PHOTOREACTIVITY OF *p*-PHENYLENEDIACRYLIC ACID
DERIVATIVES IN THE CRYSTALS AND LANGMUIR-
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Study of chemical reactions in various organized systems is of interest from the view points of both preparation of novel compounds and investigation of reaction mechanism. We have extensively studied photoreaction of olefinic compounds in the crystalline state and Langmuir-Blodgett (LB) films [1,2]. In these systems molecular arrangement plays an important role for reaction to proceed and the construction of various reaction systems may be possible by controlling chemical structure of compounds. We have prepared a series of *p*-phenylenediacyrylic acid (*p*-PDA) monoesters (I) [3] and investigated the influence of alkyl ester residues on crystal packing and photoreactivity. In this communication we will report photoreactivity of *p*-PDA monoamide (II) with relation to the molecular arrangement and compared with that of *p*-PDA monoester.

The amide function plays an important role by forming hydrogen-bonding which is a useful tool for molecular architecture. We expect to be able to control molecular arrangement by introducing an amide group instead of an ester group of *p*-PDA monoester. *p*-PDA monoamide with various alkyl chains ($n=2,4,10$) were prepared by condensation of corresponding *p*-formylcinnamide with malonic acid in the presence of piperizine. As the typical example, *p*-PDA monodecylamide

(p-PDAmAC₁₀) was described. p-PDAmAC₁₀ was recrystallized from ethanol giving white crystals (M.p. 242°C, Elementary analysis Calcd. for C₂₂H₃₁NO₃(%) C;73.91 H;8.74, N;3.92, Found C;74.33, H;8.80, N;3.90). The absorption maximum of UV spectrum of p-PDAmAC₁₀ in chloroform was observed at 318 nm. In order to check photoreactivity of p-PDA mAC₁₀ crystals, the KBr pellet embedded this crystals was irradiated with a 500 W high pressure mercury lamp. IR spectrum of irradiated KBr pellet showed the appearance of carbon dioxide to some extent. However, when the crystals dispersed in water were irradiated with the same lamp for 9 hours, they showed almost no changes in the IR,UV spectra and the molecular weight determined by G.P.C. Therefore we concluded that p-PDAmAC₁₀ crystals are photostable. This photochemical behaviour is quite different from that of corresponding p-PDA monodecyl ester. The result of crystal structure analysis of p-PDAmAC₁₀ could explain this behaviour. The molecular packing of p-PDAmAC₁₀ is shown in Fig.1. It exhibits that two molecules of p-PDA mAC₁₀ form a dimer by hydrogen-bonded carboxylic acids and the monoamide hydrogen-bonded networks between adjacent molecules produce ribbon packing. Photo-reaction can not take place within a ribbon because the linear amide-amide hydrogen-bond requires a 5 Å repeat axis whereas a 4 Å separation of double bonds is required for reaction[4].

The photoreaction between ribbon layers is also impossible because the distance between double bonds of ribbon layers is longer than 4 Å. In the case of p-PDA monodecylester the dimer is formed but molecular packing is different. The distance of double bonds between imprinted layers of dimers is 3.8 Å,

Fig.1 Molecular packing diagram of p-PDAmAC₁₀

which makes reaction proceed. Thus the remarkable difference in molecular arrangement and photoreactivity was observed by replacing an ester group into an amide group. Though p-PDAmAC₁₀ crystals are photostable, they can be photoactive by preparing the LB film. The detail of the LB film is under investigation.

References 1.M.Hasegawa, *Chem. Rev.*, **82**, (1983) 507. 2.F.Nakanishi, S.Okada, H.Nakanishi, *Polymer*, **30**, (1989) 1959. 3.F.Nakanish, H.Nakanishi, *Mol. Cryst. Liq. Cryst.*, in press. 4.G.M.J.Schmidt, *Pure and Appl. Chem.*, **27**, (1971) 647.