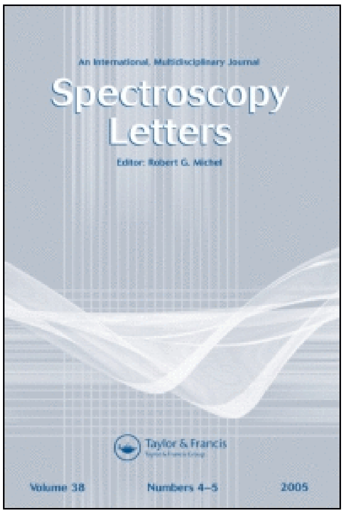

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RA-IR Studies on the Structure of Mercapto-Ended Azobenzene Derivatives in Self-Assembled Monolayers

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RA-IR STUDIES ON THE STRUCTURE OF MERCAPTO-ENDED AZOBENZENE DERIVATIVES IN SELF-ASSEMBLED MONOLAYERS[⋆]

Key words: FT-IR spectroscopy, self-assembled monolayer, azobenzene, contact angle of water

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ABSTRACT

Self-Assembled Monolayers (SAMs) were prepared from mercapto-ended azobenzene derivatives with the structure of n-$C_nH_{2n+1}AzoO(CH_2)_mSH$ (n=4,6,8,10,12; m=3,5). The structure of these SAMs was thoroughly studied with grazing-angle incident reflection absorption FTIR technique and wettability measurement. The results suggested that the plane of Azobenzene system of the assembling molecules in the SAMs lies on its back with an approximate angle of 22^0 included between the substrate surface normal and the Azobenzene plane. Tail alkyl groups (n-C_nH_{2n+1}) in these assembling molecules were considered to be in an all-trans conformation, as if they were in a crystalline-like environment. And the C-C-C plane of these all-trans tail alkyl groups, while $n \geq 8$, lies also on its back with an angle about 70^0 between its plane and the substrate surface normal. The conformation of these head groups ($-O(CH_2)_mSH$) in SAMs are disturbed by many structural factors. While m=3 or 5, the head group chain was proposed to remain in a gauche conformation to fit the upright orientation of the Azobenzene plane. The packing

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density was investigated by measuring the contact angle of water on these SAMs. The results showed that the self-assembled monolayer films are perfectly packed and the coverage density might be improved with increasing the length of both tail and head alkyl chains.

INTRODUCTION

During the past decade, the molecular self-assembling technique has been shown to be a convenient and effective method for constructing artificial monolayers, and has attracted considerable attention[1,2]. Self-assembled monolayers (SAMs) are useful for studying a variety of phenomena such as wetting, adhering, lubrication, electrochemical processes, and resistance to corrosion. Particularly, the azobenzene functionalized assembles have offered a promising approach to fabricating a new organic information storage device, because of two types of reversible processes of the azobenzene system, i.e., photochemical cis-trans isomerization, and electrochemical oxidation-reduction. This azobenzene functionalized system can be interconverted photochemically or electrochemically between these chemical states. Therefore, this system is expected to provide a potential storage process for ultra-high storage density, multi-function memory, and non-destructive information readout[3].

In previous research, we synthesized a several of azobenzene SAMs and studied extensively the physicochemical behavior of these structures[4,5,6,7]. Recently, we prepared a series of SAMs from mercapto-ended azobenzene derivatives with the structure of n-$C_nH_{2n+1}AzoO(CH_2)_mSH$ (n=4,6,8,10,12; m=3,5). The properties of these SAMs were studied by wettability measurement and grazing incidence infrared spectroscopy.

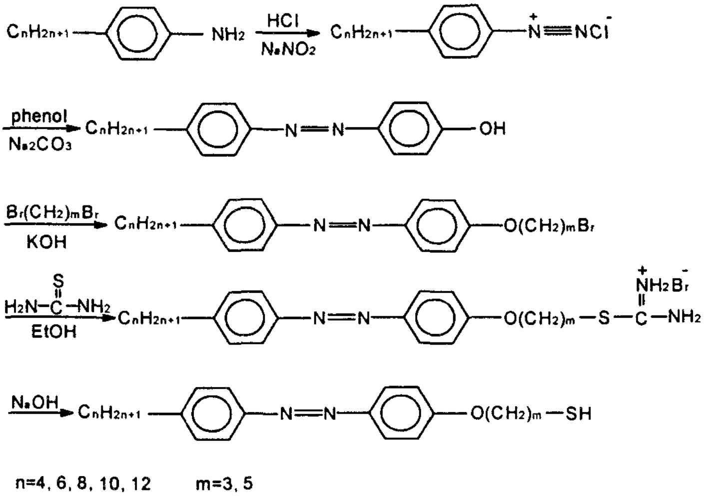
EXPERIMENTAL SECTION

The Synthesis of Assembling Materials

Self-assembling material, mercapto-ended azobenzene derivatives n-$C_nH_{2n+1}AzoO(CH_2)_mSH$ (n=4,6,8,10,12; m=3,5), were synthesized conveniently following the steps shown below in Scheme 1[8].

The Preparation of SAMs

Monolayers were formed by self-assembling technique on gold substrate. The substrates were prepared by evaporating 150 nm thick gold (99.99%) on a glass slide pre-coated with 15nm chromium. Such prepared gold substrates were first cleaned in hot piranha solution (30% H_2O_2 and 70% concentrated H_2SO_4) and rinsed with milli-Q water



Scheme 1

and absolute ethanol. They were then immersed into 1.0 mM ethanol solutions of self-assembling materials (n-$C_nH_{2n+1}AzoO(CH_2)_mSH$, n=4,6,8,10,12, m=3,5) for 24 h to reach a saturated coverage. Before characterization, the SAMs were washed with ethanol, water and then dried in pure N_2.

Infrared Spectroscopy Measurements

All the Infrared spectra were obtained with a Perkin-Elmer system 2000 FTIR spectrometer with an MCT detector cooled by liquid nitrogen. A variable angle reflection attachment was used for reflection measurements at an incidence angle of 86-degree (near grazing angle) for p-polarized infrared radiation. The resolution was 4 cm^{-1}. Reflection spectra were recorded with the background of bare gold. The sample chamber was purged with dry N_2 to eliminate the interference of water in air.

Contact-Angle Measurements

A JJC-2 Model contact-angle goniometer (The Fifth Optical Instrument Factory of Changchun, China) was employed to conduct contact-angle experiments, using yellow light to illuminate the water droplet, under ambient conditions (15-20°C, 50-60% relative humidity). All the angle values in Fig.7 were an average of three measurements.

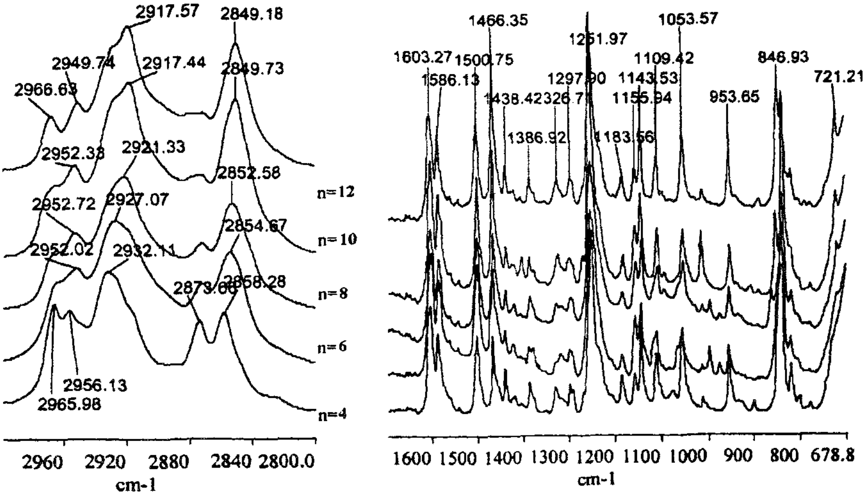


Fig. 1 FTIR of n-$C_nH_{2n+1}AzoO(CH_2)_3SH$ in KBr Pellet

RESULTS AND DISCUSSION

The Orientation of Azobenzene Plane

It is well known that all atoms in an Azobenzene system, including atoms in the two benzene rings and two nitrogen atoms, are in the same plane. The oxygen atom and the ϕ-o bond are in this plane too. This conjugate Azobenzene flat system was named *Azo plane* as a convenience to this discussion. In order to understand the packing structure of molecules in the SAMs, the orientation of the Azo plane must be studied first.

The IR spectra of n-$C_nH_{2n+1}AzoO(CH_2)_mSH$ in solid crystalline phase are shown in Fig. 1 (m=3) and Fig. 2 (m=5). The RA-FTIR spectra of SAMs are given in Fig. 3 (m=3) and Fig. 4 (m=5). Peak positions and band assignments, based on previous studies[9,10,11,12], are tabulated in Table 1. It can be found from the spectra of SAMs that the heights and positions of peaks associated with an azobenzene system, such as 1603 cm^{-1}, 1586 cm^{-1}, 1501 cm^{-1}, 1249(1254, m=5) cm^{-1}, 842 (837 cm^{-1}, m=5) cm^{-1}, are almost independent from assembling materials with different tail alkyl chain lengths. This suggests that the lengths of tail alkyl chains do not affect the packing structure of the Azo plane in SAMs.

The C-H out-of-plane wag mode gives a very weak absorption near 842 or 838 cm^{-1} in spectra of SAMs (Fig.3 and Fig. 4), while it presents a strong peak near 846 cm^{-1} in

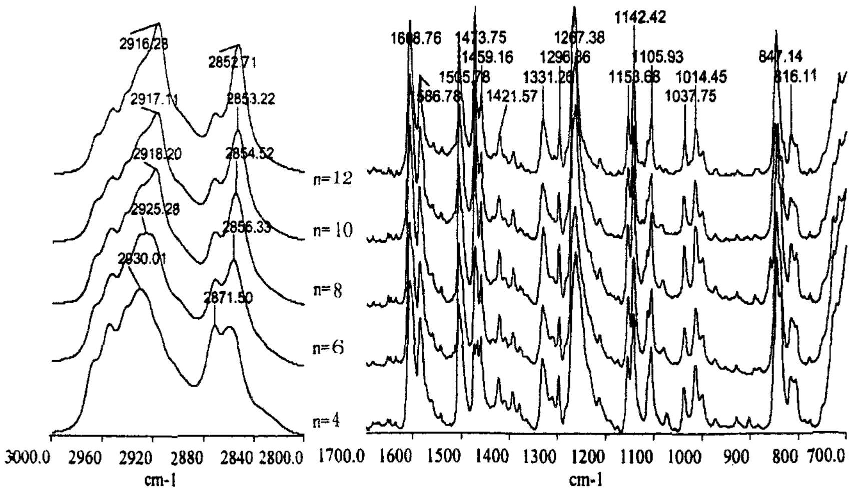


Fig. 2 FTIR of n-C_nH_{2n+1}AzoO$(CH_2)_5$SH in KBr Pellet

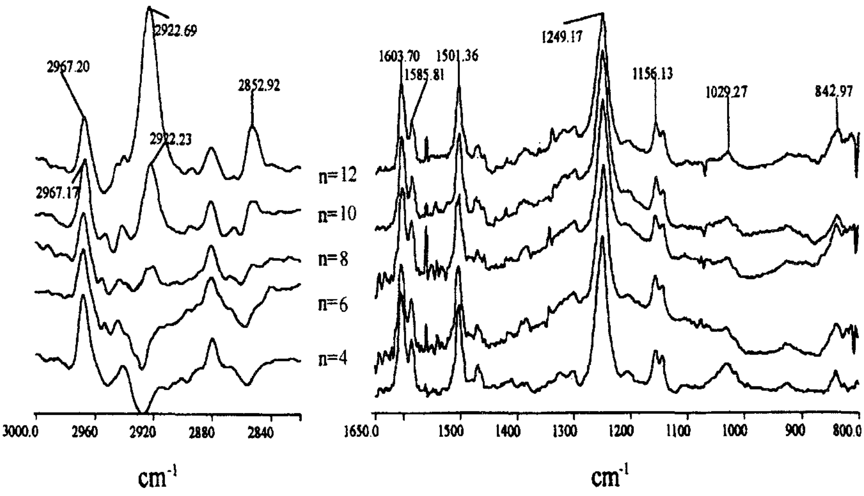


Fig. 3 RA-FTIR of n-C_nH_{2n+1}AzoO$(CH_2)_3$SH in SAMs on gold

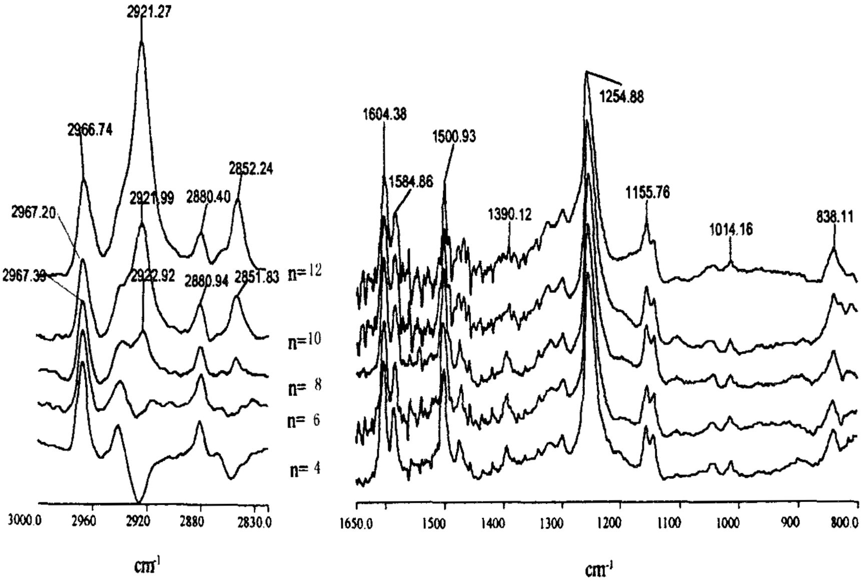


Fig. 4 RA-FTIR of n-$C_nH_{2n+1}AzoO(CH_2)_5SH$ in SAMs on gold

crystalline phase spectra (Fig.1 and Fig.2). The transition dipole moment of this band is perpendicular to the Azo plane. Other modes, in contrast, create peaks in SAMs with an intensity the same as or even much stronger than the same bands in crystalline state, such as bands near $1501cm^{-1}$, $1585\ cm^{-1}$, $1603cm^{-1}$, associated with para-substituted benzene ring stretch vibration modes, and in $1254cm^{-1}$ ($1249\ cm^{-1}$ for m=3) related to ϕ-O stretch vibration mode. Transition dipole moments of those all parallel to the Azo plane. These changes in the band intensity propose that the Azo plane in SAMs is in a special orientation state. According to the selection rule in RA-IR spectroscopy[11,12], vibration modes with their transition dipole moments parallel to the substrate surface normal are enhanced in absorption intensity and others perpendicular to the surface normal may be reduced in peak intensity. Therefore, based on the above discussion, an upright plane model can be suggested for the orientation of the Azo plane in the monolayer. In this model, the Azo plane is nearly perpendicular to the substrate surface. Hence, transition dipole moments of modes in $1605cm^{-1}(\nu_\phi)$, $1585cm^{-1}(\nu_\phi)$, $1503cm^{-1}(\nu_\phi)$, $1254cm^{-}$

TABLE 1.
Assignments of main peaks for n-$C_nH_{2n+1}AzoO(CH_2)_3SH$ in both Crystalline and SAMs

Peak Position(cm^{-1})		Assignment	Direction of Dipole Moment
in KBr m=3(m=5)	in SAMs m=3(m=5)	(vibration mode)	(in molecular coordinates)
2966	2967	CH_3, C-H str. (asym,ip) $\nu_{CH_3(a,ip)}$	⊥ C-CH_3 bond,ip C-C backbone
2949	---	CH_3, C-H str. (asym,op) $\nu_{CH_3(a,op)}$	⊥ C-C backbone plane op
2917	2922	CH_2, C-H str. (asym.) $\nu_{CH_2(a)}$	ip HCH,// to axis through H atoms
2873	2880	CH_3, C-H str. (Sym.) $\nu_{CH_3(s)}$	// C-CH_3 bond
2849	2852	CH_2, C-H str. (Sym.) $\nu_{CH_2(s)}$	ip HCH, bisect HCH
1603(1608)	1603	ring str. ν_ϕ	ip ϕ-ring
1586	1585	ring str. ν_ϕ	ip ϕ-ring
1500(1505)	1501	ring str. ν_ϕ	ip ϕ-ring
1466(1473)	1469	CH_2 scissors def., δ_{CH_2}	ip HCH, bisect HCH
1251(1267)	1249(1254)	ϕ-O str., $\nu_{(\phi\text{-}O)}$	// C-O bond
1143	1146	ϕ-N str, $\nu_{(\phi\text{-}N)}$	// C-N bond
1109(1105)	---	ip C-H bending	ip ϕ-ring, ⊥ axis through para pair substitute atoms
1053	---	O-C str, $\nu_{(c\text{-}o)}$	// C-O bond
846	842(838)	=C-H bend(op), $\delta_{(\phi\text{-}H)}$	⊥ ring plane

^{1}(1249cm^{-1} for m=3)($\nu_{\phi\text{-}o}$) parallel to the Azo plane, exactly, to the axis though ϕ-o bond, are also parallel to the substrate surface normal. The transition dipole moment of absorption near 843 cm^{-1} is perpendicular to the Azo plane and the normal too. In a previous discussion, the Azo plane was considered nearly perpendicular to the surface meaning that the angle between the Azo plane and the substrate surface normal is near zero. In other words, there is a small angle θ between the Azo plane and the surface normal. The value of θ will be estimated below.

The peak intensity can be expressed as

$$I \propto KE^2\mu^2 COS^2\theta \qquad (1)$$

Here, I is the spectrum intensity. K represents a constant for a given spectrum. E and μ represent the scalar of the surface electric field amplitude, which is a constant in a certain spectrum; and the oscillator transition dipole moment, which is a constant for a certain

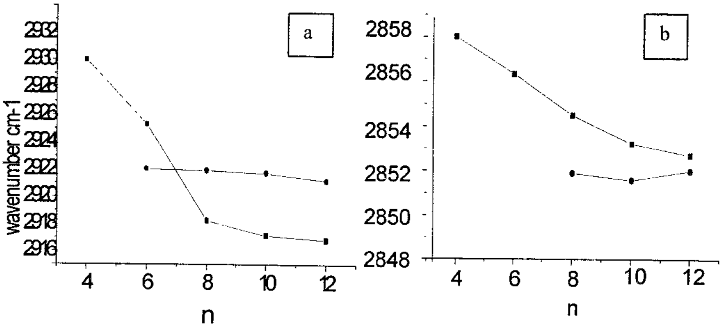


Fig.5 The relationship between absorption peak locations of ν_{as} (CH_2) (a) and ν_s(CH_2) (b) and the tail alkyl chain length n in the transmission spectra of solid state (■)and RA-IR spectra of SAM (●)

vibration mode, respectively. And θ is the angle included between $\bar{E}$ and $\bar{\mu}$. To obtain the RA-IR spectra, p-polarized radiation was employed at an incidence angle of 86^0. So the $\bar{E}$ is almost in the same direction as the normal of the substrate surface, as shown in Figure 5. Therefore, θ is also the angle between $\bar{\mu}$ and the normal. Before the calculation, it would be assumed that the Azo plane lies on its back instead of on its side. Such an assumption seems reasonable. The direct evidence supporting this is that the middle strong absorption near 1109 cm^{-1} (1105 cm^{-1}, m=5) in the crystalline state, attributed to the ϕ-H in-plane bending mode, has almost disappeared in the spectra of SAMs. With the selection rule of RA spectroscopy, the transition dipole moment of this mode must be perpendicular to the normal. This transition dipole moment is, as shown in Table 1, perpendicular to the axis through the ϕ-o bond. Therefore, as illustrated in Fig. 5, the Azo plane can only lie on its back.

Considering above discussion, the following equations can be derived from Equation (1)

$$I^T_{//} \propto K_T E_T^2 \mu_{//}^2 \qquad (2)$$

$$I^T_{\perp} \propto K_T E_T^2 \mu_{\perp}^2 \qquad (3)$$

$$I^{\Re}_{//} \propto K_{\Re} E_{\Re}^2 \mu_{//}^2 COS^2\theta \qquad (4)$$

$$I^{\Re}_{\perp} \propto K_{\Re} E_{\Re}^2 \mu_{\perp}^2 COS^2(\theta + 90) \qquad (5)$$

Here the subscripts // and ⊥ associate the absorption peaks with their transition dipole moments parallel or perpendicular to the axis through ϕ-o bond, respectively. The superscript T and R relate to the transmission spectra of the bulk solid samples and the RA-IR spectra of SAMs, respectively. So, as shown in Fig. 7, the angle between $\bar{E}_R$ and $\bar{\mu}_{//}$ is θ and between $\bar{E}_R$ and $\bar{\mu}_{\perp}$ is θ $+90^0$. Then (2) divided by (3), and (4) by (5). We get

$$I_{//}^{T} / I_{\perp}^{T} = \mu_{//}^{2} / \mu_{\perp}^{2} \qquad (6)$$

$$I_{//}^{\Re} / I_{\perp}^{\Re} = \mu_{//}^{2} COS^{2}\theta / \mu_{\perp}^{2} COS^{2}(\theta+90) = \mu_{//}^{2} ctg^{2}\theta / \mu_{\perp}^{2} \qquad (7)$$

combining (6) and (7)

$$tg^{2}\theta = I_{\perp}^{\Re} I_{//}^{T} / I_{//}^{\Re} I_{\perp}^{T} = \frac{I_{\perp}^{\Re}}{I_{//}^{\Re}} \frac{I_{//}^{T}}{I_{\perp}^{T}} \qquad (8)$$

$I_{\perp}^{T}$ and $I_{\perp}^{\Re}$ represent the absorption intensities of the vibration mode with their transition dipole moments perpendicular to the substrate normal in both transmission spectra of the solid state and RA-IR spectra of SAMs, respectively. $I_{//}^{T}$ and $I_{//}^{\Re}$ represent the absorption intensities of a mode with their transition dipole moments parallel to the normal in both solid state transmission spectra and RA-IR spectra of SAMs, respectively. The monolayer nature and the packing densities are very important for the grazing incidence IR evaluations. Different packing densities will result in different peak intensities. In equation (8), comparing relative ratios of two specific peak areas of different spectra are used to compute θ value. For example, peaks (bands) at 846cm^{-1}($\delta_{(\phi\text{-H})}$, op) and 1254cm^{-1} ($\nu_{\phi\text{-o}}$) were chosen for the ⊥ and // modes, respectively. Then, substituting these unknown terms in equation (8) with the intensities of peaks selected above, the value of θ was obtained as about 23^0. While these peaks in 1603cm^{-1}, 1585cm^{-1}, 1501cm^{-1} were selected in order for the // mode, several data of the value of θ was obtained between 20.5^0 and 25.6^0. The average value of θ is 22.6^0.

The Orientation of Tail Alkyl Groups

As shown in Fig.1 and Fig.2, the strong bands near 2917cm^{-1} and 2849cm^{-1} are assigned to asymmetric and symmetric stretching modes of -CH$_2$- in the hydrocarbon chain, respectively. These two bands are sensitive to the extent of lateral interactions between long n-alkyl chains[13]. In other words, these peak positions may reveal the chain conformational information. A downward shift of these bands is a characteristic of a highly ordered (trans-zigzag) alkyl chain conformation, whereas an upward movement is indicative of the increase in chain disorder (gauche conformation). Therefore, those two bands were selected for structural interpretation. A comparison of the frequencies of mode ν_{as} (CH_2) or ν_s(CH_2) indicates that there is, in the solid state, a tendency toward lower frequencies as the length of the alkyl chain increases, exactly, from 2858cm^{-1} to 2850cm^{-1} for ν_s(CH_2) and from 2932cm^{-1} to 2917cm^{-1} for ν_{as} (CH_2) in Fig. 1 (from 2930cm^{-1} to 2917cm^{-1}, 2859cm^{-1} to 2852cm^{-1} in Fig. 2) with a growth in tail alkyl chain length from $n = 4$ to $n = 12$. The immediate conclusion is that the conformation of tail chains in the bulk crystalline phase (solid state) tends to get more ordered with the increase in their length. While $n>10$, these tail chains might nearly be in an all-trans zigzag structure.

The RA-FTIR of SAMs are given in Fig. 3 (m=3) and Fig. 4 (m=5), respectively. It could be made out at a glance that the absorption frequencies for these two structure sensitive modes appeared near 2921cm^{-1} for ν_{as} (CH_2) and 2850cm^{-1} for ν_s(CH_2); these are independent of the length of tail alkyl chains when $n \geq 8$. The locations of these two absorption peaks in SAMs are far from those found in the bulk solid state with a short chain length (n=4), but, instead, very near to that in the solid state with a long chain length (n=12). These facts from Fig.5 indicate that the tail alkyl groups in SAMs are in an well-arranged packing situation, approximately in an all-trans conformation structure, as if in a crystalline-like environment.

Absorption peak positions in SAMs spectra for both ν_{as} (CH_2) or ν_s(CH_2), shown in Fig.3 and Fig.4, remain unchanged with a different n, but the intensities grow gradually with the increase in the length of tail alkyl chain. In general, the absorption intensity is related to the number of -CH_2- units per alkyl group, but this contribution, in this case, is subtle. If not, the two peaks for n=4 or 6 would appear stronger than they do in Fig.3 and Fig.4. The major contribution to the increase in intensity may result from the orientation of the tail alkyl chain, more precisely, a reorientation of the transition dipole moments of these two modes with an increase in chain length. As tabulated in Table 1, these transition dipole moments for both ν_{as}(CH_2) and ν_s(CH_2) are all perpendicular to the all-trans alkyl chain axis. If the chain axis is parallel to the normal, i.e., the $\bar{E}$ direction, the transition dipole moments must be vertical to the $\bar{E}$ direction and these absorption intensities would appear weak, and, on the contrary, a strong absorption would correspond with vertical direction of the chain axis to the normal. Therefore, it can be deduced that, in SAMs, all these tail alkyl chains keep in an all-trans conformation and the angle included between normal and the chain axis may increase with a growth in chain length.

Furthermore, it is obvious that the absorption peaks of $\nu_{as}(CH_2)$ in Fig.3 and Fig.4 are much stronger than that of $\nu_s(CH_2)$. The transition dipole moments of $\nu_{as}(CH_2)$ (with the axis parallel through these two H atoms) and $\nu_s(CH_2)$ (axis bisecting the HCH angle) are perpendicular and parallel to the -C-C-C- plane, respectively; though they are all perpendicular to the all-trans -C-C-C- chain axis. This reveals that the transition dipole moment of $\nu_{as}(CH_2)$ is more parallel to substrate normal than $\nu_s(CH_2)$ when $n \geq 8$. Therefore, the plane of tail alkyl chain (i.e. C-C-C plane) in SAMs would prefer to lie on its back (shown in Fig.7) as the Azo plane does. Because the absorption of $\nu_{as}(CH_2)$ is much stronger than that of $\nu_s(CH_2)$, the angle between the normal and the -C-C-C- plane is quite large. The value of this angle can also be reconciled with Equation (1). The computational result showed this angle to be near 70^0. The $-CH_2-$ deformation vibration around 1469 cm^{-1} is also significantly diminished in the SAMs spectra. This is because the transition dipole moment of this mode is in the same direction as $\nu_s(CH_2)$.

It is hard to determine the relative position of the tail alkyl chain plane to the Azo plane with the experimental results.

The Wettability of SAMs

Fig. 6 gives the relationship between contact angles of water on the SAMs surface and the chain length of both the head and tail alkyl groups. The contact angles experimentally measured are within $104\text{-}110^0$. The contact angle evidently rises with an increase in the length of these two terminal groups. This is because, as discussed previously, the increases in chain lengths can improve the chain orientation to an all-trans conformation structure and this benefit the packing density in SAMs. This results in a rise in the contact angle.

The Conformation structure of head groups of $-O(CH_2)_mSH$

Head groups, referred to the chains of $-O(CH_2)_mSH$ (m=3,5), could exist without any disturbance in an all-trans conformation. However, this all-trans structure can be easily perturbed by many structure factors. In SAMs, molecules of $n\text{-}C_nH_{2n+1}AzoO(CH_2)_mSH$ pack tidily on the substrate surface. These head groups are no longer keeping in a random-like state. One end of the SAMs is bonded to the gold substrate through a sulfur atom and another is linked with a large and almost upright Azo plane. Therefore, a gauche

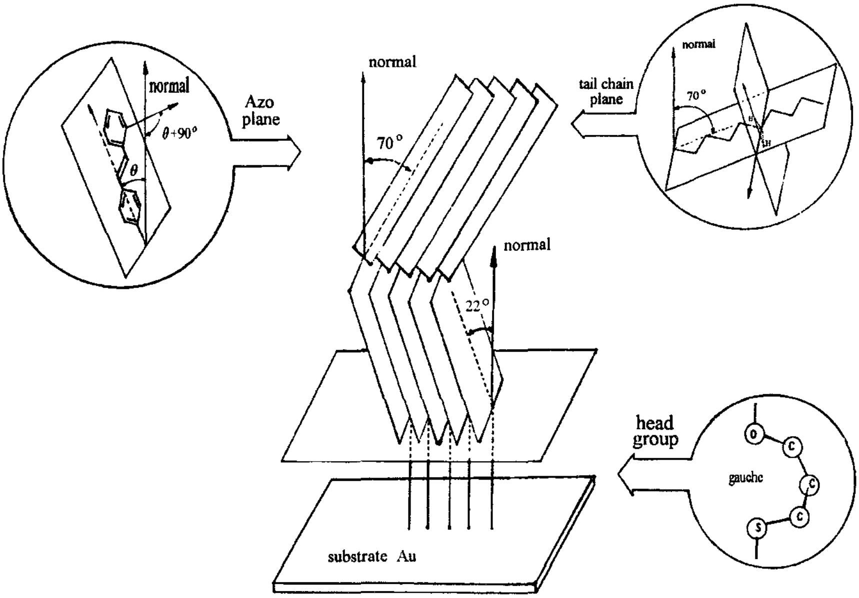


Fig. 6 Structure model for molecules in SAMs

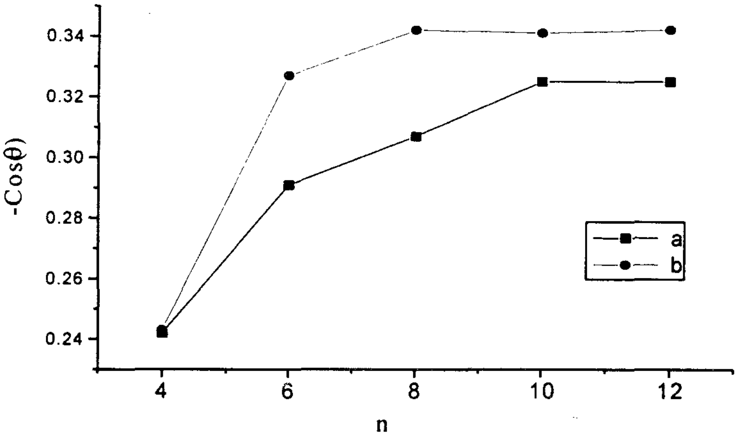


Fig.7 Contact angle of water on the SAMs from n-C_nH_{2n+1}AzoO$(CH_2)_m$SH (a: m=3; b: m=5)

conformation was proposed for head groups (m=3 or 5) in SAMs to fit the packing structure. The middle strong absorption of the $\nu_{(c\text{-}o)}$ mode in 1053 cm^{-1} in the bulk solid spectrum (Fig.1) became very weak in the RA-IR spectrum of the SAMs (Fig. 3). This evidence implies that the C-O bond, in SAMs, is vertical to the normal, and that is consonant with the result from the gauche conformation.

CONCLUSION

Considering the above discussion, several conclusions about the packing structure of assembling molecules in SAMs were obtained.

(1) The plane of the Azo system of the assembling molecules in the SAMs may lie on its back with an approximate angle of 22^0 included between the surface normal and the Azo plane. This orientation of the Azo plane is independent to the length of both tail group and head group.

(2) The tail alkyl groups of the assembling molecules in the SAMs exist in a quite orderly packing structure with an all-trans conformation, as if they were in a crystalline-like environment. All-trans conformation ensures all the carbon atoms in a tail alkyl chain lie in one plane. The angle between the substrate normal and this carbon atom plane increases with a growth in the chain length. While the tail alkyl chain is long enough ($n \geq 8$), the chain plane may lie on its back with an angle about 70^0 to the substrate normal.

(3) The packing structure of the head group $-O(CH_2)_mSH$ in SAMs might be disturbed by many structural factors. While m=3 or 5, head group chains can only keep in a gauche conformation to fit for the upright orientation of the Azo plane.

(4) The self-assembling monolayer film is perfectly packed. The coverage density can be improved with increasing the length of both tail and head alkyl chains.

REFERENCES

1. Ullman A. An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to *Self-Assembly*, New York: Academic press, 1991.

2. Roberts G. G. *Langmuir-Blodgett Films*, New York: Plenum, 1990.

3. Liu Z. F., Hashimoto K., Fujishima, A. Photoelectrochemical Information Storage Using an Azobenzene Derivative. Nature. 1990; 18: 658-660.

4. Liu Z. F., Zhao C. X., Zhang J., Tang M., Zhu T., Cai S. M. Molecular level Interface Designs Using Self-Assembling Technique for Stabilizing Langmuir-Blodgett Films. Phys. Chem. 1997; 101: 1-8.

5. Zhang H. L., Zhang J, Zhao J., Wang Y. Q., She J., Yu H. Z., Li H. L., Liu Z. F. New Approach on the Synthesis of Functionalized Alkanethiols and the Structural Characterization of Their Self-Assembling Monolayers. ACTA Physico-chimica Sinica. **1997**; 6: 515-524.

6. Zhao J., Zhang J., Ulman A., Liu Z. F. Fourier Transform Infrared Spectroscopy Evidence of a Two-Dimensional Hydrogen-Bonded Structure in Langmuir-Blodgett Films of a Novel Azobenzene Compound. Langmuir 1997; 13: 2359-2362.

7.Wang Y. Q., Yu H. Z., Cheng J. Z., Zhao J. W., Cai S. M., Liu Z. F. End-Group-Dominated Electrochemical Kinetics of Azobenzene Self-Assembled Monolayers on Gold. Langmuir 1996; 12: 5466-5471.

8. Li H. Y., Liu Z. F. A Convenient Synthesis of Novel Mercapto-Ended Azobenzene Derivatives. Synthetics Communications 1998; 28: 3779-3785.

9. Colthup N. B., Daly L., Wiberley S. E. *Introduction to Infrared and Raman Spectroscopy.* Academic Press, Inc.: 1990.

10. Porter M. D., Bright T. B., Allara D.L., Chidsey C.E.D. Spontaneously Organized Molecular Assemblies. 4. Structural Characterization of n-Alkyl Thiol Monolayers on Gold by Optical Ellipsometry, Infrared Spectroscopy, and Electrochemisty. J. Am. Chem. Soc. 1987; 109: 3559-3568

11. Nuzzo R G, Dubois L H, Allara D L. Fundamental Studies of Microscopic Wetting on Organic Surfaces. 1. Formation and Structural Characterization of a Self-Consistent Series of Polyfunctional Organic Monolayers. J. Am. Chem. Soc. 1990; 112: 558-569.

12. Nuzzo R G, Fucus F A, Allara D L. Spontaneously Organized Molecular Assemblies. 3. Preparation and Properties of Solution Adsorbed Monolayers of Organic Disulfides on Gold Surfaces. J. Am. Chem. Soc. 1987; 109: 3258-2368

13. Kutayama K., Zaki Y., Seki T., Tamaki T., Iriyama K. FT-IR study of Molecular Orientation and Anisotropy in "Command Surfaces" Formed by Langmuir-Blodgett Films of Azobenzene Amphiphilic Polymers. Langmuir 1994; 40: 1898-1902.

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