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STUDIES OF MONOMER AND POLYMER MONOLAYERS USING OPTICAL SECOND AND THIRD HARMONIC GENERATION

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Authors
Berkovic, G.
Shen, Y.R.

Publication Date
1987-04-01

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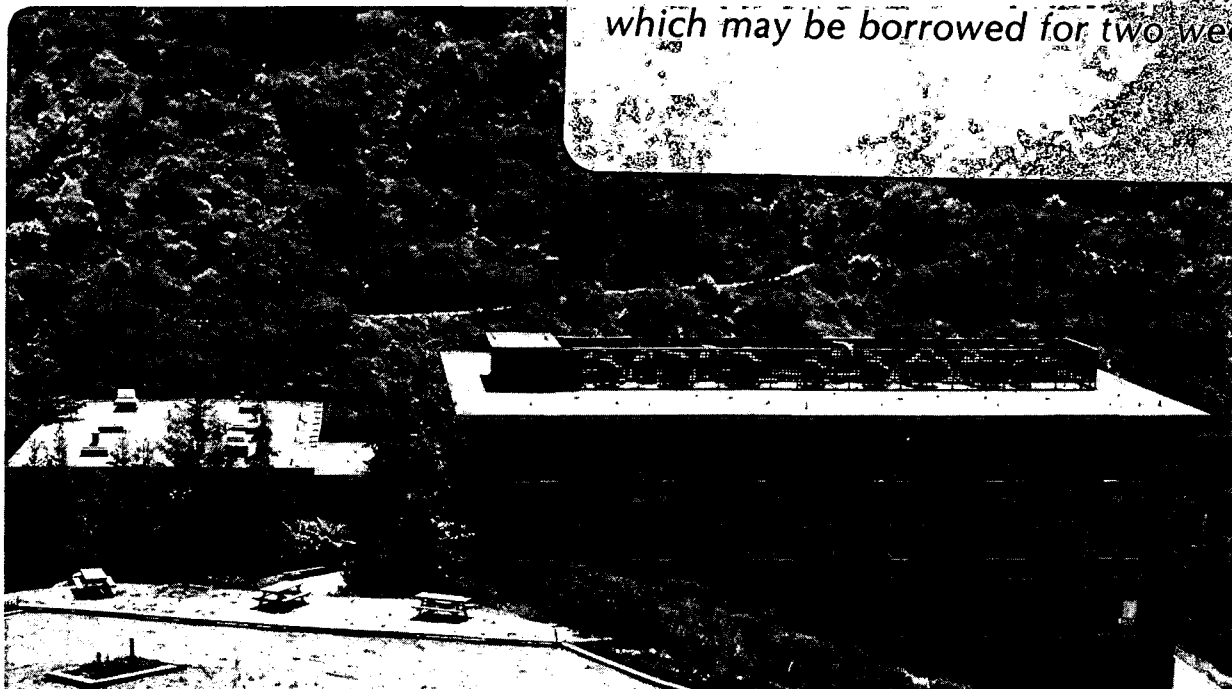## Materials & Chemical Sciences Division

JUL 8 1987

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STUDIES OF MONOMER AND POLYMER MONOLAYERS USING OPTICAL SECOND AND THIRD HARMONIC GENERATION

G. Berkovic and Y.R. Shen

April 1987

DISCLAIMER

STUDIES OF MONOMER AND POLYMER MONOLAYERS USING OPTICAL SECOND AND

THIRD HARMONIC GENERATION

Garry Berkovic and Y. R. Shen

Department of Physics, University of California
Center for Advanced Materials, Lawrence Berkeley Lab.
Berkeley, California 94720

Optical second harmonic generation (SHG) is a highly surface
sensitive technique for studying ultrathin molecular layers. This
technique has been used to study monolayers of various organic monomers
-- vinyl stearate, octadecyl methacrylate and some diacetylene
derivatives -- and their corresponding polymers spread at air/water
interfaces. Different SHG signals are obtained from a pure water
surface, and from water covered with monomer and polymer monolayers.
During polymerization of monomer monolayers the SHG signal intensity is
observed to change continuously from the monomer monolayer value to the
polymer monolayer value. Monolayer polymerization of some amphiphilic
diacetylenes was also studied by third harmonic generation (THG), which
unlike SHG is not a surface sensitive probe. However, the extremely
high third order nonlinearity of polydiacetylenes enables THG from a
single monolayer to be observable above the water background signal.
In addition, evaluation of surface molecular orientations and molecular
nonlinear optical coefficients from monolayer SHG and THG is also
discussed.

INTRODUCTION

Monolayers of polymerizable material have been the subject of
numerous studies in many fields of basic and applied chemistry
research. Polymerizable monolayers have been employed as ultrathin
coatings in device technology in microlithography[1] and
microelectronics,[2] and show potential for application in nonlinear
optical devices.[3] More basic research has involved studying monolayer
polymerization as two dimensional systems in which molecular
separations and orientations may be varied by the experimentalist in
order to study the basic factors affecting reactivity and kinetics.[4]
In biological chemistry polymerizable monolayers have been employed to
fabricate synthetic lipids[5] and vessicles.[6]

Unfortunately, characterization and analysis of monolayers and
ultrathin films is made difficult by two interrelated limitations --
the small number of molecules in a monolayer, and the fact that a
monolayer must invariably be supported on some much thicker substrate
which will often interfere with or mask the adsorbate analysis.
Removal of the monolayer film into solution may enable more convenient

analysis, but only at the price of removing the monolayer from its environment of interest. Although some very recent advances have enabled a small number of in situ studies of monolayers using specially designed and adapted instrumentation for infrared[7] and X-ray diffraction analysis,[8] there clearly is a need for other special experimental techniques for the study of monolayers.

One technique which provides in situ, nondestructive, surface sensitive analysis for monolayers is second order nonlinear optics. Using the processes of second harmonic generation (SHG) and sum frequency generation (SFG) a variety of studies of molecular monolayers have been performed. Using merely the SHG of a fixed frequency laser input it is possible to observe the surface concentration,[9] orientation[9,10] and two dimensional phase transitions[11] of molecular monolayers on various substrates. Using tunable frequency input it is possible to measure the electronic[12] and vibrational[13] absorption spectrum of the adsorbed monolayer.

Second harmonic generation in a medium arises from the second order polarization $\vec{P}^{(2)}$ induced in a medium by an applied electric field $\vec{E}$, given by

$$\vec{P}^{(2)} = \overset{\leftrightarrow}{\chi}^{(2)} : \vec{E}\vec{E} \tag{1}$$

where $\overset{\leftrightarrow}{\chi}^{(2)}$ is the second order nonlinear susceptibility. It then follows that a laser field at frequency ω (i.e. $E = E_o e^{i\omega t}$) will generate a second order polarization oscillating at frequency 2ω. This polarization is observable as photons generated at frequency 2ω, whose intensity is proportional to $|P(2\omega)|^2$. Sum frequency generation is the analogous process using two input laser fields of different frequencies.

The reason that SHG is a surface sensitive probe is that it follows from Eq. (1) that $\chi^{(2)} = 0$ in a medium possessing a center of symmetry. However, it is well established[14] that this is not strictly correct in a centrosymmetric medium, which usually has a weak second order polarization resulting from a weak quadrupole contribution that has been neglected in Eq. (1).[14] Nevertheless SHG is sufficiently repressed in a centrosymmetric or isotropic bulk medium to generally enable easy observation of SHG from a non-centrosymmetric monolayer adsorbed on it.

The second harmonic signal, $I(2\omega)$, generated in reflection from a monolayer covered water surface is given by[9]

$$I(2\omega) = \frac{32\pi^3\omega^2}{c^3\varepsilon(\omega)\varepsilon^{1/2}(2\omega)} |\vec{e}_{2\omega}\overset{\leftrightarrow}{\chi}_s^{(2)} : \vec{e}_\omega\vec{e}_\omega|^2 I^2(\omega), \tag{2}$$

where $\hat{e}_\Omega = L_\Omega\hat{e}_\Omega$ with $\hat{e}_\Omega$ denoting the unit polarization vector of the field at frequency Ω, and L_Ω the Fresnel factor for the field; $\varepsilon(\omega)$ is the substrate dielectric constant; $I(\omega)$ is the laser intensity and $\chi_s^{(2)}$ is the (complex) surface second order susceptibility tensor.

The contributions to $\overset{\leftrightarrow}{\chi}_s^{(2)}$ may be represented by

$$\overset{\leftrightarrow}{\chi}_s^{(2)} = \overset{\leftrightarrow}{\chi}_w^{(2)} + \overset{\leftrightarrow}{\chi}_m^{(2)}, \tag{3}$$

where $\overset{\leftrightarrow}{\chi}_w^{(2)}$ and $\overset{\leftrightarrow}{\chi}_m^{(2)}$ are the susceptibilities of the substrate (water) and the adsorbate monolayer, respectively. Any interaction between adsorbate and substrate may be taken into account[14] by including an additional term $\overset{\leftrightarrow}{\chi}_I^{(2)}$ in $\overset{\leftrightarrow}{\chi}_s^{(2)}$. As discussed above, due to its isotropy, $\overset{\leftrightarrow}{\chi}_w^{(2)}$ is not expected to be strong, and thus the monolayer

2

susceptibility is readily observable.

The next higher order nonlinear optical process is third harmonic generation (THG) caused by a third order polarization, $\vec{P}^{(3)}$, given by

$$\vec{P}(3) = \overset{\leftrightarrow}{\chi}(3) \vdots \vec{E}\vec{E}\vec{E}. \tag{4}$$

However, THG is electric dipole allowed in all media, and so is not surface specific like SHG. The third harmonic signal, $I(3\omega)$, reflected off a monolayer covered water surface is

$$I(3\omega) = \frac{576\pi^4\omega^2}{c^4\varepsilon(\omega)\varepsilon(3\omega)} |\vec{e}_{3\omega}\overset{\leftrightarrow}{\chi}_s^{(3)} \vdots \vec{e}_\omega\vec{e}_\omega\vec{e}_\omega|^2 I^3(\omega), \tag{5}$$

where $\overset{\leftrightarrow}{\chi}_s^{(3)}$ is the effective surface third order susceptibility given by:[15]

$$\overset{\leftrightarrow}{\chi}_s^{(3)} = \overset{\leftrightarrow}{\chi}_m^{(3)} + i\overset{\leftrightarrow}{\chi}_w^{(3)}\ell_{eff} \tag{6}$$

with

$$\ell_{eff}^{-1} = (3\omega/c)(n_\omega\cos\theta_\omega + n_{3\omega}\cos\theta_{3\omega}). \tag{7}$$

Here, $\overset{\leftrightarrow}{\chi}_m^{(3)}$ is the third order susceptibility of the monolayer and $\overset{\leftrightarrow}{\chi}_w^{(3)}$ is the susceptibility of a unit volume of water. The effective interaction depth, ℓ_{eff}, is defined by the refractive index (n_Ω) and propagation direction (θ_Ω) of the fundamental and third harmonic beams in the water. For 1.06 μm light incident on water at an angle of 60°, we calculate $\ell_{eff} = 280$ Å. Thus, in order to observe THG from an adsorbate monolayer, its third order susceptibility must be at least comparable to that of a 280 Å thickness of water. Since monolayer thicknesses are of the order of 10 Å, THG from adsorbate monolayers should only be observable from adsorbates whose molecular third order polarizability is very much greater than that of water. We also note in Eq. (6) that in the effective surface susceptibility $\overset{\leftrightarrow}{\chi}_s^{(3)}$ there is a phase factor i associated with the bulk term $\overset{\leftrightarrow}{\chi}_w^{(3)}$.

In this paper we describe some of our experiments using nonlinear optics to probe monomer and polymer monolayers spread at an air/water interface. The materials studied are all spreadable on water by virtue of being amphiphilic, i.e. they contain both hydrophilic and hydrophobic parts. We have used SHG to study the polymerization of two long chain monomers -- vinyl stearate (VS) and octadecyl methacrylate (ODMA) -- shown in Fig. 1. Although these materials do not have large second order nonlinearities it is shown that the SHG signal can still be used to follow the extent and kinetics of polymerization undergone by the monomer, without disturbance or destruction of the monolayer film. The orientation of molecules at the air/water interface could also be deduced from the polarization of the SHG signal.

We have also used SHG to probe the polymerization of some amphiphilic diacetylenes (see Fig. 2). It was found that the SHG signals from these monomers and their corresponding polymers did not differ sufficiently to allow SHG to monitor the extent and rate of the polymerization reaction. However, we have also been able to use THG to monitor the polymerization of a diacetylene monolayer in spite of the fact that THG is not surface-specific. This is because of the very high third-order nonlinearity of polydiacetylenes. We have also used THG to monitor the very interesting phase transition of one diacetylene polymer, poly-4-BCMU (see Fig. 2), from its "yellow" form to its "red" form when its monolayers on water are compressed above a certain density.[16]
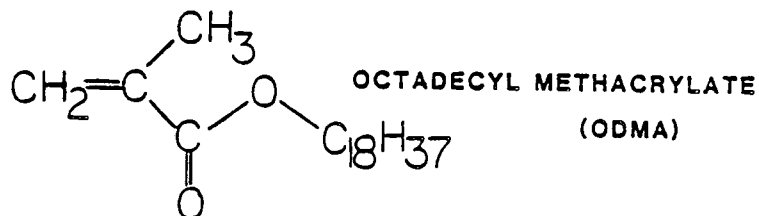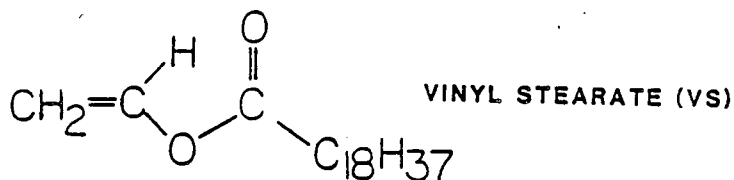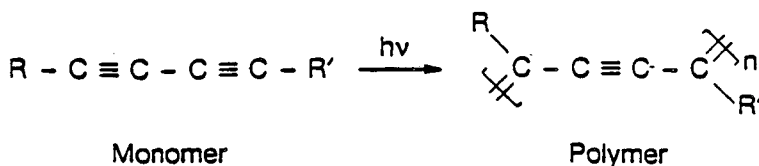
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VINYL STEARATE (VS)

OCTADECYL METHACRYLATE (ODMA)

Fig. 1.

Monomer

Polymer

MONOMER	POLYMER	SUBSTITUENTS
12-8 DA	Poly-12-8 DA	$R = C_{12}H_{25}$ $R' = C_8H_{16}COOH$
9-9 DA	Poly-9-9 DA	$R = C_9H_{19}$ $R' = C_9H_{18}COOH$
4-BCMU	Poly-4-BCMU	$R,R' = (CH_2)_4OOC-$ $NHCH_2COOC_4H_9$

Fig. 2. Diacetylene monomers and polymers used in this study.

Finally, we show how monolayer SHG and THG data may be analyzed to evaluate molecular nonlinear optical constants. This represents a convenient alternative method[17] for evaluation of molecular nonlinearities.

EXPERIMENTAL

Our experimental set us is depicted in Fig. 3. Laser light is focused onto the surface of a Langmuir trough onto which a monolayer of the material under study has been spread by pipetting an appropriate volume of a solution in a volatile solvent. Before reaching the water surface the laser light passes through a narrow bandpass color filter which transmits only the fundamental frequency, and thus blocks any pregenerated harmonic radiation. Light reflected from the water
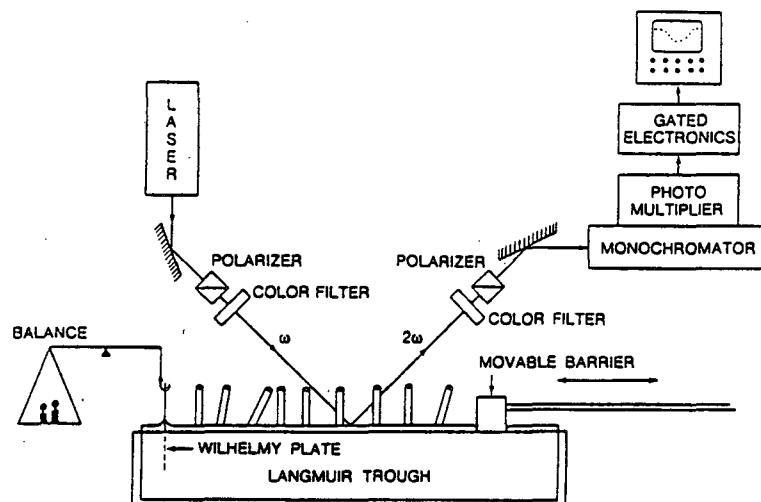
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Fig. 3. Schematic of experimental set up.

surface passes through a second color filter, which blocks the
fundamental, but transmits the desired harmonic frequency (2ω or 3ω).
Harmonically generated photons are detected through a monochromator and
a gated photon counting system, and averaged over at least 3×10^4
laser pulses. These signals were verified as being from true harmonic
generation by virtue of their very sharply peaked, background free
responses detected when the output monochromator is scanned through the
harmonic wavelength, and the correct dependence of the signal intensity
on input laser power.

The laser employed was a 500 Hz Q-switched Nd:YAG laser, where each
Q-switched envelope contained approximately 10 mode-locked pulses of 60
ps duration. The laser light was incident on the water surface at 60°
from the normal, and was focused onto the surface using lenses of 15-30
cm focal length. For THG measurements the laser output at 1.06 μm was
employed; while for SHG both this wavelength and the frequency doubled
output (532 nm) were employed. Pulse energies at these wavelengths
were 0.7 mJ (1.06 μm) and 0.3 mJ (532 nm) per Q-switched pulse.

RESULTS AND DISCUSSION

SHG Studies of Polymerization of Vinyl Stearate and Octadecyl
Methacrylate Monolayers

The SHG signal generated from a pure water surface has been
compared with that of a water surface covered with a monomer monolayer
of vinyl stearate (or octadecyl methacrylate), and with water covered
with a monolayer of a commercially available bulk polymerized sample of
the corresponding polymer.[18] As shown in Table I for both VS and ODMA
the SHG signal intensity shows clear differences between pure water,
monomer covered water and polymer covered water. Furthermore, after
monomer monolayers were irradiated for 2 hrs with a weak UV lamp under
nitrogen atmosphere the SHG signals became very similar to those of the
authentic polymer monolayers, indicating that the monomer monolayer had
undergone almost complete UV initiated polymerization (no change was
induced in the absence of UV radiation by either the probe laser or the
ambient thermal conditions).

The observation that, in our case, SHG from monomers is larger than

5

Table I. Relative intensities and polarization of second harmonic
generation from a water surface covered with various
monolayers.

System	Relative SHG Intensity[a]	Polarization Ratio[b]
Water only	100	2
Water + VS monolayer (27 A^2/molecule)	260	1.5
Water + poly VS monolayer[c] (27 A^2/monomeric unit)	170	0.5
Water + VS monolayer after UV irradiation	180	
Water + ODMA monolayer (26 A^2/molecule)	370	
Water + poly ODMA monolayer[c] (26 A^2/monomeric unit)	220	0.5
Water + ODMA monolayer after UV irradiation	250	

[a]The total output SHG signal generated using an input 532 nm laser
field polarized at 45° to the plane of incidence.
[b]The ratio of s-polarized to p-polarized SHG output.
[c]Bulk polymerized polymer spread on water.

that of their corresponding polymers can be understood as follows:
Second order optical nonlinearity of molecules arises mainly from
chemical bonds in which the electron distributions are more readily
distorted by optical excitation.[19] In VS and ODMA the π electrons in
the double bonds are likely to dominate the nonlinearity. Since the
polymerization process breaks a carbon-carbon double bond, the optical
nonlinearity decreases. It thus may also be expected that SHG from
bulk and surface polymerized samples of the same polymer should be
essentially the same, although their molecular weight distributions may
be quite different.[20]

In order to follow the kinetics of polymerization we also made SHG
measurements during the UV irradiation.[18] As shown in Fig. 4 the SHG
intensity decreases continuously during the reaction. Unfortunately,
due to the low optical nonlinearity of these materials and the
relatively small changes in signal intensity during polymerization our
measurement was not accurate enough to equivocably distinguish between
first and second order kinetics for the polymerization.

SHG and THG Studies of Diacetylene Monolayer Polymerization

In a similar way we have used SHG to study polymerization of the
two monomeric diacetylenes 12-8 DA and 9-9 DA (see Fig. 2).[21] Once
again, the SHG signal changes noticeably when water is covered with a
monomeric monolayer. However, in this case, not much change occurred
in the SHG signal when the monomer monolayer was polymerized by UV
irradiation. This behavior was observed for both 12-8 DA and 9-9 DA,
using different fundamental laser wavelengths (1.06 μm or 532 nm, as
well as 640 nm and 590 nm generated from a dye laser). Results from a
typical experiment are shown in Table II.

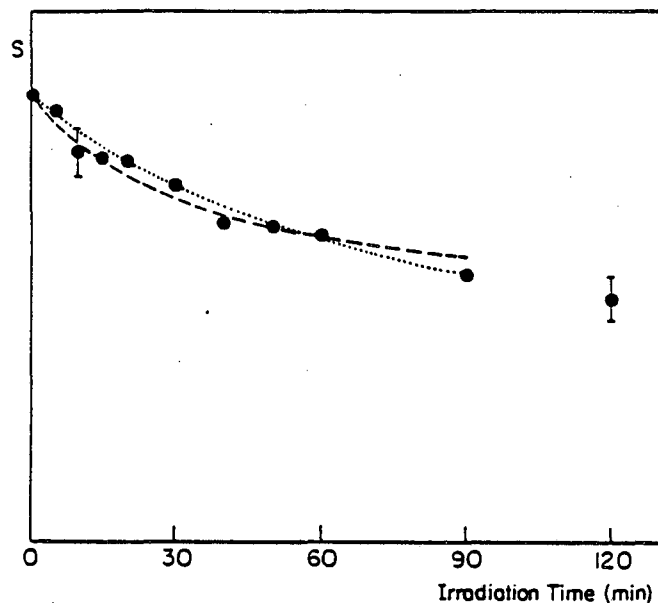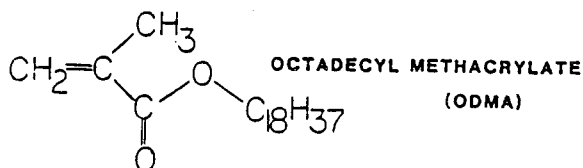The fact that the SHG signal is essentially unchanged after

6

Fig. 4. The relative SHG intensity (S) is plotted against irradiation time for UV polymerization of ODMA. The data (•) can be fitted satisfactorily by both first order (•••) and second order (---) kinetics (see the text). All experimental data points have the same uncertainty, although error bars for most points have been omitted for clarity.

Table II. Relative second harmonic generation intensities from water and water covered with monomeric and UV polymerized 12-8 DA monolayers.[a]

Sample	s-polarized SHG output	p-polarized SHG output
Water only[b]	100	60
Water + 12-8 DA monolayer (25 A^2/molecule)	180	200
Water + 12-8 DA monolayer after UV irradiation	160	180

[a] Measurements were performed using a 1.06 μm input laser field polarized at 45° to the plane of incidence. Relative SHG intensities have an uncertainty of ± 5%.
[b] The water SHG signal is set on a relative scale at 100 units in the s-polarized output.

polymerization indicates that the SHG arises from a part of the diacetylene molecule unchanged by polymerization. It is reasonable to

7

attribute the signal to the carboxylic acid end group. The magnitude of the signal relative to water and the stronger p-polarized component are in agreement with studies of other molecules where the SHG signal arises mainly from a carboxylic acid end group,[11] which has larger nonlinearity than a hydrocarbon chain.[17]

The lack of SHG from the diacetylenic core of both monomers and polymers is understood by the fact that this part of the molecule is essentially centrosymmetric -- its symmetry is only broken by the carboxylic acid group which is at least 8 carbon atoms away. Significant SHG from diacetylenes has only been reported[22] when two different, highly asymmetric groups are substituted immediately after the diacetylene bond.

Due to the very large third order nonlinearity of polydiacetylene we also examined the possibility of using THG to study the polymerization of diacetylene monomers.[21] Since THG is an electric dipole allowed process in all media, the water substrate had, as expected, a large THG signal. Addition of a monomer monolayer of 12-8 DA or 9-9 DA did not cause a noticeable change in THG. However, when these monolayers were polymerized the THG signal increased significantly, but exhibited large fluctuations both from experiment to experiment and from within one experiment. It generally varied between 3-10 times that of pure water. This variation apparently comes from nonuniformity of the polymer density in the monolayer film.[23] As the higher density regions float in and out of the laser beam the THG signal should fluctuate strongly (such fluctuations were not evident in the SHG studies because of the much smaller magnitudes and differences in the SHG signals from water, monomer and polymer).

THG Study of 2-Dimensional Conformational Phase Transition in Poly-4-BCMU

Poly-4-BCMU is a diacetylene polymer soluble in some organic solvents which may then be directly spread to give a monolayer on water.[16] In bulk phases this material exhibits two structural conformers -- the "red" and the "yellow" forms, in which there is stronger intramolecular hydrogen bonding in the former.[24] It was recently shown that when monolayers of this material are spread on water the yellow form is obtained at low surface densities, while if the monolayer is compressed to higher densities the red form is obtained.[16] We have studied this transformation using THG.[21] The good surface spreading characteristics of this material enabled stable, reproducible THG signals, unlike the in situ polymerized monolayers of 12-8 DA and 9-9 DA. Figure 5 shows the THG signal from water covered with poly-4-BCMU at various surface densities of the monolayer. It is seen that at low coverages ($\geq$ 120 A^2/repeating unit) the THG signal increases only slightly from the pure water value. However, at about 100 A^2/repeating unit the THG signal increases abruptly in the s-polarized output (the p-polarized output remains very weak). This surface density is in excellent agreement with the density at which the red form has been reported to appear.[16] Furthermore, the much higher THG signal observed when the red form appears also agrees very well with results from four wave mixing experiments in bulk phases of poly-4-BCMU which also showed[25,26] that the red form has a much higher third order nonlinearity than the yellow form.

An additional feature evident in Fig. 5 is that at higher surface densities (< 50 A^2/repeating unit) the polarization of the THG output changes significantly. This can be attributed to a change in the orientation of the polymer chains at the water surface when the
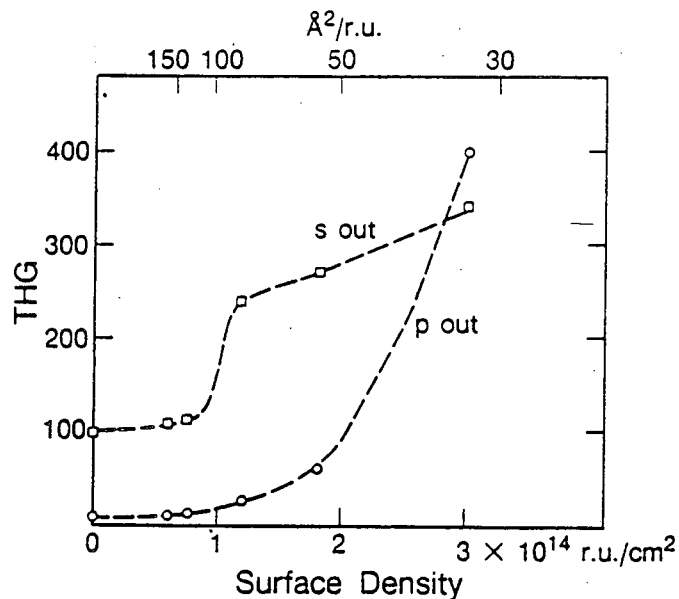
Fig. 5. Third harmonic generation from water covered with a monolayer of poly-4-BCMU at various surface densities [expressed as either number of polymer repeating units (r.u.) per cm^2, or A^2/r.u.]. The input laser field was polarized at 45° to the plane of incidence; THG was measured for both s- and p-polarized outputs. The s-polarized pure water (zero surface density of polymer) THG signal is set at 100 arbitrary units. The broken curve joining the data points is for guidance only.

monolayer is compressed to such high densities (see below).

Evaluation of Molecular Orientations and Molecular Nonlinearities from Monolayer SHG and THG Measurements

In many cases, both molecular orientations and molecular nonlinearities may be calculated from monolayer SHG and THG measurements such as those described above. When measurements are made relative to the "internal standard" provided by the pure water substrate whose nonlinear coefficients are known, the absolute values of surface susceptibility components are thus determined. Subtraction of the substrate contribution from the total surface susceptibility can be made if the relative phases of the substrate and total surface susceptibilities are known. A simple method for determining these relative phases has been described.[9,27]

Although there are in principle 18 independent components of the second order surface susceptibility tensor $\overset{\leftrightarrow}{\chi}_s^{(2)}$, the situation is greatly simplified in the case of a surface isotropic (on the scale of the laser spot size) about its normal. This condition, which should generally hold for monolayers, reduces the number of independent nonvanishing components of $\overset{\leftrightarrow}{\chi}_s^{(2)}$ (and $\overset{\leftrightarrow}{\chi}_m^{(2)}$) to three.[14] A further simplification occurs if the polarizability tensor of the molecule forming the monolayer is dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along some molecular axis ξ. In such cases the only nonvanishing components of $\overset{\leftrightarrow}{\chi}_m^{(2)}$ are $\chi_{m,zzz}^{(2)}$ and $\chi_{m,zii}^{(2)} = \chi_{m,izi}^{(2)}$ (i = x,y), which are simply related to $\alpha_{\xi\xi\xi}^{(2)}$ and θ, the average orientation of ξ to the surface normal.[9,17] Equation (2) demonstrates that, depending on the input (fundamental) and output (harmonic) polarizations employed, each SHG measurement yields a certain linear combination of the nonvanishing components of $\overset{\leftrightarrow}{\chi}_s^{(2)}$ (and hence $\overset{\leftrightarrow}{\chi}_m^{(2)}$). Thus in this special case just

9

two independent SHG measurements (such as the s- and p-polarized SHG outputs following 45° polarized input) are sufficient to evaluate $\chi_{m,zzz}$ and $\chi_{m,zii}$, which then yield $\alpha_{\xi\xi\xi}^{(2)}$ and θ.

Thus in the case of poly–VS and poly ODMA, where the nonlinearity is expected to be dominated along the C=O bond, such analysis of the SHG signal intensity and polarization ratio (see Table I) has been performed.[18] After showing that the monolayer SHG signal is in phase with that of water, it was deduced that the C=O bond is essentially perpendicular to the water surface and $\alpha_{\xi\xi\xi}^{(2)} \sim 3 \times 10^{-32}$ esu (poly VS) and $\alpha_{\xi\xi\xi}^{(2)} \sim 5 \times 10^{-32}$ esu (poly ODMA). The conclusion that the C=O bond is directed perpendicular to the water surface is in agreement with both theoretical predictions[28] and infrared analysis of monolayers which had been transferred onto various substrates.[29-31]

The SHG data of VS and ODMA monomers cannot unfortunately be analyzed by this model. The nonlinearity of these molecules is expected to arise from both their C=C and C=O bonds which are not collinear, and thus it is not reasonable to represent their nonlinearity by only one tensor component.

In an analogous way, the THG data of poly-4-BCMU can be analyzed[21] to find the dominant tensor component of the molecular polarizability $\alpha_{\xi\xi\xi\xi}^{(3)}$ along the polydiacetylene chain, and the orientation of the chain segments relative to the water surface. We found $|\alpha_{\xi\xi\xi\xi}^{(3)}| \sim 9 \times 10^{-34}$ esu for the yellow form and $|\alpha_{\xi\xi\xi\xi}^{(3)}| \sim 6 \times 10^{-33}$ esu for the red form. This value extrapolates to a value of $\chi_{xxxx}^{(3)} \sim 3 \times 10^{-11}$ esu for bulk poly-4-BCMU in its red form, which agrees well with other measurements of the third order nonlinearity of polydiacetylenes at 1.06 μm.[32-34]

Analysis of the change in THG polarization as the monolayer is compressed to high density (see Fig. 5) yielded[21] the result that the polymer chain segments lie quite flat (~ 70° to the normal) at low surface densities, but lie at ~ 40° to the normal when at a surface density of 30 Å²/repeating unit.

CONCLUSION

We have shown that monolayer SHG and THG measurements are a sensitive probe for monolayer polymerization reactions, phase transitions and molecular surface orientation, and can be used to evaluate molecular nonlinear optical coefficients. SHG measurements can be applied to monolayers of molecules of quite low nonlinearity (such as vinyl stearate and octadecyl methacrylate monomers and polymers). However, THG measurements on monolayers are only applicable to materials of very high third order nonlinearity like polydiacetylenes.

ACKNOWLEDGEMENTS

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