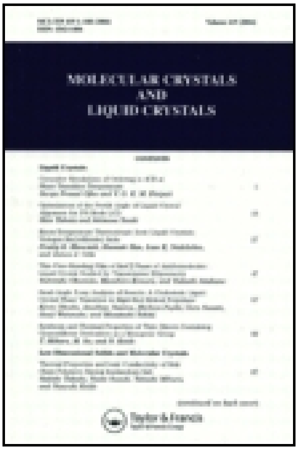


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Investigation of Poled Film of Styrene Copolymer With p-Dicyanovinyl Azo Dye Side Chain

Cheng Ye [a], Zhiming Feng [a], Jiafw Wang [a], Hui Shi [a] & Haiou Dong [a]

[a] Institute of chemistry, Academia Sinica, Beijing, 100080, China

Version of record first published: 04 Oct 2006.

To cite this article: Cheng Ye , Zhiming Feng , Jiafw Wang , Hui Shi & Haiou Dong (1992): Investigation of Poled Film of Styrene Copolymer With p-Dicyanovinyl Azo Dye Side Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 165-170

To link to this article: http://dx.doi.org/10.1080/10587259208047034

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 165–170
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

INVESTIGATION OF POLED FILM OF STYRENE COPOLYMER WITH *p* –DICYANOVINYL AZO DYE SIDE CHAIN

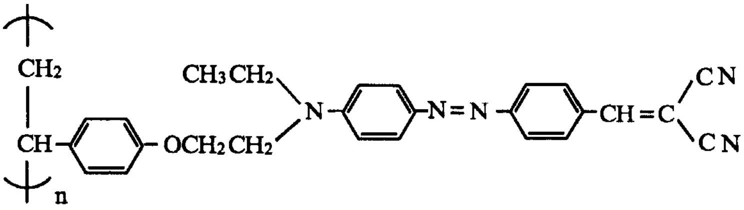
CHENG YE, ZHIMING FENG, JIAFU WANG, HUI SHI, HAIOU DONG
Institute of chemistry, Academia Sinica, Beijing 100080, China.

Abstract In this paper the poling properties of copolymer (PS)O-DCV film have been investigated by the absorption and IR spectra. The relations between corrected electrochromism and poling conditions were discussed. From IR spectra a useful information about chromophore orientation was obtained.

Nonlinear optical materials are currently of great scientific and technological interest. For second harmonic generation (SHG), a major challenge is to construct necessarily noncentrosymmetric molecular assembilies having high structural order and suitable processability. One of approches is to incorporate organic chromophore molecules possessing large second - order nonlinear optical susceptibilities into side chain of glassy polymer and poling with an electric field[1]. As known, SHG coefficient d_{33} of poled polymer films can be analyzed according to the theoretical expression for uniaxial materials [2] and the noninteracting oriented molecular gas model[3], it is linearily dependent on the chromophore number density (N), the molecular hyperpolaribility (β), dipole moment (μ) and the magnitude of the poling field (E_p), that is:

$$d_{33} \propto N \cdot \beta\mu \cdot E_p \qquad (1)$$

High chromophore number density will favor to increase d_{33} for functionalized polymer with same chromophore side chain and backbone. The copolymer of *p*-hydroxystyrene and *p*- [4-(2,2-dicyanovinyl)-4'-(N-ethyl-N-2-oxyethyl)azobenzene] styrene ((PS)O-DCV), with quite high N, had been prepared previously[4]. In this paper the poling properties of (PS)O-DCV film were investigated by spectroscopics, and the relations between N and poling conditions (temperature, time and voltage) were discussed.



EXPERIMENTAL

1. Thin film preparation

Films were made by spin-coating the solution of (PS)O-DCV in 1,2-dichloroethane onto transparent microscope slide or KBr crystal plate (for measuring polarized IR spectra). The film thickness was 1-3 μm measured by the interference microscopy. After the spinning, the samples were dried under vacuum at 60°C for at least 2 hours followed by elevated temperature (100°C) for more 6 hours to remove solvent completely.

As comparison, PMMA films doped with chromophore 4-(2,2-dicyanovinyl)-4'-(N-ethyl-N-2-oxyethyl)azobenzene (DCV) was prepared following same procedure, too. The dopant content in the films was 4 mol%.

2. Poling

Poling was carried out using a disk top electrode configuration described previously[5]. The substrate was placed film side up onto a ground plannar Al electrode. A Cu foil top electrode (Φ8mm disk) was placed 13 mm above the Al electrode. The temperature of the film could be raised by a heating plate positioned under the Al electrode and controlled with a thermocouple. A high dc voltage was applied and the poling current was monitored. Poled for a preset time the film was cooled to room temperature during 30 mins, then the voltage was removed.

RESULTS AND DISCUSSION

1. Absorption spectra

The absorption of the films were measured with JASCD UVIDEC-320 spectrometer. Fig. 1 is the typical absorption spectra of the unpoled and poled (PS)O-DCV film. The

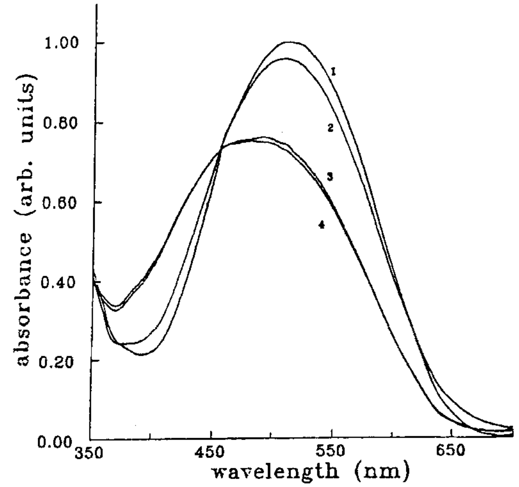


FIGURE 1 absorption spectra of poled (PS)O-DCV films
1. unpoled 2. heated only
3. poled 4. 3days after poling

poling were performed at 117°C (T_g is 106°C measured with DuPont Delta ser. DSC7 calorimeter), applied voltage was 10KV and time was 15.33 hours. There no chemical change under these poling conditions manifested by elemantal analysis and IR spectra. A decrease in absorbance was observed after poling. In contrast with common electrochromism[6], a hypsochromic shift was observed. The absorption peak was shifted from 510 nm to about 500 nm (dependent upon the efficiency of poling), and within other 3 days λ_{max} was continually shifted to about 490 nm with a slight decrease in absorbance (curve 4). Then above changes stopped and the spectroscopic absorption characteristics remained constent. Compared with the absorption of unpoled film (curve 1), the absorption band was broadened.

Recently, electrochromism had been used to monitor the induced alignment and its temporal decay in a poled film[7]. The observed decrease in absorbance can be used to described the order of the dipole alignment:

$$\Phi = 1 - A_{\perp} / A_0 \qquad (2)$$

However, our experiments indicated the observed decrease in absorbance were caused by the field and heating (the absorption of the films were decreased after heating without field at 117°C for 3 hours (curve 2 in Fig.1)). Therefore, a thermochromic correction must be introduced.

The dependence of the decrease in absorbance of poled (PS)O-DCV films upon the poling time, temperature and voltage had been investaged. The decrease in absorbance with thermochromic correction was linear with poling time. Since the thermodynamic equilibrium was not established even after more 15 hours poling in our experiments. Suitable poling temperature for (PS)O-DCV and DCV/PMMA were found to be 117°C and 87°C, respectively. At higher temperature (such as 147°C for (PS)O-DCV and 100°C for DCV/PMMA) the structural change of chromophore unit has been observed. The decrease in absorbance was proportional to the poling field as predicted from Eq.(1).

In addition, we had found that the poling current and the shift of absorption band may be used as probes for the poling level. However, there was much difficulty in quantitative analysis due to thermochromism.

Sohn et al[8] had found that the increase in N of the copolymer (DCV-MMA) with respect to the doped system (DCV/PMMA) is not translated into the second harmonic coefficient d_{33}. They considered this may be attributed to restricted motion and formation of centrosymmetric aggregates of the chromophore units. The N of our (PS)O-DCV sample ($14 \times 10^{20}/cm^3$) is near twice of DCV$\leftrightarrow$MMA ($8 \times 10^{20}/cm^3$), the motion of DCV will be more difficult and the possibility of aggregation will be higher. So, a higher poling temperature would be required, the poling efficiency would be reduced and the larger thermochromism would be produced.

2. IR and polarized IR spectra

Each vibrational mode of a molecule has a transition moment vector **M** associated with it. When IR radiation is plane-polarized such that the electric vector **E** is parallel to **M**, strong absorption occurs; if it is perpendicular, no absorption occurs. The absorption of each mode is proportional to the square of the scalar product of **E** and **M**. IR and polarized IR spectroscopy are the most powerful characterizing and reaserch means for orientation and has been widely used in oriented polymer system[9,10]. However, few paper on the investigation of poled polymer film by IR and/or polarized IR has been published so far. The IR and polarized IR spectra of (PS)O-DCV films have been measured with PE 983 spectrometer. The spectra of poled films were essentially the same as that of unpoled films, except of height of peaks. The absorption of 1507 cm^{-1} due to stretch vibration of phenyl ring was increased remarkably after poling. Its height was even higher than that of 1582 cm^{-1}, but the 1507 cm^{-1} absorption was weaker than that of 1582 cm^{-1} in the unpoled films. Moreover, the height of 1507 cm^{-1} peak was decreased with the film exposed in IR radiation for a long time due to the relaxation of orientation. So the peak of 1507 cm^{-1} can be used to monitor the poling efficiency and investigate the poling and relaxing processes.

The absorption of all other vibration modes of phenyl ring, 1597, 1582 and 852 cm^{-1}, were increased obviously. These results indicated the phenyl ring was aligned perpendicular to the substrate after poling. The vibration mode of ether bond of poled films at 1242 cm^{-1} was increased due to -C_6H_4-O align perpendicular to the substrate, too.

The dichroic ratio ($R=A_{\parallel}/A_{\perp}$) of unpoled films was 1.00 ± 0.02, here the error can be considered as the error of the measurements. However, R of most peaks in poled films were about 1.1, meaning that chromophore units had been oriented after poling. Therefore, IR and polarized IR spectra are the convenient and useful means for charactering of orientation of poled films. The detail will be published elsewhere.

CONCLUSIONS

The absorption spectra of poled (PS)O-DCV films had been investigated. Although the electrochromism can be used to monitor the poling, the thermochromism correction should be considered. It made the quantitative analysis further complication.

High chromophore number density will favor to increase the nonlinear optical susceptibility, but high possibility of aggregation, caused by strong polarity of DCV chromophore, requires longer poling time and higher poling temperature. To obtain the most effective poling, higher and more uniform poling field is necessary. The electrode configuration should be improved.

We had demonstrated that polarized IR spectra offer a simple and practical method to estimate the induce alignment of chromophore qualitatively. Due to thermochromism can be neglected for IR measurement, the result is straightforward.

ACKNOWLEDGMENTS This research was supported by The National Natural Science Foundation of China and The State Commission of Science and Technology of China.

REFERENCES

1. C.Ye, T. J. Marks, J. Yang and G. K. Wong, Macromolecules, 20, 2322 (1987).
2. K. D. Singer, M. G. Kurzk and J. E. Sohn, J. Opt. Soc. Am., B, 4, 968(1987).
3. J. Jerphagnon and S. K. Kurzk, J. Appl. Phys., 41, 1667 (1970).
4. C. Ye, H. Dong, Acta Polymerica Sinica (in Chenese), No. 3, 280 (1991).
5. C. Ye, H. Dong, J. Wang, Chinese J. poly. Sci., to be published (1991).
6. a) E. E. Havinga and P. Van Pelt, Ber. Bunsenges. Phys. Chem., 83, 816 (1979).
   b) E. E. Havinga and P. Van Pelt, Mol. Cryst. Liq. Cryst., 52, 145 (1979).
7. a) M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, A. Dienes, J. Opt. Soc. Am., B, 6, 733 (1989).
   b) R. H. Page, M. C. Jurich, B. Reck, A. Sen, R. J. Twieg, J. D. Swalen, G. C. Bjorkland, C. G. Willson, J. Opt. Soc. Am., B, 7, 1239 (1990).
8. J. E. Sohn, K. D. Singer, M. G. Kuzyk, W. R. Holland, H. E. Katz, C. W. Dirk, M. L. Schilling and R. B. Comizzoli, NATO ASI Ser. E, vol.162, 291 (1989).
9. R. S. Stein, Rubber Chem. & Tech., 49, 458 (1976).
10. J. L. Koening, S. W. Correll, D. E. Witennafeer, J. Polym. Sci., A-2, 5, 301 (1967).