

Filamentous Virus-Based Assembly: Relationship between Their Oriented Structures and Thermal Diffusivity

Organic polymers are generally regarded as thermal insulators because amorphous arrangement of molecular chains reduces the mean free path of heat-conducting phonons. However, recent studies revealed that highly oriented single polymeric chains could have higher thermal conductivity than bulk polymers because stretched polymer chains effectively conduct phonons through polymeric covalent bonds. Here, we demonstrate the possibility of non-covalent virus assembly prepared by simple flow-induced methods toward the creation of high thermal conductive polymeric materials. Films with high thermal diffusivity composed of non-covalent bond-based assemblies of liquid crystalline filamentous viruses were prepared using a simple flow-induced orientation method. Structural and thermal characterization demonstrated that the highly oriented structures of the viruses in the films affected the high thermal diffusivity.

Organic polymers with high thermal conductivity have been of great interest for flexible electronic devices due to their lightweight and (typically) electronic insulation properties. However, the thermal conductivity of bulk polymers is very low because of strong phonon scattering caused by various defects, interfaces, and the isotropic molecular orientations in amorphous regions. Highly oriented polymers such as liquid crystalline polymers are promising candidates because the well-oriented polymer chains effectively conduct phonons through polymeric covalent bonds. Although significant efforts have focused on the development of various technologies to increase their thermal conductivity, the design of a simple control method to achieve high thermal conductivity via non-covalently assembled structures has attracted little attention.

M13 bacteriophage (phage), one of the filamentous viruses [Fig. 1(a)], is a regular assembly of plural proteins and genetic DNA. Recently, it has been reported that the phages can be utilized as a material component in various fields due to their unique functions, which are easily integrated into the phages by genetic or chemical modification of the coat proteins on surfaces. Further-

more, the frameworks of phages are competent liquid crystal mesogens that are capable of forming various phases due to their high aspect ratio (4.5 nm width and 900 nm length), dipole properties, and charge densities. The liquid crystalline structures are controlled using various methods, and, in particular, a method using substrates (i.e., solid/liquid interfaces) has recently been used to create liquid crystalline virus materials, such as sensors, electronics, and devices.[1, 2] Although a phage comprises a supramolecular assembly of well-packed coat proteins, the phage acts as a potential thermal conductive material component due to its filamentous structure and liquid crystallinity.

Here, we demonstrate a straightforward technique for the preparation of phage films with highly oriented liquid crystalline structures using flow-induced methods and glass plates circularly patterned with a highly water-shedding coating [Fig. 1(b)]. The thickness of the outside of the film was visibly thicker than other positions on the film. Because a drop of solution on a solid surface leaves a dense ring-like deposit along the perimeter (coffee-ring effect), the increased thickness on the film outside may be caused by the capillary

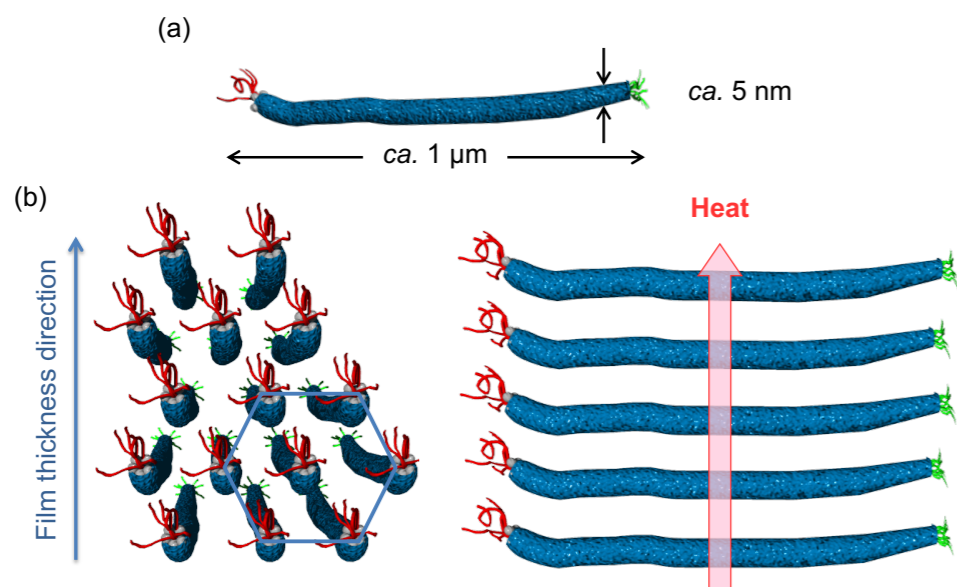


Figure 1: Schematic representations. (a) Phage and (b) hexagonally assembled structures of the phages in the film.

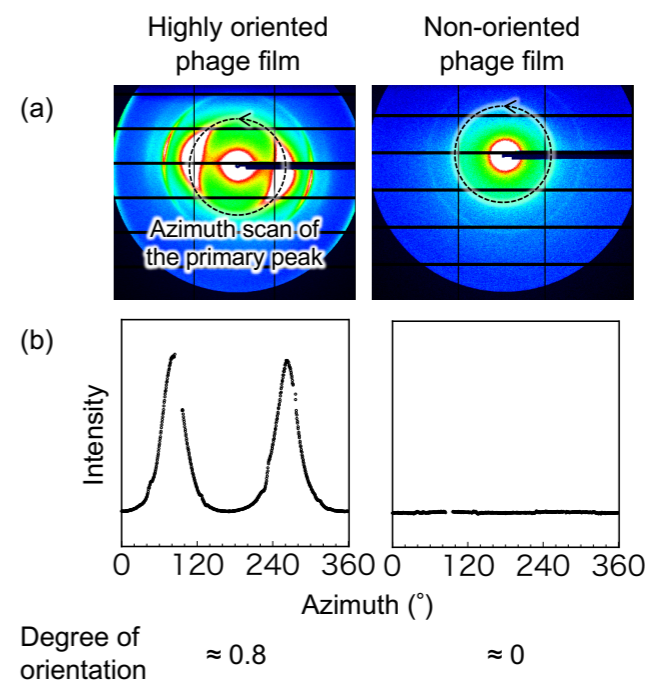


Figure 2: SAXS analyses of the phage films. (a) Two-dimensional patterns for the highly oriented (outside) and non-oriented phage films. (b) Azimuth scan of the primary peaks and resultant degree of orientation values.

flow of solutes. Thermal diffusivity values of the phage films at the outside, midpoint, and center of the film in a perpendicular (thickness) direction were measured by temperature wave analysis. The thermal diffusivity value on the outside ($6.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$) was approximately 10 times greater than that of the non-oriented film and approximately 7 times greater than those at other points, demonstrating the extremely high thermal diffusivity on the outside of the film.

To characterize the oriented structures of the phages, small-angle X-ray scattering (SAXS) experiments were performed on the outside, midpoint, and center of the film as well as the non-oriented film. Typical results are shown in Fig. 2. In the resulting scattering profiles for all the positions, intense peaks with a reciprocal d -spacing ratio of $1:\sqrt{3}:2$, which indicates hexagonally packed structures of the phages, were observed. The primary peak intensities and positions (7.9–8.3 nm) were comparable irrespective of the positions, and so packing of the phages on a molecular level is essentially the same. To quantitatively investigate the oriented structures of the phages, an azimuth scan of the primary peaks at approximately 8 nm was performed. Full width at half maximum (FWHM) was determined by fitting with the pseudo-Voigt function to calculate the degree of orientation, which indicates the orientation of the phages within the volume of irradiation. In this calculation, the degree of orientation ranges from 0 to 1, and a higher value represents a higher degree of orientation. The resulting degree of orientation of the outside of the film (0.81) was extremely high compared with those of the other positions, suggesting that the assembled phages on the outside of the film are highly oriented. The de-

gree of orientation for the non-oriented film with the lowest thermal diffusivity could not be determined because no peaks for the azimuth scan were detected. A comparison of the values of thermal diffusivity and orientation degrees indicated that no linear correlation existed between them, and only films with a high degree of orientation (0.81) exhibited high thermal diffusivity. These results suggested that the highly oriented structures of the assembled phages with a scale of several hundred μm (area measured by SAXS) resulted in a high thermal diffusivity, which may be due to highly efficient phonon transport. Therefore, the increase in the thermal diffusivity was not substantially influenced by the moderate orientation of the domains of the assembled phages. Based on all the structural and thermophysical characterizations, the thermal diffusivity of the liquid crystalline phage film measured in the perpendicular direction substantially increased due to the highly oriented assembly of the phages, which may be due to a decrease in phonon scattering at structural defects in the phage-assembled structures [3].

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BEAMLINES

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T. Sawada^{1,2}, Y. Murata¹, H. Marubayashi¹, S. Nojima¹, J. Morikawa¹ and T. Serizawa¹ (Tokyo Tech.² JST)