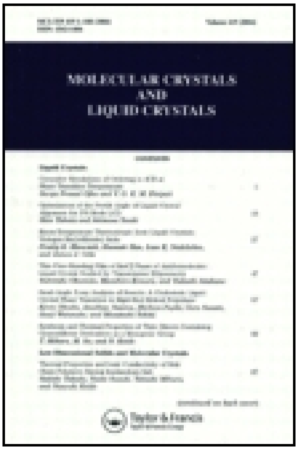

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An Effective Poling of High Tg NLO Polymer

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An Effective Poling of High Tg NLO Polymer

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It was found that the electric conductivity of both polymer film and substrate were critical factors for the preparation of a poled polymer using corona-poling technique. The polymer used in this study was a copolymer of 4-[N-(2-maleimidoethyl)N-methylamino]-4'-nitroazobenzene (MENA) and α-metylstyrene, which has a large optical nonlinearity and high glass transition temperature (Tg). The highest possible dipolar orientation could be achieved by optimizing the electric resistance of the substrate (Rs) corresponding to the electric properties of the polymer, i.e., the electric conductivity and breakdown threshold. For example, the poled polymer prepared onto a 0.4 mm-thick soda glass (Rs = 0.45 GΩ at 160 °C) exhibited a large SHG coefficient (d_{33}) of 268 × 10^{-9} e.s.u., which is ~70% larger than that for a 1.2 mm-thick soda glass (Rs = 1.4 GΩ at 160 °C).

Keywords: Poled Polymer; Corona-poling; SHG; Dipolar Orientation; Glass Substrate; Electric Resistance

INTRODUCTION

Poled polymer systems have attracted much attention as ultrafast and low voltage electro-optic (EO) devices. In recent years, many kinds of polymeric materials with high EO coefficients, good long-term stability, low optical propagation loss, and good processability have been reported. Maleimide-based polymers with NLO-active azo-dye side chain [1]-[3] are, in particular, thought to be good candidates for practical use. Recently, we demonstrated that the polymer shown in Fig. 1 showed a large optical nonlinearity and good structural and chemical stability [3]. The polymer , coated onto 0.8 mm-thick glass substrate and treated with corona-poling under 5kV/cm at 160°C, exhibited

d_{33} ~195×10^{-9} e.s.u. at 1.064μm measured by the second harmonic generation (SHG) technique . This poled polymer was quite stable, maintaining d_{33} ~175×10^{-9} e.s.u even after heating treatment at 80°C for more than 20 days, even though there was a quick initial decay of ~10% .

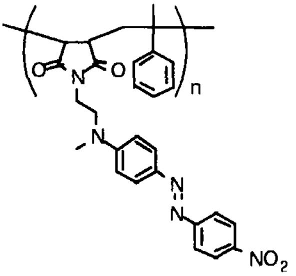

FIGURE 1 Chemical Structure of Poly(MENA-co-α-MS).

On the other hand, the study on the optimization of poling conditions has been so far directed to poling temperature[4]-[6], applied voltage[4],[5], atmosphere[4],[7], annealing procedure and so on [8]. However, in order to get higher dipolar orientation by the corona-poling method, we came to believe that we should pay attention to the electric resistance of the substrate. Here, we will show experimental data regarding the influence of the electric resistance (related to the substrate thickness and the electric conductivity) of the glass substrate on the poling efficiency, and will point out optimized conditions for the preparation of a poled polymer.

EXPERIMENTAL

The precursor polymer was prepared by radical polymerization of [N-2-(maleimidoethyl)-N-methyl]aniline (MEA) [9] and α-methylstyrene in THF at 60 °C. The copolymerization ratio of MEA to α-methylstyrene was 47% to 53% estimated by absorption spectrum. It was converted to a copolymer of 4,4-{N-[2-maleimidoethyl]N-methylamino}-4'-nitro-azobenzene (MENA) and α-metylstyrene (Poly(MENA-co-α-MS)) by a polymer reaction of azo coupling with 4-nitrobenzene diazonium chloride. Azo-dye content of obtained Poly(MENA-co-α-MS) was 57% estimated from the absorption spectrum. The molecular weight (Mn) and the glass transition temperature (Tg) was 1.7 × 10^4 and 221.4 °C, respectively.

This copolymer is soluble in dichloromethane and chloroform. Thin films of about 1000 Å thickness were prepared on various kinds of glass substrates by spin-coating. The film thickness was measured with a mechanical stylus profiler. Corona-poling was carried out in the conditions detailed below; a tungsten needle was kept at 5 kV, the electrode gap was 1 cm, poling temperature was 160 °C, poling time was 20 min, and after that, the polymer film was cooled to room temperature at the rate of 3 °C/min. In this report, the following five different substrate thicknesses were examined: 0.14, 0.4, 0.8, 1.2 and 1.6 mm. SHG coefficient of poled polymers were determined by Maker-fringe method using Q-switched Nd:YAG laser (λ = 1064 nm, pulse duration = 8ns, repetition frequency = 10 Hz, pulse power = 10 mJ / pulse) as the fundamental light source. The temperature dependence of the electric resistance of the substrate was measured in the range from 60 °C to 200 °C.

RESULTS AND DISCUSSION

Figure 2 shows the relationship between SHG coefficient (d_{33}) of poled polymer and the electric resistance that is proportional to the thickness of glass substrate. As is clear from the dashed line of Fig. 2, SHG coefficient (d_{33}) reaches its peak of ~ 280 × 10^{-9} e.s.u. at around 0.3 G Ohm (corresponding

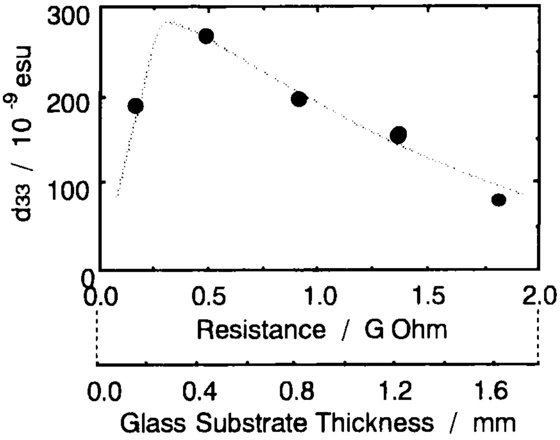

FIGURE 2 The dependence of SHG coefficient (d_{33}) on the electric resistance and the thickness of glass substrate. The electric resistance shown in this figure is the value at 160 °C.

to 0.27 mm-thick). So far, a 1.0 ~ 1.2 mm-thick soda-lime slide glass was usually employed for the preparation of the poled polymer. Therefore, it was demonstrated that the poled polymer treated under the optimized condition should exhibit 60 ~ 80 % larger SHG coefficient (d_{33}) than that prepared by conventional ways.

These observations can be interpreted by the relationship between the electric resistance of the substrate and the electric resistance and breakdown threshold of the polymer. Figure 3 shows the Maxwell-Wagner two-layer capacitor and its equivalent circuit. The dielectric consists of a polymer thin film and a glass substrate is characterized by their dielectric constant, conductivity and thickness, (ε_1, σ_1, d_1) and (ε_2, σ_2, d_2) respectively.

When a DC field is suddenly applied, the final distribution follows from the condition of electric current density continuity: $J_1 = J_2$ which can be written as $E_1 / E_2 = \sigma_2 / \sigma_1$, where E_1 and E_2 are the electric field applied at each dielectric, respectively. If we assume that the applied total voltage ($V = V_1 + V_2$) is constant in corona poling, the electric field applied to a poled polymer is given by

$$E_1 = \frac{\sigma_2 V}{\sigma_2 d_1 + \sigma_1 d_2} \quad . \tag{1}$$

The SHG coefficient (d_{33}) of the poled polymer is given by

$$d_{33} = N f_\omega f_\omega f_{2\omega} L(a) \beta_{xxx} \quad , \tag{2}$$

where N is the number of NLO active group in unit volume, f_ω and $f_{2\omega}$ are the local field factors, $L(a)$ is the third-order Langevin function and β_{xxx} is the first-order hyperpolarizability of NLO active group.

$$L(a) = \frac{\mu E_1}{5 k_B T} \quad , \tag{3}$$

where μ is the dipole moment of NLO active group, k_B is the Boltzmann constant and T is the temperature.

From the Eq.(1)-(3), the SHG coefficient (d_{33}) of poled polymer is found to be a monotonous decreasing function of the thickness of glass substrate (d_2). If we assume the case of $\sigma_1 = 10^{-13}$, $\sigma_2 = 10^{-9}$ S/cm (at 160 °C) and $d_1 = 1000$ Å, the predicted relation between d_{33} and d_2 is shown in Fig.4. The experimental data of the right slope shown in Fig.2 is well characterized by this relation. The observed quick drop of d_{33} in the thinner (low resistance) region in Fig.2 is thought to be based on the electric breakdown of dielectric.

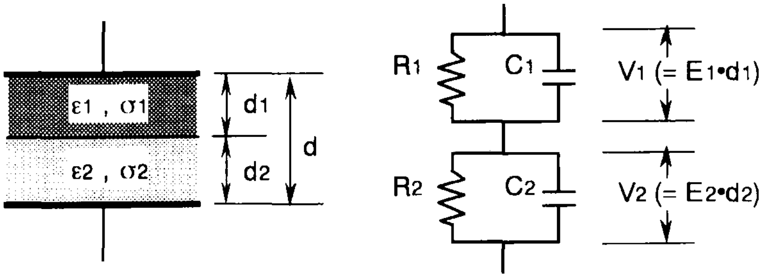

FIGURE 3 Maxwell-Wagner two-layer capacitor and its equivalent circuit.

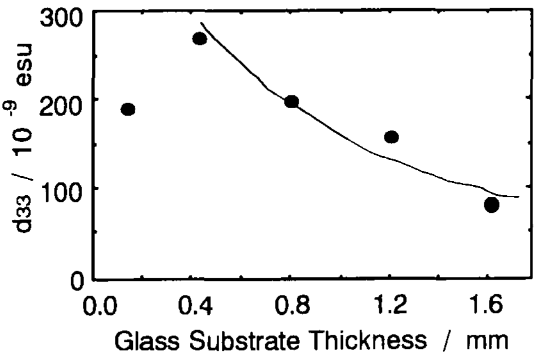

FIGURE 4 The predicted relation between the SHG coefficient (d_{33}) of poled polymer and the thickness of glass substrate (d_2) according to the model above. The scale of the vertical axis of calculated curve (Solid line) was adjusted to fit the experimental data (Solid circles).

Figure 5 is the experimental set-up for in situ current measurement on corona poling. When 5 kV were applied at 160 °C, ~60 nA was observed. Because the electric resistance of the poled polymer, the film and the substrate thickness are ~30 MΩ, 1000 Å and 1.2 mm, respectively, the actual voltage and the electric field applied to the polymer layer are estimated at ~1.8 V and 18 kV/mm, respectively. This value is a few times smaller than the electric breakdown threshold (E_{th}) of the polymer. Suppose that we can evaluate the order parameter of dipolar orientation from Eq.(3), the averaged tilt angle (θ_{tilt}) from the surface normal is then 73.0°. (The dipole moment of NLO active group was calculated to be 8.7 Debye by a semi-empirical molecular orbital method with a PM3.) From these results, the value of E_{th} is expected to be 32 kV/mm and θ_{tilt} is to be 69° at the optimized condition.

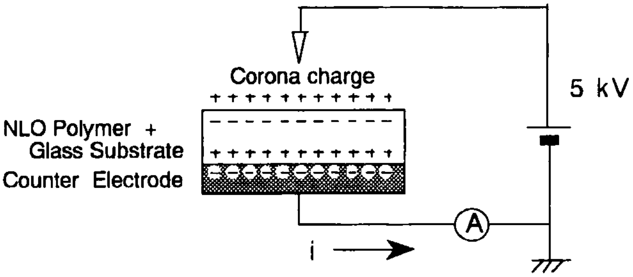

FIGURE 5 Experimental set-up for in situ current measurement on corona poling. A is a picoammeter.

CONCLUSION

On the preparation of the poled polymer using corona-poling technique, it was demonstrated that the electric conductivity of both polymer film and substrate were critical factors, and it was suggested that the highest possible dipolar orientation could be achieved by optimizing the electric resistance of the substrate.

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