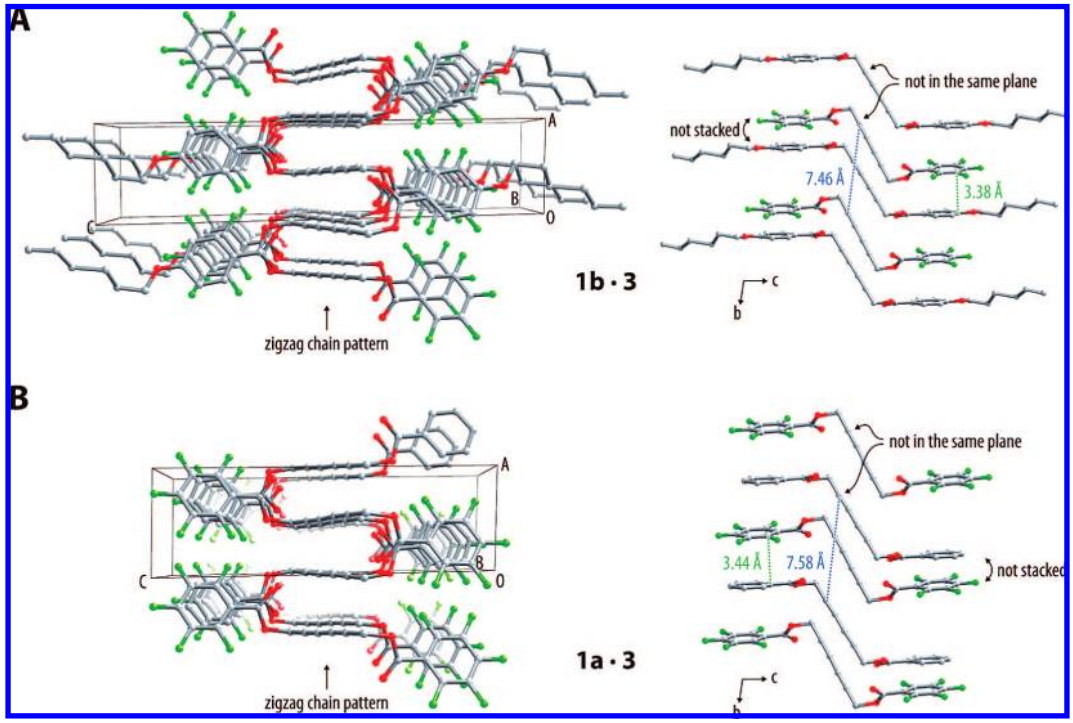


Figure 2. (A) Crystal structure of the cocrystal **1b·3** and, for comparison, (B) the related crystal structure of the cocrystal **1a·3**;[34] in both cases, the characteristic packing of the molecules into a "*zigzag chain*" pattern along the [1 0 0] axis and the almost perfectly eclipsed perfluorophenyl−phenyl stacking were preserved in spite of the presence of the alkyl substituents in **1b**; the diacetylene functions of adjacent molecules in the [0 1 0] direction were not placed in the same plane so that identity periods of 7.46 and 7.58 Å were observed, respectively.

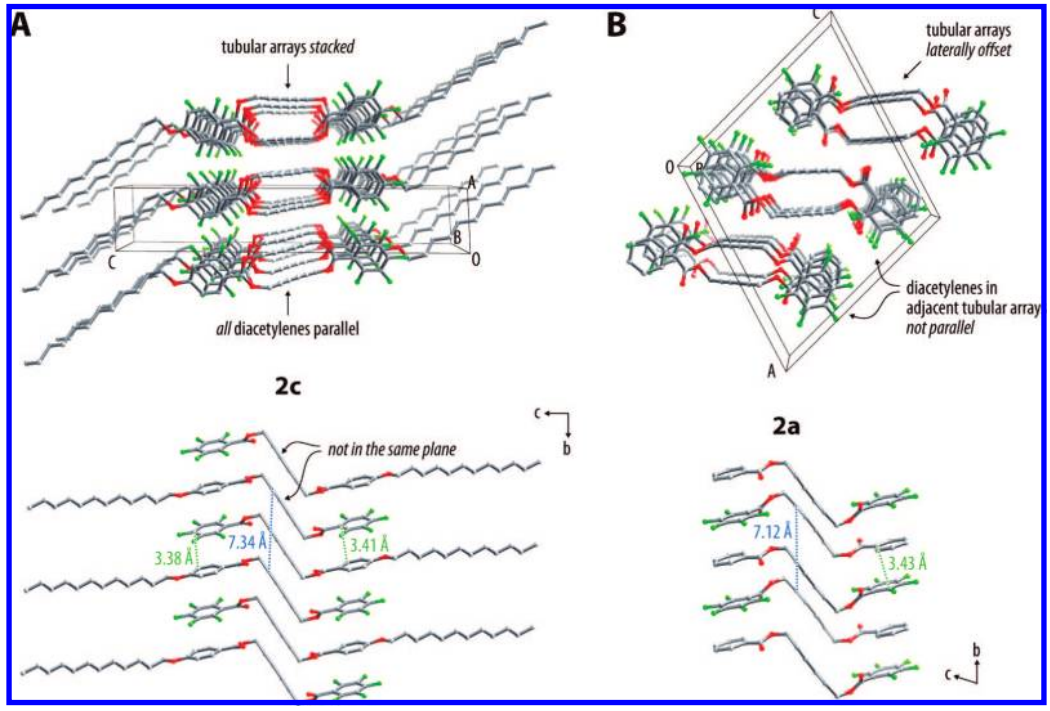


Figure 3. The crystal structure of both (A) **2c** and, for comparison, (B) **2a**[34] exhibited "*tubular arrays*" obtained via stacking dimers connected with perfluorophenyl−phenyl interactions along the [0 1 0] axis; the relative orientation of these "*tubular arrays*" was different, however; the perfluorophenyl−phenyl interaction not only was preserved in the dodecylated derivative **2c** but also showed an almost perfectly eclipsed stacking; the diacetylene functions of adjacent molecules in the [0 1 0] direction were not placed in the same plane so that identity periods of 7.34 and 7.12 Å were observed, respectively.

substituents. In all cases, the alternating perfluorophenyl and phenyl groups exhibited an almost perfectly eclipsed stacking with only a minimal parallel displacement and centroid−centroid distances close to the closest contact distances (Table 2). The alkoxy chains of adjacent stacks in **1b·3** and **2c** were interdigitated in order to accommodate the perfluorophenyl−phenyl stacking, and even the details of the diacetylene packing were virtually identical as compared to the respective nonalkylated siblings **1a·3** and **2a**. Thus, the molecular packing in the cocrystals **1a·3** and **1b·3** gave rise to a characteristic

Table 2. Comparison of Diacetylene Packing Parameters and Side Group Interactions in the Case of **1a**−**c** and **2a**−**c**, as well as **1a·3** and **1b·3**

	diacetylene packing parameters				side group interaction		
	lattice direction	diacetylene distance d[a] (Å)	inclination angle ϕ[b]	reactive carbon distance[c] (Å)	close contact distance[d] (Å)	centroid distance[e] (Å)	mode
1a	[0 1 0]	4.35	59°	4.02	3.60	4.35	parallel displaced
1b	[0 1 0]	7.756	57°	−	4.356	7.756	−
1c	[0 1 0]	7.670	58°	−	4.345	7.670	−
1a·3	[0 1 0]	7.56	35°, 38°[f]	−	−[h]	−[h]	−[h]
1a·3	[1 1 0]	4.62, 4.78[f]	51°, 54°[f]	3.84	3.48	3.82	eclipsed
1a·3	[1 −1 0]	4.80, 5.10[f]	46°, 53°[f]	3.79	3.44	3.76	eclipsed
1b·3	[0 1 0]	7.464	35°, 38°	−	−[h]	−[h]	−[h]
1b·3	[1 1 0]	4.59, 4.69[f]	52°, 53°[f]	3.80	3.385	3.75	eclipsed
1b·3	[1 −1 0]	4.76, 5.03[f]	48°, 51°[f]	3.77	3.402	3.72	eclipsed
2a	[0 1 0]	7.12	38°	−	3.25	3.78, 3.69	staggered, eclipsed[i]
2b	[1 0 0]	8.54	49°	−	n.a.	6.06[j]	edge-to-face[j]
2c	[0 1 0]	7.341	36°	−	−[h]	−[h]	−[h]
2c	[1 1 0]	4.840, 4.984[g]	53°, 45°[g]	3.929, 3.535	3.320	3.684	eclipsed
2c	[1 −1 0]	4.757, 4.380[g]	51°, 57°[g]	3.792, 3.910	3.284	3.660	eclipsed

[a] Identity period d along the [0 1 0] axis; in the case of **1a·3**, **1b·3**, and **2c** in the [1 1 0] and [1 −1 0] direction, the two different end-to-end distances between adjacent diacetylenes were given. [b] Inclination angle between the diacetylene axis and the respective crystallographic axis. [c] Distance between the two reactive carbon centers in adjacent diacetylenes. [d] Shortest contact distance between two carbons in the aromatic side groups of two adjacent molecules. [e] Distance between the centroids of the aromatic rings of two adjacent molecules. [f] The diacetylene moieties of **1** and **3** in the **1a·3** cocrystal and **1b** and **3** in the **1b·3** cocrystal were not aligned exactly parallel with respect to one another. [g] Both ends of each diacetylene of **2** have the same distance to the respective diacetylene ends adjacent, but the distance to the diacetylene above was different from the distance to the diacetylene below; accordingly, there were also two inclination angles. [h] The phenyl−perfluorophenyl pairs stacked along the [0 1 0] axis connected adjacent molecules in **1a·3**, **1b·3**, and **2c** in the [1 1 0] and [1 −1 0] directions, respectively; therefore, they were listed in the rows below. [i] There were two groups of disordered perfluorobenzoate groups in **2**, showing a staggered and an eclipsed face-to-face packing, respectively. [j] The edge-to-face interaction of a phenyl ring pointing toward the center of a perfluorophenyl ring in **2** did not involve adjacent molecules along the [1 0 0] axis.

"*zigzag*" chain of the molecules along the [1 0 0] axis for symmetry reasons, whereas they were arranged into "*tubular arrays*" along the [0 1 0] axis in the case of **2a** and **2c**.[45] As a result, the diacetylene moieties of adjacent monomers in the [0 1 0] direction were placed in different layers in all cases, so that the identity periods of the diacetylenes were twice the perfluorophenyl−phenyl stacking distance (Table 2) and, hence, inappropriate for a topochemical polymerization.

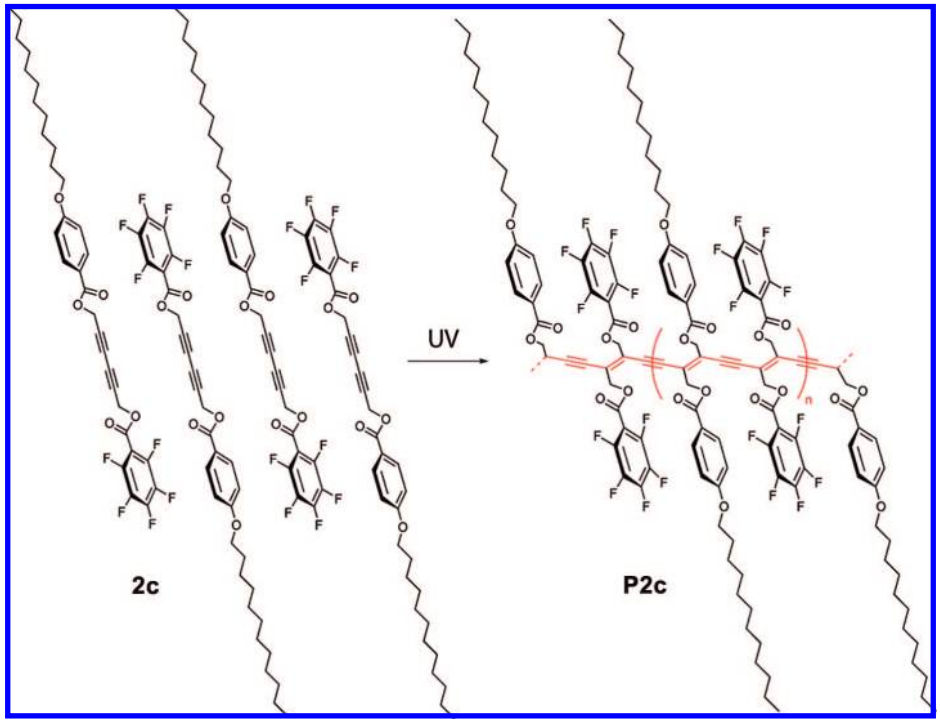
Due to the "lamellar packing" of the molecules and the interdigitation of the dodecyloxy chains in **2c**, however, the relative orientation of the "*tubular arrays*" was different from that in **2a**. In the crystal structure of **2a**, the diacetylene moieties in adjacent "*tubular arrays*" related by the glide-plane were not parallel to one another, and the "*tubular arrays*" were laterally offset. By contrast, all diacetylene functions had to be parallel by symmetry (inversion center) in **2c**, and additionally, adjacent "*tubular arrays*" were stacked on top of each other. As a consequence of this difference, **2c** featured continuous two-dimensional arrays of parallel diacetylene groups and geometries appropriate for topochemical polymerizations along the [1 1 0] and [1 −1 0] directions, as did **1a·3** and **1b·3** (Table 2).

From all of these experimental observations, one may conclude that, similar to the case of the alkoxy substituted derivatives **1b** and **1c** and by analogy with ABA triblock copolymers, the dodecyloxy chains in both **1b·3** and **2c** added an element of *phase segregation* between the aliphatic segments and the diacetylene cores.[45] However, this appeared to be rather an *additional factor* controlling the overall crystal structure which, at the same time, accommodated and preserved the perfluorophenyl−phenyl stacking. In fact, the crystallization of the dodecyl chains even appeared to *improve* the overall order in the perfluorophenyl−phenyl stacks and also induced a different packing of the stacks relative to one another. The most important consequence was that **2c**, similar to **1a·3** and **1b·3** but contrary to its nonalkylated sibling **2a**, featured *two-dimensional* ("*lamellar*") arrays of the diacetylene moieties and a diacetylene packing with an appropriate geometry for a topochemical polymerization *diagonal* to the lattice axes.

Topochemical Polymerization and Characterization of the Soluble Poly(diacetylene)s. The above analysis of the monomer crystal structures helped to identify both **1b·3** and **2c** as possible candidates for topochemical diacetylene polymerizations, exhibiting essentially the same geometric features as the polymerizable cocrystal **1a·3**.[34] Surprisingly, however, only the unsymmetrically substituted monomer **2c** was experimentally found to undergo a clean topochemical polymerization, producing the novel soluble poly(diacetylene) **P2c** (Scheme 2) in preparatively useful yields.[47] Thus, UV irradiation of the acetone-soluble, colorless monomer **2c** led to an instantaneous color change to bright red-orange. The material turned partially insoluble in acetone but remained soluble in DCM or chloroform. These solubility properties allowed separation of the polymer from the residual monomer by extraction with acetone and characterization of both the reaction mixture and the obtained pure poly(diacetylene) **P2c** in solution.

(47) The other monomers (**1a**−**c** as well as **2a** and **2b**) were not polymerizable, in agreement with the geometric features inappropriate for a topochemical polymerization. In the case of **1b·3**, UV irradiation caused a significant color change to bright orange. However, acetone extraction of the sample after 3 h of irradiation only yielded 3% of insoluble material; longer irradiation generated more material, but only in total isolated yields of below 5%. Nevertheless, the ^{1}H NMR and Raman spectra of the obtained material were consistent with poly(diacetylene) formation and resembled those of polymer **P2c**. As the crystal structure of **1b·3** was found to be similar to those of **1a·3** and **2c** and, in particular, the geometric parameters of the diacetylene packing were almost identical, the surprising lack of bulk polymerizability may tentatively be attributed to the overall poor crystal quality.

Scheme 2. Preparation of the Soluble Poly(diacetylene) **P2c** by Topochemical Polymerization of **2c** upon UV Irradiation



After acetone extraction, the pure poly(diacetylene) **P2c** was obtained as a deep red-orange powder. The polymer formed yellow solutions in DCM or chloroform, and the corresponding UV spectra[45] showed a maximum at $\lambda_{max} = 465$ nm with a molar extinction coefficient of $\varepsilon = 9.4 \times 10^6$ cm^2 mol^{-1}. Solid films obtained via dropcasting from DCM solution were red and exhibited two absorption maxima at $\lambda_{max} = 525$ nm as well as 485 nm. The solid state Raman spectrum obtained from **2c** after UV irradiation also showed that the monomer diacetylene absorption at 2264 cm^{-1} was replaced by the typical bands of poly(diacetylene) backbone double and triple bonds at 1509 and 2106 cm^{-1} (Figure 4A). A comparison of the solution-phase ^{13}C NMR spectra (Figure 4B) of **2c** and the corresponding poly(diacetylene) **P2c** proved that the four acetylene peaks at 71.8, 71.6, 69.9, and 68.2 ppm in the monomer spectrum had completely disappeared in the spectrum of the polymer, and the methylene groups attached to the diacetylene moieties were shifted from 54.1 and 52.3 ppm to 65.1 and 63.6 ppm, similar to what had been observed in the solid-state NMR spectra of **1a·3**.[34] Additionally, the new polymer backbone carbons could be observed as small, broad peaks at 128.5 and 127.4 as well as 99.8 and 98.4 ppm.

Furthermore, a comparison of the ^{1}H NMR spectra of the monomer **2c** with both the reaction mixtures during UV irradiation of the single crystals (after dissolution of the latter in $CDCl_3$) and the final polymer **P2c** (after acetone extraction) revealed several new or shifted peaks (Figure 5A). The aromatic proton signals were shifted from 8.0 to 7.7 ppm and from 6.9 to 6.7 ppm; the two signals of the CH_2 groups adjacent to the diacetylenes at around 5 ppm experienced a slight downfield shift; the dodecyloxy CH_2O group signal was shifted from 4.0 to 3.9 ppm; and all polymer peaks appeared broadened. The isolated yield of the pure polymer **P2c** after acetone extraction was determined to be 37% gravimetrically, which turned out to be acceptably consistent with the conversion of around 38% determined from the relative integration of the aromatic protons at 8.0 and 7.8 ppm in the ^{1}H NMR spectra of the reaction mixture obtained from the dissolved irradiated crystalline material. Therefore, the polymerization kinetics could conveniently be followed by irradiating crystalline powders of **2c**, dissolving samples after different time intervals in $CDCl_3$, and determining the conversion via integration in the ^{1}H NMR spectra (Figure 5B). Thus, in representative polymerization experiments, a maximum conversion of about 40% was already reached after around 360 min of UV irradiation. The reaction kinetics could be reasonably well described with a fitting function $x_p(t) = x_\infty \cdot t/(a + t)$ which had previously been used in the literature[48] as well as, even better, a second-order exponential function. Both types of functions, however, are unfortunately devoid of any mechanistic meaning. The limiting factor for a higher conversion appeared to be mainly the crystal quality, as was confirmed by irradiating larger single crystals in a separate experiment, resulting in 51% yield after 20 h of UV irradiation (Figure 5B).

GPC measurements of polymer **P2c** in chloroform at 35 °C suggested a molecular weight of $M_n = 2 \times 10^6$ (PDI = 4.5). However, the very broad multimodal elution peak near the upper exclusion limit may as well suggest (partial) aggregation and shear-induced degradation of the polymer on the column. Therefore, the molecular weight of polymer **P2c** was also evaluated by static light scattering. Polymer **P2c** exhibited a radius of gyration $R_g = 80$ nm. Comparing this value with the radius of gyration and molecular weight of poly(diacetylene)s reported in the literature[49] resulted in an estimated molecular weight of $M_w = 9 \times 10^5$ which may be a more reliable approximation than the value derived from GPC.

(48) Tieke, B.; Wegner, G. *Makromol. Chem.* **1978**, *179*, 1639–1642.
(49) Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837–850.

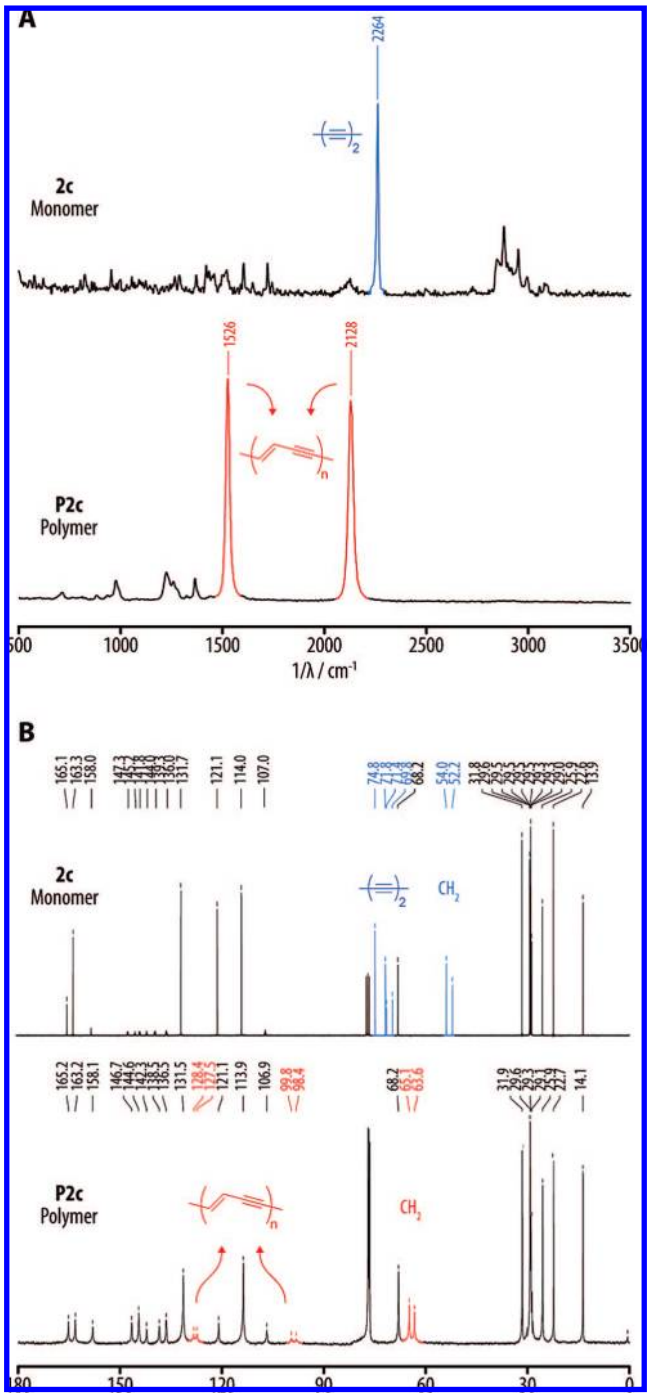


Figure 4. (A) Solid-state Raman spectra and (B) high-resolution solution-phase ^{13}C NMR spectra of diacetylene **2c** and the pure poly(diacetylene) **P2c** after UV irradiation of **2c** and extraction of residual monomer with acetone.

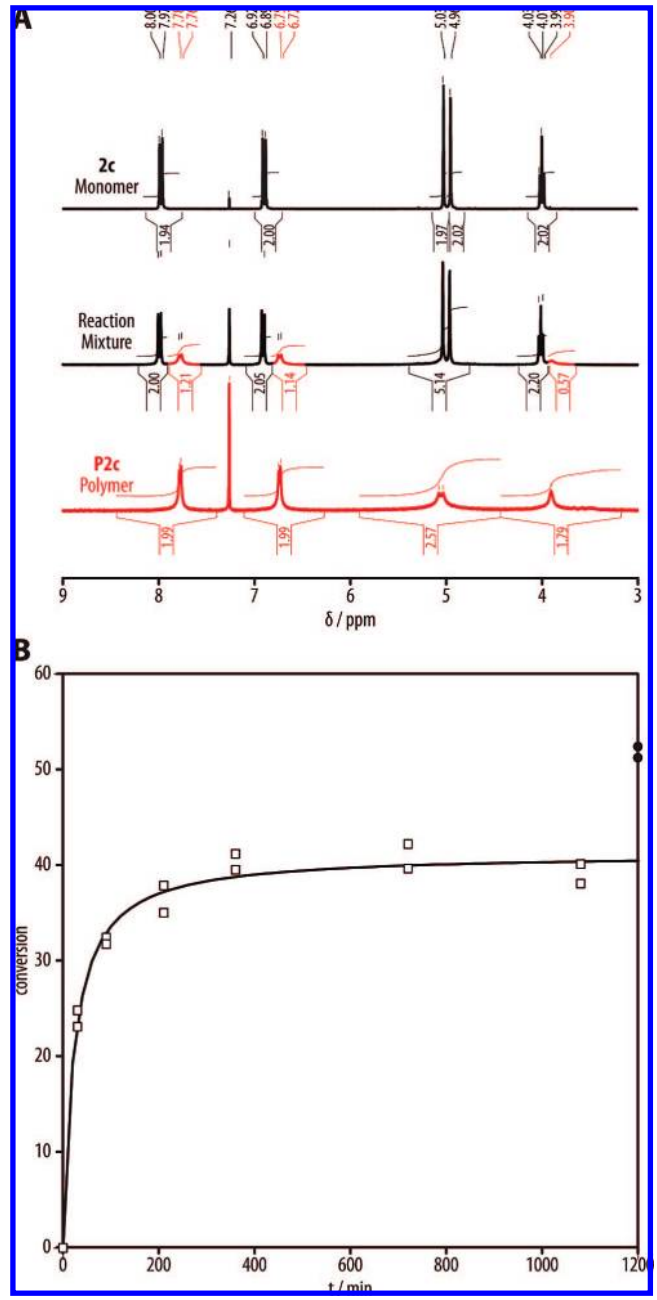


Figure 5. (A) Relative integration of the polymer and the monomer peaks in the ^{1}H NMR spectra of **2c** after different periods of UV irradiation and dissolution in $CDCl_3$ allowed following the polymerization kinetics; (B) in representative experiments (□), a maximum conversion was reached after about 360 min of irradiation, and the kinetics were reasonably well described by the function $x_p(t) = x_\infty \cdot t/(a + t)$ (solid line); however, irradiation of larger single crystals led to higher conversion (●), indicating that the crystal quality was the limiting factor for conversion.

Finally, the crystal structure of **2c** after 18 h of irradiation could be solved as a superposition of the monomer **2c** (85%) and the polymer **P2c** (15%), which helped to unambiguously confirm the polymer structure (Figure 6C). While **P2c** may formally be regarded as an alkylated sibling of the previously described alternating copolymer **P(1a·3)**, the polymer microstructure is noticeably different, featuring an alternating sequence of two different types of symmetrically substituted olefin bonds along the backbone, carrying two alkoxyaryl or two perfluoroaryl residues, respectively. The X-ray structure analysis of the poly(diacetylene) **P2c** not only unambiguously confirmed the polymer structure but also provided more details about the process of polymer formation. Similar to what we had previously reported for **1a·3**,[34] geometric parameters approximately in the range of those required for a topochemical polymerization were observed along both of the crystallographic [1 1 0] and the [1−1 0] directions in the crystal structure of **2c** (Table 2). The more optimal *average* packing parameters were observed in the [1 1 0] direction (Table 2), and accordingly, the polymerization was found to proceed along this axis. Interestingly, the polymerization direction coincided with the perfluorophe-

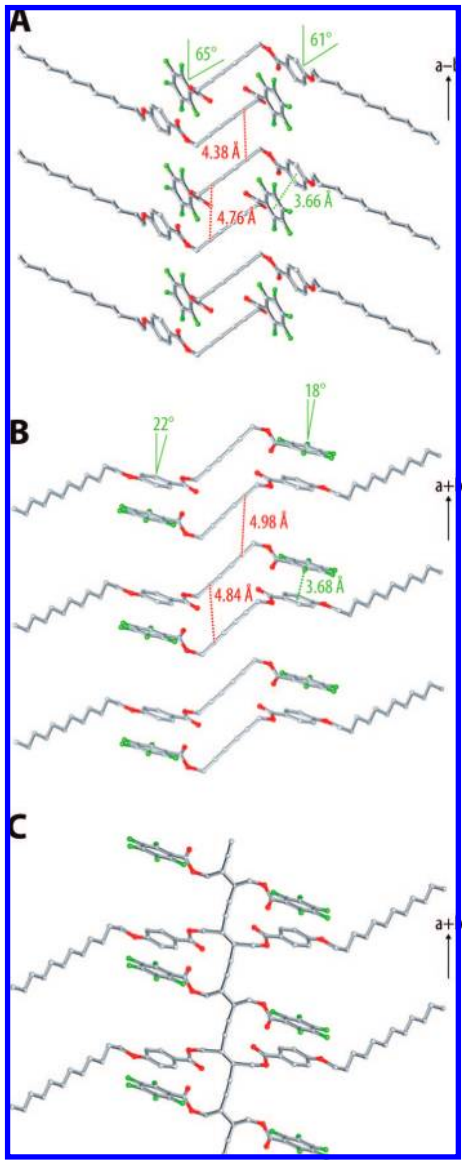


Figure 6. (A,B) Parameters appropriate for a topochemical polymerization were observed along both the crystallographic [1−1 0] and the [1 1 0] direction, but the more optimal parameters were observed in the latter case; furthermore, the perfluorophenyl−phenyl stacking direction was almost parallel to the [1 1 0] axis; (C) the crystal structure of the obtained poly(diacetylene) **P2c** (solved as a superposition of monomer and polymer structure from a UV irradiated and partially polymerized crystal of monomer **2c**) proved that the polymerization proceeded along [1 1 0] and the perfluorophenyl−phenyl interaction persisted in the side chains of the polymer.

nyl−phenyl stacking direction, as the normal vectors of the phenyl (perfluorophenyl) ring planes were inclined only 21.9° (17.8°) against the [1 1 0] axis (Figure 6B) but 60.6° (64.9°) against the [1−1 0] axis (Figure 6A). As had been the case for **1a·3**, the perfluorophenyl−phenyl interaction in **P2c** persisted almost unchanged between the side groups, although, this time, the phenyl and perfluorophenyl ring planes were not exactly parallel anymore in the polymer. Nevertheless, it appeared as if the perfluorophenyl−phenyl interaction "stitched together" the polymer so that the "mechanical properties" of the ester group as the flexible hinge only allowed the polymerization to proceed along the specified lattice direction.

Conclusions

Based on the successful synthesis and recrystallization of different diacetylene monomers and the comparison of their (co)crystal structures, it may be concluded that the phenyl−perfluorophenyl interaction qualifies, in most cases,[46] as a reliable supramolecular motif in the crystalline state, in the sense that it can be utilized to establish a certain molecular packing even when combined with other supramolecular synthons. Thus, the characteristic packing features including the appropriate arrangement of the diacetylene moieties for a topochemical polymerization already observed in the cocrystal of the two mutually complementary, unsubstituted diacetylenes **1a** and **3** were preserved in the case of the dodecyloxy-substituted self-complementary diacetylene monomer **2c**. The latter was successfully polymerized by UV irradiation, affording the soluble poly(diacetylene) **P2c** in preparatively useful yields. According to the crystal structure of this polymer, the perfluorophenyl−phenyl interactions appeared to determine the direction of the polymerization and persisted as a side group interaction in the final polymer. This fact combined with the solubility profile of **P2c** makes it an interesting candidate for processing into oriented thin films, the optoelectronic properties of which are currently under investigation.

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Note Added after ASAP Publication. Due to a production error the version published on the Web July 25, 2008, contained errors. These errors have been corrected in the version published on the Web July 31, 2008, and in the print issue.

Supporting Information Available: Detailed experimental procedures; ^{1}H and ^{13}C NMR spectra of **1b**, **1c**, **2b**, **2c**, **4a**, and **4b**; ^{19}F NMR spectra of **2b** and **2c**; UV spectra of **P2c** and other additional or enlarged figures; complete crystallographic data (CIF files) of **1b**, **1c**, **2b**, **2c**, **1b·3**, and **P2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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