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Photorefractive effect of a novel conjugate polymer containing transition metal complex

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Abstract. The photorefractive effect (PR) of a novels $\sigma-\pi$ alternating polymer having 2,2'-bipyridyl in the polymer backbone and their ruthenium complexes has been investigated. The ruthenium complex was used as the charge generator, the $\sigma-\pi$ alternating polymer backbone as the charge transporting channel and second-order nonlinear (NLO) optical chromophore. The photorefractive properties were demonstrated by two-beam coupling (2BC), degenerated four-wave mixing (DFWM) and field-induced orientation birefringence at wavelength of 532 nm. This polymer shows a enhanced photorefractive effect due to the efficient photoinduced metal-to-ligand charge transfer (MLCT) inside the ruthenium complex. A net optical gain of about 22 cm^{-1} and the diffraction efficiency about 10% were obtained at the external electric field of 30 V/μm.

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Organic photorefractive materials have been the subject of intense research in recent years. In the year since photorefractivity (PR) was demonstrated in polymers for the first time in 1991 [1], considerable work has been carried out on all organic polymers [2–6]. As inorganic crystal such as LiN_bO_3, $BaTiO_3$, $Sr_xBa_{1-x}NbO_3$ [7,8], etc. PR polymer has potential applications such as, optical storage, signal processing, and optical switching [9]. Compared with inorganic crystals, polymer materials have many advantages including high processability, low cost, low dielectric constant, and the ability to fabricate complex structure. In order to improve the PR properties, such as gain coefficient and diffraction efficiency, increase the quantum yield of the photogeneration of charge carriers, many efforts have been done. Recently, a PR polymeric film has been shown a coupling coefficient > 200 cm^{-1} and the steady state diffraction efficiency $> 80\%$ [5]. Today some new polymer materials can compete with the well-know inorganic crystals, or even surpass them in some respects.

As we know, the photorefractive effect arises in materials combining photosensitivity, photoconductivity, and second-order nonlinear optical properties that was named linear electro-optical (EO) or Pockels effect. When the photorefractive material is illuminated by nonuniform light, the charge inside the material is photoionized and spatially redistributed. This leads to a separation of positive and negative charges and gradually a internal electric field called space-charge field is build-up. This spatially modulates the index of refraction through the EO effect. Since the change of the index is proportional to the magnitude of the space charge field, how to generate a large space field will be crucial for a high PR performance.

In order to get a polymer containing photosensitive, photoconductive, and EO active moieties, two design methods were suggested [10,11]. The first is to synthesize a fully functionalized polymer, where all functionalities are covalently bound to the polymer backbone. The second is to blend low-molecular-weight compounds into a matrix polymer. In this case, the second-order nonlinear optical polymer, charge transporting polymer or inert polymer can be fulfilled with one of the required functionalities or only be used as a binder.

Here, we reported a novel polymer system that was designed based upon the method one. Tris (bipyridyl) ruthenium complex was chosen as a photo-charge generator, which was known to exhibit a interesting metal-to-ligant transfer (MLCT) transitions [12]. The conjugated polymer was chosen to play the dual role as the electric transfer channel and the macroligand to chelate with the Ru complex. The doped conjugated polymer systems were known having a high electrical conductivity and charge transporting in the polaron or bipolaron states that reside in the forbidden gap could be very efficient. Therefore, the conjugated backbone will provide an efficient charge transfer channel and make it easy to form a space charge field.

The chemical structure of the polymer used in this study was shown in Figure 1.

The synthesis of this polymer was reported elsewhere [13]. Briefly, the molecule incorporates planar structures of a 2,2'-bipyridyl and ruthenium-containing 2,2'-bipyridyl backbones, which have been widely used as nonlinear optical chromophores, connected by a silane backbone, which offers electron conjugation and as a result electronic connection of the planar structure.

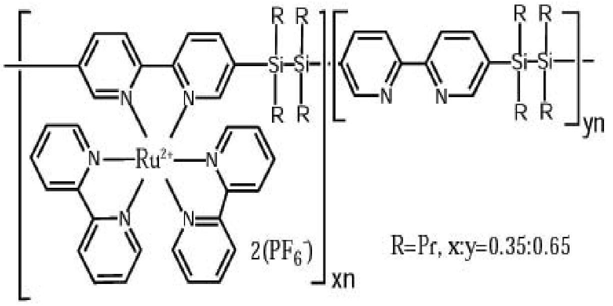

Fig. 1. The structure of the polymer, poly(dislanylene-2,2'-bipyridene-5,5'-diyl) ruthenium complex.

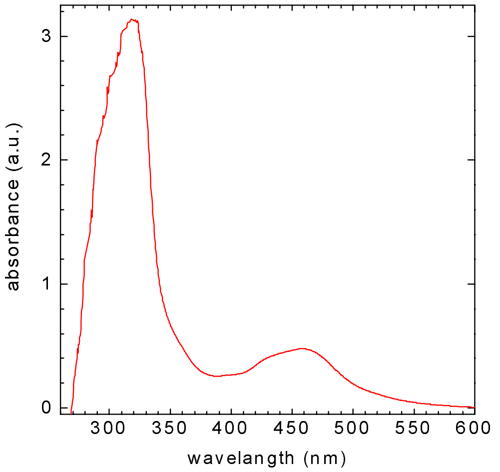

Fig. 2. UV-vis spectra of polymer in chloroform.

That means the backbone of this polymer combines the π-conjugated units and σ-conjugated Si–Si bonds units both of them have been already known as photoconductive materials. The ruthenium contents was determined to be about 35 mol% per bipyridine in the polymer backbone by ^{1}H NMR spectroscopy. The absorption spectra of the polymer in chloroform was shown in Figure 2.

Absorption maximum of bipyridine π–π^* transition appears at around 293 nm. Another absorption peak around 460 nm was assigned to the MLCT band. The linear absorption is low in the 400–600 nm region

We prepared the polymer film by casting chloroform solutions of the polymers onto indium-tin-oxide (ITO) covered glass substrates. The film was dried in a vacuum oven for 12 hours. For the two-beam coupling (2BC) and degenerated four-wave mixing (DFWM) experiments, the film thickness was guaranteed by a Teflon spacer which also acted as an insulator to resist the high voltage applied between the ITO transparent electrodes. The film thickness is about 100 μm.

The two-beam coupling experiment was used to investigate the photorefractive behavior of the polymer film. The laser came from a YLF laser system pumped by LED. The income 532 nm beam (p-polarized) was split into two writing beams with equal intensity (30 mW/cm^2) with a crossing angle of 20° in the air. Two beams were overlapped in the film. The normal of the sample was tilted 60° with respect to the bisector of the two writing beams in order to provide a projection of the EO coefficient. We measured the transmitted intensity of the two writing beam using a lock-in amplifier which was connected to a storage oscilloscope. From the theory of photorefractive, when the two writing beam interference in the sample, an index grating will be formed and diffracted each other. One beam is amplified and the another attenuated as a result of the nonlocal nature of the refractive index grating. That means an asymmetric energy transfer between two-writing beams will be observed when external electric field is applied. This also proves that a true photorefractive effect is present. In this case, two-beam coupling ratio (γ_0) can be obtained. Specially, if the two beams having equal intensities, an intensity increasing for one beam and an intensity decreasing for the other beam with the almost same magnitude will be observed. The gains and the loss can be calculated by the usual expression [14]

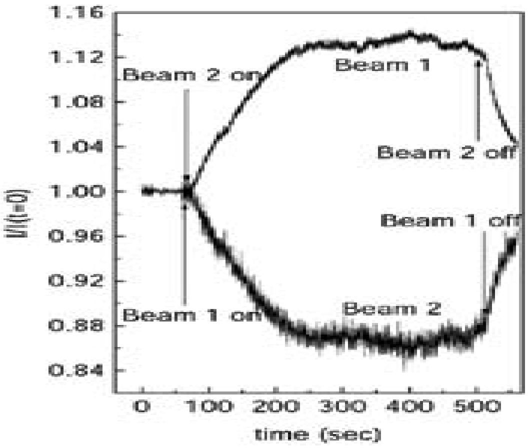

Fig. 3. The dynamics of the grating formation in the sample. The applied electric field is 30 V/μm.

$$\Gamma = \left(\frac{1}{L}\right)\left[\ln\left(\gamma_0\beta_{\mathrm{p}}\right) - \ln\left(\beta_{\mathrm{p}} + 1 - \gamma_0\right)\right] \qquad (1)$$

where L is the length of the beam experiencing gain, γ_0 is the ratio between the intensity of the beam with and without the other beam. β_{p} $(= P_{\mathrm{beam1}}/P_{\mathrm{beam2}})$ is the intensity ratio of the two incident beams (in our case $\beta_{\mathrm{p}} = 1$).

The dynamics of the grating formation in the sample was shown in Figure 3 at an applied external electric filed 30 V/μm.

A typical asymmetric behavior was obtained. As the time went by, the intensity of one beam increasing while the other one decreasing. At about 250 s, the changes of two beam intensities reached stable state. It seems that the forming process of the grating needs a long time. But after the formation of the grating, we break off one beam, the erasing of the grating was very fast.

Optical gain of the two-beam coupling as the applied external electric fields was shown in Figure 4.

The gain coefficient increases as the applied external electric fields, at the field about 30 V/μm, an optical gain of 30 cm^{-1} was obtained. The absorption coefficient (α)

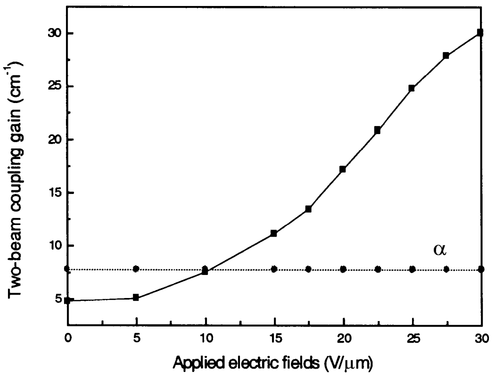

Fig. 4. The two-beam coupling gain coefficient as a function of the applied electric field.

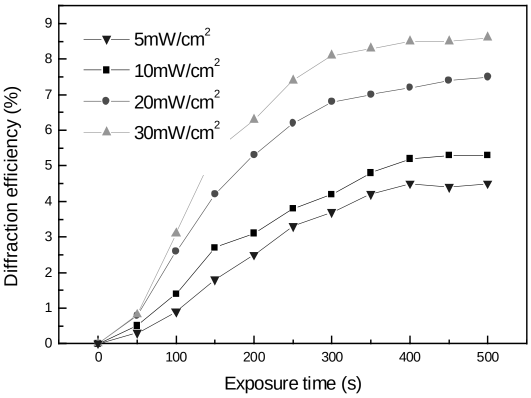

Fig. 5. Influence of varying intensities on the diffraction efficiency.

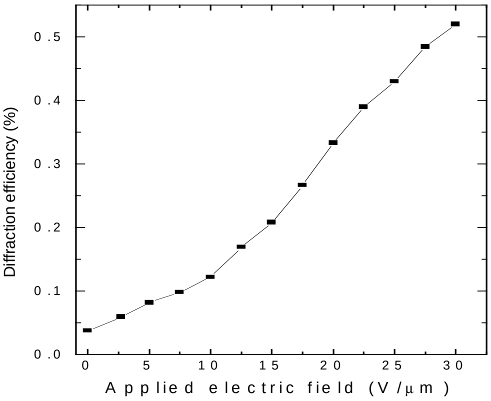

Fig. 6. The diffraction efficient as a function of the applied field.

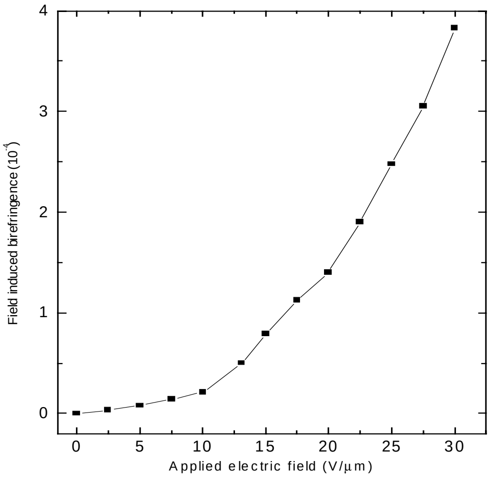

Fig. 7. The field induced birefringence as a function of applied electric field.

for this sample was 7.8 cm^{-1}, so a net gain coefficient of $(\Gamma - \alpha) = 22.2$ cm^{-1}. Here, it is very clear that external electric field plays an important role in enhancing the photorefractive efficiencies because of a higher photoconductivity and a better orientation of the second-order nonlinear optical chromophores at a high electric field.

To understand the influence of different recording beam intensities on the photorefractive performance of the film, we measured the time dependence of the diffraction efficient in the grating recorded using a two-beam interference fringe. The first-order diffraction efficiency of the grating was monitored using a He–Ne laser beam during the recording at four different recording beam intensities ranging from 5 to 30 mW/cm^2 (external field 30 V/μm) as shown in Figure 5.

The rate of the grating growth increased with an increase in the recording beam intensity. If the exposure energy lower than 10 mW/cm^2, the grating growth keeps stable even after 450 s. At higher energies, the diffraction efficiency η reached 50% of maximum value at exposure energy of 20 mW/cm^2 after 150 s.

With the same film, we demonstrated a degenerated four-wave mixing (DFWM) experiment. Two s-polarized beams (20 mW/cm^2) were used as writing beam, a p-polarized weak beam (2 mW/cm^2) counter-propagated to one of the writing beams as a probe which was chopped. The diffracted signal of the probe was detected by a photodiode connected to a lock in amplifier. The results was shown in Figure 6, also a strong electric fields dependence behavior of the diffraction efficiency was observed.

Further evidence for the PR effect comes from fields induced optical birefringence which reflects the EO effect, because PR effect is a combined phenomenon of photoconductive process and EO response. We measured the birefringence of the polymer film using an ellipsometric method with a crossed-polarizer geometry. A He–Ne laser at 632.8 nm was used as probe. The dependence of the field-induced orientational birefringence on the external electric field was shown in Figure 7.

A superlinear relationship between the birefringence and the external field was obtained.

The other nonlinear optics performance of this sample, such as optical limiting and second harmonic, have been reported else [15].

In summary, a hybridized photorefractive polymer containing an ionic transition metal complex and a σ–π conjugated polymer backbone has been synthesized. This polymer shown an enhancement in the photogeneration efficiency due to the MLCT process of the Ru complex. It was found that the photorefractivity was strongly dependent on the external applied electric field. At an applied electric field of 30 V/μm, the two-beam coupling net gain was about 30 cm^{-1} and diffraction efficiency of DFWM experiment was 0.5%. Even at zero electric field, a two-beam coupling gain of 5 cm^{-1} was obtained.

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