

current.¹⁷ But, the charging current accumulates negatively charged species in the double layer in this potential region,² which makes the *effective* mass increase because the charged species should be bound at the surface weakly or strongly in the electric field unlike those in the bulk solution.

We have calculated the charging current contribution of (bi)sulfate adsorption according to the Watanabe's opinion. The estimated charging current converted from $d\Delta M/dt$ was so small that the specific adsorption of (bi)sulfate in the double layer potential region could not explain the charging current. We took the hydroxide adsorption as an alternative choice. The current estimated from $d\Delta M/dt$ is described in Figure 4 with the assumption of the electrochemical equivalent of 17 g, where both estimated and real charging currents are comparable in magnitude. Although the assumption of hydroxide adsorption has no scientific evidence, we can say that the mass increase associated with the charging current in the double layer potential region is mainly due to adsorption of a species that has approximately 17 g of the *effective* equivalent weight in the sense of a quartz crystal.

Another remarkable thing shown in Figure 4 is that the estimated currents corresponding to the formation and the stripping of (hydr)oxides are much less than the real currents. It means that the oxidation reactions in the oxide formation region occur not only by getting hydroxides from solution but also with the hydroxides (or water according to Shimatzu and Kita¹⁷) already bound on the surface. The real current could not be also explained only with the formation of Pt-O where the equivalent weight of oxygen is 8 g. Even though the estimated current increases almost twice in this case, it is still much less than the real current.

Although many questions still remain, it was demonstrated that a low noise EQCM and its capability getting frequency derivatives can tell more details about electrochemical surface phenomena.

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Unusual Poling Behavior of Poly(p-phenylene terephthalates) with a Nonlinear Optical Sidegroup

Suck-Hyun Lee, Won-Seok Song, Myeong-Jo Jung, Il-Cheol Jeon*,
Byung-Goo Ahn**, and Seog-Jeong Song**

Department of Applied Chemistry, University of Ajou, Suwon 441-749, Korea

*Department of Chemistry, Jeonbuk National University, Jeonju 560-756, Korea

**Kolon Group Central Research Institute, Yongin-gun, Kyunggi-do 449-910, Korea

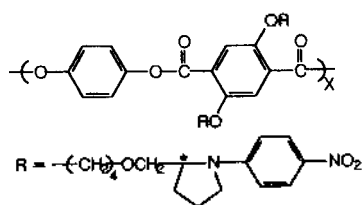
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Nonlinear optical (NLO) effects arise when light causes changes in frequency, phase or other optical properties of a

material. Substances allowing us to manipulate photonic signals efficiently are of great interest in technologies for opt-

ical communication and computing. Extensive research efforts have been directed at tailoring molecules and their arrangements to obtain the NLO materials for practical devices such as electrooptic (EO) modulators and switches.^{1,2} Here we describe unusual poling behaviors of a class of fully aromatic polyesters with NLO pendant chromophore. We have observed for the first time the domains of chromophores induced during poling by atomic force microscope (AFM).

To date, substantial progress has been made to understand how to design NLO organic molecules so as to optimize molecular first hyperpolarizability β . However, optimization of chromophore loading and chromophore order was not always easily accomplished. The electrostatic repulsion between high dipole moment chromophores opposes optimization of both of these parameters. A way to circumvent these undesired effect is to attach the chro-



mophore to a rigid chain of the polymer, for example, by using fully aromatic polyesters. In this paper are reported data on a series of poly(*p*-phenylene terephthalates) with a NLO side group. The polyester backbone chosen in this study consists of *para*-linked benzene ring connected through ester groups and is known to exhibit liquid crystalline phase due to its high chain stiffness.³ For the pendant side group, *N*-(4-Nitrophenyl)-*L*-prolinol (NPPOH) was selected. NPPOH possesses a chiral center which should resist centrosymmetric aggregation of the chromophore substituents.⁴ The repeat unit of target polymer may be represented by the structural formula,

These fully aromatic polyesters were prepared by the solution condensation of 2,5-di-substituted terephthalic acid chloride with hydroquinone. A more detailed description of the synthesis and their general properties including second harmonic generation (SHG) have been stated recently elsewhere.⁵ All of the polymers were soluble in common organic solvents such as tetrachloroethane (TCE) and CHCl_3 and optically good quality films were prepared by spin coating the freshly prepared polymer solution onto glass substrates. After the spinning, the samples were heated under vacuum at 80 °C for at least 24h. The films were poled at a corona-discharge setup with a tip-to-plane distance of 1.0 cm at a temperature 12 °C above T_g (80 °C) for a period of 5 minutes. A poling voltage of 5 kV was applied at a poling current of < 10 μA . This poling process was not optimized but standardized to conditions to compare the results for polymers with different tether length. After the poling was complete, the surface of the film was wiped with ethanol to remove any residual surface charges before measurements were made. The indices of refraction and thicknesses of the films were measured by the well known waveguide technique. Generally the thickness ranges from 0.5 to 3 μm . NLO measurements were performed using a standard Maker fringe technique.⁶ A Q-switched Nd:YAG

laser with a pulse width of 7 ns and repetition rate of 10 Hz was used as the fundamental light source (1064 nm). The SH signals were detected and amplified by a photomultiplier and then averaged in a boxcar integrator. A Y-cut quartz crystal (currently accepted susceptibility at 1.064 μm , $d_{11}=7.2 \times 10^{-10}$ esu) was used as a reference sample. Unless specified, the polarization was chosen to be in the plane of incidence (*p*-polarization). The d_{33} was evaluated following the formula given in reference.⁶ The refractive indices at 532 (SH wavelength) and 1064 nm (fundamental wavelength) were deduced from the corresponding Sellmeier's dispersion formula.⁷

We should report now unusual poling behaviors of the spin-coated films. We studied the surface topographies of the spin-coated films before and after poling using atomic force microscope (AFM). All AFM images were recorded with a Park Science Instruments Autoprobe LS, operated in the contact mode in air. Figure 1 showed that the surface of the spin coated film is clean and extremely flat. The rms roughness values obtained from the AFM software was 2.5 Å. However, this excellent quality film was drastically changed after poling resulting in numerous mountain-like structures in the surface layer, which are similar in shape and size, aligned along the poling direction (Figure 2). Similar surface morphology was also observed in other samples

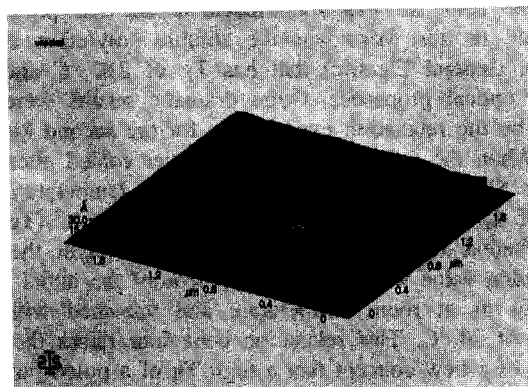


Figure 1. AFM image of spin coated films for the polymer. Note that the Z scale has been magnified in order to enhance the surface topography

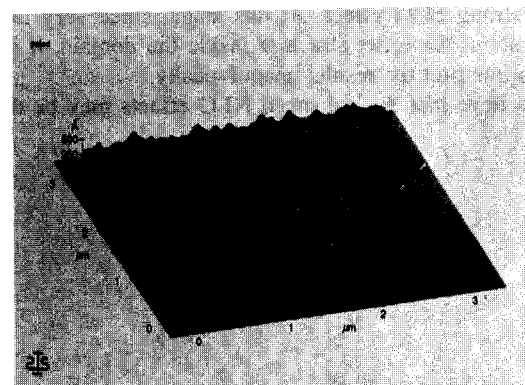


Figure 2. AFM image of spin coated film subjected to electric field (5 kV) poling at 80°C, 5 min. Note that the Z scale has been magnified in order to enhance the surface topography

by optical microscope which shows domain structures much like microphase separated block copolymers.⁸ The surface topographies shown above are characteristic of all samples although their statistical data were different in each of the samples and poling conditions studied. Polymers having larger tether length showed a less well developed structure with the smaller mean height and generally we have observed that more uniform structures give more pronounced NLO properties. With these materials, the frequency doubled blue light was strong enough to be visible to the naked eye with a pulse energy of 0.42 mJ/pulse of fundamental laser light. For example, the SHG intensity we observed for the specimen of 1 μm thick are about 8 times greater than that found for a reference quartz of 1 mm thick. If we use domain thickness estimated from AFM images for the film thickness to calculate the d value, they are found to be in the range of an order of 10^{-7} esu. To evaluate the exact d value, more data on the exact thickness of the surface domain layer should be known, nonetheless, the large relative SHG intensity confirms that these materials exhibit exceptionally high NLO effects.

As further evidence of the unusual behavior of poling, we present one attempted poling which failed. When corona poling was attempted for the films on which a 1- μm -thick polyimide barrier layer was deposited, the resulting SHG response was nearly vanished. But in case the films was corona-poled first and then a barrier layer deposited on it the SHG response was not affected at all. The polyimide we used in this work was the soluble poly(ether imide) (Ultem, General Electric) that has T_g of 210 $^{\circ}\text{C}$ and excellent optical properties. Quite dramatic results were obtained by the relaxation experiments for the second kind of film. When the polyimide layer was over coated after poling, no SHG decay was detected at room temperature and 85% of d_{33} was retained for 30 minutes at 70 $^{\circ}\text{C}$ ($T_g \sim 68$ $^{\circ}\text{C}$), whereas for the film without a barrier layer the corresponding value was approximately 48% of the initial value after 24 hr at room temperature and vanished within a minute at 70 $^{\circ}\text{C}$. This relaxation behaviour raises the possibility of a new concept that a high T_g of a poled polymer may not be essential to the long term stability of optical nonlinearities. These poling behaviours clearly demonstrated that the nanoscale domain structures in the outer layer of the film which is prone to the structural reorganization induced by the poling field may be responsible for the observed strong SHG effect. At this stage, since very little is known about the exact structure inside the domain, it is difficult to interpret the results unequivocally.

We believe that the enhanced NLO effects may be due to

the supramolecular organization of the chromophores in the domain, where the chromophores are orientationally correlated. The enhancement in bulk d value due to this effect is approximately a factor of N^2V , where N is the chromophore density and V is the volume of the domain.¹ Our order measurements confirmed this. The order parameter measured for the polymer immediately after poling by UV absorption spectra was 0.58 and to our knowledge, this value is higher than any reported values for poled polymer systems. Further, it appeared possible that even higher order parameter can be obtained in the domain layer. We observed a much higher orientation of the chromophore in the surface layer from the IR absorbance of reflectance spectra compared to transmittance spectra. The absorbance ratio for the symmetric stretching vibration of the nitro group⁹ before and after poling was 0.33 in the FTIR-ATR spectra whereas it was 0.81 in the normal FTIR transmittance spectra.

These preliminary results are particularly attractive since the nonlinearity can be increased with a scale of N^2V and also design strategies to enhance the domain formation will be valuable for improving long term stability of second order NLO properties.

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