

## EFFECT OF PIPERAZINE GROUP IN SIDE-CHAIN AZOBENZENE POLYMER ON SECOND-ORDER OPTICAL NONLINEARITY BY ALL-OPTICAL POLING

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All-optical poling of a piperazine substituted and no piperazine substituted side-chain azobenzene polymer of poly [6-[1-(4-(4-nitrophenylazo) phenyl) piperazine] hexyl methacrylate](Pda) and poly [6-(4-(4-cyanophenylazo) phenyloxy) hexyl methacrylate] (PCN6) were investigated. Optimum relative intensity of the two seeding beams was found first. The second-order non-linear optical (NLO) susceptibility of Pda was improved significantly than that of PCN6, the maximum  $d_{33}$  at saturation of Pda could be enhanced about 10 times. The normalized relaxation process of the SHG (second-harmonic generation) signal from a PCN6 film and a Pda film was also observed and explained by their donor-acceptor strength and length of side chain, at last, using short flexible spacer in Pda to enhance further the temporal stability was proposed.

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*Keywords:* Piperazine group, Polymer, All-optical poling

### 1. Introduction

Great attention has been paid to organic second-order NLO materials because of their high NLO activity, faster optical response and easy processability in fast waveguide and an electro-optic modulation etc [1,2]. Side-chain polymer with active NLO chromophore is a good candidate than guest-host systems in this field. In order to realize the noncentrosymmetry, the most common method is electric field poling. Compared with it, all optical poling (AOP) is another attractive and effective way to induce orientation for second order NLO, which has many desirable features, such as, phase matching for SHG can automatically be achieved, no electrodes are required, and micropatterning of the second order susceptibility can be simply achieved by scanning the focal area over the sample surface [3].

Currently, many efforts were spent on obtaining high second-order NLO susceptibility, large SHG conversion efficiency and long temporal stability of the polar orientation in the field of all-optical poling [4-6]. In order to obtain larger and long-term stable NLO properties, the key points are trying to make the maximum chromophore orientability and stability of orientation. Tirelli et al. [7] studied several new push-pull azobenzene dyes in guest-host systems by corona poling technique, they found rigid rod structures always presented the best orientability and stability of the nonlinear

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optical properties. Among them, MOD2 ([4-(nitrophenylazo)phenyl]piperazine) is a better chromophore which has the highest order parameter in guest-host systems [7]. Also, it has been shown that [8], if the chromophore MOD2 is directly connected to polymer backbone, namely, no flexible spacer between polymer backbone and chromophore, a lack of chromophore mobility would result in quite low orientability and rather poor stability of the polar order.

In the present paper, we first designed and synthesized a novel side-chain azobenzene polymer poly [6-[1-(4-(4-nitrophenylazo)phenyl) piperazine] hexyl methacrylate] (Pda), in which the chromophore MOD2 is connected with polymer backbone through long spacer as NLO unit. Moreover, we studied its all-optical poling behavior. In the same time, in order to investigate the effect of the key structure of piperazine group on the second-order NLO susceptibility and temporal stability in all optical poling, we also prepared a side-chain azobenzene polymer poly [6-(4-(4-cyanophenylazo) phenyloxy) hexyl methacrylate] (PCN6), in which didn't contain piperazine group. The significant difference of them on NLO susceptibility was observed. Other all-optical poling behavior, such as optimum seeding condition, and temporal stability are, also, discussed.

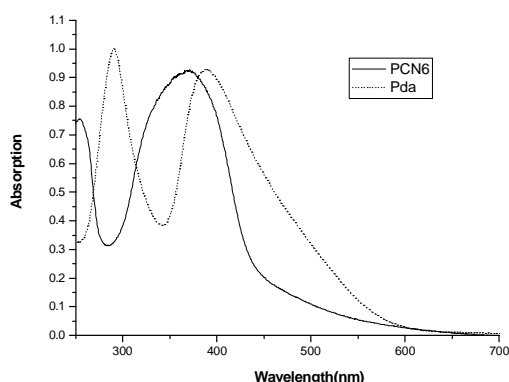


Fig. 1. Absorption spectra of PCN6 and Pda.

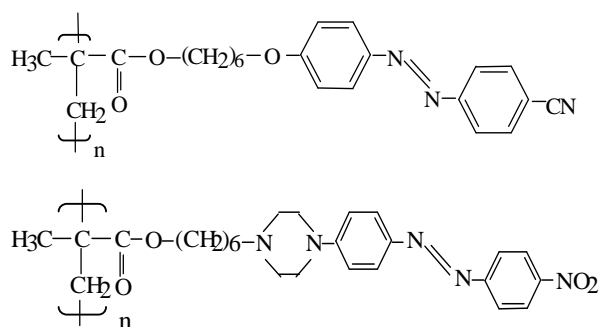


Fig. 2. Chemical structure of PCN6 and Pda.

## 2. Experiments

The polymer PCN6 and Pda were synthesized by free radical polymerization in our lab, detailed synthesis procedure of Pda will reported elsewhere. Fig. 1 shows the absorption spectrum of both PCN6 and Pda thin films. The PCN6 maximum absorption wavelength is 369 nm, which is blue shifted by about 20 nm relative to Pda. Fig. 2 shows their chemical structures. The films of PCN6 and Pda were made by spin-coating on glass substrates after dissolving in cyclopentanone. Transmittance of films was measured by Shimadzu UV-3100. Film thickness was measured with an Alpha-Step 500 Surface Profiler. The index of refraction was determined by optical waveguide experiment on a quartz substrate.

All-optical poling consists of a seeding type process. A similar experimental setup as that used by Fiorini et al. [9], in which the source was an actively and passively mode-locked YAG laser delivering 36 ps pulses at 1064 nm at a repetition rate of 10 Hz. The beam waist diameter at the sample location was 2 mm. The energy in each laser shot is 1 mJ, which gives a fluence of 0.9 GW/cm<sup>2</sup>.

### 3. Results and discussion

#### 3.1. The optimum intensity ratio of the two seeding beams

All-optical poling efficiency depends strongly on both the relative intensity  $R = I_\omega / I_{2\omega}^{1/2}$  and the relative phase  $\Delta\Phi$  of the seeding beams at  $\omega$  and  $2\omega$  frequencies. The optimum poling condition was examined by changing the power of the  $2\omega$  seeding beam, while keeping the intensity of the  $\omega$  beam constant. Fig. 3 presents the normalized SHG signal intensities of Pda and PCN6 films with different ratio of  $R = I_\omega / I_{2\omega}^{1/2}$ . The strong dependence of the SH signals on the relative intensities of two seeding beams can be considered by the physical origin of the  $\chi^{(2)}$  recording. Indeed, the excitation probability, which is at the origin of the selective excitation of the molecules (orientational hole burning), is the sum of three terms:  $I_{2\omega}$ ,  $I_\omega^2$  and  $I_\omega I_{2\omega}^{1/2}$  [10], only the last term is polar and enables centrosymmetry breaking inside the sample, its relative weight determines the efficiency of the process. Therefore, the SH signal intensity generated after saturation should have the following dependence [11]:

$$I_{2\omega} \propto \left( I_\omega I_{2\omega}^{1/2} / (I_\omega^2 + I_{2\omega}) \right)^2 = [R / (R^2 + \gamma)]^2 \quad (1)$$

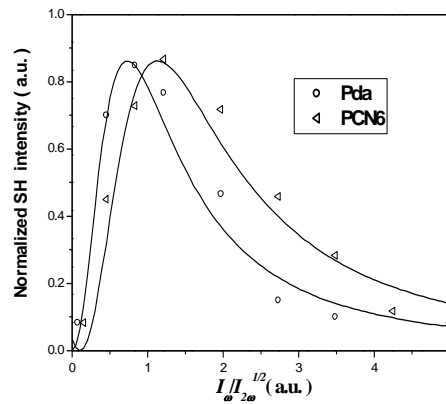


Fig. 3. Normalized SH intensity of PCN6 and Pda against the different intensity ratio,  $I_\omega / I_{2\omega}^{1/2}$ , of two seeding beams.

where  $R = I_\omega / I_{2\omega}^{1/2}$  and  $\gamma$  is a proportionality factor depending only on the dipole moment difference between the ground states and excited states of the nonlinear molecules in the case of two-level model. The solid curve in Fig. 3 is the fitting result given by equation (1). The agreement between the theoretical fit and experimental data is fairly good. The optimum intensity ratio  $R$  was 0.73 and 1.15 for PCN6 and Pda in our experiment.

#### 3.2. Photoinduced SHG intensity and relaxation

To investigate the influences of the piperazine group in Pda on the photoinduced SHG, we measured the evolution of the SHG signals from a PCN6 film and a Pda film under the optimum relative intensities of two seeding beams, respectively. As shown in Fig. 4, after seeding process for about 70 minutes, the signals from the PCN6 film and the Pda film became saturated. The saturated

photoinduced SHG intensity of Pda film is about three times than that of PCN6 film. By comparing with  $d_{11}$  of the quartz ( $d_{11} = 0.5$  pm/V), the induced second-order nonlinear optical coefficients  $d_{33}$  at saturation were estimated to be 4.21 and 53.25 pm/V for PCN6 and Pda, respectively, that is, the  $d_{33}$  value of Pda containing piperazine substituted structure was enhanced about 10 times than in the case of PCN6. The  $d_{33}$  value was determined from the SHG intensity with the following equation [9]:

$$I_{2\omega}^{SHG} = \frac{\omega^2 d_{eff}^2}{4n^2 c^2 10^{OD}} I_{\omega}^2 l^2 \quad (2)$$

where  $I_{2\omega}$  and  $I_{\omega}$  are the SHG signal intensity and the input intensity of the  $\omega$  beam, respectively. Here,  $l$  is the sample thickness, which is 1750 nm and 850 nm for PCN6 and Pda, respectively;  $d_{eff}$  is the effective second-order nonlinear coefficient of the sample; OD is the optical absorption density, which is 0.06 and 1.01 for PCN6 and Pda, respectively; the refractive index at the frequency  $2\omega$  is 1.62 and 1.64 for PCN6 and Pda, respectively;  $c$  is the velocity of light.

This result is significant and can be related to their chemical structure. From Fig. 2 we can see, the two polymers contain the electron-donor and electron-acceptor groups at both ends of the NLO azobenzene chromophore. When we didn't consider the small difference of electron-accepting ability between  $-\text{NO}_2$  and  $-\text{CN}$ , the main difference between them lies in the different electron-donating ability of oxygen atom in PCN6 and piperazine group in Pda. Obviously, the strength of electron-donating ability piperazine group is stronger than that of oxygen atom, because the delocalization of  $\pi$  electrons in strong donor-acceptor substituted structure probably caused the red-shift of the absorption peak [12], as shown in Fig. 1. Furthermore, in strong donor-acceptor substituted system, a large value of hyperpolarizability  $\beta$  can be attained [13]. This is the reason for the significant enhancement of  $d_{33}$  value in Pda.

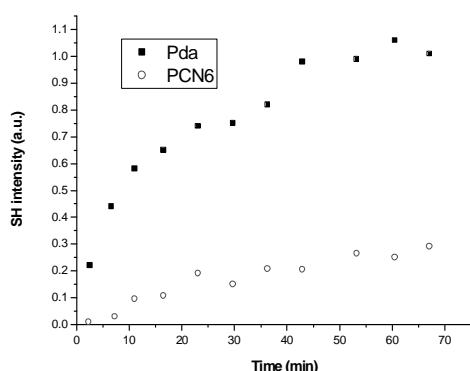


Fig. 4. Evolution of the induced SHG signal from Pda and PCN6 in all optical.

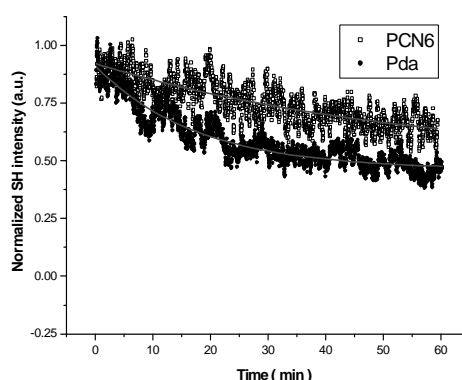


Fig. 5. Decay of normalized photoinduced SHG of Pda and PCN6.

Usually, there are two decay processes in optical poling: the thermal back-reaction process of cis-to-trans isomerization, corresponding to the fast decay component, and disorientation of trans-molecules by thermal motion, and reorientation by non-polar fundamental radiation [14], corresponding to the slower decay component. Fig. 5 shows the relaxation of the SHG signal from a PCN6 film and a Pda film. Obviously, the first decay process in Pda film is faster than that in PCN6. This fact can be also explained by strong donor-acceptor substituted structure in Pda, as reported in previous study. The rate of cis-trans isomerization of azobenzene dyes increases with the increase in

the donor-acceptor strength [13], therefore, the obvious first decay process in Pda film is observed. However, as for the slow decay component, we couldn't compare them clearly, because no better biexponential fitting data was obtained [15]. Even so, we attempted to explain the different temporal stability by comparing the molecule structure of the two polymers. We found the side chain length of Pda is relatively longer than that of PCN6 from Fig. 2. Thus, the limitation from polymer backbone to the thermal motion and reorientation of chromophore in Pda became relatively weak, as a result of the more easy rotation of chromophore after poling in Pda, that probably resulted in the decreasing temporal stability. On the other hand, the analysis above suggested a method to enhance the temporal stability, that is, reducing the length between the chromophore and polymer main backbone. The solid lines in Fig. 5 are the fitting results by a mono-exponential function [14]. After 60 min decay, 64.3% and 48.2% of the maximum SHG intensity for PCN6 film and Pda film remained.

Considering the application, a large second-order coefficient and good temporal stability are all required. For Pda, the enhanced  $d_{33}$  value was what we expected, but the poor temporal stability is not desirable. In the future work, we would attempt to use short flexible spacer in Pda to enhance further the temporal stability [8], in the same time, keeping the high second-order coefficient from the effective piperazine group.

#### 4. Conclusions

All-optical poling behavior of a piperazine substituted and no piperazine substituted side-chain azo polymer of Pda and PCN6 were compared. We found that the maximum  $d_{33}$  at saturation of Pda was enhanced about 10 times than that of PCN6, however, the temporal stability of Pda appeared to some decrease. We analyzed the reason and proposed the way to enhance further the temporal stability in Pda. In general, the strong donor group of piperazine in side-chain azobenzene polymer Pda is a kind of effective molecule structure to have high optical nonlinearity as second-order with NLO materials. We expect this type of polymer associated with all-optical poling will be applied to SHG waveguide devices.

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