

# The Orientation Stability and UV Irradiation of Poly(hexa-2,4-diynilene-1,6-dioxy)benzoates and Cinnamates Containing *Disperse Red 19*

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*The poling and orientation parameters of the four polymers para and meta benzoates and cinnamates containing Disperse Red 19 dye were studied. The para polymers were found to be orientated more efficiently, and their stabilities were much better than the meta polymers. The photobleaching takes place when irradiated at temperatures around  $T_g$ , but did not occur when irradiated under the poling conditions. After the photo cross-linking at around  $T_g$  the orientation maintenance of the para polymers were found to be almost indefinite. The stability of the para polymers is considered to be due to their stable main chain conformation when poled.*

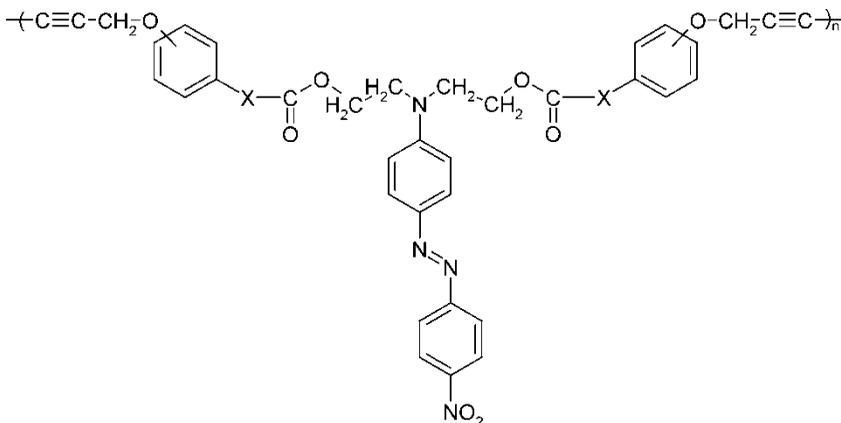
**Keywords** croceona poling, orientation parameter, photo-crosslinking, SHG stability, diacetylene-containing polymers

## Introduction

In the last decades, studies on the organic polymers having nonlinear optical properties flourished, but in recent years, the topic has become less popular because materials which satisfy every requisition to be used in devices could not be found. One of the problems to be solved for second order nonlinear optical (2-NLO) materials to be used in devices is the stability of the orientation of chromophores in the polymeric systems. Naturally, high glass transition temperature ( $T_g$ ) is thought to be an important factor to minimize the relaxation of orientated chromophores. Therefore, high  $T_g$  polyamides and polyimides have been prepared (1, 2). However, rigid polymers are quite resistant to poling, and efficient orientation cannot be achieved, thus 2-NLO responses are very poor. Crosslinking to increase  $T_g$  has been studied earlier, using monomers, which have cross-linkable structures, such as epoxide (3–5) and a cinnamate (6). The decrease of 2-NLO coefficients with time is suppressed by cross-linking. However, when crosslinking points increase, increases the difference in refractive indices between the cross-linked part and uncrosslinked part, causing light scattering of the films.

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X = none or  $\text{-CH=CH-}$

**Scheme 1.** General structure of poly(benzoates) and poly(cinnamates).

Present authors have reported previously series of novel polymers consisting of hexa-2,4-diyne-1,6-dioxydibenzoates and dicinnamates in the main chains and *Disperse Red 19* chromophore in the side chains (7, 8), as shown in Scheme 1. The 2-NLO coefficients ( $d_{33}$ ) of some of these polymers were high being over  $250 \text{ pm/V}$  (9, 10), and the  $d_{33}$  depended most significantly on the main chain conformation, the *para*-polymers showing about 5 times greater  $d_{33}$  than the corresponding *meta*-polymers. The  $d_{33}$  stability of the *para*-polymers was superior to the *meta*-polymers. Thus it can be concluded that the main chain conformation is very important for 2-NLO properties of polymers, both response and stability, as the orientation of chromophores is determined by the main chain conformation of poled polymers. When these polymers were irradiated by UV light at around  $T_g$  temperatures, cross-linking takes place giving films which are not only insoluble but they do not swell in solvents. The structures of these polymers are uniform, each monomer unit contains one chromophore, and they are amorphous and give films with excellent optical quality by spin coating from dimethylformamide (DMF) or N-methylpyrrolidone (NMP) solutions. This paper reports the poling and the effect of cross-linking on the relaxation of chromophores of these poled films investigated by the visible absorption spectroscopy.

## Experimental

### Materials

Synthesis of the four polymers of which structures are shown in Scheme 1, were reported previously (7, 8). Their films were prepared on an ITO coated glass substrate from their NMP solutions at  $80^\circ\text{C}$  using a spin-coater equipped with heating gadget, and films with thickness of around 500 nm were prepared. After spinning, the films were dried at  $80^\circ\text{C}$  in a vacuum oven for 2 h. The films were then subjected to poling at the temperatures around  $T_g$  of each polymer with a needlepoint cathode fixed at a distance of 10–14 mm from the film surface with a voltage of 4.5–5.0 kV.

Poly(methyl methacrylate) containing *Disperse Red 1* (PMMA-DR1), was synthesized by the free radical polymerization of methacryloyl chloride. After evaporating solvent and excess methacryloyl chloride, which was then reacted with DR1, followed

by the reaction with methanol. The elemental analysis indicated that the ratio of MMA units to DR1 units was 5.2, the dye content being about 33%.

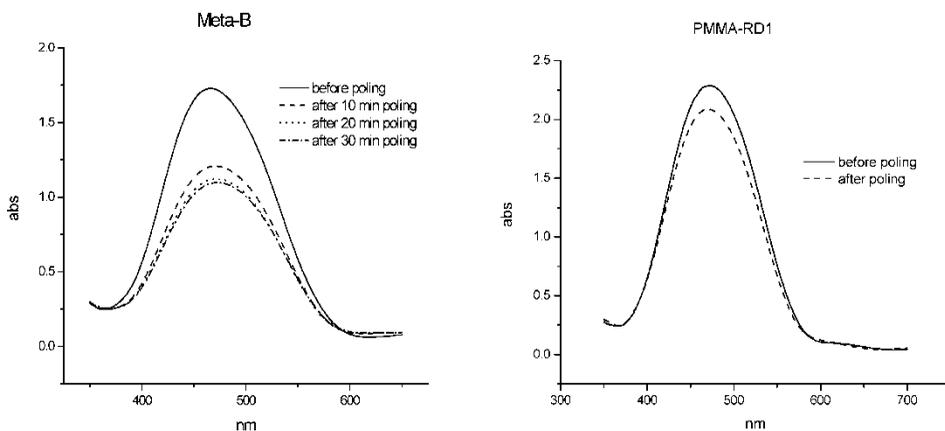
The order parameter,  $\Phi$ , which is a measure for the 2-NLO reponse, was calculated from the relationship,  $\Phi = 1 - (A_2/A_1)$  where  $A_1$  and  $A_2$  are the absorption maxima of film before and after poling, respectively.

UV irradiation was carried out using a 400 W medium pressure immersion mercury lamp of AceGlass Co., at a distance of 30 cm.

## Results and Discussion

Figure 1 shows an example of poling for the *meta* benzoate polymer. It seems that 30 min poling is sufficient, and further poling did not increase the orientation. The poling of PMMA is also shown for comparison. The orientation efficiency is much less than that of the *meta* benzoate, and prolonged poling caused a surface damage. Table 1 shows the order parameters of the four polymers under the optimum poling conditions, and Figure 2 shows the decreases in absorption by the optimum poling. It can be clearly seen that the *para* polymers can be orientated more efficiently than the *meta* polymers. This is in accordance with the observation that the former showed much higher SHG coefficients than the latter (9, 10). The order parameters of these polymers are considerably higher than those of commonly known polymers such as polymetacrylates containing *Disperse Red 1* (11). The experiment was repeated and the relaxation of poled chromophores is shown in Figure 3 and Table 2. The order parameter decreased after left to stand for several months at room temperature. The *para* cinnamate polymer maintained its orientation better than the others, and the *meta* cinnamate was the poorest in maintaining the orientation. It seems that the *meta* cinnamate polymer main chain has a more winding nature.

Diacetylene-containing polymers can be cross-linked by radiation or heating through opening of triple bonds. In the case of crystalline polymers, whose crystalline structures satisfy the requisition of topochemical polymerization, the crosslinking takes place by UV irradiation at room temperature. In the cases of amorphous polymers, such as the polymers of this work, photo cross-linking usually does not take place at temperature

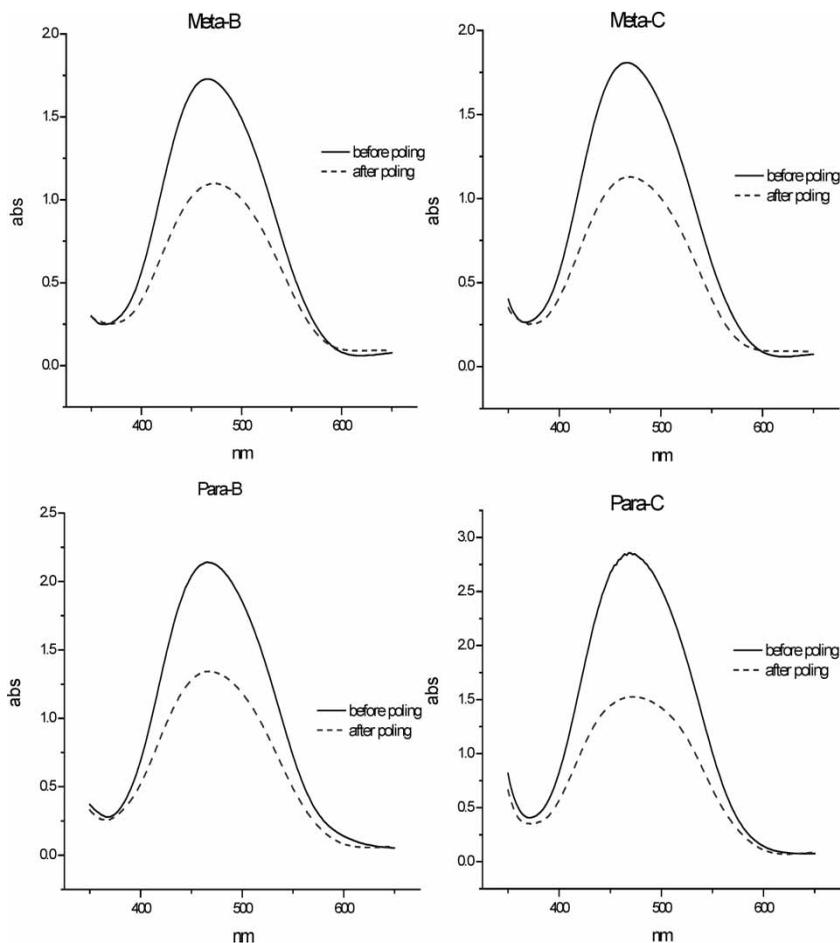


**Figure 1.** The poling effect of the *meta* benzoate polymer (left) at 115°C and PMMA containing *Disperse Red 1* (right) at 110°C for 20 min.

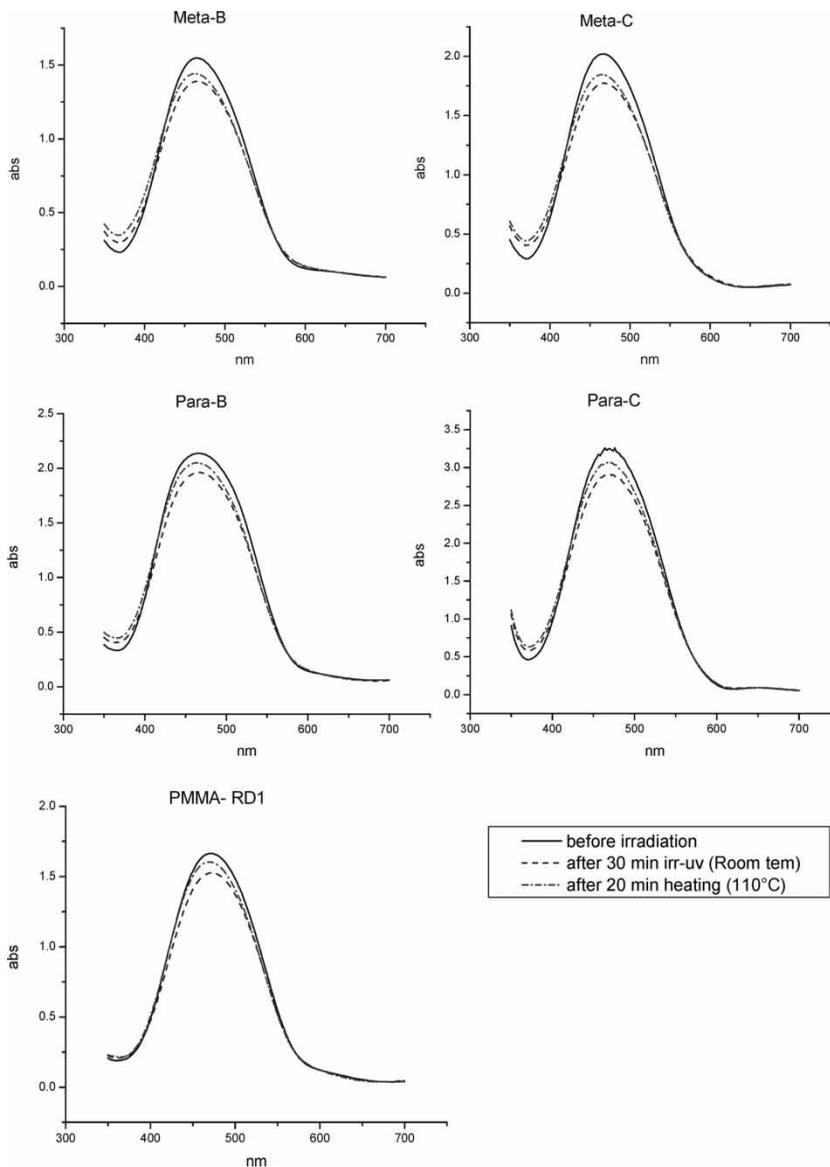
**Table 1**  
Optimum poling results of the four polymer films

Polymer	Poling temp (°C)	Heating rate (°C/h)	Discharge (kV)	Poling time (min)	Needle-film distance (mm)	Order parameter ( $\phi$ )
Para-C	135	120	4.5	90	10.0	0.466
Meta-C	120	60	5.0	20	12.0	0.376
Para-B	115	90	4.5	30	14.0	0.373
Meta-B	115	120	4.5	30	13.0	0.364

below  $T_g$ , because the diacetylene groups are not in the position to react each other. The crosslinking through diacetylene groups is a free radical reaction, and diradicals are formed initially, and if they are far apart from each other, crosslinking is not possible. Therefore, it is necessary to raise temperatures to about  $T_g$  of polymers so that two diacetylene groups get close enough by thermal motion in order to be



**Figure 2.** Decrease in the absorption maxima with poling under the conditions shown in Table 1.



**Figure 3.** Relaxation of poled chromophore with time at room temperature.

cross-linked photochemically. The crosslinking takes place when two diacetylene groups approach each other to form dimeric diradicals, as shown in Scheme 2. The diacetylene-polymers containing hexa-2,4-diynylene-1,6-dioxy groups undergo thermal reaction of diacetylene groups at temperatures over  $140^{\circ}\text{C}$  giving completely crosslinked materials (10, 12).

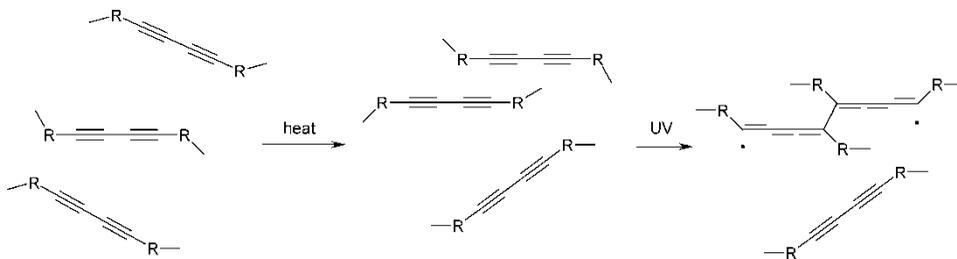
However, this temperature is too high for poling, as thermal energy overcomes the orientation.

In order to see the effect of UV irradiation, the films were irradiated at room temperature and at  $110^{\circ}\text{C}$ , and the spectra are shown in Figures 4 and 5. In many cases, irradiation

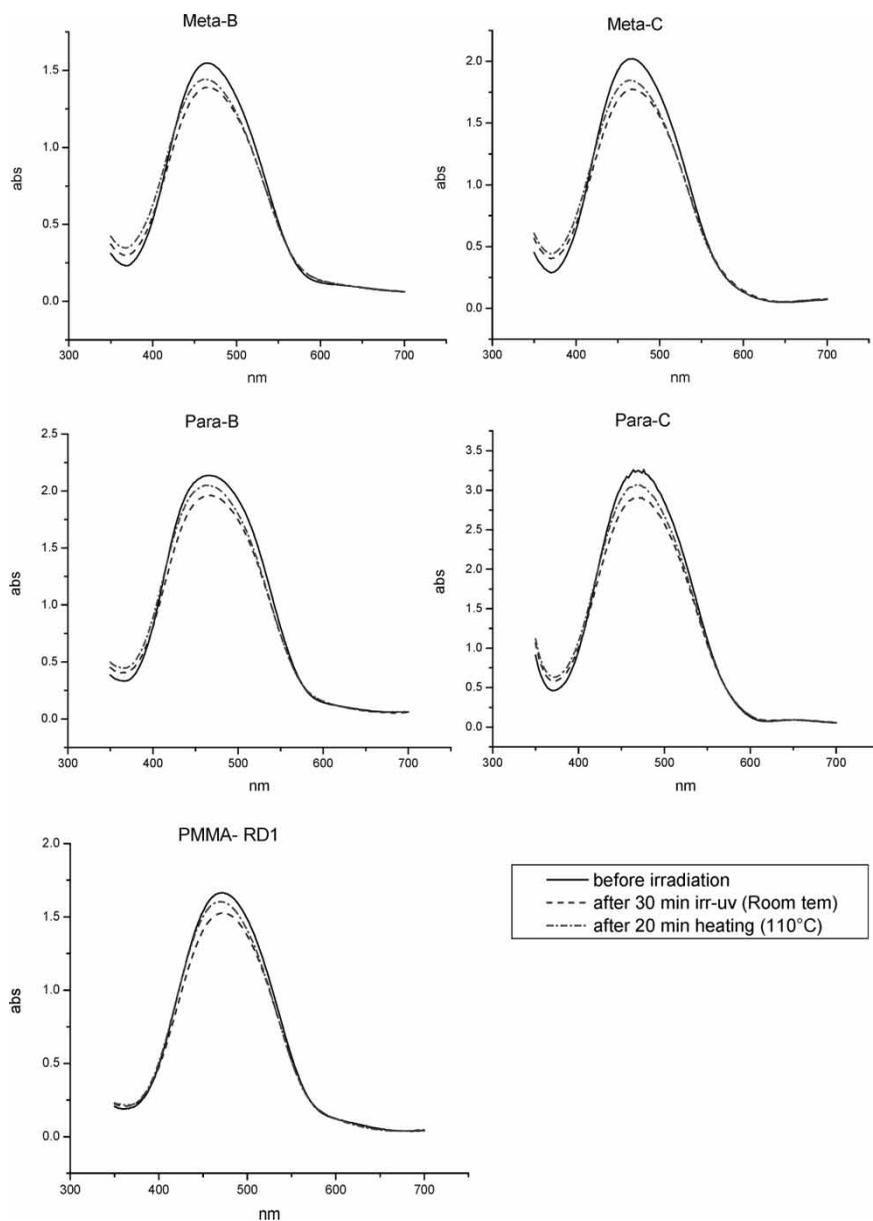
**Table 2**  
Relaxation of orientated chromophores at room temperature

Polymer	Relaxation time (months)	Order parameter ( $\phi$ )		Orientation % after relaxation time
		After poling	After relaxation time	
Meta-B	9	0.323	0.257	79.6
Para-B	6	0.170	0.132	77.7
Meta-C	6	0.268	0.047	17.5
Para-C	10	0.370	0.312	84.3

of UV or visible light fades color of dyes, although the precise mechanism of photofading or photobleaching, has not been well established. It has been reported that photofading of azo dyes occur by the electron transfer from dye molecules to oxygen by visible light (13). Yamaguchi has reported that the contribution of the singlet oxygen is small (14). As can be seen in Figure 4, all of the films showed decrease in absorption. The cause for this can be the *trans* to *cis* photo-isomerization of the dye or the photobleaching by oxidation. Dalton and coworkers have reported previously a few polymers containing *Disperse Red 19* in the side chains, and the polymer films suffer photobleaching as the absorption peak decreased 50% after 35 min of irradiation at room temperature (15). Therefore, the decrease in the absorption by irradiation at room temperature in Figure 1 can be due to the photobleaching. However, regaining of absorption on heating in dark, suggests that the *cis* to *trans* isomerization also took place, and therefore, both the isomerization and photo bleaching take place. There is almost no difference in photobleaching among the four polymers. Since this occurs on the surface of films, the thicker the films less effect will be observed. The apparent less photobleaching of PMMA is due to its less dye content than the others and its film is thicker, thus the surface damage being relatively small. When the films were irradiated at temperatures around Tg, the photobleaching is significantly enhanced, as shown in Figure. 5. The absorption did not increase by heating after irradiation, indicating that *trans* to *cis* isomerization did not occur at the elevated temperature, and the decrease in absorption is due to photobleaching alone. The difference among the four was almost negligible, as the dye molecules are being attacked. Photochemical



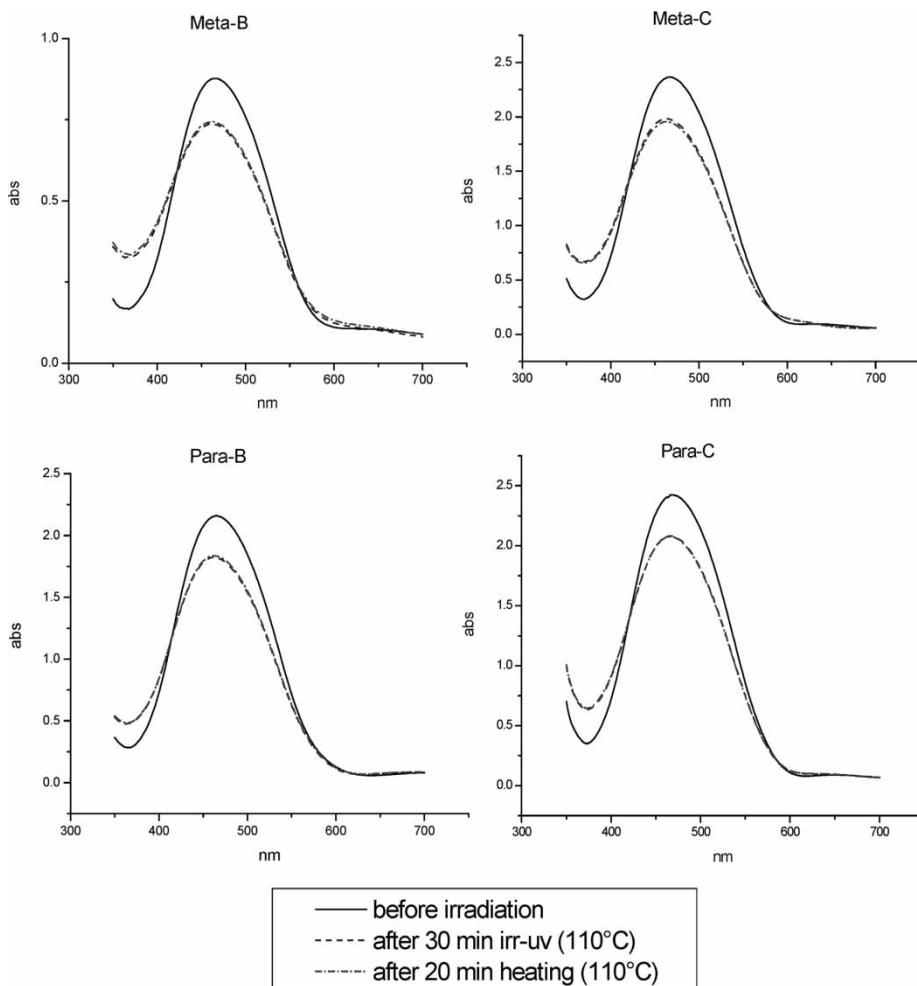
**Scheme 2.** Crosslinking mechanism of amorphous diacetylene-containing polymers. -R- is polymer chain component.



**Figure 4.** The effects of UV irradiation at room temperature of the four polymers and PMMA containing DR1.

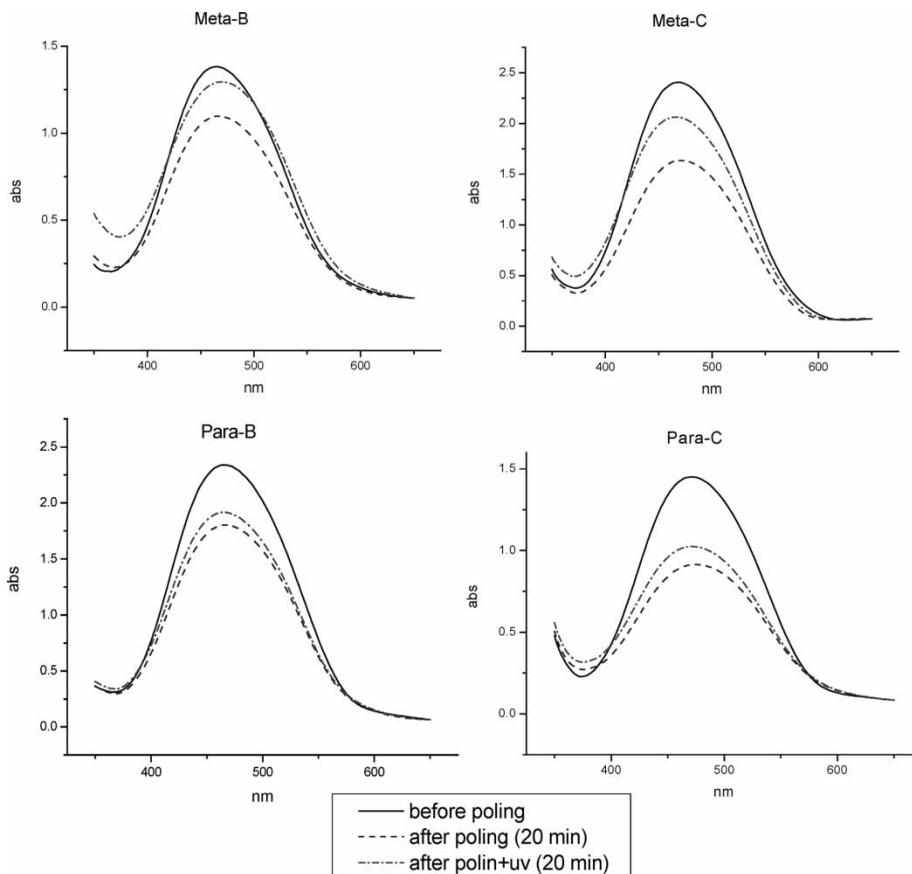
process must be independent of temperature in general. The increase in photobleaching with temperature seems to be due to the increase in diffusion of oxygen from air into films as the polymers become soft at  $T_g$ .

Figure 6 shows the absorption spectra of the four polymer films poled and cross-linked. The spectra changes are quite different from those without poling shown in



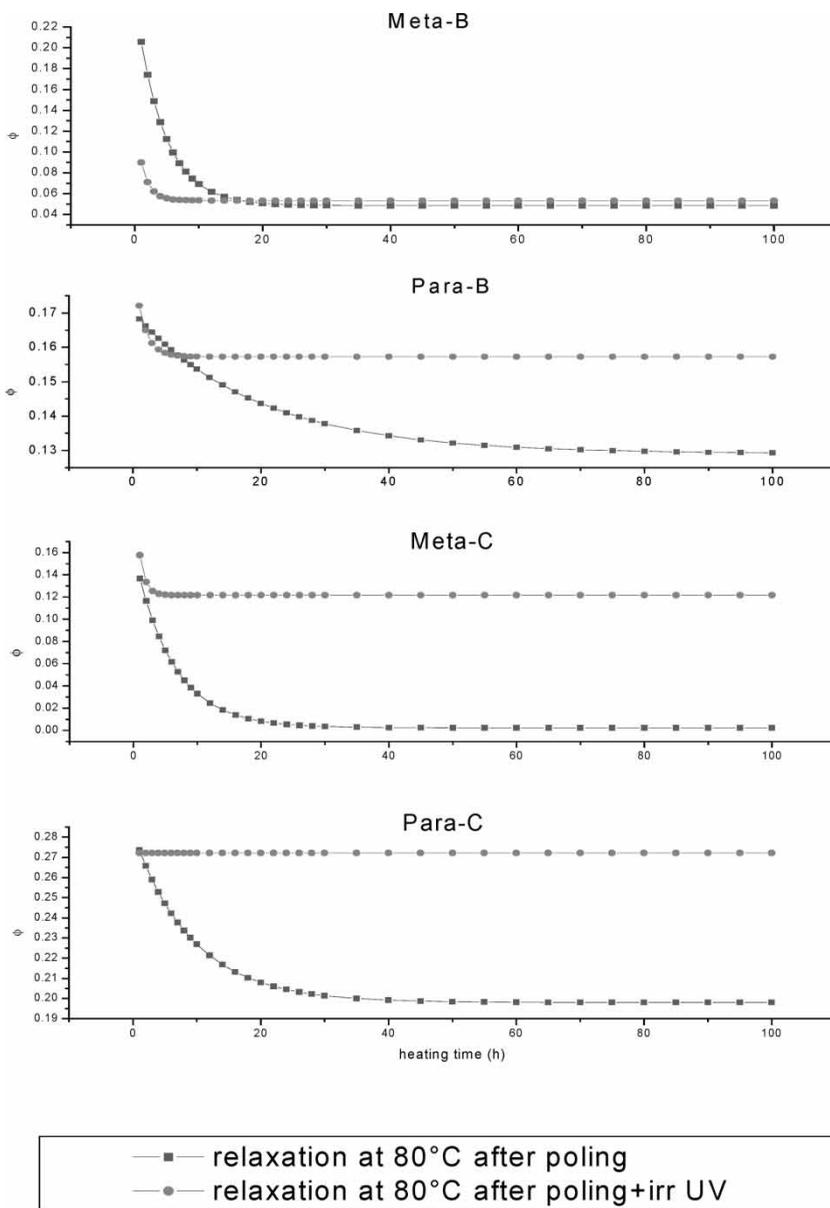
**Figure 5.** Effects of UV irradiation of the four polymers at 110°C.

Figure 5. The poled films were then irradiated but there was no decrease in the absorption, but on the contrary it increased on irradiation. The reason why the decrease in the absorption did not occur under the poling conditions, is intriguing, and the mechanism is not clear. The surface of the films is covered with positive charges, which might block the penetration of oxygen to the films. The increase in absorption on irradiation is thought to be due to the cross-linking, and the polymers are converted to rigid, insoluble and infusible thermoset resins. This causes disorder in the polymer chain conformation, resulting in relaxation of poled dye molecules. It can be seen that the *para* cinnamate polymer is the best among the four polymers, followed by the *para* benzoate polymer. The meta polymers were found to be the poorest, and this was expected from the main chain conformation. As can be seen from Figure 7, the crosslinked films of *para* polymers maintain the orientation of chromophores for many hours at 80°C. The two-dimensional drawings of the four polymers are shown in Scheme 3, which suggest that the *para* cinnamate may be the best candidate for 2-NLO polymer.



**Figure 6.** Effects of UV irradiation under the poling conditions.

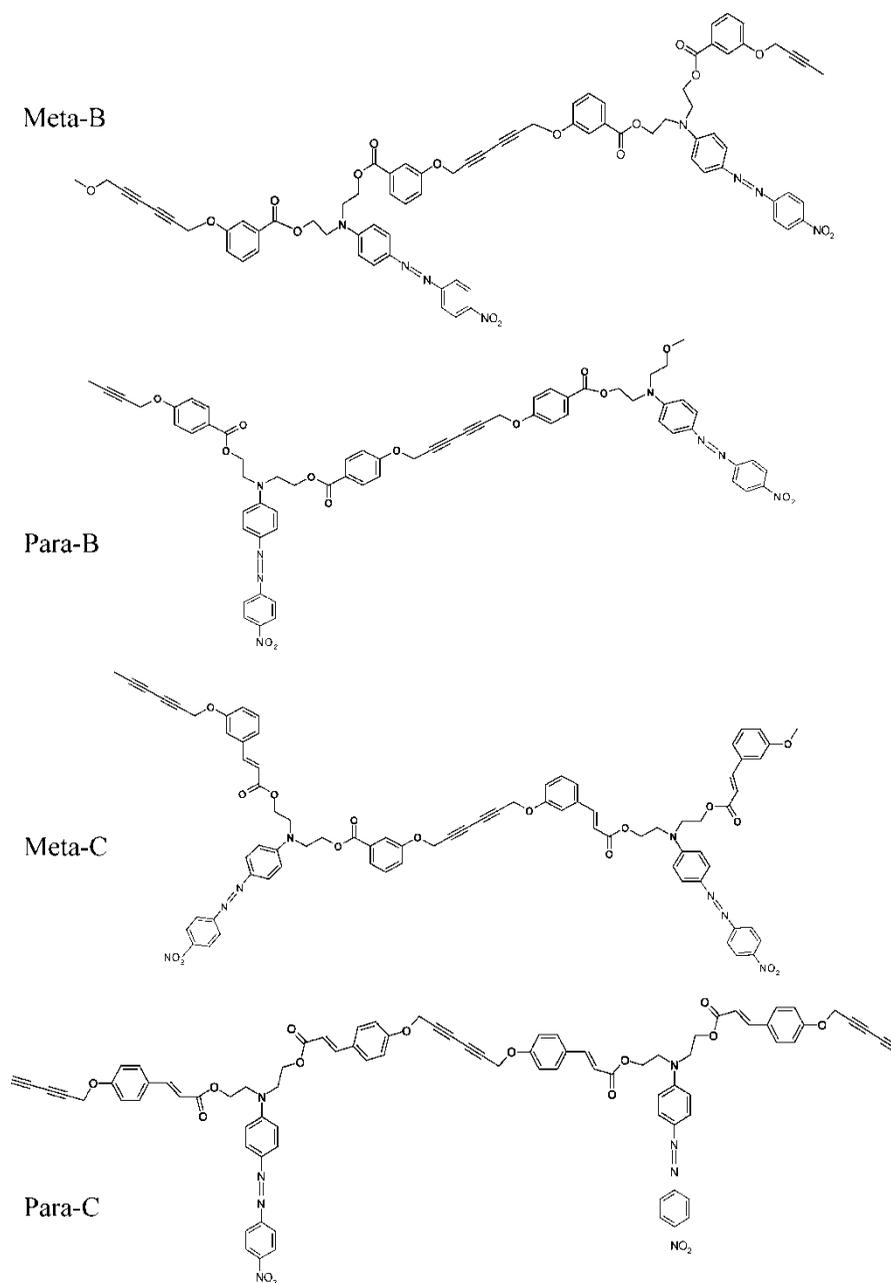
The four polymers studied in this work have high chromophore concentration (MW of dye/MW of monomer) 48.8% for the cinnamates and 53% for the benzoates. Compared with the commonly studied polymethacrylates, which are copolymers of methylmethacrylate and dye-containing methacrylates, the polymers of this work have a uniform composition, each monomer unit containing one dye. However, because of the high chromophore content, agglomeration of polymer chains can take place due to the dipole-dipole interaction of dyes. Therefore, the polymer solution in DMF is not stable, as the polymers precipitate on standing for a few days to weeks. This tendency is more enhanced for the *para* cinnamate polymer, and the *meta* polymers have less tendency of coagulation. The precipitated polymers can be dissolved again in hot N-methylpyrrolidone, as the coagulation is not due to cross-linking. If polymers have many dipole-dipole interactions, their poling efficiency is thought to decrease, and consequently their 2-NLO responses may not be as high as expected. It was found that the Langmuir-Blodgett membranes of these four polymers clearly showed the difference in morphology, as the *para* polymers demonstrated the self-assembly nature (16). If such self-assembly takes place for the spin-coated films, the decrease in absorption may not be used for the evaluation of poling efficiency.



**Figure 7.** Changes in order parameters at 80°C after poling and UV irradiation of the four polymers. Before 60 h: Experimental data; after 60 h calculated tendency.

## Conclusion

Although there exist some factors such as dipole-dipole interaction and possible self-assembly nature, to be included in consideration, it was shown that the main chain conformation is an important factor for 2-NLO polymers. The rather rigid main chains of the *para* benzoate and cinnamate are very much effective in maintaining the orientation, compared with the more flexible *meta* polymers, which have more freedom of main chain rotation. The high 2-NLO coefficients previously observed for the *para* polymers,



**Scheme 3.** Two dimensional drawings of the four polymers.

are in agreement with the orientation characteristics described in this work. The orientation stability is satisfactory for the *para* polymers, and it can be maintained permanently at room temperature. It was rather unexpected that photobleaching is avoided when irradiated under poling conditions, but this indicates that photo cross-linking can be applied simultaneously with poling to obtain highly stable 2-NLO polymers.

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## References

1. Miller, R.D., Burland, D.M., Jurich, M., Lee, V.Y., Lundquist, P.M., Moylan, C.R., Twieg, R.J., Thackara, J.I., Verbiest, T., Sakkat, Z., Wood, J., Aust, E.F., and Knoll, W. (1995) High-temperature Nonlinear Optical Chromophores and Polymers. In *Photonic and Optoelectronic Polymers*; ACS Symp. Ser. 672, Am. Chem. Soc., Washington, DC., 100–122.
2. Wenije, D.Y., Gharavi, L.A., and Yu, L.. Highly Stable Copolyimides for Second Order Nonlinear Optics. *ibid.*, 123–132.
3. Eich, M., Reck, B., Yoon, D.Y., Willson, C.G., and Bjorklund, G.C. (1989) Novel Second Order Nonlinear Optical Polymers Via Chemical Cross-Linking-Induced Vitrification Under Electric Field. *J. Appl. Phys.*, 58: 3241.
4. Jungbauer, D., Reck, B., Twieg, R., Yoon, D.Y., Willson, C.G., and Swalen, J.D. (1990) Highly Efficient Stable Nonlinear Optical Polymers Via Chemical Cross-Linking Under Electric Field. *Appl. Phys. Lett.*, 56: 2610.
5. Jungbauer, D., Teraoka, I., Yoon, D.Y., Reck, B., Swalen, D., and Twieg, R. (1991) Second Order Nonlinear Optical Properties And Relaxation Characteristics of Poled Linear Epoxy Polymers with Tolan Chromophores. *J. Appl. Phys.*, 69: 8011.
6. Mandel, B.K., Chem, Y.M., Lee, J., Kumar, J., and Tripathy, S. (1991) Cross-linked Stable Second Order Nonlinear Optical Polymer by Photochemical Reaction. *Appl. Phys. Lett.*, 58: 2459.
7. Hernandez, S., Beristain, M.F., and Ogawa, T. (2002) Diacetylene-containing Polymer XII. Synthesis and Characterization of Dye-Containing Poly(hexa-2,4-butadiynylenoxydibenzoates). *Designed Monomers and Polymers*, 5 (1): 125–138.
8. Miura, H. and Ogawa, T. (2002) Diacetylene-containing Polymers. XIII. Poly(hexa-2,4-diynylene-1,6-dioxydicinnamates) Containing an Azo Dye, *Disperse Red 19. Polym. Bull.*, 49: 103–110.
9. Hernandez, S., Ogawa, T., Watanabe, T., and Miyata, S. (2002) Novel Diacetylene- and Chromophore-Containing Polymers and their Second Order Nonlinear Optical Properties. *Mol. Cryst. Liq. Cryst.*, 374: 503–512.
10. Hernandez, S., Miura, H., Beristain, M.F., Ogawa, T., Watanabe, T., and Miyata, S. (2003) Novel Diacetylene-Containing Polymers for Second Order NLO Applications: Effects of Main Chains and Structure Property Relationship. *Macromol. Symp.*, 192: 123.
11. Kajzar, F., Chollet, P.A., Ledoux, I., Le Moigne, J., Lorin, A., and Gadret, G. (1991) Organic Thin Films For Quadratic Optics. In *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J., ed.; Kluwer Academic Publishers: Dordrecht, 403–432.
12. Ramirez, C., Beristain, M.F., and Ogawa, T. (2004) Diacetylene-containing Polymers XV. Synthesis and Characterization of Poly(dipropargyloxybenzoates) Containing *Disperse Red 1*. *Des. Monomers and Polymers*, 7: 85.
13. Batchelor, S.N., Carr, D., Coleman, C.E., Fairclough, L., and Jarvis, A. (2003) The Photofading Mechanism of Commercial Reactive Dyes on Cotton. *Dyes and Pigments*, 59: 269–275.
14. Yamaguchi, S and Sasaki, Y. (2001) Spectroscopic Determination of Very Low Quantum Yield of Singlet Oxygen Formation Photosensitized NY Industrial Dyes. *J. Photochem. Photobiol., A: Chemistry*, 142: 47–50.
15. Chen, M., Yu, L., Dalton, L.R., Shi, Y., and Steiner, W.H. (1991) New Polymers with Large and Stable Second-Order Nonlinear Optical Effects. *Macromolecules*, 24: 5421.
16. Carreon, M.P. and Ogawa, T. unpublished results.