Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1523 - 1528

STUDY ON THE ALL-OPTICAL POLING BEHAVIOR OF A SERIES OF SIDE-CHAIN AZO COPOLYMERS AND HOMOPOLYMER

B. Guo[a,c*] F. S. Liu[b], L. J. Zhu[a], Y.Chen[a], Q. J. Zhang[c], G. M. Wang[d]

[a]College of Information, Nanjing Forestry University, Nanjing 210037, China
[b]Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China
[c]Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China
[d]Department of Optical Science and Engineering, Fudan University, Shanghai 200433, China

All-optical poling of a series of side-chain azobenzene copolymers with different azo content and homopolymer was experimentally investigated. The maximum photoinduced SHG was observed when the weight percent of azo in copolymer attained to about 60%. The photoinduced SHG decay process show that copolymers and homopolymer all have higher temporal stability than typical guest-host DR1-PMMA system; moreover, no obvious difference was observed between copolymers and homopolymer. The results indicated that optimal NLO copolymer could be obtained by controlling the azo content of molecule structure in all optical poling.

(Received after revision May 18, 2005; accepted May 26, 2005)

Keywords: Azo, Copolymer, Homopolymer, All-optical poling

1. Introduction

Great attention has been paid to second-order nonlinear optical (NLO) polymeric materials because of their high NLO activity, faster optical response and easy processibility in fast waveguide and an electro-optic modulation etc [1,2]. To achieve second-order NLO effect, macroscopic noncentrosymmetric structure is the requirement. At present, several methods have been developed to realize this noncentrosymmetric structure. They are: electric field poling, photoassisted poling, all optical poling, etc. Among them, all optical poling (AOP) has many desirable features over the others, such as, phase matching for SHG can automatically be achieved, no electrodes are required, and micropattering 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 contrast to guest-host systems, side-chain polymer with active NLO chromophore has larger optical nonlinearity and better temporal stability, e.g., the highest d_{33} value was estimated at around 70 pm/v in DR1 molecules grafted PMMA copolymer (MMA-DR1)[7]. Besides, other reported side-chain polymers included poly (urethane-imide)(PUI)[8], PMMA-co-PNA [5], copolymer (PO-MA)[9], and poly-norbornene [10] etc.

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, which is associated to the microstructure of materials. Tirelli etc.studied the structure-activity relationship of several NLO

---

[*] Corresponding author: gbm@ustc.edu

side-chain polymers containing different push-pull azobenzene dyes by corona poling technique [11]. However, in the field of all-optical poling, to the best of our knowledge, no related study has been reported concerning the relationship between NLO performance and microstructure of the side-chain polymer. Here, we prepared an azobenzene monomer of CN2 (2-[4-(4-cyanophenylazo) phenoxy] 2-methylene methacrylate), and synthesized homopolymer and a series of copolymers with MMA monomer. What we focused on is to understand the influence of the azo ratio in copolymer microstructure on chromophore orientability and stability of orientation in all-optical poling.

In the present paper, The dependence of SH intensity on intensity ratio of the two seeding beams, the relationship between photoinduced SHG intensity with different azo content, and the decay process of the induced SHG were studied in details.

2. Experimental

The monomers in this study were MMA (methyl methacrylate) and an azobenzene monomer of CN2 (2-[4-(4-cyanophenylazo) phenoxy] 2-methylene methacrylate), which was prepared according to the previously reported [12]. The samples of copolymer were labeled PCNx, where x denotes the weight percent of CN2 monomer in the initial monomer feed. The homopolymer was labeled PCN. The copolymers and homopolymer were synthesized by free-radical polymerization in anhydrous THF at 60 °C for 48 h with AIBN (1wt %), purification was performed for three times by dissolution in THF and precipitation from methanol, finally dried under vacuum at 50 °C. Details on the identification label, initial feed monomer, the copolymer composition, and glass transition temperatures are presented in Table 1.

Table 1. Details of Sample.

Sample	Initial feed (CN2, wt %)	Copolymer composition[1] (CN2, wt %)	Copolymer composition[1] (CN2, mol %)	Glass transition temp[2] (^{o}C)
PCN4	4	4.23	1.3	100
PCN10	10	9.39	3.0	103
PCN33	33	39.48	16.3	112
PCN50	50	59.63	30.6	118
PCN75	75	84.69	62.3	120
PCN	100	100	100	123

Note: 1. Calculated by the results of elementary analyzer (Elementar Vario EL)
2. Determined by DSC (Shimadzu DT-50 thermal analyzer).

Fig. 1 shows the chemical structures and typical absorption spectrum of the samples. The films of copolymer and homopolymer were made by solution casting method on glass substrates after dissolving in cyclopentanone. Absorption and transmittance spectrum of films was obtained by using Shimadzu UV-3100. Film thickness was measured with an Alpha-Step 500 Surface Profiler. The refractive index of sample was determined by optical waveguide experiment on a quartz substrate. The DR1-doped pure PMMA (1% mass ratio) film was also fabricated in comparison by spin coating.

All-optical poling consists of a seeding type process. The typical experimental setup can be found in Ref. [13], 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 1mJ, which gives a fluence of 0.9 GW/cm^2.

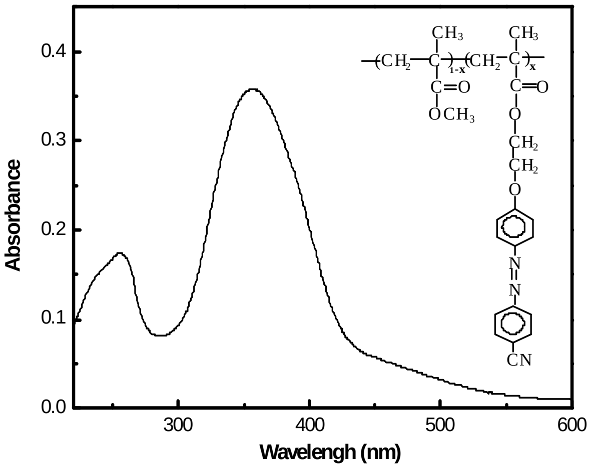

Fig. 1. Absorbance spectrum and chemical structure of azobenzene containing copolymer.

3. Results and discussion

3.1. 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 ω and 2 ωfrequencies. The optimum poling condition was examined by changing the power of the 2 ωseeding beam, while keeping the intensity of the ω beam constant. Fig.3 presents the SHG signal intensities of PCN film 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 $I_\omega I_{2\omega}^{1/2}$ [14], only the last term is polar and enables cenrtosymmetry 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 [15].

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

where $R = I_\omega / I_{2\omega}^{1/2}$ and γ 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. 2 is the fitting result given by equation (1). The agreement between the theoretical fit and experimental data is fairly good. From Fig. 3, we can obtain the optimum intensity ratio R was 1.15 for PCN in our experiment. Similar results were also observed in PCNx films.

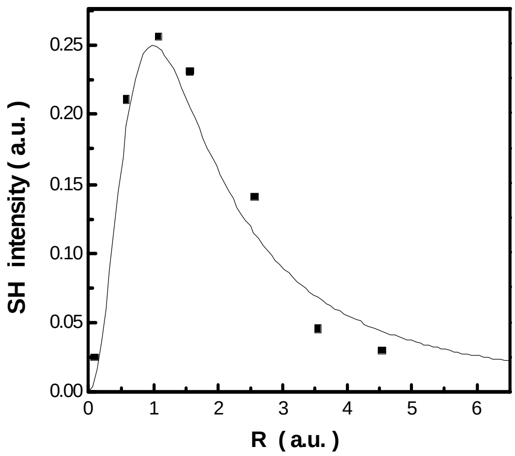

Fig. 2. SH intensity against the different intensity ratio R of two seeding beams.

3.2. Effect of azobenzene content on photoinduced SHG

At the optimum intensity ratio R of 1.15, the measurements were made after the photoinduced SHG of the films increased to their saturation values. The d_{33} value was determined from the SHG intensity by following equation [13]:

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

where $I_{2\omega}$ and I_{ω} are the SHG signal intensity and the input intensity of the ω beam, respectively. Here, l is the sample thickness, and deff is the effective second-order nonlinear coefficient of the sample; OD and n are the optical absorption density and the refractive index of the sample at frequency $_{2\omega}$, respectively, and c is the velocity of light.

The related physical parameters chosen in Eq. (2) can be seen in Table 2.

Table.2. Physical parameter of PCNx and PCN film.

Sample	Thickness (μm)	n	Transmittance (100%)	d_{33} (pm/v)
PCN4	28.27	1.50	81.18	0.51
PCN10	23.24	1.52	80.3	1.33
PCN33	29.59	1.53	28.4	5.42
PCN50	19.47	1.55	20.26	12.69
PCN75	10.85	1.58	54.4	6.44
PCN	18.63	1.62	17.2	6.09

Fig. 3 shows the second-order nonlinear coefficient d_{33} from different azo content in copolymer and homopolymer. Obviously, when the azo weight percent changed from 4~60, the d_{33} value increased; on the contrary, the d_{33} value decreased when the azo weight percent changed from 60~100. That is to say, there is an optimal azo content to obtain the maximum second-order nonlinear coefficient.

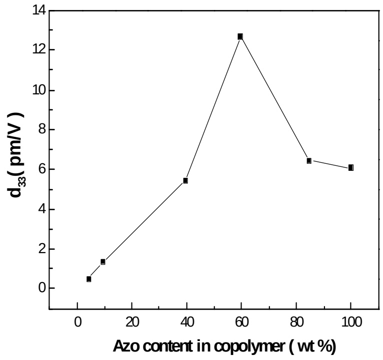

Fig. 3. Effect of azo content in copolymer on second-order nonlinear coefficient d_{33}.

From the microscopic point of view, the above two processes corresponded different mechanism, and it can be explained as follows: the chromophore orientability is related to their different microscopic environments. When the azo content changed from 4~60 wt%, the corresponded molar percent is 1.3~30.6, the relative low concentration has no obvious effect on chromophore mobility, they all can orient freely under polar optical poling. Therefore, azo content plays the key role to increase the d_{33} value in this process, more oriented chromophores at higher concentration resulted in enhanced d_{33} value. However, when the azo weight percent continued to increase from 60~100, it is not the case. The major factor lies in chromophore orientability, not azo content. Because the further increased azo content in copolymer will accordingly reduce its mobility and restrict its orientability, so the d_{33} value decreased. The feature in molecule structure of copolymer creates an optimal order of non-centrosymmetry and second-order nonlinearity observed in the above experiments.

3.3. Effect of azobenzene content on decay process of photoinduced SHG

According to the mechanism of all-optical poling, when the seeding process is just finished, there are two kinds of noncentrosymmetries contributing to the SHG. One of them comes from the cis isomer produced by the photoinduced trans-to-cis isomerization during seeding; the other comes from the polarly oriented trans molecules [16]. Considering this fact, that relaxation evolutions of photoinduced SHG can be described by a bi-exponential function, which represents the following two processes: the thermal backreaction process of cis-to-trans isomerization, corresponding to the faster decay component, and the loss of the polar order of the trans molecules by thermal diffusion, corresponding to the slower decay component.

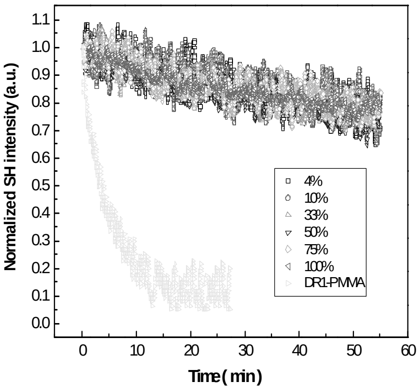

Fig. 4. Decay of normalized photoinduced SHG of PCN, PCNx and DR1-PMMA.

After the photoinduced SHG signal intensity increased to the saturation value, the 2 ωω beam was blocked and the decay evolution was measured. Fig. 4 shows the decay of the normalized SHG induced in DR1-PMMA, PCN and PCNx samples. It was found that the faster and slower process in DR1-PMMA was obvious; on the contrary, the two processes were not discriminable in PCN and PCNx. After about 20min, SHG signal of DR1-PMMA decreased to the minimum value, about 12% of the initial value. In the same time, about 78% of the initial value could be maintained in PCN and PCNx after about 54min. This result showed that the temporal stability of PCN and PCNx is much higher than DR1-PMMA, in which the azo chromophore is not bonded to the polymer.

Because of the fluctuation of the laser power, there is an uncertainty range of ±0.1 for SHG signal intensity. Therefore, From Fig. 4, no obvious difference was observed for PCNx and PCN samples. In other words, it is difficult to discriminate them accurately on our present experimental conditions. So we believe that they have same temporal stability. This result could be explained by the molecule structure in PCNx and PCN. Generally, there are two possible molecule structrue factors in side-chain polymer to influence the decay process, one is that the spacer between the main chain and the azo group could restrict the disorientation of trans molecules by thermal diffusion; the other is that the intermolecular interactions between side chains could lead to overcome the decay process. From our experimental results, different azo content copolymers and homopolymer have no difference. But, it is also certain that intermolecular interactions between side chains will increase with increased azo content in copolymers. Consequently, we can conclude that the major and effective factor maybe the existing “spacer” to determine the higher temporal stability in side-chain polymer.

4. Conclusion

In conclusion, we have investigated the all-optical poling behavior of a series of side-chain azobenzene copolymers with different azo content and homopolymer. The dependence of SH intensity on intensity ratio of the two seeding beams, dependence of SHG on azo content in copolymer, decay process of photoinduced SHG were studied in details. The results showed that the maximum second-order optical nonlinearity and higher temporal stability could be obtained when the weight percent of azo in side chain copolymer attained to about 60%.

References

[1] F. Kajzar, K. S. Lee, A. K. Y. Jen, Adv. Polym.Sci. **161**, 1 (2003).
[2] S. K. Yesodha, C. K .S. Pillai, N .Tsutsumi, Prog. Polym. Sci. **29**, 45 (2004).
[3] J. H. Si, J. Qiu, Z. Meng, K .Hirao , J. Appl. Phys. **95**, 3837 (2004).
[4]. J. Si, J.Qiu, K. Kitaoka, K. Hirao, J. Appl. Phys. **89**, 2029 (2001).
[5] C. Fiorini, F. Charra, P. Raimond, A .Lorin, J.M. Nunzi, Opt. Lett. **22,**1846 (1997).
[6] G. Xu, X .Liu, J. Si, P. Ye, Z .Li, Y. Shen, Appl. Phys.B. **68**, 693 (1999).
[7] W. Chalupczak, C. Fiorini, F. Charra, J.-M Nunzi, P. Raimond, Opt. Commun. **126,** 103 (1996).
[8] Y. Sui, X. Yu, J. Yin, X. Zhong, Q. Li, Y. Chen, Z. Zhu, Z. Wang, Opt. Commun. **191,** 439 (2001).
[9] C. Fiorini, J.-M. Nunzi, F. Charra, F. Kajzar, M. Lequan, R.-M. Lequan, K. Chane-Ching, Chem. Phys. Lett. **271,**335(1997).
[10] V. M. Churikov, M. F. Hung, C. C. Hsu, C. W. Shiau, T. Y. Luh, Chem. Phys. Lett. **332,** 19 (2000).
[11] N. Tirelli, A. Altomare, R. Solaro, Polymer **41,** 415 (2000).
[12] R. Ruhmann, Poly. Int. **43,** 103 (1997).
[13] C. Fiorini, F. Charra, J.-M. Nunzi, P. Raimond, J. Opt. Soc. Am. B **14,** 1984 (1997).
[14] C. Fiorini, F. Charra, J.-M. Nunzi, J. Opt. Soc.Am. B **11,** 2347 (1994).
[15] N. Matsuoka, K. Kitaoka, J. Si, K. Fujita, K. Hirao, Opt. Commun. **185,** 467 (2000).
[16] G. Xu, J. Si, X. Liu, Q. Yang, P. Ye, Z. Li, Y. Shen, J. Appl. Phys. **85**, 681 (1999).