Second-Harmonic Generation by Spontaneous Self-Poling of Supramolecular Thin Films of an Amylose−Dye Inclusion Complex

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For second-harmonic generation (SHG), nonlinear optical (NLO) materials require a noncentrosymmetrical molecular arrangement in the bulk. This can be achieved most commonly for polymeric systems by electrical poling. However, there are some drawbacks,[1−3] resulting mainly from thermal reactions of chromophores, particularly in the poling of high temperature polymer systems. The LB film techniques are, on the other hand, known to be an alternative approach for constructing the non-centrosymmetry with a controlled dimension and a high degree of molecular order.[4] An improved assembly technique has been developed recently,[5,6] in that chromophores are covalently linked between the layers. The practicality of such multilayer assembly systems has a limitation, however, due to the lack of thermal stability and mechanical integrity resulting from the flexible amphiphilic chains.

We have developed a new strategy not only for thermal and mechanical stabilities but also to search for the possibility of a spontaneous dipolar alignment of chromophores by employing a supramolecular architecture. In this approach, the chromophore is uniaxially included in the helical cavity of amylose (Figure 1), forming a rigid-rod supramolecular complex.[7] It was anticipated that upon casting a thin film from the supramolecular solution, a self-assembly process for dipolar alignment would take place, if a polar orientation is initiated by a specific interface interaction between the supramolecules and the substrate, and a chiral and/or a donor−acceptor[8,9] recognition occurs in the subsequent ordering of the rigid-rod supramolecules in the film-forming process.

The obvious merit of the inclusion state is that the guest chromophores are completely screened from each other (no dimeric association), and are mechanically reinforced and thermally shielded by the host molecule such that they can benefit from thermal and photochemical stability.[10,11] Additional advantages are the facts that dry amylose has virtually no glass transition temperature (T_g),[12] and forms lateral H-bonding among ordered molecules; these can contribute further to the polar stability of the guest chromophores.

We report herewith the first observation of SHG signals from solution-cast thin films of the hemicyanine−amylose supramolecule without any external poling, and their outstanding long-term polar stability.

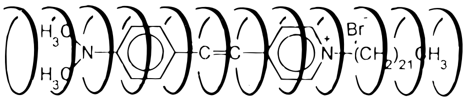

Figure 1. Supramolecular amylose−DASPC$_{22}$ inclusion complex.

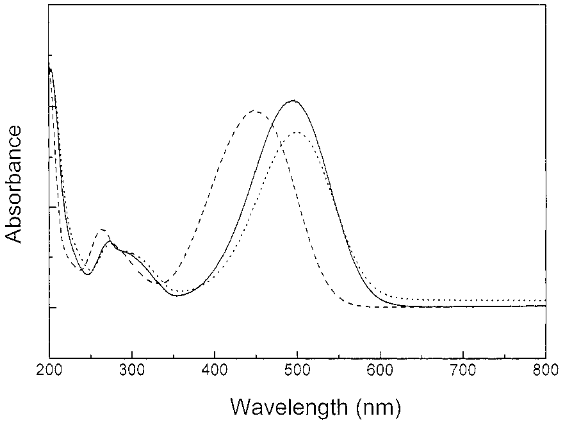

Figure 2. UV−vis spectra of free dye and dye−amylose supramolecules: DASPC$_6$ solution (in water), 3.7×10^{-5} M (− −); DASPC$_{22}$−amylose supramolecular solution (in water), 4.0×10^{-5} M (—); DASPC$_{22}$−amylose supramolecular solid thin film (ca. 1.0 μm thick) (- - -).

Amylose is a rod-like polymer consisting of α-1,4-glucosidic units, whose helical cavity is capable of including hydrophobic organic molecules, forming a six-fold helix. Once included, the guest chromophore is stretched out along the helical axis and rigidified by loss of conformational freedom due to the chromophore binding to the host, as indicated by induced circular dichroism and enhanced fluorescence intensity.[7] Among homologs of various alkyl tail lengths, a hemicyanine dye, 4-[4(dimethylamino)styryl]-1-docosylpyridinium bromide (DASPC$_{22}$), was selected as guest for the inclusion complex because of its strong hydrophobicity, a large molecular hyperpolarizability, and a large molecular length scale matching that of the host amylose[13] and thus, only one chromophore can be incorporated into the host cavity to form a 1:1 complex.[16]

Amylose−DASPC$_{22}$ supramolecular complex was prepared as we reported earlier,[7] using a low molecular weight amylose[13] in a DMSO−H$_2$O mixture. The complex was then subjected to exhaustive dialysis to remove DMSO, after which the solution was concentrated and unreacted insolubles were separated out by centrifugation. The resulting red-pink solution was subjected to freeze-drying to obtain a floppy solid which is soluble in water, while the dye itself is insoluble in water, and the solution-cast supramolecular films, however, become insoluble (in water) due to the interchain H-bonding between the host amylose. The supramolecular complexation in the thin film was confirmed and identified by UV−vis spectra, FTIR, C-13 NMR, X-ray diffraction and elemental analysis which indicated a nearly 1:1 stoichiometry. As seen in Figure 2, the solution spectra (λ_{max} = 498 nm) (by redissolving) of the supramolecular solid complex in water indicate that there is no or negligible uncomplexed free (λ_{max} = 451 nm)[17] and dimeric (λ_{max} = 420 nm, observed for DASPC$_{22}$ in water-rich DMSO−H$_2$O mixture)

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(13) A low molecular weight amylose (Mw ≈ 4500; Pn ≈ 26) was used for better solubility.[14] Since each turn of the amylose helix consists of six glucose units and the distance of the helical pitch is assumed to be ca. 10 Å in the solid state,[15] the length of the helical supramolecular rods in the film is around 45 Å.

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(16) When more than one chromophore is included in the amylose cavity, nonlinear susceptibility of supramolecular films can be reduced unless the chromophores are directionally ordered in the cavity.

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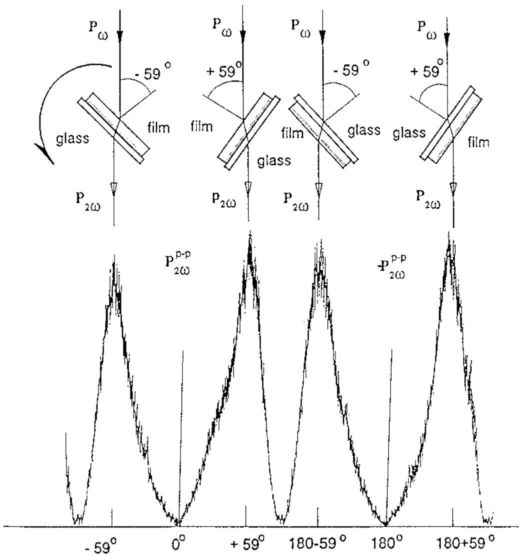

Figure 3. The SHG Maker fringes of an amylose–DASPC$_{22}$ supramolecular film of 0.1 μm thickness—dependence of SH output power for p–p polarization on the incidence beam angle.

dye molecules present.[7] The red-shift of the absorption bands of the solid thin film ($\lambda_{\max} = 502$ nm) as well as the solution ($\lambda_{\max} = 498$ nm) of the inclusion complex (relative to the uncomplexed free dye) can be attributed to the less polar hydrophobic environment in the host cavity, since hemicyanine dyes exhibit a negative solvatochromism.[18] The shift between the absorption bands of supramolecular solid thin film and its solution seems to reflect some differences in their inclusion states.[19] As anticipated, the solid inclusion complex exhibited a significant increase (ca. 30 °C) in the thermal stability[10] of the chromophore and also other interesting properties such as photochemical stability and unusual thermochromism,[11] in that the color becomes darker upon heating and reverses upon cooling.

SHG of the thin films was measured using s- or p-polarized light from a Q-switched Nd:YAG laser (the fundamental wavelength, $\lambda = 1064$ nm) at a pulse width of 10 ns and repetition rate of 10 Hz. The nonlinear susceptibility, $\chi_{33}^{(2)}$, of film samples was determined by comparing the Maker fringes of the film with those of a Y-cut quartz plate as reference (d_{11} of quartz). When the fundamental beam was incident to a thin film of 0.1 μm thickness, a $\chi_{33}^{(2)}$ value[20] of 9×10^{-9} esu was measured. As seen in Figure 3, the profile of Maker fringes of the SH output power for p–p polarization, $P_{2\omega}{}^{p-p}$, is symmetrical with SH power peaks at ±59° and no output power at 0°, showing a standard SH Maker fringe.[21] This seems to suggest that supramolecular dipoles are uniformly aligned[22] with a directional order, being tilted to the surface normal. From the ratios of the polarization-dependent SHG output power, $P_{2\omega}{}^{p-p}/P_{2\omega}{}^{s-p}$ (at the same incidence angle), and second-order nonlinear coefficients, $\chi_{31}^{(2)}/\chi_{33}^{(2)}$, the tilt angle of the supramolecules was estimated[23] to be around 40° with respect to the normal of the film surface.

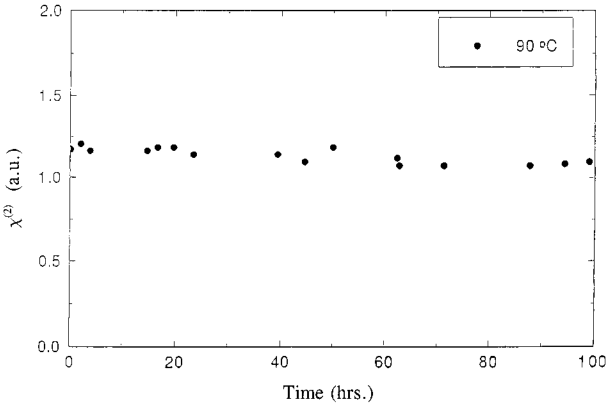

Figure 4. Temporal stability of a DASPC$_{22}$–amylose supramolecular film at 90 °C in air.

A similar tilt angle of chromophores was reported[4,24,25] with LB films (on a glass substrate) made from the same hemicyanine dye, DASPC$_{22}$, and its homologs, suggesting that the donor head group (*N*,*N*-dimethylamino) of the chromophore is bound to the glass substrate (H-donor) by H-bonding. Although the mechanistic aspect of the self-poling of the present system is unknown, it is likely that such an interface interaction[26] of the supramolecules plays a crucial role in initiating the polar orientation and influencing the subsequent dipolar alignment of the rigid-rod supramolecules, forming a self-assembly; no SHG signals were detected with the supramolecular films cast on poly(methyl methacrylate)-coated substrate, and also with poly(vinyl pyrrolidone)–DASPC$_8$ composite films (no inclusion) on the glass substrate. In order to elucidate the propagation of the polar orientation, it is still considerable to postulate a chiral and/or dipolar recognition of supramolecules in a parallel arrangement of ordering.

Supramolecular films of the present dye–amylose complex demonstrated an excellent long-term polar stability: no decay of $\chi^{(2)}$ at room temperature for at least 5600 h (probably no limit) and at 90 °C for more than 100 h (Figure 4). Such a pronounced polar stability is a rare example, except for some polymer systems whose poled chromophores are incorporated into a cross-linked polymer network or high-temperature polymer matrix such as polyimides. Such unusual stability of the self-poled supramolecule is clearly the result of the inherent tendency[27] of helical amylose as host to align, associate, and H-bond.

In summary, we have shown that supramolecular solid thin films of an amylose–hemicyanine dye inclusion complex exhibit a self-poling of the chromophore and an excellent long-term polar stability. Such novel NLO properties are due to the merit of supramolecular architecture based on inclusion of the chromophore, helical rigid-rod structure, and H-bondings at the interface as well as among aligned supramolecules.

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[17] Since DASPC$_{22}$ is insoluble in water, a water-soluble homolog, DASPC$_6$, was used as a representative of the free dye in water. DASPC$_6$ would not form dimeric aggregates at the concentration used due to a weak hydrophobicity unlike DASPC$_{22}$.

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[19] Only a slight decrease in the fluorescence intensity ($\lambda_{\text{em}} = 620$ nm) of the solid thin film (compared to that of the solution) upon increasing the temperature seems to suggest a rather strong chromophore binding (to the host) in the solid state than in the solution.

[20] The $\chi^{(2)}$ values observed for the present supramolecular films are somewhat smaller compared to other material systems comprising similar chromophores. A particularly large difference (nearly 100 fold) in $\chi^{(2)}$ values is noticed when they are incorporated in covalently self-assembled multilayers.[5] This is most likely due to the very low chromophore number density (one per 5000 D), due to supramolecular formation. Other reasons may involve counterion effect,[4] chromophore packing density, and local environmental effects.

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[22] A preliminary investigation with a 6 μm thick film to which the fundamental beam was incident through two different interfaces (glass-film or air-film) suggested that the polar order is reasonably uniform throughout the film thickness but is around 16% lower in the layer close to the air interface compared to that close to the glass interface.

[23] The average tilt angle was estimated using the following equations: $\chi_{33}^{(2)} = B\langle\cos^3\varphi\rangle$ and $\chi_{31}^{(2)} = {}^1/_2 B\langle\cos\varphi\,\sin^2\varphi\rangle$ where B is a parameter which is independent of the molecular tilt angle, φ (with respect to the normal of film surface).

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