

Photoinitiated Polymerization of Columnar Stacks of Self-Assembled Trialkyl-1,3,5-benzenetricarboxamide Derivatives

Mitsutoshi Masuda,[†] Pascal Jonkheijm, Rint P. Sijbesma,* and E. W. Meijer*

Contribution from the Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

Received August 14, 2003; E-mail: r.p.sijbesma@tue.nl; e.w.meijer@tue.nl

Abstract: A disk-shaped molecule, *N*-(5-sorbyl-pentyl)-*N,N'*-di(*n*-octyl)benzene-1,3,5-tricarboxamide (**1**), has been synthesized and assembled into a columnar stack in cyclohexane. Using a photoinitiated process, we polymerized monomer **1** in its self-assembled state and analyzed the resulting **poly-1**. On cooling a boiling cyclohexane solution of **1**, the molecules aggregate via amide hydrogen bonds, as supported by the position of the N–H stretching band in FT-IR spectroscopy. Evidence of helical columnar stacking of **1** in the aggregate is provided by an induced CD effect upon blending **1** with a chiral side-chain homologue **3** in a so-called “sergeants and soldiers” experiment. The columnar assembly in cyclohexane was polymerized by UV light (365 nm) irradiation in the presence of 2,2-dimethoxy-2-phenylacetophenone as radical photoinitiator. The polymerization occurs selectively to give 1,4-polymer with isolated trans C=C bonds, as shown by FT-IR, and ¹H and ¹³C NMR spectroscopy. Lack of polymerization of methyl sorbate (**4**) under identical conditions, and low incorporation of **4** in copolymerizations with **1** in cyclohexane, suggests that the polymerization preferentially occurs within the columnar assembly. Size exclusion chromatography shows that the degree of polymerization (X_n) based on number average molecular weight is approximately 65. Incorporation of small amounts of nonpolymerizable derivatives **2** and **3** into the columns has no effect on X_n and conversion. Molecular models show that the polymerizable sidearm of **1** is long enough to span the distance between the monomers in the chiral stack. Under the atomic force microscope (AFM), purified samples of polymerized **1** displayed nanometer-sized fibrous morphologies with a high-axial-ratio (> 150), uniform width (60 nm), and a thickness (1.0 nm) which corresponds to the width of the benzene tricarboxamide core of **1**, whereas aggregates of nonpolymerized **1** yield a featureless image due to their instability.

Introduction

Self-assembled columnar structures of stacked aromatic compounds are attractive building blocks for supramolecular electronics,^{1–3} because they possess the necessary one-dimensional nanometer-sized architecture to function in charge or energy transport. 1,3,5-Benzenetricarboxamides are synthetically easy to access and self-assemble in the crystal,⁴ in the liquid crystalline state,⁵ and in both organic and aqueous media to form columnar structures via triple amide hydrogen bonding.⁶ In previous work, we have studied derivatives with chiral side chains, which express supramolecular helicity within the column due to helical strands of amide hydrogen bonds. Addition of

chiral components to columnar assemblies of achiral 1,3,5-benzenetricarboxamides was shown to bias their helicity^{6d} in a supramolecular form of the “sergeants and soldiers” principle.⁷

Covalent fixation of self-assembled objects is an important issue in supramolecular chemistry,^{8,9} and polymerization of a chiral or helical arrangement of molecules in liquid crystalline phases has important technological applications.¹⁰ Polymerization of columnar aggregates fixes and stabilizes objects with a well-defined structure and enables further processing such as modification and positioning. So far, many attempts have been

[†] Current address: Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

(1) Neher, D. *Adv. Mater.* **1995**, *7*, 691–701.
(2) Disch, S.; Finkelmann, H.; Ringsdorf, H.; Schuhmacher, P. *Macromolecules* **1995**, *28*, 2424–2428.
(3) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyonovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384–387.
(4) Lightfoot, M. P.; Mair, F. S.; Pritchard, R. G.; Warren, J. E. *Chem. Commun.* **1999**, 1945–1946.
(5) (a) Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197–3198. (b) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. *J. Am. Chem. Soc.* **2001**, *123*, 8157–8158.

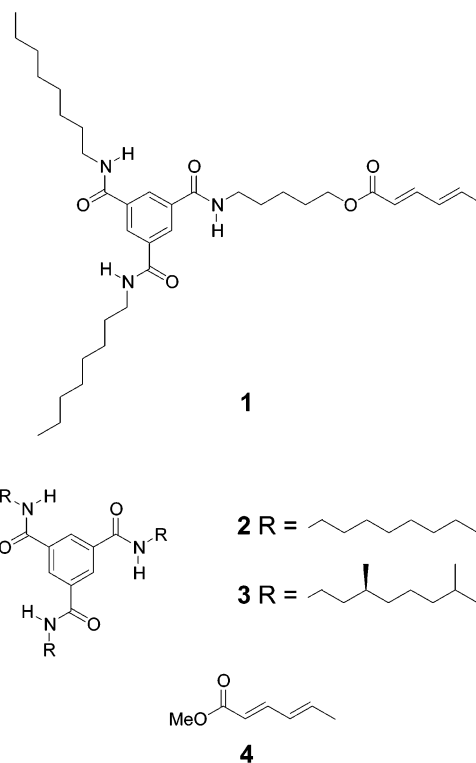
(6) (a) Yasuda, Y.; Iishi, E.; Inada, H.; Shirota, Y. *Chem. Lett.* **1996**, 575–576. (b) Hanabusa, K.; Koto, C.; Kimura, M.; Shirai, H.; Kakehi, A. *Chem. Lett.* **1997**, 429–430. (c) Matsunaga, Y.; Miyajima, N.; Nakayasu, Y.; Sakai, S.; Yonenaga, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 207–210. (d) Brunsveld, L.; Schenning, A. P. H. J.; Broeren, M. A. C.; Janssen, H. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Lett.* **2000**, 292–293. (e) Gorp, J. J. v.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 14759–14769.
(7) Green, M. M.; Reidy, M. P.; Johnson, R. D.; Darling, G.; O’Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452–6454.
(8) For reviews, see: (a) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153–180. (b) Mueller, A.; O’Brien, D. F. *Chem. Rev.* **2002**, *102*, 727–758. (c) Tajima, K.; Aida, T. *Chem. Commun.* **2000**, 2412, 2399–2412. (d) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113–158.
(9) For examples, see: Gray, D. H.; Hu, S.; Juang, E.; Gin, D. L. *Adv. Mater.* **1997**, *9*, 731–735.
(10) Broer, D. J.; Lub, J.; Mol, G. N. *Nature* **1995**, *378*, 467–468.

reported concerning polymerization of self-assemblies in organic and aqueous media, but relatively few successful attempts have been reported for polymerization of columnar structures^{5a,11} or other one-dimensional assemblies such as nanoscale fibers¹² or giant wormlike micelles.¹³ Major issues that complicate the covalent fixation of columnar aggregates by means of polymerization are the possibility of cross-linking between columns and incompatibility of the repeat distance of the polymer chain with the stacking distance of the monomers in the column.

Molecular Design

To polymerize columnar self-assemblies based on C_3 -symmetrical benzene-tricarboxamides with minimal distortion of the well-defined architecture, we focused on two additional requirements for the molecular design of the polymerizable group: (1) avoiding cross-linking and (2) compatibility of the repeat distance. Two completely different strategies to prevent intercolumnar reaction can be envisaged. In one strategy, either a step polymerization or a chain polymerization of molecules with multiple reactive groups is used, and placing the reactive groups away from the periphery prevents intercolumnar reaction.^{11e} A strategy using multiple reactive groups has been shown to work well in self-assembled polymer aggregates,^{13,14} or in condensed phases, where the dynamics of the self-assembly processes are slow. In solution, where the dynamics are much faster, an alternative strategy to prevent cross-linking is proposed by using a chain polymerization and a single polymerizable group per molecule. When a chain polymerization is used to connect consecutive layers of columnar aggregates of benzene-tricarboxamides, the polymerizable group attached to the self-assembly unit is required to give a polymer chain with a distance between repeating units that is equal to, but not shorter than, the stacking distance of the columnar assemblies, which is 0.36 nm.⁴ If the distance is less, the length of the polymer chain does not match the columnar length, the polymerization will terminate early, or the columnar architecture may even be lost. Furthermore, the angle between consecutive monomers (ca. 60° in the crystal structure of a benzene-1,3,5-tricarboxamide derivative⁴) requires additional length. This requirement precludes the use of efficient 1,2-polymerization processes such as the radical polymerization of (meth)acrylates, which give a repeating distance of around 0.25 nm. 1,4-Chain polymerizations, on the other hand, give a repeating unit distance around 0.48 nm,¹⁵ giving some freedom in the offset of groups from disk to disk. Polymerizations of diacetylenes and dienes have been used extensively in topochemical reactions in the crystalline state,¹⁶ in thermoplastic

elastomers,¹⁷ and for the polymerization of bilayer¹⁸ and monolayer^{16c,19} membranes and hexagonal mesophases.^{11f,20} However, the strict steric requirements for the 1,4-polymerization of diacetylenes limit the use of this functional group in less ordered phases. Therefore, we have chosen the sorbate moiety as a polymerizable unit in trialkyl-benzenecarboxamide derivative **1**. In this Article, the synthesis of the monomer **1**, its self-assembly properties, the polymerization within the assemblies, the studies of the stereochemistry, and the morphology of the polymers obtained are disclosed.



Results

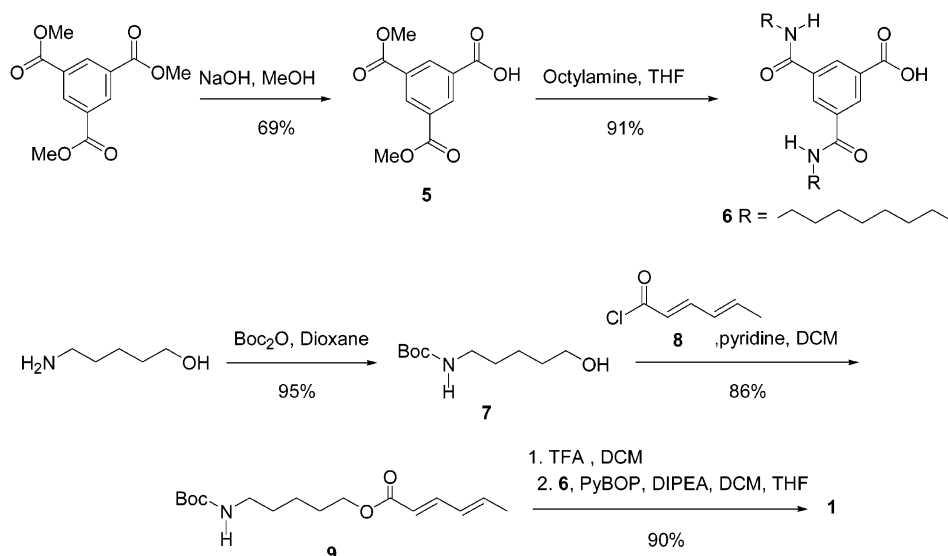
Synthesis. Monomer **1** was synthesized by the hydrolysis of one of the methyl ester groups of benzene-1,2,3-tricarboxylic acid trimethylester using 1 equiv of sodium hydroxide in 69% yield, followed by amidation of the two remaining ester groups with *n*-octylamine in 91% yield and the condensation of the carboxylic acid group with 6-aminopentyl sorbate in 90% yield (Scheme 1). Monomer **1** was fully characterized by ¹H and ¹³C NMR, FT-IR spectroscopy, and elemental analysis. The stereochemistry of the sorbyl group in **1** was confirmed to be more than 98% of the *E,E*-configuration based on ¹H NMR spectroscopy. The synthesis of the nonpolymerizable derivatives, achiral **2** and chiral **3**, has been reported previously.^{6c,d}

Neat monomer **1** forms an enantiotropic columnar mesophase at elevated temperature (melting temperature (T_m) = 158–161

- (11) (a) Percec, V.; Ahn, C.-H.; Ungar, G.; Yearley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161–163. (b) Percec, V.; Ahn, C.-H.; Barboiu, B. *J. Am. Chem. Soc.* **1997**, *119*, 12978–12979. (c) Percec, V.; Schlueter, D. *Macromolecules* **1997**, *30*, 5783–5790. (d) Percec, V.; Holerca, M. N. *Biomacromolecules* **2000**, *1*, 6–16. (e) Percec, V.; Ahn, C. H.; Bera, T. K.; Ungar, G.; Yearley, D. J. P. *Chem.-Eur. J.* **1999**, *5*, 1070–1083. (f) Drager, A. S.; Zangmeister, R. A. P.; Armstrong, N. R.; O'Brien, D. F. *J. Am. Chem. Soc.* **2001**, *123*, 3595–3596.
- (12) (a) Masuda, M.; Hanada, T.; Yase, K.; Shimizu, T. *Macromolecules* **1998**, *31*, 9403–9405. (b) Inoue, K.; Ono, Y.; Kanekiyo, Y.; Hanabusa, K.; Shinkai, S. *Chem. Lett.* **1999**, 429–430. (c) Tamaoki, N.; Shimada, S.; Okada, Y.; Belaisaoui, A.; Kruk, G.; Yase, K.; Matsuda, H. *Langmuir* **2000**, *16*, 7545–7547.
- (13) Won, Y. Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960–963.
- (14) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384–389.
- (15) Natta, G.; Farina, M.; Donati, M. *Makromol. Chem.* **1961**, *43*, 251–254.
- (16) (a) Tieke, B. *J. Polym. Sci., Polym. Chem.* **1984**, *22*, 2895–2921. (b) Matsumoto, A.; Nagahama, S.; Odani, T. *J. Am. Chem. Soc.* **2000**, *122*, 9109–9119. (c) Tieke, B. *Colloid Polym. Sci.* **1985**, *263*, 965–972.

- (17) (a) Agrawal, R. N.; Rubner, M. F. *Macromolecules* **1990**, *23*, 1017–1025. (b) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1991**, *24*, 526–529. (c) Beckham, H. W.; Rubner, M. F. *Macromolecules* **1993**, *26*, 5192–5197. (d) Hammond, P. T.; Rubner, M. F. *Macromolecules* **1995**, *28*, 795–805.
- (18) (a) Sission, T. M.; Srisiri, W.; O'Brien, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 2322–2329. (b) Lamparski, H.; O'Brien, D. F. *Macromolecules* **1995**, *28*, 1786–1794.
- (19) Barraud, A.; Rosilio, C.; Ruauel-Teixier, A. *Polym. Prepr.* **1978**, *19*, 179–182.
- (20) Srisiri, W.; Sission, T. M.; O'Brien, D. F.; McGrath, K. M.; Han, Y.; Gruner, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 4866–4873.

Scheme 1



°C, clearing temperature (T_c) = 171 °C) as concluded from the flowerlike texture observed for a sample under polarized optical microscopy and the miscibility with the known columnar mesophase of **2**, indicating that the monomers stack on top of each other. Compound **1** has a higher melting point but a lower clearing temperature than the saturated chain chiral analogue **2** (T_m = 102 °C, T_c = 204 °C) and achiral analogue **3** (T_m = 119 °C, T_c = 236 °C).

Self-Assembly in Cyclohexane. Cyclohexane was chosen as solvent for the self-assembly and the polymerization of **1** for its low polarity, its compatibility with amide hydrogen bond formation, and its low reactivity toward growing radicals.²¹ Monomer **1** is soluble in boiling cyclohexane (approximately 1×10^{-2} mol/L), and solutions become slightly viscous on cooling, indicating self-assembly formation similar to other 1,2,3-benzenetricarboxamide derivatives.^{6a,b} At concentrations below 1×10^{-1} M, gel formation is not observed, probably due to the absence of physical cross-links between columns, whereas longer chain homologues do form gels at similar concentrations.^{6b} In FT-IR spectra of cyclohexane solutions of **1** (Figure 1b–d), an amide N–H stretching band is observed around 3241 cm^{-1} at 22 °C. The appearance of the NH stretch region does not change upon dilution to a concentration of 1×10^{-4} M, and N–H bands attributable to molecularly dissolved species, which are observed in CHCl_3 solution (Figure 1a), remain absent. A non-H-bonded amide I band of **1** in CHCl_3 appears at 1665 cm^{-1} . In cyclohexane, this band appears at 1647 and 1630 cm^{-1} . These results indicate that the monomers are stacked on top of each other via amide hydrogen bonds as has been observed for the columnar self-assemblies of **2**, **3**, and their mixtures. The hydrogen-bonded stacks are in agreement with an X-ray structure of a model benzene 1,3,5-tricarboxamide.⁴

The self-assembly in dilute solution was investigated using CD spectroscopy on mixtures of **1** and **3** in cyclohexane (Figure 2). Obviously, a solution of achiral monomer **1**, at a concentration of 3.35×10^{-5} mol/L, does not show a Cotton effect. However, upon mixing this solution with a small amount of a

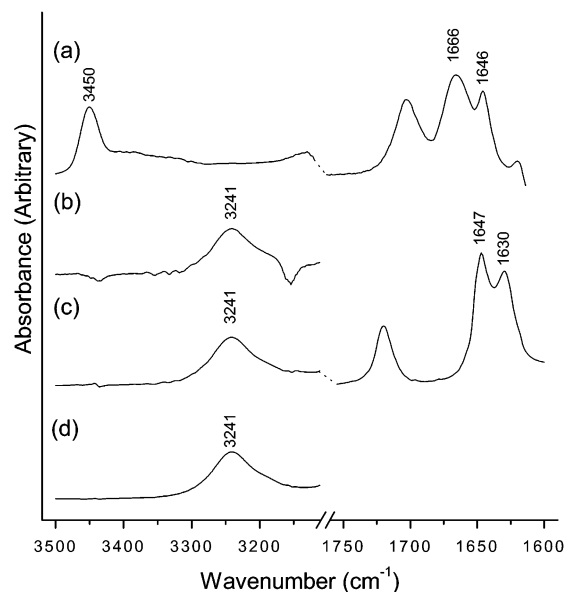


Figure 1. Solution IR spectra of **1** at 22 °C. (a) 1.18×10^{-4} mol/L in CHCl_3 , (b) 8.92×10^{-5} mol/L in cyclohexane, (c) 8.92×10^{-4} mol/L in cyclohexane, and (d) 8.92×10^{-3} mol/L in cyclohexane.

solution of chiral **3**, a negative Cotton effect was observed at the absorption maxima of the phenyl and sorbyl chromophores. A strong sergeant and soldiers effect⁷ was observed. At a wavelength of 222 nm, the Cotton effect reaches saturation at 5% of **3** (Figure 2, inset), indicating that a small amount of **3** controls the helicity of columns of **1** in a highly cooperative self-assembly process. The CD spectra also show a significant Cotton effect at 250 nm, the absorption maximum (λ_{max}) of the sorbyl group, confirming that the molecules of **1** are incorporated in the helical assemblies and that the sidearm as well as the benzene tricarboxamide core are in a well-defined chiral environment.

Variable-temperature (VT) CD spectra of a solution of a mixture of **1** and **3** containing 6.75% **3**, at a total concentration of 6.7×10^{-5} M, indicate that the ellipticity is gradually lost upon heating and reversibly disappears at 75 °C (Figure 3). The loss of ellipticity upon heating in this experiment is presumably the combined result of the loss of helicity of the columns and

(21) Odian, G. *Principles of Polymerization*, 3rd ed.; A Wiley-Interscience Publication: New York, 1991.

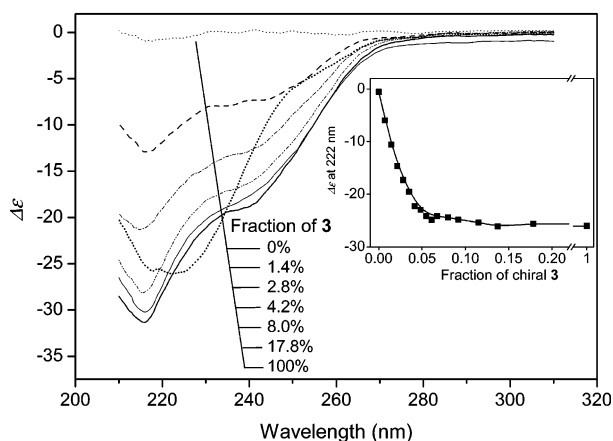


Figure 2. CD spectra of mixtures of **1** and **3** in cyclohexane at 22 °C at a total concentration of 3.3×10^{-5} mol/L. Inset: $\Delta\epsilon$ value at 222 nm as a function of the mole fraction of chiral **3**.

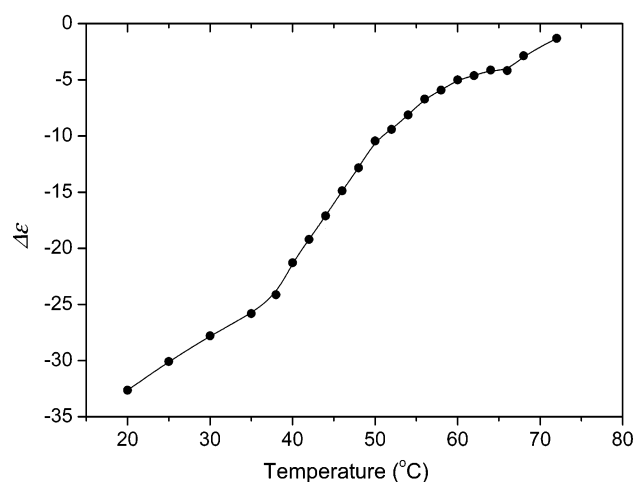


Figure 3. Temperature dependence of the Cotton effect at 222 nm of a solution of **1** mixed with 6.75 mol % of **3** in cyclohexane.

a decreasing average column length. The latter decreases both the cooperativity and the strength of the sergeant and soldiers effect. To polymerize the aggregates in the helical state, polymerizations were performed at room temperature.

Polymerization. Polymerization of self-assembled **1** in cyclohexane was performed using Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) as a radical photoinitiator and UV-light ($\lambda_{\text{max}} = 365$ nm) to generate radicals. Direct photoactivation of **1**, which has been shown to give low degrees of polymerization^{18b} and mainly dimerization,¹⁹ was prevented by filtering the light through glass (cutoff wavelength 325 nm). Upon UV-irradiation at 25 °C, the cyclohexane solution of **1** became slightly turbid and more viscous. Progression of the polymerization was monitored by FT-IR spectroscopy, using the changes in intensity of the monomer band at 1000 cm^{-1} and the polymer band at 972 cm^{-1} (see below). After 5 h, the ratio of these bands did not change significantly, and irradiation was stopped. This time corresponds to approximately 4 times the half-life (70 min) of the photoinitiator under the prevailing reaction conditions. **Poly-1** was isolated by removal of the solvent and subsequent washing with diethyl ether to remove unreacted monomer. Finally, the polymer was purified by Soxhlet extraction with diethyl ether.

Spectroscopic Characterization. Polysorbates can be formed via 1,2-, 1,4-, or 3,4-polymerization. The microstructure of

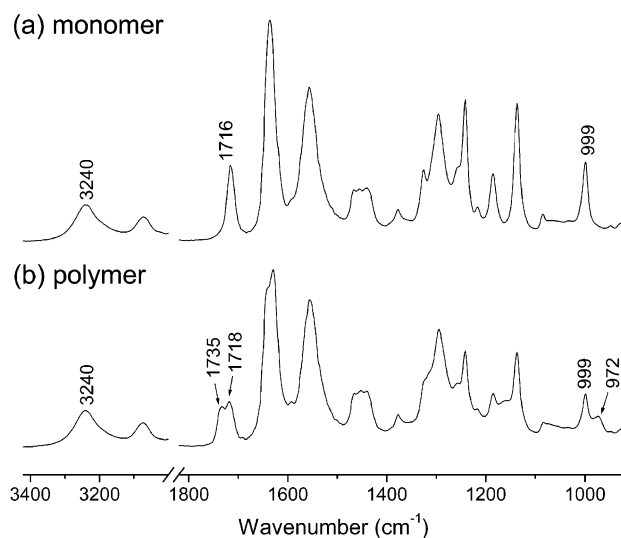


Figure 4. FT-IR spectra of **1** and **poly-1** as cast from cyclohexane.

poly-1 was characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy.^{16c,18b,22} The FT-IR spectrum of **1** displays a conjugated C=C wagging mode of the sorbyl group at 1000 cm^{-1} . The intensity of this band decreases upon irradiation (Figure 4a and b). Simultaneously, a new band appears at 972 cm^{-1} which is attributed to an isolated trans C=C bond, indicating 1,4-polymerization of **1**.^{16c} In addition, the FT-IR spectrum of the product shows a band for a nonconjugated ester carbonyl group at 1732 cm^{-1} . The hydrogen-bonded N-H stretching band is observed at the same frequency (3241 cm^{-1}) before and after irradiation, indicating that polymerization of the sorbyl ester groups does not significantly disturb the columnar structure of the self-assembled aggregates.

^1H NMR spectra of **1** and the purified **poly-1** (Figure 5a and b) indicate that irradiation results in 1,4-polymerization. The vinyl proton peaks (7.21, 6.13–6.66, and 5.75 ppm) of the sorbate monomer have disappeared, and a new single broad peak (5.36 ppm), assigned to isolated trans double bonds of 1,4-polymer, appears for polymerized **1** (Figure 5a and b). The formation of 3,4-polymer is excluded because no vinyl proton signals around 6.9–7.0 and 5.7–5.8 ppm are observed.^{18b,23} The spectral regions around 0.9 and 1.6 ppm contain the methyl signals of 1,4-polymerization product (*a* in Figure 5b) and 1,2-polymerization product, respectively. Although these signals overlap with the methyl group of the octyl chain (*n*) and with a number of methylene protons (*g*, *i*, and *l*), respectively, the integral ratio of these areas shows that 1,4-addition accounts for more than 95% of the polymerization.

The ^{13}C NMR spectrum of **poly-1** provides more specific information on the stereochemistry of the double bond. The chemical shifts of two sets of tertiary carbons adjacent to the double bond (carbon atom *b* in the structure of Figure 5b resonating at 39.6 ppm, and carbon atom *e* in the structure of Figure 5b resonating at 56.4 and 55.0 ppm²⁴) are in good agreement with the reported²⁵ peak positions of poly(methyl

(22) Tsuchida, E.; Hasegawa, E.; Kimura, N.; Hatashita, M.; Makino, C. *Macromolecules* **1992**, *25*, 207–212.

(23) Naf, F.; Degen, P. *Helv. Chim. Acta* **1971**, *54*, 1939–1949.

(24) See Supporting Information for spectra.

(25) Hertler, W. R.; Ovenall, D. W.; Reddy, G. S.; Sogah, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 5841–5853.

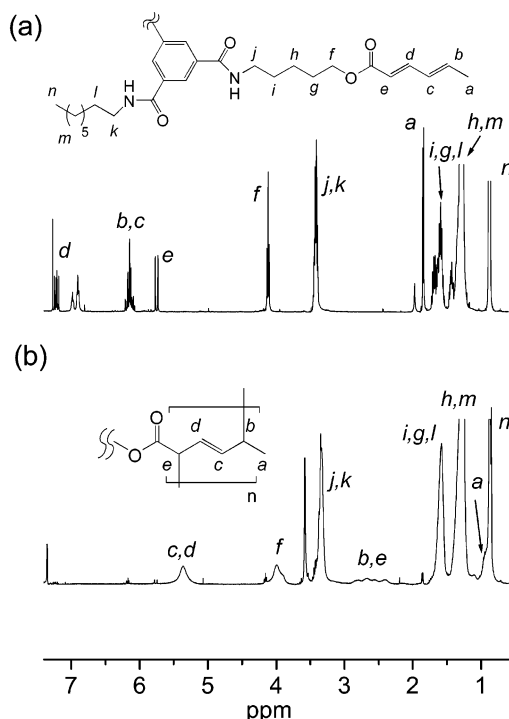


Figure 5. ^1H NMR spectra of monomer **1** in CDCl_3 (a). **Poly-1** in d_4 -methanol/ CDCl_3 9:1 v/v (b).

sorbate) having the trans conformation, and no peaks attributable to the cis conformation are observed (see Supporting Information).

Size Exclusion Chromatography. SEC analysis using THF or CHCl_3 as eluent shows that **poly-1** has a large polydispersity ($\text{PDI} > 7$) and high molecular weight ($> 10^6$) probably due to intermolecular aggregation. Therefore, the polymer was treated with hydrochloric methanol to disconnect the benzene tricarboxamide unit by transesterification as reported for polysorbyl esters by Tsuchida²² and O'Brien.^{18b} After transesterification, a polymer was obtained that is soluble in CDCl_3 . The ^1H NMR spectrum of the treated **poly-1** shows that more than 95% of the benzene tricarboxamide units have been detached from the polymer backbone. Subsequent molecular weight analysis using GPC reveals definitive evidence of polymerization. The degree of polymerization (X_n) values based on number-average molecular weight, conversion, and polymerization conditions are summarized in Table 1. The polymerization of **1** shows constant X_n (around 56–66, runs 1 and 2 in Table 1) against the variation of $[\text{M}]$ to $[\text{I}]$ ratio, while it is proportional to $[\text{I}]$ for polymerization within bilayer membranes.^{18b}

Evidence of Polymerization within the Assemblies. To investigate whether polymerization selectively occurs within the columnar assemblies, copolymerization of self-assembled **1** with methyl sorbate **4** was studied, using a solution with a monomer ratio $[\text{4}]/[\text{1}]$ of 2. The copolymer obtained shows a polymer incorporation ratio of $[\text{4}]/[\text{1}]$ of 0.14 based on NMR integral ratios, while the X_n decreases from approximately 60 for the homopolymerization of **1** to $X_n = 8$ for the copolymer (Table 1, entries 6–7). Under the same conditions, attempts to polymerize **4** do not give polymer, but dimers and trimers are obtained with low conversion even when the concentration was increased to 1 M. The very low polymerizability of the molecularly dispersed sorbyl ester **4** is attributable to the low

Table 1. Polymerization Condition, Number Average Degree of Polymerization (X_n), Polydispersity (PDI), and Conversion of Polymer **1**

run	monomer	$[\text{M}]$ (mol/L)	additive	$[\text{M}]/[\text{I}]$	PDI (M_w/M_n)	conversion (%)	X_n^a
1	1	1.03×10^{-2}		50	1.52	37.2	65.5
2	1	1.06×10^{-2}		15	1.75	46.7	56.5
3	1	1.03×10^{-2}	2 ^b	50	1.58	32.1	65.4
4	1	1.03×10^{-2}	2 ^c	50	1.64	37.4	80
5	1	1.06×10^{-2}	3 ^d	50	2.70	59.7	45.8
6	1/4 ^e	3.63×10^{-2}		5	1.90	29 ^f	7.5
7	1/4 ^e	3.63×10^{-2}		50	1.80	5.0 ^g	8.0
8	4	1.00×10^{-2}		50	<i>h</i>	trace	2–3
9	4	1.00×10^{-1}		50	<i>h</i>	trace	2–3
10	4	1.00		50	1.12	6.4	3

^a X_n values were calculated after methanolysis. ^b $[\text{2}]/[\text{1}] = 0.5$. ^c $[\text{2}]/[\text{1}] = 0.1$. ^d $[\text{3}]/[\text{1}] = 0.05$. ^e $[\text{4}]/[\text{1}] = 2$. ^f 12 mol % of **4** was incorporated. ^g 25 mol % of **4** was incorporated. ^h Not determined.

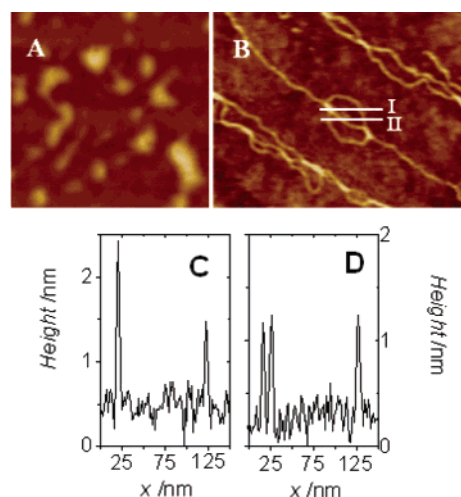


Figure 6. AFM image (730 × 730 nm) of columnar structures of **1** (A) and AFM image (950 × 730 nm) of the purified **poly-1** (B). Line scan corresponding to line I in (B) (C) and line II in (B) (D).

reactivity of allylic growing radicals and to competing degradative chain transfer to the methyl group.²⁶ It also implies that nonaggregated molecules of **1** will not polymerize readily and that polymerization of **1** therefore takes place predominantly, if not exclusively, within the columnar assembly. The strong reduction of X_n upon addition of **4** suggests that, when this compound copolymerizes, it acts as a terminator for the polymerization of the self-assemblies. This is further substantiated by the MALDI-TOF mass spectrum of the copolymerization product, which shows that the oligomeric products are predominantly terminated by methyl sorbate (see Supporting Information).

The sensitivity of the polymerization within columns of **1** to the presence of nonpolymerizable molecules was investigated in mixtures of **1** with **2** (entries 3–4 in Table 1). The addition of **2** shows little or no effect on X_n and conversion. Therefore, it is concluded that the pentyl linker unit of the polymerizable arm in **1** is long enough to allow polymerization of molecules of **1** across intervening molecules of **2** or that the unreactive **2** is dynamically exchanged within the column of the growing polymer. No evidence is found that unreactive **2** is incorporated in the polymer by unexpected side reactions.

(26) (a) Kamachi, M.; Umetani, H.; Kuwae, Y.; Nozakura, S. *Polym. J. (Tokyo)* **1983**, *15*, 753–761. (b) Matsumoto, A.; Horie, A.; Otsu, T. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 681–685.

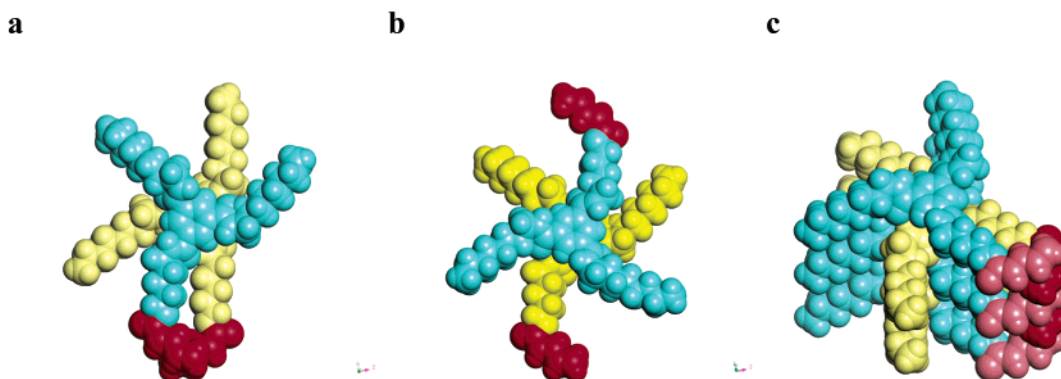


Figure 7. CPK models illustrating the relative orientation of molecules of **1** required for polymerization of sorbyl groups. Stacking geometry of the benzenetricarboxamides cores was taken from the crystal structure of *N,N,N'*-tris(2-methoxyethyl)benzene-1,3,5-tricarboxamide.⁴ Dimer with syn orientation of the sorbyl containing side chains (a). Dimer with anti orientation of the sorbyl containing side chains (b). Pentameric stack with syn orientation of the sorbyl containing side chains (c). Terminal sorbyl methyl groups have been omitted for clarity.

Stability of the Aggregates. Covalent fixation of the columns of **1** by polymerization is expected to stabilize the morphology significantly. Therefore, the persistence of the columns of **1** and of **poly-1** upon removal of solvent was investigated using atomic force microscopy (AFM). Drop casting a cyclohexane solution of **1** and **poly-1** on silicon oxide wafers reveals noticeable differences in structure between **1** and **poly-1** (Figure 6). Monomer **1** appears as large irregular-shaped objects probably due to collapse of the columnar structures at the interface during evaporation of cyclohexane (Figure 6a). On the other hand, purified **poly-1** (monomer content < 0.001%), which is drop cast after being redispersed in cyclohexane by solvent exchange, appears as high-axial-ratio (>150) fibers (Figure 6b). The fibers have a uniform height of approximately 1.0 nm, while at the intersection of the two fibers the height is measured at 2.0 nm (Figure 6c). The widths of the ribbons are constant, approximately 60 nm, but require correction due to the broadening effect of the finite radius of the tip (15 nm).²⁷ The apparent width of the fibers gives an upper limit for the width of 50 nm. At first glance, the AFM data suggest **poly-1** has a very high degree of polymerization; however, SEC shows that the length of the polymeric columns cannot be larger than approximately 20 nm. Therefore, we propose that the fibers consist of polymeric columns, which form fibers upon drop casting by lateral as well as terminal aggregation.

Discussion and Conclusions

The successful photoinitiated polymerization of **1** confirms the validity of our design and suggests the use of benzenetricarboxamides with a single polymerizable sorbyl ester group as a general method for the polymerization of columnar assemblies. In the crystal structure of *N,N,N'*-tris(2-methoxyethyl)benzene-1,3,5-tricarboxamide,⁴ the side chains of consecu-

tive molecules in the columns are rotated by 60° relative to each other. In columnar aggregates of **1**, this orientation leads to an arrangement of sorbyl groups, which is either syn (Figure 7a) or anti (Figure 7b). Polymerization of consecutive molecules can only occur in the syn orientation.

In this respect, the successful polymerization requires an explanation. The undiminished polymerizability of columns of **1** containing 33% of **2** indicates that the chain end is able to “skip” a layer in the column. The columns are dynamic structures, and skipped molecules may be expelled later. Finally, the stability of the radical at the growing chain end is enhanced by conjugation^{18b,26a} and may provide sufficient lifetime to wait for molecular rotation from anti to syn to occur. The AFM results show that the stability of the columns is greatly enhanced by polymerization and allows the formation of stable mesoscopic objects. Future work will be directed toward the introduction of benzenetricarboxamide derivatives with photophysical functionality and the exploration of the supramolecular chirality inherent to these self-assembled structures.

Acknowledgment. We thank Dr. A. J. Wilson for useful discussions and comments, Dr. X. Lou and Mr. R. A. A. Bovee for performing MALDI-TOF measurements and SEC molecular weight analysis, and Ms. J. J. van Gorp for the synthesis of the starting compounds and useful discussions. The research of Dr. M. Masuda has been made possible by funding of the Dutch polymer institute (DPI).

Supporting Information Available: Experimental procedures, ¹H and ¹³C NMR spectra of compounds **1**, **6–9**, and **poly-1**, UV absorption spectra of glass filter, monomer, and polymer in cyclohexane, VT-CD spectra of monomer **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Samori, P.; Francke, V.; Mangel, T.; Müllen, K.; Rabe, J. P. *Opt. Mater.* **1998**, *9*, 390–393.

JA037927U