1. Two-dimensional (2D) periodic surface: various preparation methods

1.1. Recent achievements to obtain periodic 2D single-layered surface (Figure 1)

(a) Exfoliation of aggregated sheets: 3D → 2D (mica, molybdenite, graphene)
- Mechanical (exfoliation by scotch-tape) or solvent treatment (obtaining dispersion)
  ✓ Easy method, large scale production
  X Limited structure of sheets, harsh synthetic condition

(b) Self-assembly of monomer and tuning the structure with additives: 0D → 2D (Figure 2)[1]
- Tuning of molecular orientation and size of oriented domains by changing an additive
  ✓ Easy fabrication and tuning of surface properties
  X Limited substrate for fabrication
  X Structural weakness (solved by cross-linking)
  X Difficulty in finding the condition of controlling molecular ordering

(c) Covalent linkage: 0D → 1D → 2D (Figure 3)[2]
- Anisotropic polymerization by different terminal halogen atom
  ✓ Ability to tune the structure, surface energy, etc.
  X Defects originating from <100% reactivity
- In general, polymer bearing two-dimensional periodicity has rarely been synthesized.
1.2. This work: polymerization of pre-organized crystal
(d) Strategy: 0D → 3D → 2D
✓ Polymerization using cyclization with complete site-selectivity to obtain periodic structure
✓ Preparation of polymer sheets without any supporting surface
X Complicated synthetic method

2. Synthesis, crystallization of monomer, and photopolymerization
2.1. Overview of synthesis of monomer (Scheme 1)[3]
• C₅-symmetrical monomer 6 bearing terphenylene bridge (TPB) and diethynylanthracene (DEA) unit by sequential Sonogashira coupling and final capping by esterification

Scheme 1. Synthesis of monomer 6
2.2. Crystallization, photopolymerization, and single-layer exfoliation

- **C$_3$-symmetrical layered structure** with separation of TPB and DEA
  - Prevention of interlayer polymerization by TPB “insulator”
- Plate or rod structure with hexagonal face (Figure 5)
- Exfoliation by heating in solvent (NMP)
- AFM image (Figure 6)
  - Single layered sheets with 1-2 µm lateral size

**Plausible reason of exfoliation**
1. Conformational relaxation: destabilization of stacked state due to shrinkage of crystal size
2. Shear force induced by thermal treatment and by internal strain

**Figure 4.** Crystallization of monomer 6

**Figure 5.** Optical microscopic images of the crystal before photopolymerization and after polymerization and exfoliation

2.3. Insights into chemical structure (Figure 7)

- Photopolymerization reaction using a model compound $\rightarrow$ [4 + 4] cycloaddition
- Raman spectra of polymer (Figure 8): decrease in C≡C bond signal by 50%, increase in C=C bond signal, disappearance of anthrène signals
  - $\rightarrow$ [4 + 2] cycloaddition of anthrène unit
- Difference in reaction type: structural strain in the

**Figure 6.** An AFM image of polymer sheets on mica, whose height well agreed with that of expected single layer

**Figure 7.** Plausible cyclization pathway
crystal which prohibiting \([4 + 4]\) addition in the crystal

3. **Properties of two-dimensional polymer**

3.1. **Internal periodicity**
- TEM of eight layered sheets (single layer was unstable against electron beam, Figure 9)
- Periodic structure with diffraction similar to that of monomer crystal
- Retaining of structure after polymerization

3.2. **Structural rigidity**
- Chemical tolerance: highly stable against CHCl₃, TCE, etc. (Figure 10) for >4 months
- Mechanical stability: unlike graphene, no folding of polymer sheets on Cu grid
- Polymerized structure with rigid chemical bonding (norbornene bridge)
- Mw > 10⁸ Da for >1 μm² sheet: one of the largest polymer (cf. cellulose and polyethylene: ~10⁶ Da)

4. **Conclusion and perspective**
- Two-dimensional polymer bearing internal periodicity and structural rigidity was prepared by bottom-up synthesis.
- Utilization of this polymer sheets: functionalization of capped part by ester exchange for filtration of small molecules or bottom-up construction of 3D structure

5. **References**