Topochemical Polymerization using Bis-thyminyl

Monomers

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Crystal Data and Methods

CCDC depositions 841955, 841956, 841957, 888374, 948169, 948168, 948167 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>. As the individual crystal sizes were small (i.e. in the range of 40-60 μ m) or produced weak diffraction patterns, structural analyses were performed on the MX1 micro-crystallography beam-line at the Australian Synchrotron, Clayton, Victoria. The end station comprised a φ goniostat with a Quantum 210r area detector. Data were collected using the Blue Ice GUI³ and processed using the XDS software. Due to hardware constraints (fixed detector angle, minimum detector distance) the maximum obtainable resolution at the detector edge was approximately 0.81Å. The structures were solved and refined using the programs SHELXS-97 and SHELXL-97, respectively. The program X-Seed⁷ was used as an interface to the SHELX programs, and for preparation of the figures. Plausible positions of hydrogen atoms in water molecules and the amide, were located in the difference Fourier map, and were refined such that O-H distances were restrained to reasonable values (0.88-0.98Å); all other hydrogen atoms were placed in calculated positions using a standard riding model.

Crystal structure of **1** (CCD 841955), crystal structure of **3** (CCD 841957), and crystal structure of **7** (CCD 841956) are reported in our previous paper. Ref 15) P. Johnston, C. Braybrook and K. Saito, *Chem. Sci.*, **2012**, *3*, 2301-2306. Crystal structure of **2** (CCD 888374) is reported in Ref 20) P. Johnston, E. I. Izgorodina and K. Saito, *Photochem. Photobiol. Sci.*, **2012**, *11*, 1938-1951.

Crystal structure of 5 (CCD 948167):

Triclinic crystals that were suitable for structural analyses were difficult to obtain for **5**. After repeated attempts to produce adequate crystals and data from the Synchrotron, the crystal structure of **5** was finally determined by merging two partial datasets to give the structure shown in **Figure S1**. Referring to the structure of **5** in **Figure S1**, incorporation of the odd numbered *N3-N3* C₃ alkyl spacer appeared to cause non-equivalence of the two thyminyl propanoate moieties due to the alkyl spacer adopting a cisoidal conformation close to one of the rings (α N3-C-C-C = -56.5°). Subsequently, the orientation of the two thyminyl rings in the monomer approached perpendicularity (α C6- α N3- β N3- β C6 = 74.1°), whereas in the C₄ **1** and C₆-linked **7** (see below) monomer structures, the thyminyl rings were coplanar (C6-N3-N'3-C'6 = -180°).



Figure S1 Crystal structure of **5**. (a) Monomer alignment occurring along a row with the α and β *N*1-chain conformations indicated. In this structure, the *N*1 chains of the α - α pairs bend inward toward the *trans-anti* TA ring stack (**Type II**), while the linear β - β pairs form **Type III** *trans-anti* (TA) thyminyl ring stacks. (b) Closest thyminyl pairing is observed between **Type III** pairs to give an olefinic separation distance of 3.74 Å. (c) Monomer packing diagram. (d) Monomer with α and β -*N*1 chains and a cisoidal *N*3-*N*3 propyl bridge.

Crystal structure of 9 (CCD 948168):

Monoclinic crystals of **9** were obtained by crystallisatio from EtOAc. The crystal structure of **9** in **Figure S2** reveals that the thyminyl rings are co-planar in each monomer molecule, while the core aryl ring lies along a plane roughly perpendicular to the plane of the thyminyl rings. The core aryl unit joins to the thyminyl ring at the *N*3 position through a bond angle of 113.3° (N3-C16-C17). The *N*1 propanoate chains adopt the usual bent (α) conformations, although there appears to be some unresolved disorder in the ester moieties which leads to larger than normal thermal ellipsoids for the O15, O13 and C14 atoms of the ester moiety. There is also some residual electron density near the carbonyl O13 (q = 0.68; q-O13 d = 1.009 Å) that can be attributed to the unresolved disorder. These

factors indicate that the ester carbonyl groups possess some conformational variation that was unable to be sensibly modelled.

Referring to the crystal structure of **9**, it can be seen that monomer molecules form rows in a direction perpendicular to the b-axis, and the rows stack down the b-axis to give the overall structure. Proximity related thyminyl pairs are generated along the c-axis, although the olefinic separation distance is too great for photo-reaction (d = 4.97 Å). Proximity related thyminyl pairs are generated from thyminyl rings possessing bent (α) propanoate chains that fold inwards into the ring stack **Figure S2** (**Type II**). Close **Type II** stacking was inhibited in the dimethoxyaryl-linked monomer structure due to the perpendicular orientation of the aryl core (in relation to the thyminyl rings) and the protruding alkoxy chains which sterically blocked **Type II** stacking was displaced which lead to the large olefinic separation distance of 4.97 Å. Close C2=O⁻⁻H6C contacts (2.35 Å, torsion angle -174°) were also observed in the structure, which may have stabilised or at least contributed to the displacement of the **Type II** stacks.



Figure S2 Crystal structure of 9. (a) Shows the extended alignment of the closest related monomers. (b) Shows olefinic alignment in the closest thyminyl pair (atoms involved the C=C bonds are represented as spheres). (c) Monomer packing diagram. (d) Close C6H^{$\cdot\cdot$}O=C2 contacts (2.35 Å).

Crystal structure of 10 (CCD 948169):

A photo-stable crystalline sample of **10** was obtained by recrystallisation of the monomer from EtOAc. It was difficult to find suitable analytical quality crystals in the sample, as the mounted crystals generally produced twinned diffraction patterns. After several attempts, the structure in **Figure S3** was eventually obtained. However due to a combination of poor quality crystals and hardware limitations at the Australian Synchrotron MX1 beamline (i.e. fixed detector angle, minimum detector distance allowing a maximum obtainable resolution at the detector edge of approximately 0.81Å), the data completeness of the solved structure was low (83%). Nevertheless the structure solution obtained, gave a reasonable refinement (R = 0.0768) and molecules of the diethoxyaryl-linked monomer, **10**, were found to possess similar conformations to molecules of **9**.

The crystal structure of **10** contains two crystallographically independent monomer molecules (henceforth denoted *A* and *B*) in the asymmetric unit cell. In both cases, the thyminyl rings are co-planar, while the core aryl rings lie along a plane roughly perpendicular to the thyminyl ring plane. However in molecule *A* (**Figure S3a**), the core aryl unit joins to the thyminyl ring at the *N*3 position through a bond angle of 115.05° (N3-C16-C17), while in the second molecule (*B*) the bond angle is slightly less (111.91°, N25-C38-C39). The ethoxy chains branching from the aryl moieties are also different between the molecules: for *A* the torsion angle of the ethoxy chain is -166.0° (C19-O20-C21-C22), and for B it is +175.1° (C40-O41-C42-C43). In both *A* and *B*, the *N*1 propanoate chains adopt bent (α) conformations that are roughly perpendicular to the thyminyl ring (for *A*, C4-C10-C14 = 86.9°; for *B*, C26-C32-C36 = 83.26°), although there appears to be some conformational disorder in the ester moieties of both molecules which causes larger than normal thermal ellipsoids for atoms O15, O13 and C14 in molecule *A*; and O37, O35 and C36 in *B*.

Upon examination of the extended monomer packing, it was noticed that the *A*-type monomers formed continuous rows in a direction perpendicular to the c-axis. Proximity related thyminyl pairs of type *A* are generated by stacking down the c-axis, although the olefinic separation distance was outside of the photo-reactive range (d = 4.670 Å).^[25] The *B*-type monomers formed rows in a direction perpendicular to the b-axis, and proximity related thyminyl rings stacked down the b-axis. In the latter case, the proximity related rings possessed a large olefinic separation distance of 4.94 Å. Rows of type *A* molecules and type *B* molecules stacked in an alternating pattern to give the overall structure shown in **Figure S3c**. Large solvent-accessibe channels run down the a-axis in the structure (**Figure S3d**), which are proposed to contain disordered solvent molecules (not included in the refined structure).



Figure S3 Crystal structure of **10**. (a) Shows the extended alignment of the closest related type A monomers. (b) Shows the olefinic alignment in the closest thyminyl pair (Type A monomers, atoms involved the C=C bonds are represented as spheres) (c) Monomer packing diagram: A-type monomers are shown in red, and B-type monomers are shown in blue (viewed down the c-axis). (d) View down the a-axis reveals the large channels that are proposed to contain disordered solvent molecules. (e) Partial structure with some of the short C2=O⁻H6C contacts indicated.

Powder (P-XRD)

The powder X-ray diffraction data were collected using a Bruker D8 Focus powder diffractometer with CuK α radiation (1.5418 Å) at 40 kV and 30 mA. The powdered crystalline samples were analysed between 2 θ angles of 5°- 60°, and the samples were scanned at a rate of 1 deg.min⁻¹ (step size $2\theta = 0.02^{\circ}$).



Figure S4 P-XRD of compounds. exp = experiment, sim = simulation