

Hydrogen-Bonding Molecular Assemblies of Alkylamide-Substituted Isophthalic Acid Derivatives with Different Alkyl Chain Lengths

○Chao Lv¹, Takashi Takeda^{1,2}, Norihisa Hoshino^{1,2}, Tomoyuki Akutagawa^{1,2}

¹ Graduate School of Engineering, Tohoku University, Japan

² Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Japan

[Abstract] Alkylamide-substituted isophthalic acid derivatives can form interesting hydrogen-bonding molecular assemblies. Gelation behavior and liquid crystal (LC) formation are evaluated in the structural parameter of alkylamide chain length (n) at $-\text{CONHC}_n\text{H}_{2n+1}$. All compounds ($n = 6, 10, 14,$ and 18) show the gelation behavior in the mixed solvent system of $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$, where H_2O is necessary for the gelation behavior, suggesting in the formation of tubular assembly structure with the hydrophilic inside pore. In addition, different LC phases of hexagonal columnar (Col_h) and lamellar phases ($\text{D}_{\text{L}1}$) are observed by changing in the structural parameter of n and introducing guest H_2O molecules.

[Introduction] Bottom-up molecular assemblies using non-covalent intermolecular interactions such as hydrogen-bonding, π - π stacking and amphiphilic interactions have been attracted much interest because of its potential applications for functional supramolecular assemblies. We have designed the ferroelectric hydrogen-bonding assemblies of alkylamide-substituted benzene derivative and fluorescent ferroelectric hydrogen-bonding pyrene derivative, where the dynamic motion of one-dimensional hydrogen-bonding chain plays an important role to appear the ferroelectric response.^[1,2] In this work, we focused on alkylamide-substituted isophthalic acid derivatives of C6, C10, C14 and C18 ($n = 6, 10, 14, 18$) to develop the novel hydrogen-bonding molecular assembly structures (Fig. 1).

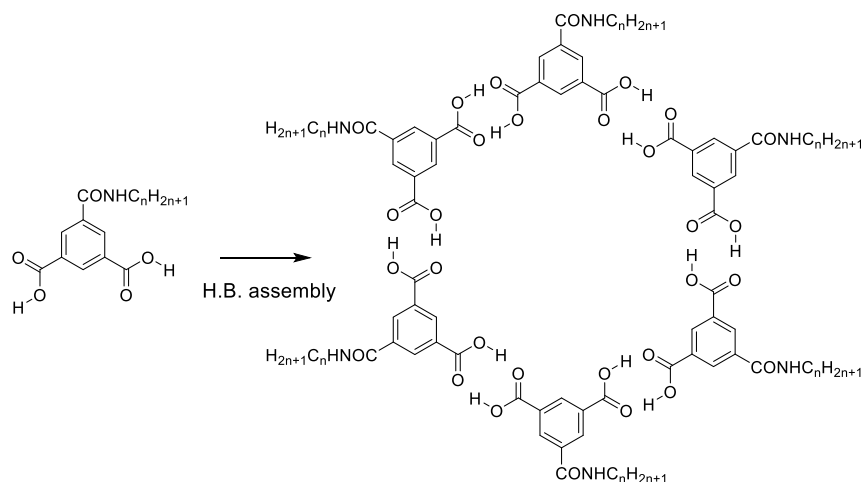


Fig. 1. Possible hydrogen-bonding hexamer structure of C14 ($n = 14$).

[Experimental] Alkylamide-substituted isophthalic acid derivatives of C6, C10, C14, and C18 were prepared from starting material of trimethyl-1,3,5-benzenetricarboxylate. One equivalent sodium hydroxide (NaOH) yielded the corresponding monocarboxylic acid and reaction of thionyl chloride (SOCl_2) generated the corresponding acid chloride, which was further reacted with alkylamine ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$) to form monoalkylamide-dimethylester derivative. Hydrolysis of methylester-groups using lithium hydroxide (LiOH) formed the corresponding C6, C10, C14, and C18 derivatives. Gel states of all the compounds were

confirmed in the mixed solvent system of C₂H₅OH-H₂O and the corresponding xerogel state were prepared by a drop cast method on mica and/or HOPG surfaces with a vacuum dry. LC states of C14 and C18 were observed by a heating of powder sample and/or xerogel of C14 and C18.

[Results and Discussion] Both C14 and C18 can form gel states in the mixed solvent system of C₂H₅OH-H₂O, where the H₂O molecules are necessary to appear gel. From the ¹H NMR measurements, xerogel state included H₂O in the absence of C₂H₅OH. Thermogravimetric analyses of xerogel states of C14 and C18 (Fig. 2) showed the weight-loss of 7.1 % at 120 °C, corresponding to the elimination of eleven molar H₂O per six molar C14 or C18 molecules. Herein, we assumed the formation of O-H•••O= hydrogen-bonding hexamer unit (Fig. 1) to explain the xerogel formula of C14•11(H₂O) and C18•11(H₂O). The diameter of one hexamer is approximately 11 Å and the π-π stacking distance is around 3.5 Å, resulting in the hexamer inside pore volume of around 330 Å³. The volume of eleven H₂O molecules (30 Å³ x 11 = 330 Å³) is consistent with the hexamer inside pore volume above.

Powder samples of C14 and C18 can form thermotropic LC phases (Fig. 3). Depending on the alkylchain lengths, different kinds of LC phases of hexagonal columnar (Col_h) for n = 14 and lamellar (D_{L1}) for n = 18 are observed at the temperatures above 450 and 440 K, respectively. The molecular assembly structures in LC phases are influenced by the existence of H₂O molecules. The xerogel of C14•11(H₂O) can form only the Col_h phase. On the contrary, the xerogel of C18•11(H₂O) results in the Col_h phase, which is different from the D_{L1} phase of powder C18 sample. The H₂O molecules inside the hydrophilic pore stabilize the hydrogen-bonding hexamer structure and Col_h phase.

[Conclusion] Molecular assembly structures and phase transition behaviors of C6, C10, C14, and C18 derivatives were examined. All compounds can form gel states in the existence of H₂O, and C14 and C18 ones can form different LC phases. The TG analyses of xerogels of C14 and C18 are consistent with the hydrogen-bonding hexamer molecular assemblies. The guest H₂O molecules stabilized the hexamer arrangement and also Col_h phase, whereas the D_{L1} phase could be stabilized by the long alkylchain of n = 18 in the absence of H₂O molecules. The LC phases of C14 and C18 can be governed by the alkyamide chain lengths and guest H₂O molecules.

[References]

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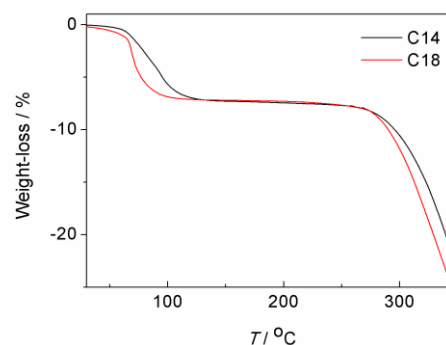


Fig. 2. TG of xerogels of C14 and C18.

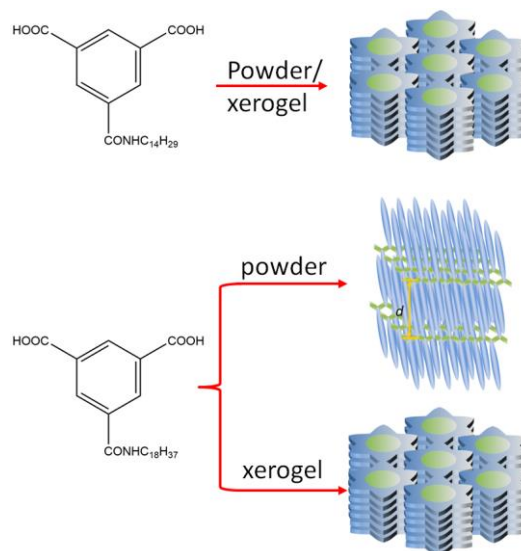


Fig. 3. Assemblies structures of C14 and C18.