New polymer mesophase structure discovered

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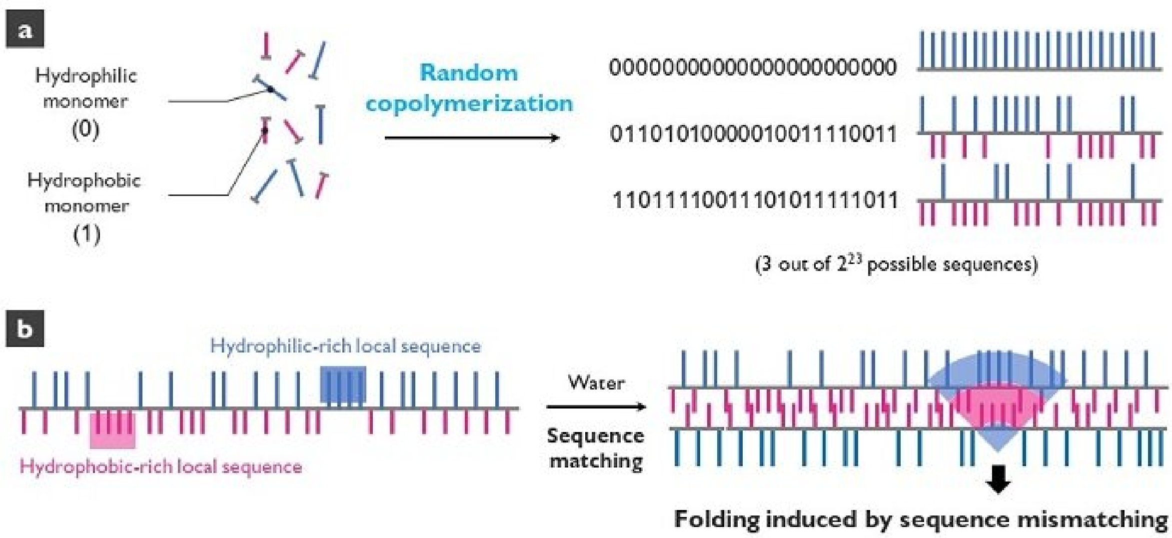

(a) Random copolymerization of hydrophilic and hydrophobic monomers. Three binary sequences that can be generated by the random copolymerization are given as examples for the copolymer consisting of 23 repeating units. (b) A random sequence can be drastically heterogeneous and contain hydrophilic- and hydrophobic-rich local sequences. When the chains associate in water via hydrophobic interaction, local sequence mismatches can take place for long chains leading to folding because of the curvature instability.

Credit: Korea Advanced Institute of Science and Technology

Polymers, large molecules made up of repeating smaller molecules called monomers, are found in nearly everything we use in our day-to-day lives. Polymers can be natural or created synthetically. Natural polymers, also called biopolymers, include DNA, proteins, and materials like silk, gelatin, and collagen. Synthetic polymers make up many different kinds of materials, including plastic, that are used in constructing everything from toys to industrial fiber cables to brake pads.

As polymers are formed through a process called polymerization, the monomers are connected through a chain. As the chain develops, the structure of the polymer determines its unique physical and chemical properties. Researchers are continually studying polymers, how they form, how they are structured, and how they develop these unique properties. By understanding this information, scientists can develop new uses for polymers and create new materials that can be used in a wide variety of industries.

In a paper published in *Nature Communications* on May 4, researchers describe a new structure found in an aqueous solution of an amphiphilic copolymer, called a bilayer-folded lamellar mesophase, that has been discovered through a random copolymer sequence.

"A new mesophase is an important discovery as it shows a new way for molecules to self-organize," said Professor Myungeun Seo at the Department of Chemistry at KAIST. "We were particularly thrilled to identify this bilayer-folded lamellar phase because pure bilayer membranes are difficult to fold thermodynamically."

Researchers think that this mesophase structure comes from the sequence of the monomers within the copolymer. The way the different monomers arrange themselves in the chain that makes up a copolymer is important and can have implications for what the copolymer can do. Many copolymers are random, which means that their structure relies on how the monomers interact with each other. In this case, the interaction between the hydrophobic monomers associates the copolymer chains to conceal the hydrophobic domain from water. As the structure gets more complex, researchers have found that a visible order develops so that monomers can be matched up with the right pair.

"While we tend to think random means disorder, here we showed that a periodic order can spontaneously arise from the random copolymer sequence based on their collective behavior," said Professor Seo. "We believe this comes from the sequence matching problem: finding a perfectly complementary pair for a long sequence is nearly impossible."

This is what creates the unique structure of this newly discovered mesophase. The copolymer spontaneously folds and creates a multilamellar structure that is separated by water. A multilamellar structure refers to plate-like folds and the folded layers stack on top of each other. The resulting mesophase is birefringent, meaning light refracts through it, it is similar to liquid crystalline, and viscoelastic, which means that it is both viscous and elastic at the same time.

Looking ahead, researchers hope to learn more about this new mesophase and figure out how to control the outcome. Once more is understood about the mesophase and how it is formed, it's possible that new mesophases could be discovered as more sequences are researched. "One of the obvious questions for us is how to control the folding frequency and adjust the folded height, which we are currently working to address. Ultimately, we want to understand how different multinary sequences can associate with another to create order and apply the knowledge to develop new materials," said Professor Seo.

More information: Minjoong Shin et al, Bilayer-folded lamellar mesophase induced by random polymer sequence, *Nature Communications* (2022). DOI: 10.1038/s41467-022-30122-z

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