



Chirality-controlled spontaneous twisting of crystals due to thermal topochemical reaction

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Crystals that show mechanical response against various stimuli are of great interest. These stimuli induce polymorphic transitions, isomerizations, or chemical reactions in the crystal and the strain generated between the daughter and parent domains is transcribed into mechanical response. We observed that the crystals of modified dipeptide LL (N_3 -L-Ala-L-Val-NHCH₂C≡CH) undergo spontaneous twisting to form right-handed twisted crystals not only at room temperature but also at 0 °C over time. Using various spectroscopic techniques, we have established that the twisting is due to the spontaneous topochemical azide–alkyne cycloaddition (TAAC) reaction at room temperature or lower temperatures. The rate of twisting can be increased by heating, exploiting the faster kinetics of the TAAC reaction at higher temperatures. To address the role of molecular chirality in the direction of twisting the enantiomer of dipeptide LL, N_3 -D-Ala-D-Val-NHCH₂C≡CH (DD), was synthesized and topochemical reactivity and mechanoresponse of its crystals were studied. We have found that dipeptide DD not only underwent TAAC reaction, giving 1,4-triazole-linked pseudopolypeptides of D-amino acids, but also underwent twisting with opposite handedness (left-handed twisting), establishing the role of molecular chirality in controlling the direction of mechanoresponse. This paper reports (i) a mechanical response due to a thermal reaction and (ii) a spontaneous mechanical response in crystals and (iii) explains the role of molecular chirality in the handedness of the macroscopic mechanical response.

chirality | mechanoresponsive crystals | topochemical reactions | twisting | spontaneous

There is tremendous interest in the study of stimuli-induced molecular level changes leading to macroscopic mechanical motion or changes in crystals. Such mechanically responsive crystals are expected to find use in a variety of practical applications (1–3). Various stimuli such as light, heat, and pressure induce conformational changes, packing changes, isomerizations, or chemical reactions inside the crystal. Such molecular-level responses to stimuli often result in the development of local packing strain between the parent and daughter domains (4, 5). Relaxation of such strain can manifest in a mechanical response at the macroscopic level (whole crystal) (1). There are two pathways of relaxation leading to different kinds of mechanical responses: (i) slow and continuous relaxation of strain, as and when generated, by mechanical reconfiguration of the crystal leading to bending (2, 4–31), twisting (6, 10, 14, 32, 33), coiling (16, 34), shape change (35), or size change (7, 25, 31, 36–38) or (ii) sudden relaxation leading to stimuli-salient effects (2, 9, 12, 39–50) such as jumping, hopping, exploding, displacement, and so on, after accumulation of stress over an induction period, to a critical level. All of the known mechanical responses in crystals are due to (i) photoisomerizations (16, 24–31, 34, 43), (ii) photochemical reactions (2, 5–23, 32, 33, 35–37, 39–42), (iii) pressure-induced change in molecular packing (44, 51–57), or (iv) heat-induced polymorphic transitions (4, 38, 44–50). As many photochemical processes (photochemical reactions or photoisomerizations) are reversible, light-induced mechanical responses in crystals are often reversible. To the best of our knowledge there is no mechanical response reported as a result

of thermal reaction. Also, the role of molecular chirality in macroscopic mechanical behavior of a crystal has not been addressed so far. Herein, we report a spontaneous twisting of the crystals due to a thermal cycloaddition reaction between azide and alkyne and also the role of molecular chirality in dictating the direction of twisting.

Results and Discussion

Recently we reported a method for the synthesis of pseudopolypeptides by the topochemical polymerization of a small peptide (58, 59). Dipeptide LL (N_3 -L-Ala-L-Val-NHCH₂C≡CH) has the complementary reactive motifs azide and alkyne at its termini crystallized in parallel β -sheet packing, which brings the azide and the alkyne motifs of adjacent molecules to proximity. The rectangular plate-like crystals of LL upon heating at 85 °C underwent crystal-to-crystal topochemical azide–alkyne cycloaddition (TAAC) reaction, forming 1,4-triazole-linked pseudoproteins (58) (Fig. 1).

We have serendipitously noticed that the crystals of dipeptide LL stored at room temperature for several weeks showed twisted morphology. However, freshly made crystals of LL were not twisted and showed normal rectangular plate-like morphology. This suggested that the crystals of LL undergo spontaneous twisting at ambient conditions. To confirm this, crystals of freshly crystallized dipeptide LL were kept at room temperature and were monitored regularly. To our surprise, these crystals were

Significance

Recently many crystals have been reported to show various mechanical responses when triggered by stimuli (heat, light, and pressure). Such properties are attributed to polymorphic transitions, conformational changes, packing changes, isomerizations, or chemical reactions inside the crystal and the consequent strain developed between parent and daughter phases. The role of molecular chirality in such macroscopic phenomena is yet to be established. In the present study we found that crystals of dipeptide LL undergo right-handed twisting and those of its enantiomer, dipeptide DD, undergo left-handed twisting upon heat-induced topochemical azide–alkyne cycloaddition. This study provides clear evidence for the role of molecular chirality in controlling the direction of macroscopic twisting of crystals.

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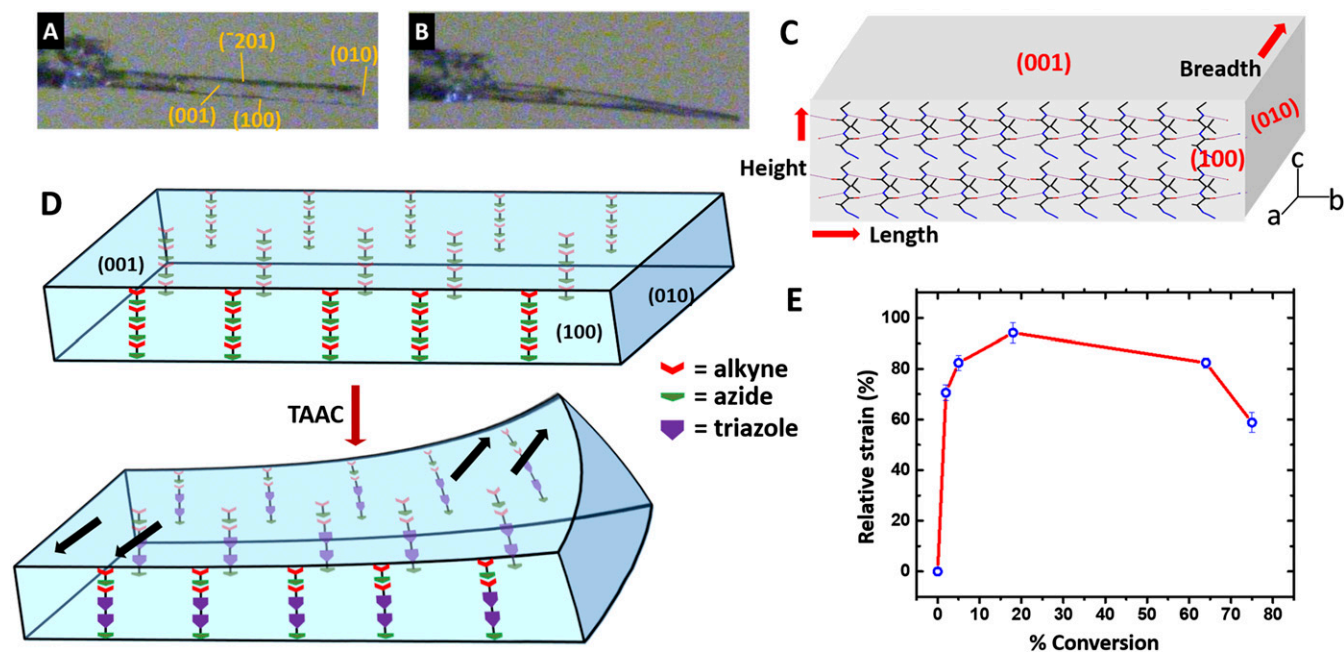


Fig. 3. (A) Photograph of the LL crystal and face indices before twisting of the crystal (0.250 mm \times 0.080 mm \times 0.030 mm). (B) Appearance of the crystal (0.250 mm \times 0.080 mm \times 0.030 mm) after heating at 85 °C for 30 min on the goniometer. (C) Representation of a long rectangular plate-like crystal with various planes. Directions of TAAC reaction (c) and β -sheet formation (b) are also shown. (D) Schematic representation of generation of asymmetric distribution of product and reactant domains (layers) due to the nonuniform thermal stimuli and subsequent twisting. The triazole motif is color-coded as a violet pentagon, unreacted azide as a green arrowhead, and alkyne as red arrow tail (arrow indicates plausible direction of strain generated during the reaction). (E) Plot of the change in strain with the progress of the TAAC reaction (percent conversion) at 85 °C for LL (error bar shown in relative strain is obtained by the SD method).

diffraction (PXRD), and differential scanning calorimetry] revealed that the crystals had undergone a spontaneous topochemical reaction to give oligomers (*SI Appendix*, Fig. S1) and that the TAAC reaction was the cause of twisting of the crystals.

This previously unnoticed, interesting phenomenon of spontaneous TAAC reaction and the consequent twisting at room temperature (rt) motivated us to investigate whether such a mechanical response can happen during the thermally activated TAAC reaction of LL, leading to the formation of higher oligomers. We heated a freshly crystallized sample of the dipeptide LL at 85 °C for 3 d, and these crystals were imaged using optical polarizing microscopy (Fig. 2 C and D). As expected, all of the crystals were twisted without losing their birefringence (*SI Appendix*, Fig. S2 A–D). This suggests that their crystalline nature is maintained even after twisting.

Hot-stage polarizing microscopic study revealed that the twisting happens gradually (*Movie S1*). We heated a crystal of LL gradually in a hot-stage polarizing microscope at a heating rate of 10 °C/min (Fig. 2E). The crystal started twisting without losing its birefringence at 75 °C and continued twisting up to 90 °C. Further heating did not result in more twisting, but the birefringence of these crystals completely disappeared at 150 °C, suggesting the loss of crystallinity at this temperature; ^1H NMR of these heated crystals showed 10% conversion (reaction). This suggests that the twisting of the crystals occurs as a result of topochemical reaction (*SI Appendix*, Fig. S4). Cooling of the twisted crystals did not show any untwisting (*SI Appendix*, section 3C and Fig. S3). This irreversible nature of the mechanical response is not surprising as the TAAC reaction, the basic process responsible for the mechanoresponse, is irreversible. This is in contrast to photoinduced twisting in crystals, which is reversible.

To correlate the direction of the TAAC reaction with twisting, crystal-face indexing was done (*SI Appendix*, Fig. S7). The (100), (010), (001), and ($\bar{2}01$) planes were identified as various faces of

the crystal (Fig. 3C). A probable mechanism for twisting may be similar to the one proposed by Naumov et al. (1). It is clear from the face indexing that the reaction occurs along the height (c-direction) of the crystal. Since the reaction involves the formation of covalent linkages, there will be a reduction in the thickness of the crystal. Upon heating, molecules at the heat-exposed face of the crystal would react faster, thereby reducing d-spacing between the (001) planes present at the exposed face (shrinking of the crystal along the c-direction or height of the crystal) while the d-spacing at the unexposed (unreacted) part remains intact (Fig. 3D). This asymmetric distribution of product and reactant domains (layers) due to the nonuniform thermal stimuli leads to a layered bimorphic structure and generates interfacial strain between the layers (10). Also, the energy released in the reaction, the reduction in the thickness (height) of the crystal due to the cycloaddition reaction along that dimension, and the change in the crystal volume would contribute to the overall strain. To release this strain the crystal undergoes a gradual relaxation by ribbon twisting along the length of the crystal contemporaneously with the reaction (Fig. 3D). It is noteworthy that in such layered bimorphic structures ribbon twisting is a predicted mode of relaxation (10, 32, 60). As the reactive motifs, azide and alkyne, are not in a reactive orientation in the monomer crystal, for the reaction to happen the monomer molecules have to twist to align the reactive motifs parallelly, and this molecular motion (twisting) of the homochiral monomer would influence the direction of the macroscopic twisting. As the polymerization/oligomerization reaction leads to oligomers/polymers of different sizes the heterometry in the crystal would be sustained. This might also account for the irreversibility of the twisting.

Williamson–Hall strain analysis (61, 62) of the crystals of dipeptide LL revealed that they are inherently strained (*SI Appendix*, section 9B). Time-dependent strain analysis showed that the strain increases initially with time and later decreases,

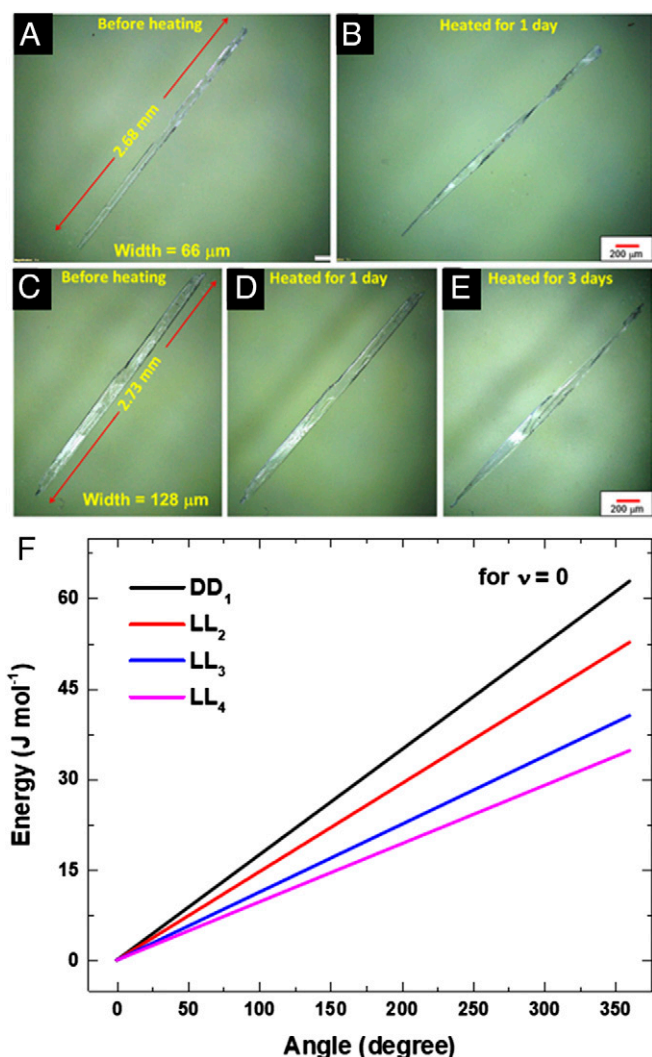


Fig. 6. Optical microscopic images of thinner crystal (A) before and (B) after heating at 85 °C for 1 d. Optical microscopic images of thicker crystal (C) before and after heating for (D) 1 d and (E) for 3 d. (F) Plot of energy versus angle of twist of various dipeptide crystals (DD and LL) having different dimensions. (Scale bar: 200 μm.)

crystals of different sizes, a thin crystal (2.7 mm × 0.07 mm × 0.015 mm) and a thick crystal (2.7 mm × 0.13 mm × 0.036 mm).

Both the crystals were heated at 85 °C and imaged through optical microscopy. The thin crystal twisted completely within a day (Fig. 6 A and B), whereas the thick crystal required prolonged heating for 3 d to undergo considerable twisting (Fig. 6 C–E). Although this suggests that the kinetics of twisting depends on the size, it is noteworthy that even large crystals undergo twisting. The influence of crystal length on the twisting was further investigated by monitoring the twisting of several crystals (of DD and LL) of different lengths heated at 85 °C for 5 d. It revealed that longer crystals underwent more twists with time, whereas shorter ones formed a few twists (SI Appendix, Fig. S18 and Table S2). It was also found that the rate of twisting is slow at lower conversion and increases rapidly at higher conversion (SI Appendix, Fig. S19). The energy required to twist the representative sample crystals by 360° was calculated (69) to be 34.5–62.8 kJ/mol (Fig. 6F and SI Appendix). This energy can be easily obtained from the heat released (–250 kJ/mol) due to the TAAC reaction (SI Appendix, Table S3). Also, plots of angle of twist versus the energy required to twist for crystals (of various dimensions) showed the influence of crystal dimensions on the ease of twisting.

Conclusions

We have presented a report of a spontaneous twisting of crystals not only at room temperature but also at 0 °C as a consequence of spontaneous TAAC reaction. The crystals of dipeptide LL undergo right-handed helical twisting, whereas its enantiomer dipeptide, DD, undergoes left-handed twisting. The inherent strain in the crystals triggers the TAAC reaction, and this reaction involves considerable rearrangement of molecules within the crystal lattice, which leads to further packing strain. To release the strain the crystal undergoes twisting in a direction dictated by the molecular chirality. This report shows a mechanical response by a crystal (i) that occurs spontaneously and (ii) is triggered by a thermal topochemical reaction and (iii) whose directionality is controlled by the molecular chirality. This study showing a trigger to initiate mechanoreponse and chirality as a tool to bias the direction of mechanoreponse might be useful for designing smart materials.

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