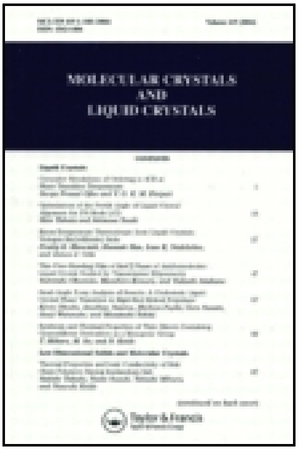

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Kinetics of Photoreaction of p-Phenylenediacrylic Acid Derivative in LB Films: An Infrared Spectroscopic Study

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KINETICS OF PHOTOREACTION OF p-PHENYLENEDIACRYLIC ACID DERIVATIVE IN LB FILMS: AN INFRARED SPECTROSCOPIC STUDY

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Abstract Photocycloaddition of LB multilayer system of a p-phenylenediacrylic acid derivative compound has been studied by infrared spectroscopy. A two-step kinetics are found. It is revealed that the reaction process results in changes in the molecular environment, which also affects the kinetics of the reaction.

Keywords: infrared spectroscopy, photocycloaddition, LB films, p-Phenylenediacrylic acid derivative

INTRODUCTION

Photo-induced reaction in LB films have been of important interests their perspective applications as well as for the fundamental research.[1] *p*-Phenylenediacrylic compounds have been proved to be photo-active materials, and studies on their reactivities in crystals as well as LB thin films have been reported, revealing the predominant process of cycloaddition.[2-3] It is known that, during cycloaddition, the molecular conformation experiences a drastic change: the hybridization of the carbon atom will change from sp^2 hybridization in the CH=CH group into the sp^3 hybridization when the cyclobutane ring is formed.[4-5] This conformation change is believed to induce changes in the status of the molecules, such as packing, orientation, and intermolecular interaction, etc. Having information on the molecular environment changes will not only reveal the behavior of the molecules during the reaction, but also provide insight into how to improve the reactivities, and to fabricate highly sensitive reactive systems.

In this paper, we report our infrared studies on thephoto-reaction of the LB multilayer of 4-(4-(2-decyloxycarbonyl)vinyl)cinnamo)benzoic acid (referred as DCAB).[2] The two olefinic groups having different molecular environments, and the hydrogen-bonding formed between amide groups will allow us to evaluate reaction kinetics and its correlation with molecular environment. The results expose the different kinetics of the two olefinic groups, and show the changes in the intermolecular interactions. The molecular environment is largely changed by photocycloaddition process, and this change in molecular environment also has great effect on reaction kinetics.

EXPERIMENT

The DCAB sample was dissolved in mixed solvent of THF and benzene (~1:3), with a concentration of 1 mM. A Lauda-MGW LB trough was used for LB film fabrication. The sample solution was spread on the subphase surface (distilled water), and film deposition was conducted at a surface pressure of ~30mN/m. It was verified that the film on the water surface at 30 mN/m is of multilayer structure, and a multilayer system is formed on the solid substrates. Hydrophobic CaF_2 plates were used as substrates. The radiation source was an extra-high pressure Hg lamp (Ushio, UI-501C), with a combination of optical filter to achieve monochromic radiation of 313 nm. The UV-visible spectra were measured by a Shimadzu UV-2500 PC photospectrometer. IR measurement was done by a Perkin-Elmer System 2000 FTIR spectrometer, equipped with a MCT detector, at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The UV-visible spectra of the DCAB multilayer upon irradiation is shown in Fig.1, which show drastic change under irradiation. Differing from the crystallite system of DCAB, which appeared to be stable under irradiation, this multilayer system greatly improves the reactivity of the molecule.

The infrared spectra also show drastic changes. Attention is paid to the bands of olefinic, amide, and alkyl groups. Figure 2 shows the absorbance of ν(C=C) at ester side and at amide side ($\nu(C=C)_I$ at 1627 cm^{-1}, $\nu(C=C)_{II}$ at 1636 cm^{-1}, respectively). The normalized absorbance is also shown. The absorbance of both bands decrease as the irradiation goes on, and the decreasing speed before ~85 s is much faster than then after. The C=C bond at ester side experiences a much faster reaction than that at amide side. The later difference of reaction speed may be attributed to the different micro-environment of two olefinic groups, because the cycloaddition process is believed to be accompanied by the movement of the molecules, and the more mobile molecules will exhibit a higher reactivity. Being influenced by the hydrophobic interaction between the alkyl chains, the mobility of C=C bond at ester side is larger than that at amide side, which is restricted by the hydrogen-bonding.

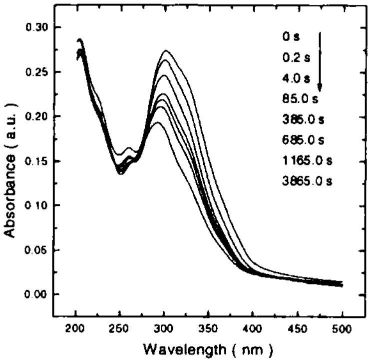

FIGURE 1 UV-visible spectra of DCAB multilayer upon irradiation.

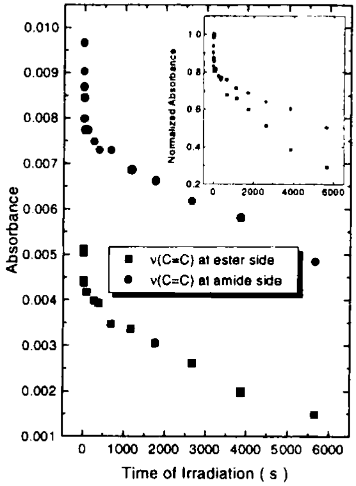

FIGURE 2 Absorbance of two ν(C=C) modes versus time of irradiation. Inset is for normalized absorbance.

The absorption frequency of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ mode is an indicator of the conformation of the alkyl chain, and their absorbance reflects the alkyl chains' orientation. In this study, the wavenumber of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ is found to increase all the way (2920→2924, 2850→2853 cm^{-1}, respectively), indicating the change of the conformation of alkyl chains towards a state of distortion upon irradiation. The absorbance of both $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ shows decreasing, indicating that the alkyl chains tilt more towards the substrate surface as the reaction goes on. Generally speaking, if the intermolecular distance remains unchanged, a tilting of the alkyl chain will result in a decrease in the distance between the alkyl chains, and will not bring about the distortion of the alkyl chains.[1] The data above show that, when two molecules form a cyclobutane-dimer, their alkyl chains tilt in different directions (most possibly in opposite directions), in other words, they "expand" in the reaction.

This kind of "expanding" behavior of the molecules may also change the hydrogen-bonding. Figure 3 is the IR spectra corresponding to the absorption band of ν(N-H) mode. The un-irradiated sample has a broad band centered at 3341 cm^{-1}, showing that the N-H of the amide group is hydrogen-bonded. Upon irradiation, a new, sharp peak begins to appear at 3391 cm^{-1}, whose intensity increases very fast during the first ~85 second, and later this increase slowed down (see the inset of Fig.4). The appearing of this sharp band shows the generation of weakly hydrogen-bonded N-H group. In the mean time, the former broad band of ν(N-H) began to decrease and also shift to lower frequency, which corresponds to an enhancement or strengthening of the hydrogen-bonding. Accordingly, the ν(C=O) mode in the amide also shows a decrease as well as a shift towards lower frequency (Fig.4), which, alone with the

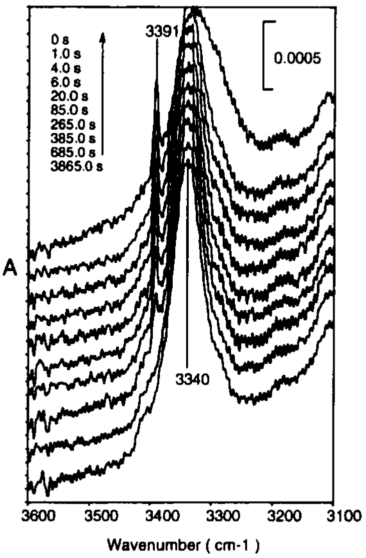

FIGURE 3 Infrared spectra of ν(N-H) of amide group.

behavior of the N-H bond, indicates that there is an enhancement of hydrogen-bonding between the amide groups, accompanied by generation of weakly hydrogen-bonded amide groups.

As described above, before cycloaddition occurs, the carbon atom of the olefinic group bears a sp^2 hybridization, which determines the CH=CH group to be co-planar with the neighboring phenyl group. After cycloaddition, the former sp^2 hybridization is changed to sp^3 conformation. Consequently, the molecule itself (the conjugation part) is no longer co-planar, and will make an angle to each other. Since the conjugated part of the molecule is rigid, and this change in conformation will result in an increase in molecular area, as well as the breaking of the hydrogen-bonding, forming weakly associated amide groups. Since in the multilayer, the molecules are closely packed (evidenced by the blue-shift in UV absorption peak and the low vibration frequency of stretching mode of the methylene group), the increase in the molecular area of the reacted molecules will result in a decrease of the molecular area of the unreacted molecules, if the two-dimensional structure of the layers have not been altered. In other words, the unreacted molecules will be pushed together by the reacted ones. This means the intermolecular distance of the unreacted molecules is reduced, which strengthens the hydrogen-bonding. This kind of reaction induced expanding and consequently compressing process of the unreacted molecules can also be evidenced in the blue-shifting in the UV-visible spectra during the reaction, showing the

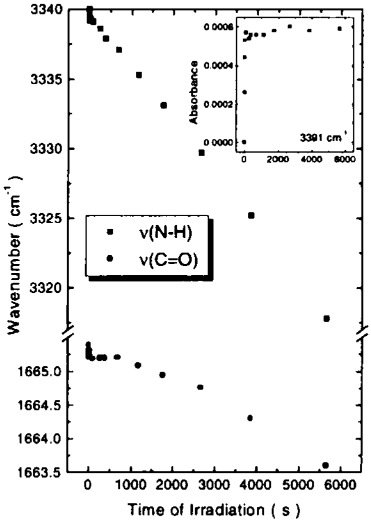

FIGURE 4 Wavenumber of ν(N-H) and ν (C=O) of amide group versus time of irradiation. Inset: Temporal evolution of absorbance of ν(N-H) at 3391 cm^{-1}.

enhancement of H-aggregation between the conjugated part of the molecules.

Regarding the reaction kinetics, all of the absorbance shows similar temporal behavior, which consists of a faster one before ~85 second, and a slower one afterwards. Referring to a report appearing in the same issue of this journal, the reaction kinetics depends largely on the molecular packing status, i.e., a very closely packed system exhibits a much slower kinetics. As to this study, it could be concluded that the different kinetics before and after ~85 second may be attributed to the changes in the molecular packing. The original film system is not "so" closely packed, and therefore, bears a faster kinetics. After the reaction goes on to some extent, the remaining unreacted molecules are "pushed together" by the reacted ones, forming a much closer packed phase, and as a result, the mobility of the molecule is reduced and the reaction kinetics slows down.

CONCLUSION

The infrared study on the photocycloaddition process of LB multilayer system of 4-(4-(2-decyloxycarbonyl)vinyl)cinnamo)benzoic acid reveals that the photo-reaction changes the molecular environment greatly, and the molecular environment change influences reaction kinetics very much. Expanding of the molecular area of reacted molecules is induced by the cycloaddition, which results in compressing of the molecular area of the unreacted molecules, forming a loser packed structure and slowing down the reaction kinetics.

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