Effect of Corona Poling during Film Casting Process of Photorefractive Polymers

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In order to reduce high external voltage application and intense light incidence necessary for driving the photorefractive (PR) polymers, corona poling was newly examined during the film casting process through achieving a well-developed uniaxial orientation of non-linear optic molecules dispersed molecularly in the polymer film. When this technique was combined with our previously reported high temperature casting method, almost the twice large diffractivity of more than 14% with a high response speed of 55 ms was obtained under a relatively moderate applied field of 60 V/µm and low light incidence of 200 mW/cm^2.

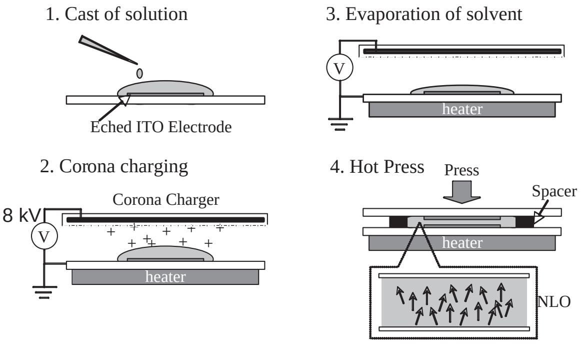

Figure 1. Procedure images of corona Poling. 1; PR polymer solution is cast on a pattern etched ITO substrate. 2, 3; Corona discharge is applied to the cast solution during the evaporation of solvent. At the same time, the temperature of the substrate is controlled by heater. 4; The resultant cast film is sandwiched with another ITO electrode.

PR effect appears only in the materials that exhibit both photoconductivity and electro-optic (EO) effect, and can modulate the refractive index of the PR media reversibly upon a coherent light irradiation. Since the first observation of PR effect in the amorphous photoconducting polymer composite dispersed with non-linear optic (NLO) molecules for EO effect, many researches have been made for achieving high PR performance and it has been revealed that the improvement of photoconductivity is effective to achieve high diffractivity and fast response speed.[1–9] On the other hand, from the principle of PR emergence itself, the pre-formed uniaxial NLO orientation state is also important to conduct a large refractive index modulation due to the EO effect, i.e., Pockels effect.[2,9] Generally, therefore, the PR polymers are operated by applying high voltage externally to obtain uniaxial NLO orientation perpendicular to the film. For the practical use, a very intense external field as high as 100 V/µm and 1 W/cm^2 of light intensity, are used to achieve high PR properties. In a previous paper,[10] we demonstrated that the introduction of high temperature casing for the film preparation brings about the increase of molar fraction of isolated NLOs to be orientated toward the external field through the thermal releasing of stable *anti*-parallel pairs formed between NLO molecules having a large dipole moment, and thereby the drastic improvement has been made in the PR performance. However, a high voltage application was still required. The pre-formation of well-developed uniaxial oreintation of NLOs in the cast polymer film would reduce the external applied field largely. To obtain such orientation state of NLOs, the PR polymer composites were often treated by high voltage poling with a sandwiched electrode configuration at high temperature above T_g (glass transition) so far. In this method, however, the device suffered high risk of the dielectric breakdown.

In this study, therefore, the corona poling was applied during the film casting process. For the PR sample preparation, usually, the polymer solution was cast on an ITO substrate at room temperature, and after the complete evaporation of solvent, the cast film heated on hot plate at about 120 °C was sandwiched with another ITO electrode using a 100 µm-thick polyimide spacer to keep a given film thickness as shown in Figure 1. However, the present corona poling technique was conducted during the solvent evaporation at room or elevated temperature by using a tungsten-wired corotron charging device, which was converted from a copy machine. The corotron device driven at +8 kV DC voltage, was set about 1 cm apart above the film sample and moved back and forth until the completion of solvent evaporation (Processes 2 and 3 in Figure 1).

The PR polymer used in this study was consisted of a photoconductive polymer, poly(*N*-vinylcarbazole) (PVK), doped with 4-(1-perhydroazepinyl)benzylidenemalononitrile (7-DCST) (35 wt %) as an NLO, the plasticizers (32 wt %), 9-ethylcarbazole (EtCz), and 1,3-bis(9-carbazolyl)propane (BisCzPro) (1:1), and C_{60} (0.5 wt %) as a sensitizer. The chemical structures of these compounds are shown in Figure 2. These materials were dissolved in the chlorobenzene, and the resulting solution was filtrated with a micro filter.

The evaluation of the diffraction efficiency was made by four-wave mixing (FWM) with two beams of equal intensity from 10 mW He–Ne laser (633 nm) overlapped in the sample

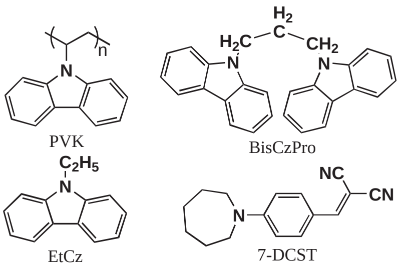

Figure 2. Chemical structures of compounds used in this study.

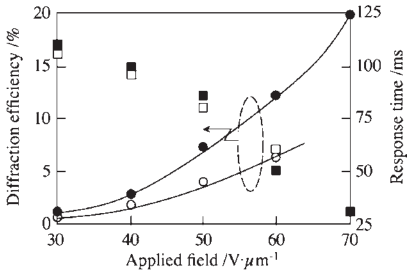

Figure 3. The effect of corona poling for the PR performance, diffaction efficinecy (circle) and PR response speed (square), virsus the external applied fields. The filled and open marks represent the values for the samples with and without corona poling during casting at room temperature, respectively. The FWM measurements were carried at room temperature.

film at incidence angles of 60° and 30° to the normal direction, respectively. The reading beam (0.5 mW) was aligned so as to propagate in the opposite direction to one of the writing beam.[11] The electro-optic coefficient, r_{33}, an effective component for PR effect, was evaluated according to the method reported by J. S. Shildkraut.[12]

In Figure 3 are compared the diffaction efficinecy and response speed for the samples with and without corona charging during casting process at room temperature. The applied fields in abscissas denote the field applied externally in the FWM measurement.

Interestingly, an explicit corona charging effect was recognized in diffraction efficiency, while little change was observed in response time. The diffraction efficiency of the sample treated with corona charging showed twice as much in the field range observable for the PR diffractivity at least. This result strongly indicates that the well-developed uniaxial orientation state of NLOs is pre-formed during casting process under the corona poling, and consequently, the larger EO effect gave rise to the larger diffraction efficiency.

Actually, the electro-optic coefficient r_{33}, which represents the coefficient perpendicular to the film plane, was evaluated. The r_{33} of the sample cast at room temperature with corona charging exhibited much larger value of 95 pm/V (measured at 80 V/μm) compared with 60 pm/V (at the same applied filed) for the sample cast at the same temperature without corona charging. In the molecularly dispersed PR polymers, the relaxation of NLO orientation is concerned because of their low T_g. Actually, the present system with corona poling tended a gradual decline of r_{33}. But after the tendency calmed down for a week, r_{33} of the sample with corona poling was still kept almost 1.2–1.5 times larger than that of the sample without corona poling. This result indicates that the NLO orientation perpendicular to the film plane attained by corona charging in the film immediately before completion of solvent evaporation is well fixed in a once-solidified film.

It should be also worthwhile to mention that the sample with corona poling during the casting process showed the larger value of r_{33} by more than 10% at least compared with the case of corona poling on a solid film.

More interestingly, the polymer film treated by positive corona charging over the film surface showed the distinct dependence of diffraction efficiency and response on the polarity of externally applied field as shown in Figure 4. For applying the reverse bias, i.e., in the opposite direction to the corona poling polarity, the diffraction efficiency was significantly decreased and the response greatly deteriorated. This result provides us an indisputable evidence for pre-formation of the uniaxial NLO orientation in the cast polymer film treated with corona charging, and seems to tell us that the NLO molecules once embedded in a solidified sample are hard to change their orientation direction largely by 180°, even if higher voltage is applied. In this sense, the present corona charge during casting process is very effective for the poling treatment.

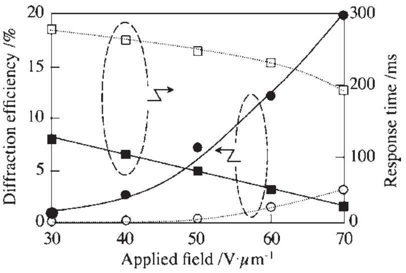

Figure 4. Applied external field dependence of the diffraction efficiency (circle) and response speed (square) for the cases of applying externally the forward bias (closed) and the reverse bias (open) with respect to the corona polarity.

Finally, combining the present corona poling technique with the high temperature casting method reported previously,[10] the sample prepared by cast at 70 °C with corona poling showed the fast response of about 55 ms and the diffractivity of more than 14% under a relatively moderate condition, applied field of 60 V/μm and light intensity of 200 mW/cm^2.

Thus, the present technique was shown to be very useful to improve PR performance based on the increase of the uniaxial orientation of NLOs to the corona field, and provides a new materialization technique for achieving the low-voltage driven PR device in the field of photonics such as transient holography, optical correlation system.

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