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Preparation and Molecular Orientation of a Regular Cast Film of Fluorocarbon Bilayers1)

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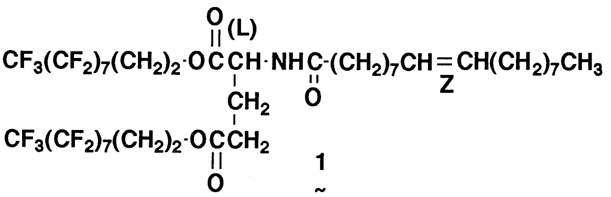
A multilayered cast film was prepared from a dispersion of a fluorocarbon/hydrocarbon amphiphile in chlorocyclohexane. Its solid-solid phase transition involved unwinding of the fluorcarbon helix and improved chain alignment.

Conventional bilayer membranes possess highly ordered two-dimensional structures and are assembled spontaneously from dilute aqueous dispersions.2) The regular bilayer structure is retained in their macroscopic films that are prepared by casting of the aqueous dispersion on solid supports.3) The unique structural characteristics of the cast film have been studied in detail.4) They can be utilized for anisotropic organization of functional molecules5,6) and as molecular templates of two-dimensional organic7) and inorganic8) networks. A few years ago we reported successful formation of bilayer assemblies in hydrocarbon solvents from novel fluorocarbon "amphiphiles" represented by N-(Z-9-octadecenoyl)-O,O'-bis(1H,1H',2H,2H'-perfluorodecyl) L-glutamate(**1**).9,10) In this novel system, bilayer formation is attained by aggregation and alignment of "solvophobic" fluorocarbon chains and solubilization of "solvophilic" hydrocarbon chains. Very recently, we demonstrated that a reversed combination of solvophobic hydrocarbon chain and solvophilic fluorocarbon chain gave rise to self assembly of the bilayer structure in a fluorocarbon medium.11)

It should be interesting in principle and useful in application, if regular cast films can be produced from these novel "amphiphilic" bilayers. We describe in this paper that a cast multilayer film is in fact obtainable from amphiphile **1** that is dispersed in an aprotic organic solvent.

A chlorocyclohexane dispersion (40 mM) of **1** was cast on a Teflon sheet. Upon drying at room temperature for 4-6 days, a translucent, self-supporting film was formed. Similar films were obtainable also from other organic solvents such as benzene and methylecyclonexane.12) Figure 1 displays differential scanning calorimetry (DSC) thermograms of this cast film. The as-cast film shows a broad endothermic peak at 44°C (peak top, ΔH = 3.9 kJ/mol) and a sharp peak at 65°C (ΔH = 20.0 kJ/mol). The latter peak invariably appeared in the repeated scans, and corresponds to melting of the film as observed by melting point measurement under a crossed Nichol prism. The former peak did not appear in the second and third scans, but appeared again at 48°C (ΔH = 5.4 kJ/mol) after the cast film was kept at room temperature for 7 days. It is clear that recovery of the original (as-cast) chain alignment is a very slow process. This thermal transition is different from the bilayer-to-monomer transition at 32°C (ΔH = 39 kJ/mol) observed for a chlorocyclohexane dispersion of **1**.13)



$CF_3(CF_2)_7(CH_2)_2\text{·}OC(=O)\overset{(L)}{C}H(CH_2C(=O)O(CH_2)_2(CF_2)_7CF_3)\text{·}NHC(=O)\text{-}(CH_2)_7CH\underset{Z}{=}CH(CH_2)_7CH_3$

1

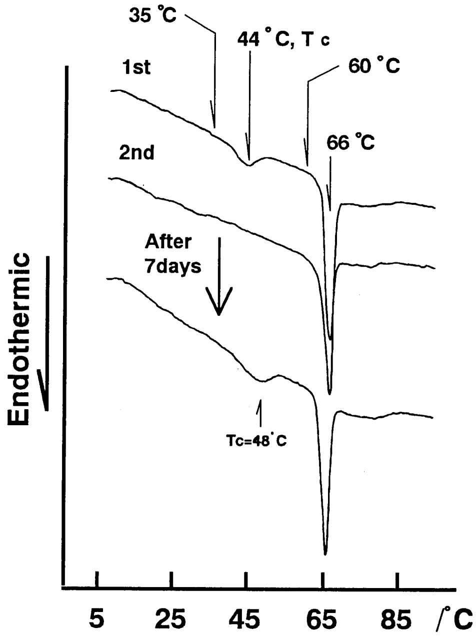


Fig.1. DSC thermograms of a cast film of 1 Seiko Instrument,SSC/5200H. Scanning range,15-80 °C. rate,1 °C/min.

Subsequently, tansition X-ray diffraction (XRD) was conducted for the vertically-positioned, as-cast film. X-ray beam was directed toward the film edge. As given in Fig.2b, regular diffractions with 58-Å spacing were found up to at least 10th order on the equatorial position. Although this number is smaller than twice the extended molecular length (34 Å), the regular layer apparently corresponds to the bilayer assembly found in the cyclohexane dispersion. The shortened spacing would arise from tilting of component molecules, as is frequently observed for aqueous

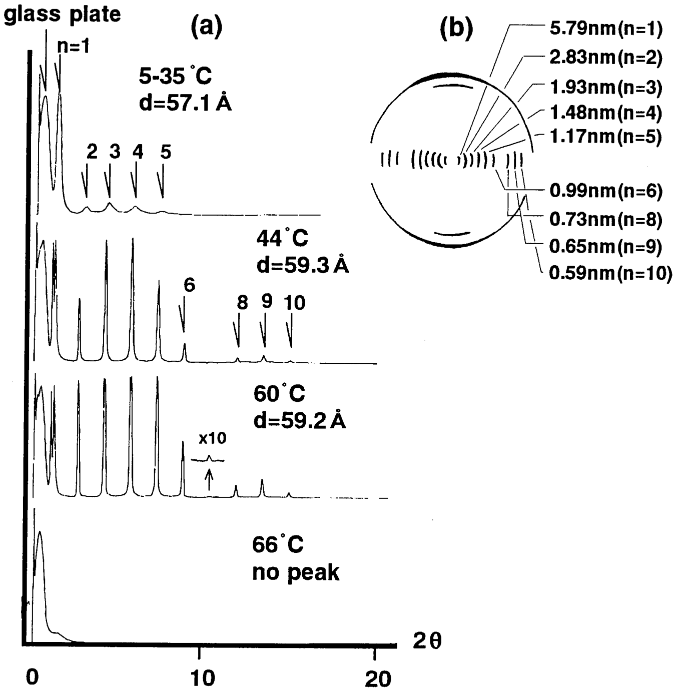


Fig.2. Temperature dependence of reflection and transmission(inset,at 20 °C)X-ray diffraction of the as-cast film. Instrument: Rigaku RAD-R-32.

bilayers and their cast films.7)

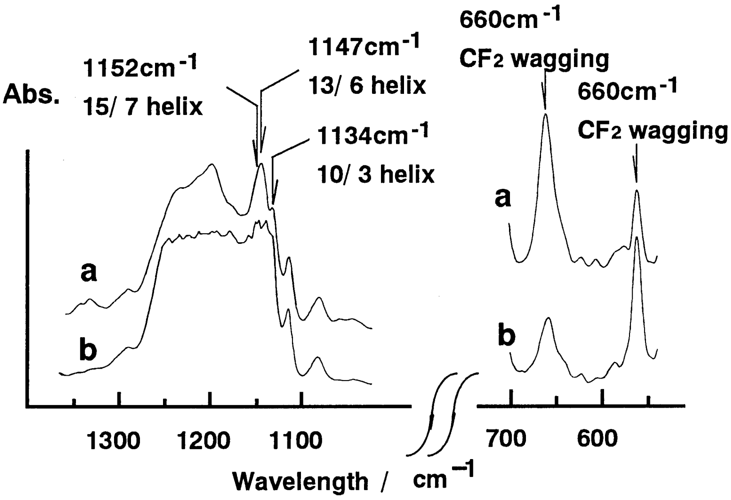


Fig.3. FT-IR spectra of 1. a: 20 °C, as-cast film, b: aged film, 55 °C,5hrs. Nicolet 710 FT-IR spectrometer.

The XRD pattern displays surprising temperature dependence that is related to DSC data. Figure 2b describes reflection XRD data at several critical temperatures. At 5-35°C which is below the first endothermic peak, a series of broad diffractions with d = 57.1 Å are observed. They are replaced by sharp diffractions of d = 59.3 Å at 44 °C which is the peak top of the first DSC peak. This pattern gets sharper up to 60 °C, but disappears at 66 °C where the second endothermic transition occurs. Clearly the first DSC peak corresponds to a solid-to-solid phase transition and the second peak to chain melting (bilayer-to-isotropic transition). The sharp diffraction peaks are retained after cooling to room temperature, and broad peaks of the original as-cast film reappears only after prolonged aging (7 days) at room temperature. This aging behavior is closely related to the disappearance of the 44 °C peak in repeated DSC scans without aging.

The nature of the solid-solid phase transition can be elucidated by FT-IR spectroscopy. It is known that a fluorocarbon chain assumes temperature-dependent helical conformations.14,15) In the case of poly(tetrafluoroethylene), the 10/3 helix with a dihedral angle of 108 ° is transformed to the 15/7 helix (dihedral angle, 168 °) at 19 °C. These conformational changes are reflected in IR vibration modes of the CF_2 unit.16-18) Figure 3 displays an FT-IR spectrum of the cast film at 20 °C. A ν_{C-F} peak characteristic of the 10/3 helix is clearly noticed at 1134 cm^{-1}, together with ν_{C-F} peaks at 1147 cm^{-1} and 1240 cm^{-1} which have been assigned to the 13/6 and 15/7 helices, respectively. At temperatures above the first transition (e.g., ca 55 °C), the characteristic peaks of the 10/3 and 13/6 helices are lessened. These IR changes are associated with partial unwinding of the fluorocarbon helix. IR spectral changes are also noted at the 550-700 cm^{-1} region. The relative intensity (I_{660}/I_{560}) of the CF_2 wagging vibration (at 660 cm^{-1}) and the CF_2 rocking vibration (at 560 cm^{-1}) is 1.56 for the as-cast film and 0.68 for its aged film (55 °C, 5 h). The plane of the wagging vibration is parallel to the CF_2 chain axis and that of the rocking vibration is normal to the chain axis, and the IR beam is directed normal to the film plane. Thus, the observed intensity change indicates that the CF_2 chain becomes aligned more perpendicular by to the film plane upon the phase transition at 44 °C. Combination of these DSC, XRD and IR data shows that this phase transition involve partial unwinding of the fluorocarbon helix, the decrease in chain tilting, and improvement in chain alignment, as schematically illustrated in Fig.4 and Fig. 5.

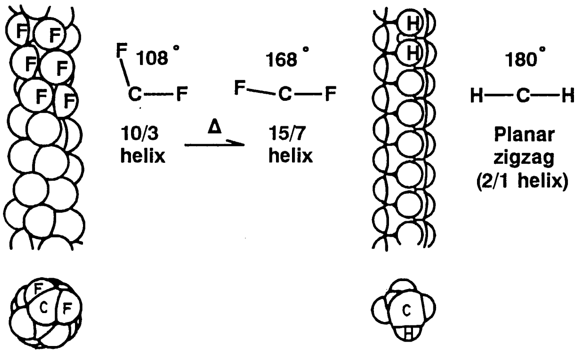


Fig.4. Conformational change of fluorocarbon helix with temperature.

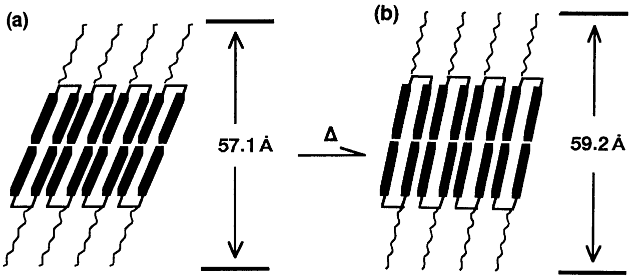


Fig.5. Structural change with temperature of the as-cast film. a: below Tc, b: above Tc.

Russell et al.19) reported that semifluorocarbons underwent crystal-to-crystal phase transitions that involve changes in helical conformation, chain orientation and packing mode. The present finding demonstrates that the helical conformation exert a very strong influence on the chain packing. The regular cast film derived from a non-aqueous dispersion would play an important role as molecular matrices similar to that of the aqueous bilayer.

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