

Tunable Plastic Films of a Crystalline Polymer by Single-Crystal-to-Single-Crystal Photopolymerization of a Diene: Self-Templating and Shock-Absorbing Two-Dimensional Hydrogen-Bonding Layers**

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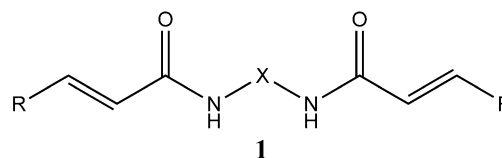
Polymerization reactions in the solid state have attracted the interest of chemists because of their fundamental and applicative aspects.^[1,2] The advantage of solid-state polymerization is that it results in the controlled formation of the product in terms of geometry and stereochemistry and often gives high yields.^[3] In particular, single crystal to single crystal (SCSC) reactions offer a detailed understanding of the structure of the product polymer.^[4] However, in most such reactions the products obtained are either amorphous or microcrystalline, thus making it difficult to characterize the product structure. Recrystallization of these products is often impossible because of the insolubility of the polymeric products. Even in soluble cases, recrystallization of the product is not guaranteed to result in the same structure as was originally formed. Therefore, reactions in which the single crystals maintain their integrity and crystalline nature are particularly noteworthy. However, such reactions are relatively rare and only a few molecules are known to undergo such SCSC transformations to yield crystalline polymers. The diacetylene, triacetylene, and muconic acid derivatives of 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethane have been shown to undergo topochemical polymerization in an SCSC fashion.^[5]

Although several bisolefins have been shown to form polymers,^[6] to date only 2,5-distyrylpyrazine (DSP) is known to undergo [2+2] polymerization in an SCSC manner to afford polymers containing cyclobutane rings. This reaction was first reported in 1905 and named a four-center type photopolymerization, but was only reported in detail in 1967 by Hasegawa.^[7a] Following this discovery, several studies have been conducted on various aspects of this reaction of DSP and several other related molecules.^[7]

The rarity of SCSC [2+2] polymerization reactions arises from the difficulty in finding suitable monomers with the required crystal packing to promote not only a reaction but also a crystal packing that can withstand the changes that occur at the molecular level over the entire course of the

reaction. Even the crystal structure of the directly obtained polymeric phase of DSP was not determined, as the original crystal developed cracks, and only the cell parameters were determined. However, Harris et al. recently used powder diffraction to determine the structure.^[8] Herein, we present two examples of molecules containing amide functionalities which undergo polymerization through a [2+2] reaction in a SCSC fashion. These monomers form N–H···O hydrogen-bonded layers which act as a self-template to promote a [2+2] reaction, and they also act as a shock absorber to enable the reaction to occur in an SCSC fashion.

The molecules of **1** are of our interest for the study of template-directed [2+2] reactions to produce tricyclic molecules by a double [2+2] reaction (Scheme 1). Indeed, recently



2: R=Ph, X=-(CH₂)₄-; **3:** R=3-pyridyl, X=-(CH₂)₄-

Scheme 1.

we have shown that Ag···Ag interactions can template such a reaction of **1** (R=4-pyridyl; X=HN–NH) to yield a tricyclic molecule with a 4-12-4 arrangement.^[9a] Furthermore, our systematic studies on bisamide derivatives indicated that this class of materials have two possible hydrogen-bonding modes: formation of a β sheet or a two-dimensional layer.^[9b] These studies hinted that the formation of two-dimensional layers between molecules of **1** brings the possibility of promoting a [2+2] polymerization reaction. Therefore, we have prepared several derivatives of **1** by introducing 3-pyridyl, 4-pyridyl, and phenyl groups as R and various aromatic and aliphatic groups as linkers (X) to explore their reactivity in crystalline solids with and without external templates. During this process we found that **2** and **3** stand out from all the other derivatives as they undergo SCSC photo-reactions. We note here that **2**, putrescine-1,4-dicinnamide, is a natural product which can be isolated from fruiting bodies of the gilled mushroom *Pholiotasporumosa* (*Basidiomycetes, Strophariaceae*), and recently it was shown to inhibit the growth of human prostate cancer cells.^[10]

Single crystals of compound **2** suitable for X-ray diffraction analysis were obtained from MeOH/DMF. In the crystal structure,^[11] the asymmetric unit contains only half of the

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molecule as there is inversion symmetry. Interestingly, the molecule does not exhibit a linear geometry, as the $\text{-N-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ fragment contains a gauche conformation with an N-C-C-C torsion (τ_1) of 62.4° . The molecules join through $\text{N-H}\cdots\text{O}$ hydrogen bonds ($\text{N}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$: $2.901(4)$ Å, 161°) to form a corrugated two-dimensional layer. Within this layer, the double bonds are aligned for a photochemical reaction, with a nonbonding distance (d_1) of 3.812 Å between the C=C atoms of two layers and a $\text{C=C}\cdots\text{C=C}$ torsion of (τ_2) 0° , thus indicating ideal conditions for a topochemical $[2+2]$ reaction (Figure 1). Such an alignment of double bonds occurs through

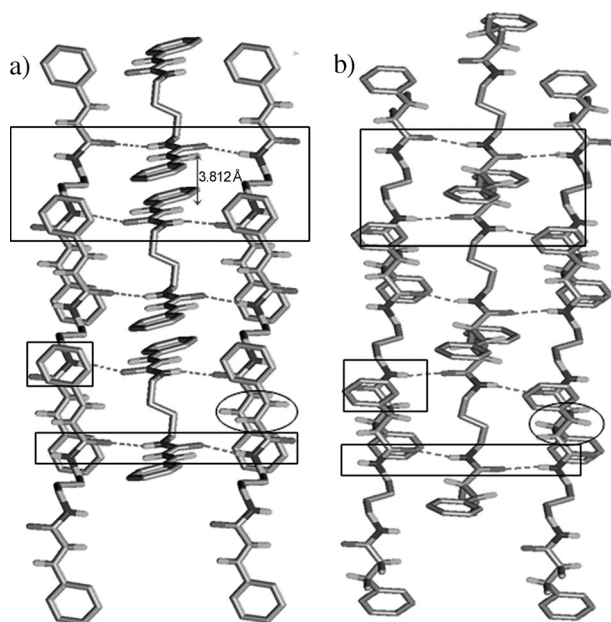


Figure 1. Illustration of the hydrogen-bonding (large rectangle) layers: a) before and b) after irradiation in **2** and **2P**, respectively (views along the a -axes). Please note the alignment of the double bonds (oval) and amide-pyridyl stacking interactions (small rectangle).

one-dimensional stacks of molecules along the a -axis arranged through $\pi\cdots\pi$ interactions between the amide and phenyl groups: The distance between the amide C atom and phenyl C atom (d_2) is 3.36 Å and the angle (τ_3) between the planes of the phenyl and amide groups is 12° .

Irradiation of crystals of **2** results in the $[2+2]$ reaction occurring in an SCSC manner to yield single crystals of the one-dimensional polymer **2P**. The volume of **2P** was found to be compressed by 6% compared to that of crystals of **2** (1765 versus 1881 Å³). The major compression occurs through the stacking axis (a -axis), which was reduced by 0.73 Å (11.83 versus 12.56 Å), while the other two axes remain almost the same. As expected, the value of d_1 decreased from 3.812 Å to 1.588 Å, while the values of τ_1 and τ_2 remain almost unaffected (68° and 0° , respectively) from those of the parent structure. The cyclobutane moiety in the polymer exhibits perfect planarity, with the groups attached to it exhibiting torsions of 6° (*cis* groups) and 125° (*trans* groups; Figure 2). Furthermore, the d_2 and τ_3 values in **2P** are 3.2 Å and 37° , respectively, which indicates a considerable change in the stacking interactions.

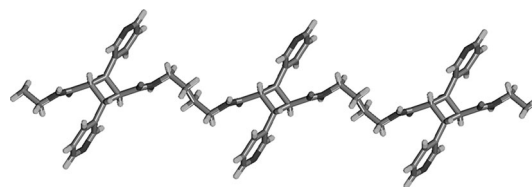


Figure 2. Crystal structure of polymer **3P**.

The 3-pyridyl (**3**) and 4-pyridyl derivatives of these compounds were prepared to analyze the generality of the reaction. Furthermore, since polymer **2P** was found to be insoluble, which makes it difficult to study its properties, it was also anticipated that the pyridyl derivatives of **2** would result in better solubility in aqueous solutions. The single crystals of **3** were not only isostructural with **2** but also underwent a similar SCSC reaction to form crystals of the corresponding polymer **3P**. Some important differences were observed in this polymer: the a -axis shrinks more than that of **2** (1.1 versus 0.731 Å) and the c -axis expands (14.400 Å in **3** versus 14.855 Å in **3P**) while it remains almost the same in the case of **2** (15.496 Å in **2** versus 15.305 Å in **2P**). In contrast, the 4-pyridyl derivative was found not to be isostructural with **2** and **3**, and was also photostable.

Full conversion of **2** into **2P** or **3** into **3P** was found to require 22 h of irradiation in sunlight. In the case of **3**, full conversion (100%) into **3P** was verified by ^1H NMR spectroscopic analysis in D_2O containing a drop of HCl . Furthermore, monitoring the conversion of **3** into **3P** at various time intervals by ^1H NMR spectroscopy indicates that the reaction occurs through an intermediate phase: the ^1H NMR spectra of a partially irradiated sample is not just a mixture of **3** and **3P**, it contains some new signals corresponding to alkyl (*n*-butyl) and pyridine protons which belong to neither **3** nor **3P**. From this observation it may be inferred that the reaction may progress through oligomer formation. For example, it was shown earlier that controlled irradiation of DSP at a wavelength greater than 400 nm resulted in formation of an oligomer.^[12] We are carrying out further studies on **3** to obtain more details of this process.

We note here that the SCSC reactions of **2** and **3** do not disrupt the hydrogen bonds involved in the layers, although small changes in the hydrogen-bonding parameters are observed ($\text{N}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$: $2.901(4)$ Å and 161° in **2**, $3.035(2)$ Å and 162° in **2P**; $2.891(3)$ Å and 172° in **3**, $2.965(3)$ Å and 164° in **3P**). The changes occurring at the molecular level are absorbed by the 2D hydrogen-bond layer, through adjustment of the interplanar angles between the hydrogen-bonded amide groups (Figure 3): the interplanar angle between two successive amide groups connected through hydrogen bonds is 68° in **2** and **3**, which decreases to 49° upon photochemical reaction (in **2P** and **3P**).

As anticipated, the polymer **3P**, unlike **2P**, was found to be soluble in formic acid, *m*-cresol, and dilute HCl or H_2SO_4 . Such solutions (formic acid and HCl) of **3P** form films upon drying in an oven at 70 – 80°C . The films were found to have a wrinkle-free nature: After twisting and turning they return to their original shape without any evident residual marks (Figure 4a, also see the video in the Supporting Information).

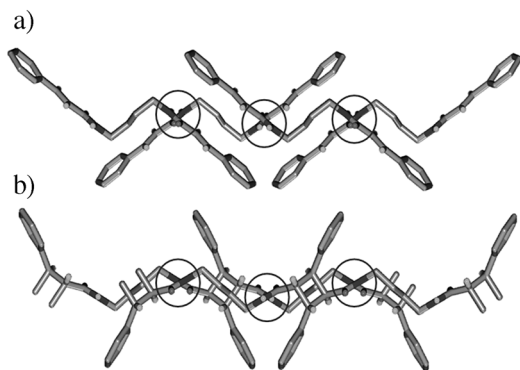


Figure 3. Illustration of the changes that occur in the hydrogen-bonding layer: a side view of the layer in the crystal structures of a) **2** and b) **2P**. Note the change in the angle between the amide planes (circles).

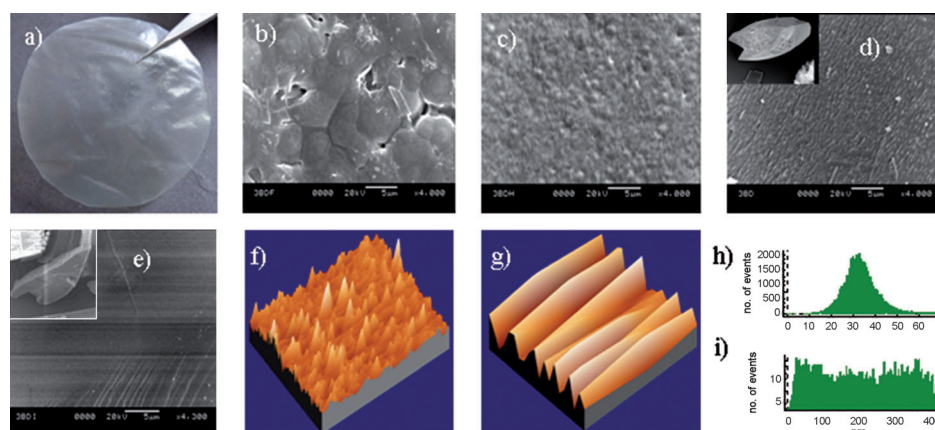


Figure 4. Film made from a) **3P**-formic acid. SEM images of the b) **3P**-formic acid film, c) **3P**-HCl film, d) crystal surface of **3** (inset: crystal image), and e) crystal surface of **3P** (inset: crystal image). 3D AFM height images of f) **3** and g) **3P**. The bar graphs indicate the different degree of roughness for h) **3** and i) **3P**.

However, the use of H_2SO_4 in place of HCl or HCOOH did not result in films. Preliminary measurements of the tensile strengths of the films of **3P**- HCOOH and **3P**- HCl indicate values of 15.99 and 7.11 MPa, respectively, with an elongation break at 20% strain. This implies that the nature of the film is tunable by changing the counterions. Scanning electron microscopy (SEM) images of both films were recorded on a JEOL-JSM 5800 scanning electron microscope. These images confirm the large structural differences between the two films (Figure 4b,c).

Thermogravimetric analysis (TGA) of the films showed that decomposition occurs at 410°C . It is interesting to note here that the as-prepared crystalline polymer of **3P** exhibits a sharp melting point of 343°C , as indicated by differential scanning calorimetry (DSC). Furthermore, polymer **2P** was found to have a higher melting point (394°C) than that of **3P**. The molecular weight of as-synthesized solids of **3P** were determined by MALDI-TOF analysis using a 2,5-dihydroxybenzoic acid matrix. The maximum molecular weight observed is 4238, which indicates a 12-mer.

The SEM images for the as-synthesized and irradiated crystals indicate significant differences. In both cases (**2** and **3**)

it was found that the irradiated crystals have smooth surfaces (Figure 4d,e). The AFM images of **3** and **3P** were also recorded using the drop-casting technique. The powder samples were dispersed in CH_2Cl_2 and drop-cast on the glass slide with a micropipette. AFM analysis of **3** indicates several peaks whereas that of **3P** indicates very smooth surfaces with several wedges parallel to each other (Figure 4f–i).

In conclusion, we have demonstrated the facile [2+2] SCSC transformation of two monomers—the first examples—to produce crystalline polymers containing pyridine/phenyl, amide, cyclobutane, and *n*-butyl moieties. The SCSC transformation was favored by the self-templating and shock-absorbing nature of the hydrogen-bonding layers. The pyridine-containing polymers were shown to be soluble and useful for making plastic films with considerable tensile strengths.

Pyridine-containing polymers have been shown to be excellent candidates for light-emitting diodes because of their high electron affinity.^[13] Currently, we are investigating the electroluminescent, photoluminescent, and tensile strengths of **2P** and **3P** in the presence of various counterions.

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- [1] a) K. Sada, M. Takeuchi, N. Fujita, S. Shinkai, *Chem. Soc. Rev.* **2007**, *36*, 415–435; b) D. J. Ahn, J. M. Kim, *Acc. Chem. Res.* **2008**, *41*, 805–816; c) G. Fernández, M. Stole, V. Stepanenko, F. Würthner, *Chem. Eur. J.* **2013**, *19*, 206–217.
- [2] a) S. Rondeau-Gagné, J. R. Néabo, M. Desroches, J. Larouche, J.-F. Morin, *J. Am. Chem. Soc.* **2013**, *135*, 110–113; b) T.-J. Hsu, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.* **2012**, *134*, 142–145; c) S. Dawn, M. B. Dewal, J. A. Krause, P. J. Pellechia, L. S. Shimizu, *J. Am. Chem. Soc.* **2011**, *133*, 7025–7032; d) A. Matsumoto, T. Odani, K. Sada, M. Miyata, K. Tashiro, *Nature* **2000**, *405*, 328–330; e) X. M. Zhang, S. D. Xu, M. Li, Y. T. Shen, Z. Q. Wei, S. Wang, Q. D. Zeng, C. Wang, *J. Phys. Chem. C* **2012**, *116*, 8950–8955.
- [3] a) Y. Sonoda, *Molecules* **2011**, *16*, 119–148; b) A. Matsumoto, *Top. Curr. Chem.* **2005**, *254*, 263–305; c) V. Rammurthy, K. Venkatesan, *Chem. Rev.* **1987**, *87*, 433–481; d) I. G. Georgiev, L. R. MacGillivray, *Chem. Soc. Rev.* **2007**, *36*, 1239–1248; e) G. K. Kole, J. J. Vittal, *Chem. Soc. Rev.* **2013**, DOI: 10.1039/c2s35234f; f) K. Biradha, R. Santra, *Chem. Soc. Rev.* **2013**, *42*, 950–967.
- [4] a) G. Kaupp, *J. Phys. Org. Chem.* **2008**, *21*, 630–643; b) T. Friščić, L. R. Z. MacGillivray, *Z. Kristallogr.* **2005**, *220*, 351–363.
- [5] a) J. W. Lauher, F. W. Fowler, N. S. Goroff, *Acc. Chem. Res.* **2008**, *41*, 1215–1229; b) L. Luo, C. Wilhem, A. Sun, C. P. Grey, J. W. Lauher, N. S. Goroff, *J. Am. Chem. Soc.* **2008**, *130*, 7702–7709; c) L. Addadi, J. V. Mil, M. Lahav, *J. Am. Chem. Soc.* **1982**, *104*, 3422–3429; d) G. Z. Wegner, *Z. Naturforsch. B* **1969**, *24*, 824–

- 832; e) G. Wegner, *Pure Appl. Chem.* **1977**, *49*, 443–454; f) T. Odani, S. Okada, C. Kabuto, T. Kimura, S. Shimada, H. Matsuda, H. Oikawa, A. Matsumoto, H. Nakanishi, *Cryst. Growth Des.* **2009**, *9*, 3481–3487; g) D. Furukawa, A. Matsumoto, *Macromolecules* **2007**, *40*, 6048–6056; h) S. Nomura, T. Itoh, H. Nakasho, T. Uno, M. Kubo, K. Sada, K. Inoue, M. Miyata, *J. Am. Chem. Soc.* **2004**, *126*, 2035–2041.
- [6] a) P. Johnston, C. Braybrook, K. Saito, *Chem. Sci.* **2012**, *3*, 2301–2306; b) G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 3641–3649.
- [7] a) M. Hasegawa, *Chem. Rev.* **1983**, *83*, 507–518; b) M. Hasegawa, C. M. Chung, N. Muro, Y. Maekawa, *J. Am. Chem. Soc.* **1990**, *112*, 5676–5677; c) see Ref. [5c]; d) S. Takahashi, H. Miura, H. Kasai, S. Okada, H. Oikawa, H. Nakanishi, *J. Am. Chem. Soc.* **2002**, *124*, 10944–10945; e) G. M. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678; f) M. Hasegawa, H. Harashina, S. Kato, K. Saigo, *Macromolecules* **1986**, *19*, 1276–1278; g) J. J. Stezowski, N. M. Peachey, P. Goebel, C. J. Eckhardt, *J. Am. Chem. Soc.* **1993**, *115*, 6499–6505; h) R. O. Al-Kaysi, R. J. Dillon, J. M. Kaiser, L. J. Mueller, G. Guirado, C. J. Bardeen, *Macromolecules* **2007**, *40*, 9040–9044.
- [8] F. Guo, J. Marti-Rujas, Z. Pan, C. E. Hughes, K. D. M. Harris, *J. Phys. Chem. C* **2008**, *112*, 19793–19796.
- [9] a) R. Santra, K. Banerjee, K. Biradha, *Chem. Commun.* **2011**, *47*, 10740–10742; b) M. Sarkar, K. Biradha, *Cryst. Growth Des.* **2006**, *6*, 202–208.
- [10] A. Russo, M. Piovano, M. Clericuzio, L. Lombardo, S. Tabasso, M. C. Chamy, G. Vidari, V. Cardile, P. Vita-Finzi, J. A. Garbarino, *Phytomedicine* **2007**, *14*, 185–191.
- [11] The crystal structure of **2** was reported earlier, but we redetermined it for the sake of completeness: M. Clericuzio, M. Piovano, M. C. Chamy, J. A. Garbarino, M. Milanesio, D. Viterbo, G. Vidari, P. V. Finzi, *Croat. Chem. Acta* **2004**, *76*, 605.
- [12] N. M. Peachey, C. J. Eckhardt, *J. Am. Chem. Soc.* **1993**, *115*, 3519–3526.
- [13] a) Y. Z. Wang, D. D. Gebler, D. J. Spry, D. K. Fu, T. M. Swager, A. G. MacDiarmid, A. J. Epstein, *IEEE Trans. Electron Devices* **1997**, *44*, 1263–1268; b) C. Wang, M. Kilitziraki, J. A. H. MacBride, M. R. Bryce, L. E. Horsburgh, A. K. Sheridan, A. P. Monkman, I. D. W. Samuel, *Adv. Mater.* **2000**, *12*, 217–222.