Structure of Two-Dimensional Polymers in Solution

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Two-dimensional (2D) polymers, which are single-molecule-thick polymer compounds, have garnered significant interest from both fundamental and applied science perspectives. The structure of 2D polymers in solution is particularly intriguing. It is hypothesized that these polymers may adopt either an extended planar structure or a crumpled form, akin to a crumpled piece of paper, depending on the rigidity of the polymer sheet. However, due to the lack of methods for synthesizing highly dispersible 2D polymers in large quantities, experimental investigations have been limited.[1]

N. Hosono and T. Uemura et al. have developed a synthesis method using metal-organic frameworks (MOFs) as templates to produce large quantities of single-molecule-thick 2D polystyrene.[2] The synthesized 2D polystyrene features polystyrene chains cross-linked within the 2D plane, allowing us to vary the rigidity of the sheet by adjusting the degree of cross-linking. These polymers are soluble in organic solvents such as toluene and chloroform and exhibit good dispersion in laser light scattering experiments. Here, our research aims to elucidate the solution structure of 2D polystyrene using neutron small-angle scattering (SANS). This study is significant as it addresses a fundamental property of 2D polymers that could impact their future applications as efficient coating agents or dispersants.

To investigate the solution structure of 2D polystyrene, we employed SANS measurement, which is suitable for examining large molecular sizes (approximately 50–100 nm) at low Q regions, beyond the capabilities of X-ray small-angle scattering. The experiments were conducted using a Peltier temperature-controlled sample changer at 25°C. We prepared four types of deuterated toluene solutions: three 2D polystyrene samples with cross-linking degrees of 1%, 3%, and 7% (molecular weight ~200,000), and one linear polystyrene sample (molecular weight ~200,000) at 2 wt% concentration.

From a fit to experimental SANS data (Fig. 1), in the q = 0.005-0.01 region, the scattering intensity for 1% and 3% cross-linked samples does not fit the q^{-2} relationship, whereas the 7% cross-linked sample does. This indicates that at cross-linking densities of 7% or higher, 2D polystyrene maintains a plate-like structure in solution. Thus, this study revealed that 2D polymer with rigidity derived from high crosslinking ratio are dissolved as a planar structure in solution.

[1] A. D. Schlüter, P. Payamyar, H. C. Öttinger, *Macromol. Rapid Commun. 37, 1638–1650 (2016).*

[2] N. Hosono, S. Mochizuki, Y. Hayashi, T. Uemura, *Nat. Commun.* 11, 3573, (2020).

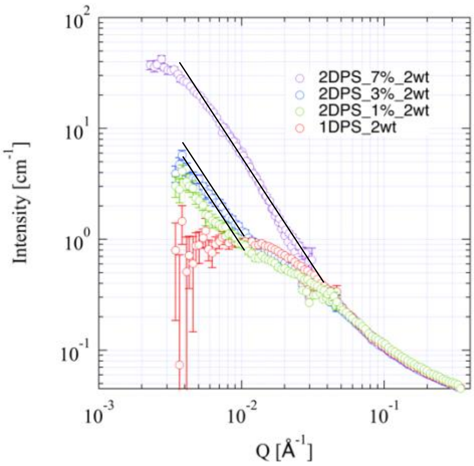

Fig. 1. Neutron diffraction scattering of 2D polystyrenes with different crosslinking ratio (7%: purple, 3%: blue, 1%: green) and 1D polystyrene as a reference (red). Solid line (black) shows the q^{-2} power law, characteristic of plate-like structures.