# EFISH 방법을 이용한 용액에서의 극성 분자 구조 규명

# Solution structure of organic polar molecules using EFISH method

Jae Woo Park, Hyung-ki Hong, Kwang-Sup Lee*, Choon Sup Yoon
Department of Physics, KAIST, Daeduck Science Town, Daejon 305-701, Korea
*Department of Polymer Science & Engineering, Han Nam University, Daejon 306-791, Korea
E-mail : csyoon@kaist.ac.kr

Polar organic molecules tend to form dimers in a concentrated solution because of their large ground state dipole moment. The molecular dimerization gives rise to undesirable effects on the solution structure such as fluorescence quenching in a dye laser and undue interruption of crystal growth. We investigate the influences of the dimerization on the crystal growth of 3-methyl-4-methoxy-4'-nitrostilbene (MMONS) using electric field induced second harmonic (EFISH)[1-3] generation. MMONS shows very large powder SHG efficiency (1250 × urea), which is one of the largest values among nonlinear optical materials.[4]

The dimerization of MMONS molecules was verified by the concentration dependence of macroscopic third-order susceptibility, $\Gamma$ which was measured by EFISH. Fig.1 shows the experimental setup, where a Nd:YAG laser of 15.8 ns pulse width and 10 Hz repetition rate was used as a pump source. A function generator synchronized with the pump laser makes square pulses of 0.4 V height and 500μs duration. The square pulse was amplified by a high voltage amplifier to 800 V so that an electric field of 800 V/mm may apply to the solution. Fig.2 shows the Maker fringes obtained, where the closed circle and solid line represent the experimental and theoretical data, respectively. The macroscopic third-order susceptibility for the solution was obtained by the analysis of the Maker fringes.

Based on the monomer-dimer equilibrium model and the assumption of a centrosymmetric dimer, $\Gamma$ is given by

$$\Gamma = f(N_{monomer}\gamma_{monomer} + N_{MEK}\gamma_{MEK}), \quad (1)$$

where $f$ is the local field factor of the solution, $N_{monomer}$ and $N_{MEK}$ are the concentrations of the solute and solvent molecules, respectively, and $\gamma_{monomer}$ and $\gamma_{MEK}$ are the molecular second-order hyperpolarizabilities of the solute and solvent molecules, respectively. Fig.3 shows the concentration dependence of $\Gamma/f$. The experimental data in Fig.3 agree well with the solid line, which is obtained by Eq. (1). The association constant for the dimer is estimated to be 0.61 $(mol/L)^{-1}$. The dashed line in Fig.3 represents the $\Gamma/f$ values when all the MMONS molecules are assumed to be in a monomer state. Fig. 3 clearly indicates that the number of MMONS monomers decreases as a result of dimerization. Fig.4 shows the number ratio of the monomer and the dimer molecules as a function of concentration.

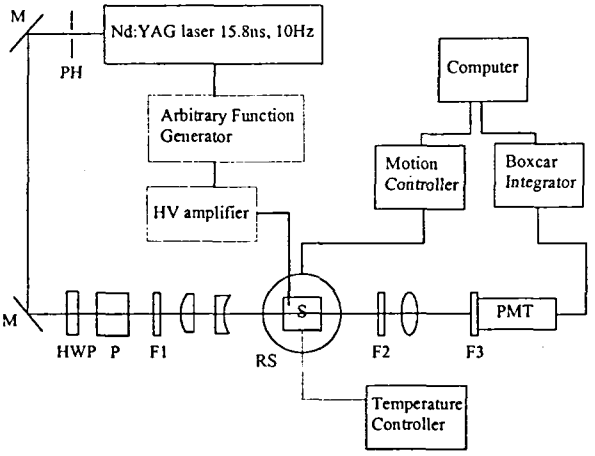


Fig.1 EFISH setup. (PH: Pin hole, M: Mirror, HWP: Half Wave Plate, P: Polarizer, F1: IR pass filter, S: Sample, RS: Rotational Stage, F2: IR cut Filter, F3: 532 nm narrow pass filter, PMT: Photo Multiplier Tube)

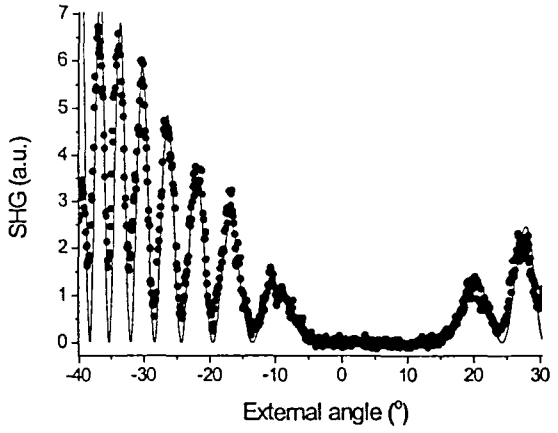


Fig.2 Maker fringes for 0.414 mol/L. The closed circle and solid line represent the experimental and theoretical data, respectively.

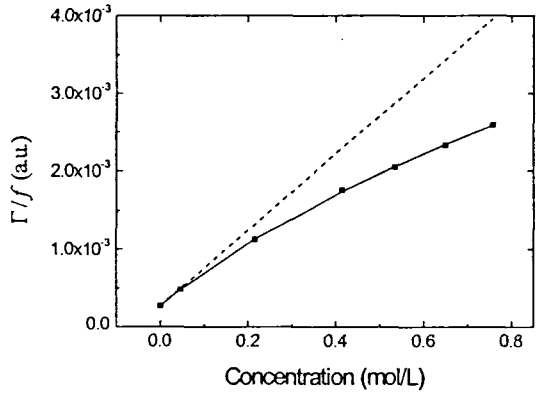


Fig.3 Dependence of $\Gamma/f$ on the solution concentration. The solid squares represent the experimental data, and the solid line is obtained by Eq. (1). The dashed line is for the case of no dimerization.

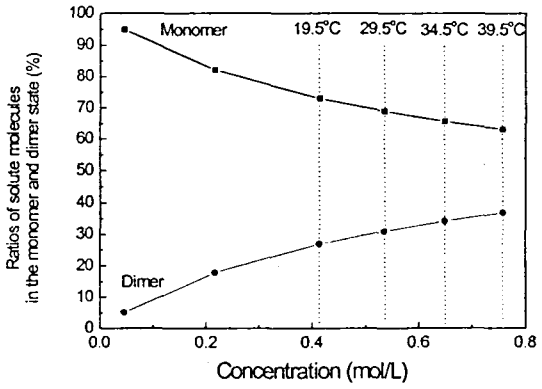


Fig.4 The number ratio of the monomer and the dimer molecules as a function of concentration.

1. B.F. Levine, and C.G. Bethea, J. Chem. Phys. **63**, 2666 (1975).
2. J.L. Oudar, J. Chem. Phys. **67**, 446 (1977).
3. T. Uemiya, N. Uenishi, and S. Umegaki, J. Appl. Phys. **73**, 12 (1993).
4. W. Tam, B. Guerin, J.C. Calabrese, and S.H. Stevenson, Chem. Phys. Lett. **154**, 93 (1989).