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Design, fabrication, and properties of macroscale supramolecular fibers consisted of fully hydrogen-bonded pseudo-polymer chains†

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Macro-scale supramolecular fibers composed of hydrogen bonded pseudo-polymer chains of guanosine derivatives were fabricated, and physical properties of the fibers were investigated.

Macroscopic-scale supramolecular materials prepared by self-assembling of molecules through noncovalent forces have been drawing a great deal of interest because these materials can offer novel functionality that can not be achieved by conventional polymer materials.[1] Macroscale fiber is the typical form of polymer materials reflecting the tough and flexible nature of the covalently bonded linear polymer chain. Supramolecular assemblies including mesoscopic-scale fibers have been reported in gels and crystals,[2] but little has been known as to the macroscale supramolecular polymers. Pourcain *et al.*[3] and Castellanno *et al.*[4] reported fabrication of supramolecular fiber, though properties of the solid state fiber were not well characterized. We report here design and fabrication of a macroscale supramolecular fiber consisting of a fully hydrogen-bonded pseudo-polymer chain, and clarify for the first time the physical properties of the fiber and the orientation of the pseudo-polymer chain within the fiber. Though hydrogen bonding is recognized as a strong and important intermolecular interaction, hydrogen bonding energy between neutral molecules normally lies in the range of 10–65 kJ mol^{-1} and is considerably weaker compared to the covalent bond.[5] However, tensile strengths of common fibers are far smaller than their ideal tensile strengths and do not directly reflect the strength of their covalent-bond main chains. Orientation of the polymer chains along the fiber axis plays an essential role in determining the tensile strength of the polymeric fibers. Therefore, hydrogen-bonded supramolecular fibers that have better main-chain orientation along the fiber axis might have a sufficiently tough nature.

For this purpose, an alkylsilylated guanosine derivative having long alkyl chains, 2′,3′,5′-tris-*O*-(octadecyldiisobutylsilyl)guanosine (**1**),‡ was selected as a building block of the supramolecular fiber. Supramolecular assemblies of guanosine derivatives have been reported.[6,7] The compound **1** was obtained as white powder (mp 55 °C), but no single crystal suitable for X-ray crystal analysis was obtained. Some of the guanine derivatives are known to form one-dimensional tape units by double hydrogen bonds from 2-NH$_2$ to 6-C=O and from 1-NH to 7-N of the adjacent guanine units in their crystal structures.[8] The same hydrogen-bonded guanine tape units were found in the crystal of 2′,3′,5′-tris-*O*-(*tert*-butyldimethylsilyl)guanosine (**2**) (Fig. 1),§ a model compound of **1** having shorter alkyl chains. The IR spectral pattern of the samples **1** and **2** were identical for the amino stretching and deformation modes in the range from 3000 to 3600 cm^{-1} and from 1600 to 1700 cm^{-1}, respectively.[9] Therefore, a similar guanine tape unit was formed in the solid sample of **1**. Though double hydrogen bonds contributed to more stable intermolecular bonding compared to a single hydrogen bond, they restricted the molecular arrangement of the guanine within the tape yielding a rigid hydrogen-bonded main chain. To fabricate macroscale fibers by aligning the hydrogen-bonded tape units along the fiber axis, we covered the rigid main chain with flexible alkylsilyl groups. The fibrous form of **1** was obtained by melt-spinning from a glass-made syringe heated to about 60–80 °C through a needle (ϕ = 0.3 mm) with take-up velocity of 0.5 m min^{-1} (Fig. 2), but **2** having shorter alkyl chains, could not be fabricated into fibrous structure. Though the spinning rate was extremely slow compared to a conventional or high-speed spinning method (10^2–10^4 m min^{-1}),[10] the fibers thus obtained were sufficiently flexible being 0.02 to 0.21 mm in

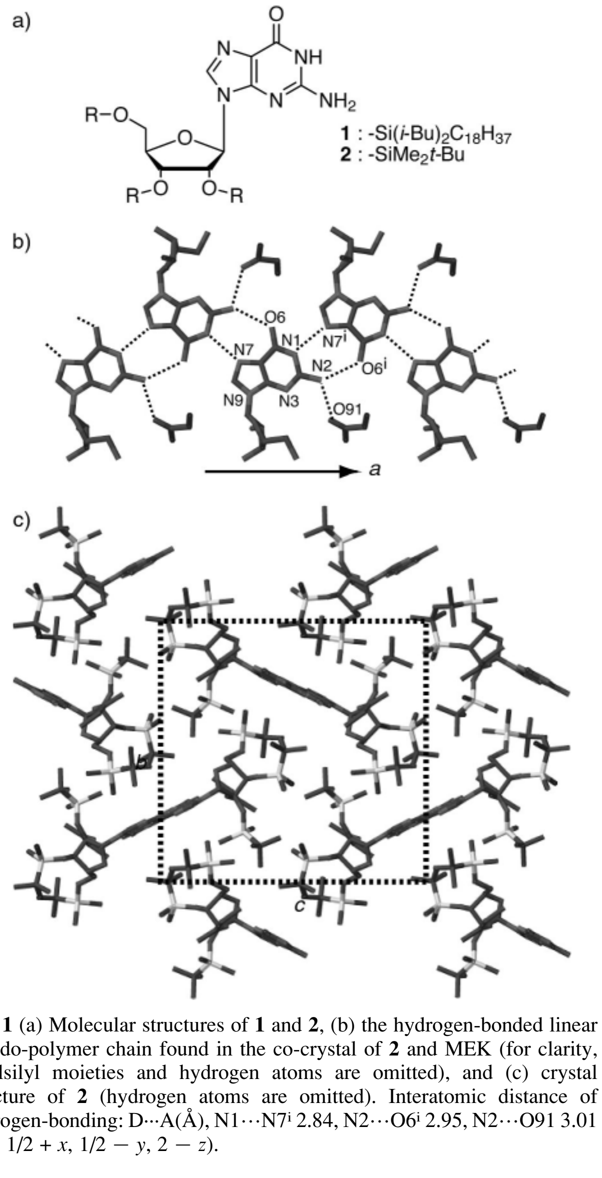

Fig. 1 (a) Molecular structures of **1** and **2**, (b) the hydrogen-bonded linear pseudo-polymer chain found in the co-crystal of **2** and MEK (for clarity, alkylsilyl moieties and hydrogen atoms are omitted), and (c) crystal structure of **2** (hydrogen atoms are omitted). Interatomic distance of hydrogen-bonding: D···A(Å), N1···N7^{i} 2.84, N2···O6^{i} 2.95, N2···O91 3.01 (i = 1/2 + x, 1/2 − y, 2 − z).

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† Electronic supplementary information (ESI) available: DSC curves of the fiber. See http://www.rsc.org/suppdata/cc/b1/b103864h/

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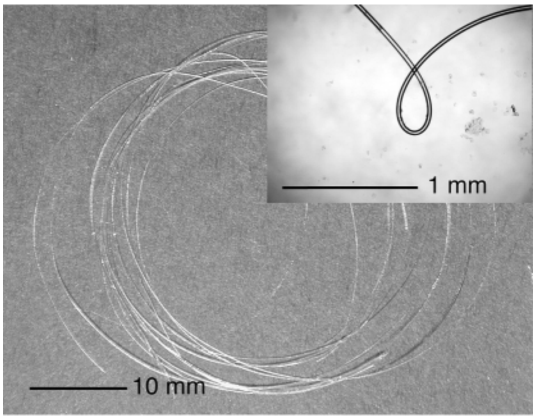

Fig. 2 Typical fibers of **1** obtained by melt-spinning (inset: microscopic view: ϕ = 0.026 mm, smallest curvature 0.23 mm).

diameter (ϕ) and infinite length. The tensile strength of the sample was measured to be 1.91 ± 0.41 MPa with an average elongation at break of 0.98 ± 0.46% (40 samples, ϕ = 0.09–0.20 mm) at ambient temperature and 2.79 ± 0.77 MPa with the average elongation at break of 0.63 ± 0.27% (27 samples, ϕ = 0.07–0.21 mm) at 5 °C.¶ In these experiments, no practical difference was noticed at all for the fibers fabricated by reuse of the fibrous samples. This confirmed the reusable nature of the supramolecular fiber, though the tensile strength of the fiber was still smaller than those of typical polymers (high-density polyethylene 17.9–33.1 MPa).[11] To test the orientation of the pseudo-polymer chain in the fiber, polarized microscopic observation of the fiber was carried out. When the fiber axis was placed 0 or 90° to the plane of polarization, no light transmission was observed at all. Highest light transmission was observed when the fiber axis was set 45° to the plane, suggesting that the orientation of the pseudo-polymer chain was parallel or perpendicular to the fiber axis. Alignment of the tape motifs along the fiber axis was confirmed by X-ray diffraction of the fiber (Fig. 3).[12] The reflection appearing in this direction was the ring at $2\theta = 8.45°$ (r = 10.5 Å) next to the innermost one, which corresponded to the repeated unit length in the pseudo-polymeric tape motif. Therefore, the pseudo-polymer chain was aligned parallel to the fiber axis. From an azimuthal intensity distribution of the innermost reflection at $2\theta = 6.65°$, the Hermans orientation function f_c of the pseudo-polymer chain along the fiber axis was estimated to be 0.20 for the sample used for the tensile strength measurement, and 0.46 for the sample prepared by the faster take-up velocity of 53 m min^{-1}. Structural ordering in the fiber was also indicated from thermal analysis. The first DSC heating curve of the fiber sample prepared by melt-spinning showed three endothermic peaks, a small and broad peak at −3.5 °C (peak top), a shoulder peak at 43 °C (peak top), and a sharp melting peak at 55.5 °C. However, the second heating curve showed only two endothermic peaks, a broad and small peak at −2.5 °C (peak top) and a sharp melting peak at 54.9 °C, which was practically identical to a bulk sample without melt-spinning. The sample became a viscous liquid above the melting point, but no birefringence was observed at all. Though more has to be studied for detailed explanation, this thermal behaviour is suggestive of the presence of the structural ordering in the fiber sample prepared by melt-spinning.

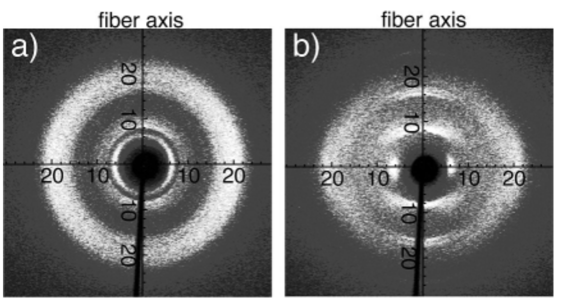

Fig. 3 X-Ray diffraction pattern of the fiber fabricated by take-up velocity of (a) 0.5 m min^{-1} and (b) 53 m min^{-1}. The fiber was placed in the perpendicular direction in these pictures.

Thus, novel molecular design of the low-molecular-weight nucleoside derivative, covering the rigid main chain with flexible alkylsilyl groups, allowed fabrication of the macroscale supramolecular fiber consisting of fully hydrogen-bonded pseudo-polymeric chains by melt-spinning. Relatively high main-chain alignment along the fiber axis was attained even by using a slow spinning rate, and mechanical and thermal properties of the fiber were clarified. The obtained supramolecular fibers were reusable and showed sufficiently flexible nature, though tensile strength of the fiber is still to be improved.

Notes and references

‡ The compounds **1** and **2** were prepared according to the method of Ogilvie *et al.*[13] **1**: FAB-MS *m/z* 1467 ([MH]$^+$ $C_{88}H_{176}N_5O_5Si_3$ requires 1467).

§ Crystallographic data and X-ray diffraction were measured by a DIP-Lab diffraction image processor (MAC Science Co., LTD.). *Crystal data* for **2**·MEK: $C_{32}H_{63}N_5O_6Si_3$, M_w = 698.14, orthorhombic, space group $P2_12_12_1$, a = 11.47600(10), b = 18.5090(2), c = 19.3310(2) Å, V = 4106.08(7) Å^3, Z = 4, T = 100 K, μ (Cu-Kα) = 1.414 mm^{-1}, D_c = 1.129 g cm^{-3}, $F(000)$ = 1520. A total of 46625 reflection data were collected, of which 7920 (R_{int} = 0.039) independent. The structure was solved by direct methods with the program SHELX97[14] and refined by full-matrix least-squares procedures. Convergence to the final R values of R_1 = 0.0434, wR_2 = 0.1132 [$I > 2\sigma(I)$] and R_1 = 0.0449, wR_2 = 0.1202 (all data). CCDC 168941. See http://www.rsc.org/suppdata/cc/b1/b103864h/ for crystallographic files in .cif or other electronic format.

¶ Melt-spinning was performed at feed velocity of 3–15 mm^3 min^{-1} and take-up velocity of 0.5 m min^{-1}. Tensile strength of the sample (length 10 mm) was measured by a Tensilon model UTM-II (Toyo Keisoku Kiki, Co.) with cross-head speed of 0.4 mm min^{-1}.

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