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Topochemical Polymerization of a Diarylbutadiyne Derivative in the Gel and Solid States

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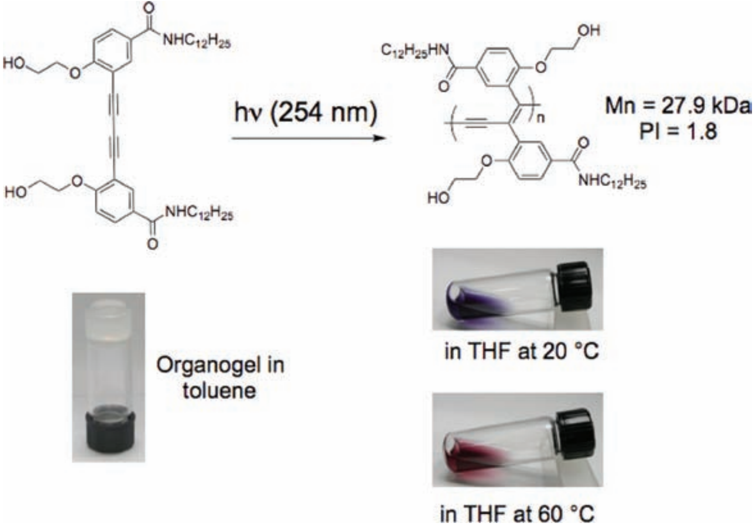
ABSTRACT



A diarylbutadiyne derivative was synthesized using a few steps and gelified in aromatic solvents. The gel prepared at low concentration is made of micrometers-long nanofibrils as shown by scanning electron microscopy. XRD of the dried gel shows sharp features, revealing a well-organized material. A topochemical reaction was performed on the dried gel, and a polydiacetylene presenting reversible thermochromism properties was obtained.

The topochemical reaction of butadiyne leading to polydiacetylene in the crystalline[1] or gel state[2] is a very elegant way of preparing very pure, well-defined conjugated polymers with unique optical and electrical properties.[3] However, to undergo such polymerization in the solid state, the butadiyne units have to be properly oriented in relation to each other. A distance of 4.9 Å between the two reactive carbon atoms and an angle of 45° relative to the butadiyne axis are necessary to perform this reaction efficiently. Because a topochemical reaction results in a change of the atomic coordinates inside the crystal, the nature of the substituents directly attached to the butadiyne unit has a significant impact on the polymerization process.[4] Indeed, these substituents should be able to accommodate structural changes within the crystal lattice,

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(1) (a) Wegner, G. *Natureforsch., B: Chem. Sci.* **1969**, *24*, 824–832. (b) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35–48.

(2) For representative examples, see: (a) Masuda, M.; Hanada, T.; Yase, K.; Shimizu, T. *Macromolecules* **1998**, *31*, 9403–9405. (b) Tamaoki, N.; Shimada, S.; Okada, Y.; Belaissaoui, A.; Kruk, G.; Yase, K.; Matsuda, H. *Langmuir* **2000**, *16*, 7545–7547. (c) Aoki, K.; Kudo, M.; Tamaoki, N. *Org. Lett.* **2004**, *6*, 4009–4012. (d) Nagasawa, J.; Kudo, M.; Hayashi, S.; Tamaoki, N. *Langmuir* **2004**, *20*, 7907–7916. (e) Shirakawa, M.; Fujita, N.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4164–4165. (f) Nie, X.; Wang, G. *J. Org. Chem.* **2006**, *71*, 4734–4741. (g) Dautel, O. J.; Robitzer, M.; Lère-Porte, J.-P.; Serein-Spirau, F.; Moreau, J. J. E. *J. Am. Chem. Soc.* **2006**, *128*, 16213–16223. (h) Fujita, N.; Sakamoto, Y.; Shirakawa, M.; Ojima, M.; Fuji, A.; Ozaki, M.; Shinkai, S. *J. Am. Chem. Soc.* **2007**, *129*, 4134–4135. (i) Jahnke, E.; Weiss, J.; Neuhaus, S.; Hoheisel, T. N.; Frauenrath, H. *Chem.—Eur. J.* **2009**, *15*, 388–404.

(3) (a) Wang, Y.; Yang, K.; Kim, S.-C.; Nagarajan, R.; Samuelson, L. A.; Kumar, J. *Chem. Mater.* **2006**, *18*, 4215–4217. (b) Pilzak, G. S.; Baggerman, J.; van lagen, B.; Posthumus, M. A.; Sudhölter, E. J. R.; Zuilhof, H. *Chem.—Eur. J.* **2009**, *15*, 2296–2304. (c) Ahn, D. J.; Lee, S.; Kim, J.-M. *Adv. Funct. Mater.* **2009**, *19*, 1483–1496.

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and this is why almost all of the topochemical reactions of butadiyne reported so far have been performed on derivatives bearing flexible alkyl chains directly attached to the butadiyne moiety.

To the best of our knowledge, very few topochemical polymerizations of butadiyne through irradiation with UV light have been reported when aryl groups were attached to both ends of the butadiyne.[5] This reaction is very difficult to achieve in crystals since the phenyl groups are expected to be too bulky to undergo significant conformational changes within the crystal. In fact, several other attempts to achieve this polymerization using UV irradiation failed,[6] and only thermal and γ-ray irradiation polymerization gave a polydiacetylene with relative success.[7]

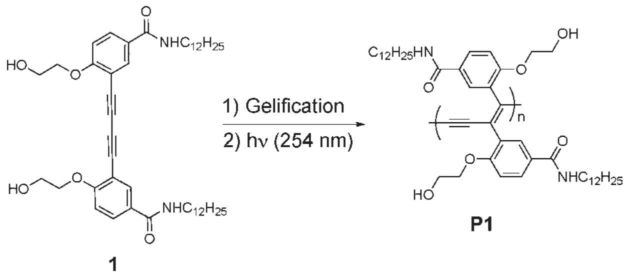


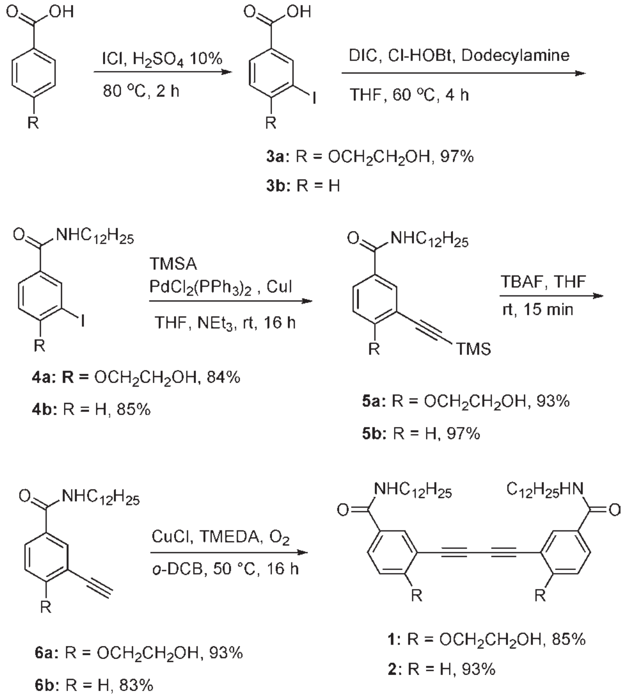
Figure 1. Compound **1** and its corresponding polydiacetylene **P1**.

Because conformational changes are known to be less demanding in an organogel than in crystals, we hypothesize that butadiyne bearing two aryl groups could be more easily polymerized within an organogel. This assumption is supported by the successful topochemical reaction of the diarylbutadiyne derivatives trapped inside polysaccharide schizophyllan in solution.[8] Herein, we report the efficient preparation of a polydiacetylene from a diarylbutadiyne derivative (**1**, Figure 1) in both gel and solid states using UV irradiation.

One of the most important design aspects of compound **1** is the presence of two amide groups, bearing a long alkyl chain, directly attached to the aryl units. The amide group is widely used to properly orient butadiyne moieties in both crystal and gel forms since the intermolecular distance between amide groups of molecules facing each other is ca. 4.8 Å, which is close to the butadiyne distance necessary to achieve a topochemical reaction.[2e,9]

The synthesis of derivatives **1** and **2** is described in Scheme 1. Compound **1** was obtained via six straightforward steps from commercialy available 4-hydroxybenzoic acid. The first reaction involves monoiodination using iodine monochloride (ICl) in hot aqueous sulfuric acid to yield compound **3** in quantitative yield. Amidation of compound **3** with dodecylamine using diisopropylcarbodiimide (DIC) and 6-chloro-1-hydroxybenzothiazole (Cl-HOBt) in refluxing tetrahydrofuran gives compound **4a** in 84% yield. Sonogashira[10] coupling with trimethylsilylacetylene (TMSA) on **4a** in THF using Pd/Cu catalysts and triethylamine as the base yields compound **5a** in 93% yield. Alkyne deprotection of **5a** with tetrabutylammonium fluoride (TBAF) gives compound **6a** in 93% yield. Finally, Glaser−Hay[11] homocoupling of **6a** in *o*-DCB using tetramethylethylenediamine (TMEDA), CuCl, and air yields compound **1** in 85% yield. The synthesis of derivative **2** was achieved by using a similar synthetic pathway starting from commerically available 3-iodobenzoic acid. All the products were obtained in good to excellent yields.

Scheme 1. Synthesis of Diarylbutadiynes **1** and **2**



The gelation properties of the two derivatives were studied in common organic solvents. First, the organogelator was mixed in a solvent and sonicated for a few minutes. The solution was then heated near the boiling

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point of the solvent and slowly cooled down to room temperature. Compound **1** showed good gelation ability in all the aromatic solvents tested (see Table S1 in the Supporting Information). In fact, aromatic solvents allowed gel formation at low concentration in *o*-DCB (2.5 mg/mL) and toluene (3.0 mg/mL). Depending on the solvent used, the gel obtained is translucid, semitranslucid, or opaque (Figure S1 in the Supporting Information). This behavior can be attributed to different solublities of compound **1** in aromatic solvents, leading to gels having various levels of crystallinity. In all the aromatic solvents tested, repeating the heating/cooling process always lead to similar gels. In nonaromatic solvents, many states are obtained including a viscous solution, solution, or simply suspension of insoluble material. In contrast to compound **1**, compound **2** was found to be insoluble at room temperature in all the solvents tested. Even after heating a suspension of compound **2** in different solvents, precipitation rather than gelification occurred. This difference between both compounds is indicative of the importance of the hydroxy-ethoxy chain attached to compound **1** for the assembly process. In addition to increasing the solubility, they are expected to participate in intermolecular H-bonding (OH..OH) that supports the formation of a gel.

In order to investigate the crystallization temperature of solvents within the gel and the thermal stability of the gel, two gel samples were prepared with either toluene or *o*-DCB as solvent at a 10 mg/mL concentration and subjected to differential scanning calorimetry (DSC). In *o*-DCB, the DSC analysis was carried at temperatures ranging from 298 to 223 K. A very sharp exotherm attribuable to the crystallization of supercooled solvent was observed at 232 K (ΔH = 11.0 kJ/mol) (see Figure S2 in the Supporting Information). This is approximatively 24 K below the freezing point of free *o*-DCB (256 K). By heating the gel from 223 to 298 K, an endotherm was observed at 257.6 K ($\Delta H = -11.1$ kJ/mol), which corresponds to the melting point of free *o*-DCB. A similar phenomenon was observed for a toluene-based gel.

To gain a better understanding of the nanoscale morphology of the organogel, a small portion of it was slowly dried under ambient conditions onto a metallic substrate and subjected to scanning electron microscopy (SEM) analysis. As shown in Figure 2, the organogel of compound **1** is made of micrometers-long 1-D wirelike fibers with diameters of a few tens of nanometers. Interestingly, most of the fibers assembled into well-ordered micrometers-wide bundles, indicating strong interfiber interactions.[12] After irradiation for 24 h, the fibrillar structure was completely lost as a possible consequence of the destruction of the H-bonding network (Figure 2b). This result is in agreement with the loss of the gel state observed upon gel irradiation.

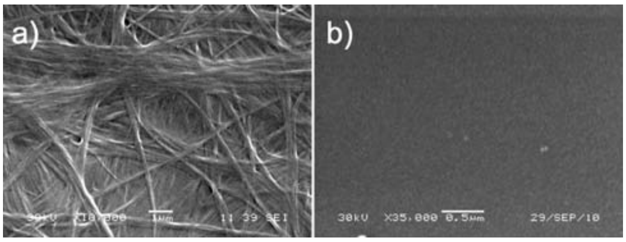

Figure 2. SEM images of organogel from compound **1** in toluene (10 mg/mL) before (a) and after (b) irradiation for 24 h at 254 nm. The scale bars are 1 and 0.5 μm for (a) and (b), respectively.

In order to study the intermolecular interactions and distances within the supramolecular assembly, a gel of compound **1** (toluene, 10 mg/mL) was deposited onto a glass slide, slowly dried at room temperature, and subjected to XRD analysis. A recording of XRD spectra was taken between angles of $2\theta = 1°$ and 15° (see Figure S3 in the Supporting Information). The diffraction pattern is characterized by three peaks at 22.9, 11.4, and 7.5 Å, which correspond to a 1:1/2:1/3 ratio. This peak pattern is indicative of the presence of a layered structure with an interlayer distance of 2.3 nm.[13] To draw a comparison, a sample of compound **1** was dissolved in MeOH and cast onto a glass slide substrate. XRD analysis after drying did not show any crystallographic peaks, thus confirming the lack of arrangement in the solid state (see Supporting Information).

Photopolymerization was achieved on a 10 mg/mL toluene gel of **1** by irradiation at 254 nm with a 120 W UV lamp at a distance of 2 cm for 6 h. The blue state generally associated with the highly extended π-delocalization along the polydiacetylene backbone[14] was never reached in the gel form. Also, after a dark orange form was obtained, a loss of the gel state and the appearance of a red, translucent solution after 6 h of irradiation were observed (Figure 3). This phenomenon observed by Moreau et al. during the photopolymerization process of alkyl-substituted butadiyne derivatives could be attributed to a significant conformational change of the aryl groups within the gel, thus disturbing the hydrogen bond network.[2g]

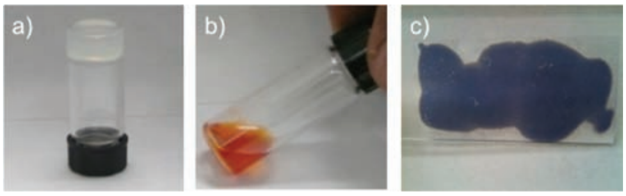

Figure 3. (a) Compound **1** in the gel form (10 mg/mL in toluene) at room temperature; (b) the same gel after irradiation at 254 nm for 4 h; and (c) the gel evaporated on a glass slide and irradiated for 24 h at 254 nm.

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Interestingly, when the initial gel was dried onto a glass slide and then irradiated, the film that was formed rapidly turned dark blue, which can be attributed to the formation of a polydiacetylene with an extended conjugation length (see Figure 3c). Unlike the case of compound **1**, the resulting solid is not soluble in methanol but readily soluble in THF. After purification of the dark material using a Soxhlet apparatus in methanol, only the polymer **P1** was recovered (with trace amounts of the starting material) for a polymerization yield of 75% yield, which is quite higher than the previous yields reported for similar topochemical reactions.[5] More importantly, size-exclusion chromatography (SEC) analysis shows a molecular weight of 27.9 kDa with a polydispersity index of only 1.8, which is surprinsingly low for a solid-state polymerization.

Using the gel rather than a solution of compound **1** to cast a film onto a glass substrate is of utmost importance to achieve the topochemical reaction in the solid state. In fact, when a solution of compound **1** in methanol is cast onto a glass slide, the film thus formed remains unchanged upon irradiation, meaning that it does not undergo the topochemical reaction to yield the polydiacetylene structure. This result is consistent with the XRD observations discussed above.

For a better insight into the topochemical reaction, the photopolymerization reaction was monitored using Fourier-transformed Raman spectroscopy (FT-Raman). Before irradiation, the Raman spectrum of compound **1** shows two peaks at 2215 and 2095 cm^{-1} attributed to the symmetrical and asymmetrical stretching modes of 1,3-butadiyne, respectively (see Figure S4 in the Supporting Information). Upon irradiation, the band at 2215 cm^{-1} completely disappeared suggesting a change in the nature of the C≡C units. The peak between 1400 and 1600 cm^{-1} generally associated with the formation of the enyne unit cannot be observed directly since this region of the spectrum contains several peaks, mainly attributed to aromatic ring stretching and bending.[15]

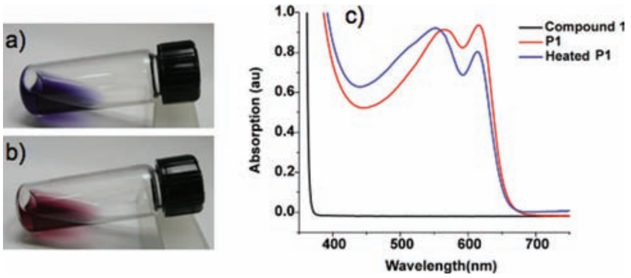

Figure 4. **P1** in THF at (a) 20 °C and (b) 60 °C. (c) UV−vis spectra of **P1** at 20 °C (red line) and at 60 °C (blue line) recorded in THF.

As in rare cases for polydiacetylenes,[3c] **P1** shows reversible thermochromism properties in organic solvents (Figure 4). When **P1** was dissolved in THF at room temperature and heated to 60 °C, the clear dark purple solution gradually turned reddish. The solution goes back to purple when cooled at room temperature. As a consequence of this color change, the intensity of the absorption band at 616 nm in the UV−vis spectrum decreased while the band at 565 nm is blue-shifted (14 nm) (Figure 3). In the solid state, the dark blue film gradually turned orange upon heating and went back to dark blue upon cooling (see Figure S5 in the Supporting Information). This rare reversibility property for a polydiacetylene opens the way to usage of this new family of conjugated polymers in sensor devices.[3c]

In summary, we have demonstrated that a high molecular weight polydiacetylene with a low polydispersity index can be obtained in good yield from a butadiyne unit substituted with sterically demanding phenyl groups using a light-promoted topochemical reaction. This reaction can be accomplished in both the gel and solid states. The synthesis of other functional diarylbutadiyne derivatives is in progress to extend the scope of this reaction to the synthesis of various electro- and photoactive diarylbutadiyne derivatives.

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Supporting Information Available. Experimental procedures and characterization data for all the new compounds, DSC, XRD, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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