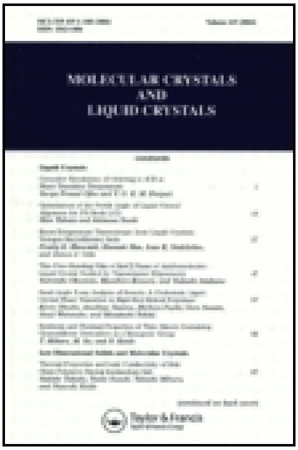

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochemical Behavior of Diolefinic Compounds with Amide Bonds: Relationship between Molecular Environment and Reaction Kinetics in the Monolayers

Jiang Zhao [a], Sung-Ae Lee [a], Haruhisa Akiyama [a], Jun'ichi Nagasawa [a] & Fusae Nakanishi [a]

[a] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

To cite this article: Jiang Zhao, Sung-Ae Lee, Haruhisa Akiyama, Jun'ichi Nagasawa & Fusae Nakanishi (2000): Photochemical Behavior of Diolefinic Compounds with Amide Bonds: Relationship between Molecular Environment and Reaction Kinetics in the Monolayers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 491-494

To link to this article: http://dx.doi.org/10.1080/10587250008024969

Mol. Cryst. and Liq. Cryst., 2000, Vol. 349, pp. 491-494
Reprints available directly from the publisher
Photocopying permitted by license only

Photochemical Behavior of Diolefinic Compounds with Amide Bonds: Relationship between Molecular Environment and Reaction Kinetics in the Monolayers

JIANG ZHAO, SUNG-AE LEE, HARUHISA AKIYAMA,
JUN'ICHI NAGASAWA and FUSAE NAKANISHI

*National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba,
Ibaraki 305–8565, Japan*

Photopolymerization has been conducted successfully in the Langmuir and Langmuir-Blodgett monolayers of *p*-phenylenediacrylic acid derivatives. We have evaluated the mutual relationship between the reaction-induced monolayer structural change and the dependence of the reaction kinetics on the monolayer structure.

Keywords: photopolymerization; *p*-phenylenediacrylic acid; Langmuir monolayer; Langmuir-Blodgett film

INTRODUCTION

As its importance in understanding the reaction mechanism in low-dimensional molecular systems as well as its future applications, photopolymerization in molecular films has been attracting research attention. The relationship between the monolayer structure, especially the microscopic molecular environment, and the reaction features, such as products and kinetics, shows its significance both at the fundamental scientific level and in the directional information for device fabrication [1]. In this work, photochemical behavior of *p*-phenylenediacrylic acid derivatives in monolayers has been evaluated from the view of the relationship between the reaction kinetics and molecular environment.

EXPERIMENT

The sample synthesis and the monolayer fabrication of the compounds adopted, 4-(4-(2-(decyloxycarbonyl)vinyl)cinnamoylamino)benzoic acid (DCAB) and 4-(4-(2-(octadecyloxycarbonyl)vinyl)cinnamoylamino)benzoic acid (OCAB), have been described in details elsewhere [2]. The photopolymerization was conducted for DCAB in the mixed Langmuir monolayers and OCAB in its LB multilayers. The reaction processes were evaluated by a combination of methods, such as π-A isotherm, UV-visible and infrared spectroscopy (UV-VIS and IR), gel permeation chromatography (GPC), and Brewster-angle microscope (BAM).

RESULTS AND DISCUSSIONS

Figure 1 shows the π-A isotherms of DCAB, DCAB+stearic-d_{35} acid (1:3), and OCAB. DCAB is difficult to form a stable monolayer by itself, and it can form a monolayer at 7.4 mN/m with the help of stearic acid. A process of stabilization occurs with this mixed monolayer, i.e., the monolayer experienced a decrease in its area, corresponding to a decrease in partial molecular area of DCAB from 0.38 to 0.26 nm^2 at a time scale of 2-3 hours. Furthermore, an increase in molecular density was observed by BAM.

Regarding the photopolymerization conducted on the water surface, the product was revealed as cyclobutane dimer by GPC, UV-VIS, and IR spectroscopy. An increase in surface pressure and

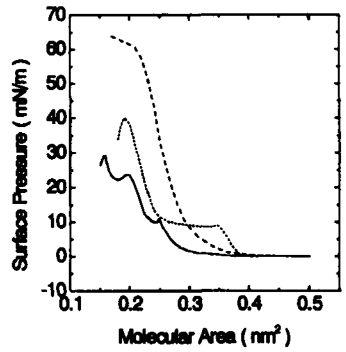

FIGURE 1. π-A isotherm of DCAB (dotted), DCAB + stearic-d_{35} acid (solid), and OCAB (dashed) on water at 20°C.

monolayer area was observed during the reaction. Importantly, an interesting feature lies in the difference in the reaction kinetics, i.e., a much faster speed is with the monolayer before stabilization than that after. This is evidenced in the GPC data, in which both dimer and monomer can be observed in the reaction in monolayer after stabili-zation at 10 minutes irradiation, while no monomer could be observed in the monolayer before stabilization even though the irradiation time was only 5 minutes. It is clear that the molecular density is higher after stabilization and therefore the molecular distance is shorter after stabilization, which should be more favorable for the reaction. The contradictory data made us attribute this phenomenon to two aspects: 1) the difference in molecular free space; 2) the difference in molecular packing.

When the cyclobutane dimer is formed, the molecules will change their shapes from the former planar conjugated configuration to the out-stretching one. This change not only results in an expansion of monolayer but also brings about the requirement for the molecular free space for the molecules to make both orientational and lateral movement during the polymerization. Therefore, the looser structure of the monolayer causes a higher reaction speed. On the other hand, the initial molecular packing is also essential. It is very likely that molecular packing differs in these two stages, considering the different molecular density. Regarding this aspect, further experiments are in progress.

As originated from the molecular conformation, the reaction induced structural change in monolayer and its effect on the reaction kinetics are also clearly observed in the IR spectra of the LB multilayer of OCAB deposited at 35 mN/m (Figure.2). A two-step kinetics (firstly fast and later slow) is found with the C=C groups. Importantly, a similar feature is with the increase in frequencies of $\nu_a(CH_2)$ and $\nu_s(CH_2)$, showing an increase in the gauche conformation number in the alkyl chains and thus the distortion of them, induced by the reaction. The good correlation of these two kinetics strongly suggests the dependence of the reaction speed on the structural change. This is very reasonable considering the dependence of the reaction on the crystalline structure in the three-dimensional crystal [3]. In conclusion, the mutual dependence of polymerization reaction kinetics and monolayer structural changes are well analyzed for amphiphilic *p*-phenylenediacrylic acid derivatives.

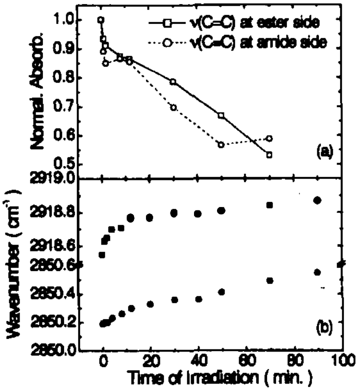

FIGURE 2. (a): Normalized absorbance of the two ν(C=C) and (b): the frequencies of $\nu_a(CH_2)$ (▪) and $\nu_s(CH_2)$ (•) versus the time of irradiation.

ACKNOWLEDGEMENTS

Financial support of STA Fellowship is appreciated.

References

[1] A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*, (Academic, Boston 1991).
[2] J. Zhao, K. Abe, H. Akiyama, Z. Liu, F. Nakanishi, *Langmuir*, **15**,2543 (1999).
[3] G. M. J. Schimdt, *Pure Appl. Chem.*, **27**, 647 (1971).