Solvent Effect on Morphology of Self-assembled Fibrous Materials Derived From an Azopyridine Carboxylic Acid

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The macroscopic morphology of fibrous materials deposited from solutions of an azopyridine carboxylic acid dissolved in organic solvents was critically corelated with solvent parameters.

Increasing interest has been focused on supramolecular self-assembly of small molecules to give self-organized materials with macroscopically well-defined shapes such as microfibers as consequences of molecular harmonization of the component molecules.[1] This sort of self-organization processes carried out predominantly in aqueous solutions[2] is affected significantly not only by molecular structures but also by various environmental factors because levels and directions of intermolecular interactions among the small molecules are markedly sensitive to ambient conditions such as temperature and solvent. For instance, aspects of the supramolecular architecturing have been modified by external stimuli such as heat[3] and light[4,5] and influenced by preparative conditions including temperature, cooling, concentrations[6] and casting solvents.[7] In this context, it has been required to unravel the relationship between macroscopic morphology of self-assembled materials and environmental conditions in order to prepare tailor-made self-assembled organic materials. We have described that the self-assembly of azopyridine carboxylic acids (Figure 1) to give microfibers deposited from alkaline aqueous solutions as a result of the gradual neutralization by atmospheric carbon dioxide is affected critically by their intrinsic chemical structures[8] and by photoisomerization to alter their geometrical molecular structures.[8b] Taking notice of reasonable solubility of the azopyridine carboxylic acids in organic solvents, we report here that the self-assembly of the compounds **1** to give fibrous materials is readily carried out in organic solvents, whereas aqueous solutions have been extensively employed so far. We present also that macroscopic organization morphology of self-assembled materials is closely related with empirical parameters of organic solvents from which the fibrous materials are deposited.

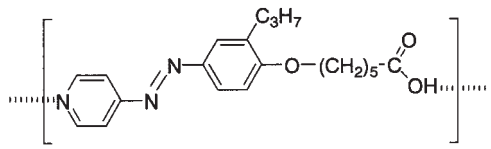

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Figure 1. Azopyridine carboxylic acid of **1** used in this study.

Self-assemblages of **1** were prepared by dissolving **1** in organic solvents under reflux for 2 min to give transparent 0.4% (w/w) solutions, followed by cooling at an ambient temperature to result in the deposition of materials within a day. The deposition was observed for many organic solvents including methanol, ethanol, acetone, ethyl acetate, chloroform, toluene, etc., whereas solutions of **1** in pyridine, acetic acid, DMF and 1,4-dioxane caused no deposition. Self-assembly experiments in less polar solvent like hexane failed because of the scarce solubility of **1**. The morphological features of the deposited materials were categorized into the following three groups. The first belongs to fibrous assemblages displaying high aspect ratios (>300) of an almost uniform diameter of 1 μm and more than several hundreds μm in length, as shown in Figure 2a. They were produced from methanol, ethanol, 1-propanol and 1-butanol and exhibit the appearance very similar to those self-organized in aqueous media as the result of the parallel orientation of the rod-like shaped molecules along the long axis of the microfibers.[8] The second group obtained from acetone, ethyl acetate and chloroform exhibited needle-like appearance with relatively small aspect ratios (10–100), as shown in Figure 2b. The third group is of leaflet crystals (aspect ratios: <5), as shown in Figure 2c, and formed from solutions of benzene and toluene.

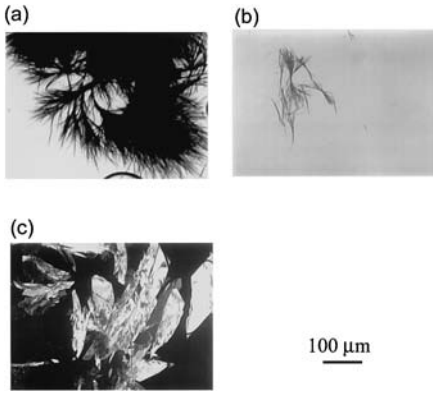

Figure 2. Optical micrographs of the molecular assemblages self-organized from (a) ethanol, (b) acetone and (c) benzene solutions in a concentration of 0.4% (w/w).

The FT-IR spectra of the molecular assemblages of each group displayed characteristic absorption bands of $\nu_{C=O}$, ν_{OH} and its Fermi resonance bands at around 1700, 2500 and 1930 cm^{-1}, respectively, indicating the formation of consecutive intermolecular hydrogen bonds in a head-to-tail manner between the pyridyl and carboxyl groups.[9] The powder X-ray diffraction (XRD) patterns of all of the deposited materials were not far from each other[10] and are also very similar to those of fibrous assemblages obtained from aqueous solutions of **1**,[8b] revealing that the organized structures of **1** in molecular levels are not

influenced by the preparation conditions. It should be stressed here that the nature of solvents affects scarcely the organized molecular arrangement of **1**, but significantly the macroscopic appearance of self-assembled materials.

In order to elucidate the solvent effect on the macroscopic self-organization, the morphologies of the deposited materials were discussed on the basis of empirical solvent parameters of π^*-, α- and β-scales.[11] As stated above, solvents with high π^*-values such as DMF, DMSO and pyridine cause no deposition of **1** because of the efficient ability to form so strong hydrogen bonds that the intermolecular hydrogen bonds among **1** molecules are suppressed, whereas solvents with low π^*-values scarcely dissolve **1** even though under reflux conditions. On the other hand, as shown above, solvents with moderate polarity are essential for the distinctive formation of supramolecular self-assemblages of **1**. The three types of them are classified by both of β-scale for solvent hydrogen-bond acceptor (HBA) basicity and α-scale for solvent hydrogen-bond donor (HBD) acidity, as summarized in Figure 3. Well-defined fibrous assemblages exhibiting high aspect ratios are deposited from solvents with high values of both α- and β-scales, while solvents having a high value of either α- or β-scales are favorable for the formation of needle-like assemblages with moderate aspect ratios. Solvents with low values of both scales give rise to the specific deposition of leaflets with small aspect ratios. This situation arises from the fact that the azopyridine carboxylic acid **1** is an amphoteric compound having both of hydrogen-bond donor (carboxyl) and acceptor (pyridyl) groups. Alcohols with high α- and β-scales and moderate π^*-values have the capability to result in the thorough dissociation of **1** under reflux and in the subsequent reconstruction of intermolecular hydrogen bonds between weakly acidic and basic groups at ambient conditions to cause gradual emergence of markedly high-aspect-ratio microstructures. It is likely that the cleavage of the hydrogen bonds of **1** occurs only partially in solvents with low α- and/or β-scales even under reflux to give microscopic hydrogen-bonded precursors, which give the needles or leaflets (Figure 2b, c).

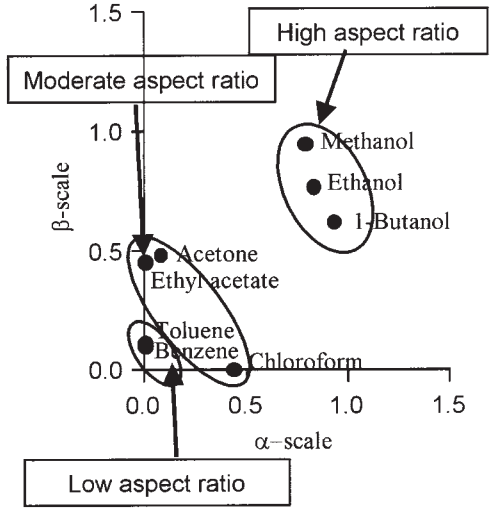

Figure 3. Correlations between the macroscopic organization morphology of **1** and the empirical parameters of the organization media of α- and β-scales.

In summary, the shapes of self-assemblages of **1** deposited from various solvents with different aspect ratios are influenced critically by empirical solvent parameters of π^*-, α- and β-scales. It follows that microfibers with high aspect ratios are obtained under specific conditions using solvents having high α-, β-scales and moderate π^*-scales due to the efficient reversibility of dissociation and formation of intermolecular head-to-tail hydrogen bonds among component molecules. In other words, the morphological features of **1** are controllable by the appropriate choice of solvents with suitable empirical solvent parameters.

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