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

Spontaneous Noncentrosymmetric Alignment of Carbazole Polymers

Su-An Choi [a b], Tatsuo Wada [a c], Yadong Zhang [c], Hiromi Kimura-suda [c], Jong-Duk Kim [b] & Hiroyuki Sasabe [c]

[a] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01, Japan

[b] Department of Chemical Engineering, KAIST, Taejon, 305-701, Korea

[c] Core Research for Evolutional Science and Technology (CREST), JST, Hirosawa 2-1, Wako, Saitama, 351-01, Japan

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 83–86
Reprints available directly from the publisher
Photocopying permitted by license only

Spontaneous Noncentrosymmetric Alignment of Carbazole Polymers

SU-AN CHOI,[a,b] TATSUO WADA,[a,c] YADONG ZHANG,[c] HIROMI KIMURA-SUDA,[c] JONG-DUK KIM[b] and HIROYUKI SASABE[a,c]

[a]Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-01, Japan
[b]Department of Chemical Engineering, KAIST, Taejon, 305-701, Korea
[c]Core Research for Evolutional Science and Technology (CREST), JST, Hirosawa 2-1, Wako, Saitama 351-01, Japan

Spontaneous noncentrosymetric in-plane alignment of carbazole polymers is demonstrated. The alignment was taken place during film preparation process, one is thermal treatment and the other is flow casting.

Keywords: second-harmonic generation; carbazole polymers; spontaneous polarization

INTRODUCTION

Second order nonlinear optical(NLO) organic materials are currently under intensive investigation for their potential application to optical modulator and frequency doubler[1]. Preparation of second-order NLO organic thin film is one of the most important issue for the applications of integrated nonlinear optical devices.

To make organic thin films show second order nonlinear optical property, the system should consist of chromophores oriented in such a way that the total system does not have center of symmetry because the second order susceptibility is a third rank tensor. Electric poling is generally used to

break the center of symmetry for polymeric systems[2]. In the poling process the organic thin film is fabricated and subjected to an intense external electric field, usually above its glass transition temperature(T_g). Alternative method is Langmuir-Blodgett(LB) technique[3]. In this method molecules with polar head groups and long aliphatic tails are transferred onto a substrate from the air-water interface. To get noncentrosymmetric film, the film deposition should be performed only on the immersion or withdrawal of the substrate which are referred to as X and Z-type LB films, respectively.

In this paper, spontaneous noncentrosymmetric alignment of carbazole polymers is described. The inversion symmetry was broken during film preparation processes. In-plane anisotropy and chromophore alignment were confirmed by second harmonic generation experiment.

EXPERIMENTAL

The carbazole polymers used in this study are presented in Fig. 1. The polymers have the same main chain containing carbazole moiety with the different groups in the side chains. The detailed synthesis scheme and material characterization were described in another paper[4].

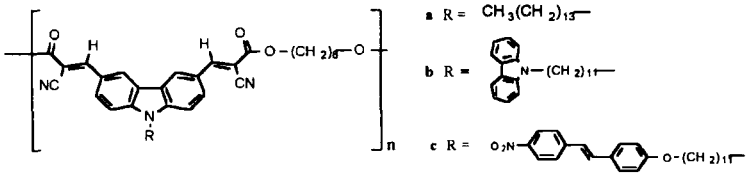

FIGURE 1 Carbazole polymers used in this study

The film preparation methods in this study were thermal treatment and flow casting. In the thermal treatment, proper amounts of the compounds were dissolved in chloroform and the solution was casted onto the slide glass.

The resulting casted film stayed overnight for solvent removal. Put the slide glass on the hot plate and raised the temperature from room temperature to 180 °C slowly. Finally, sandwiched the film between slide glasses by applying gentle pressure. After 1 hr, moved upper slide glass to one direction parallely to give shear to the film. In the flow casting, the slide glass was tilted and the solution was droped on upper part of slide glass, then flowing down to the below part.

The light source for the second-harmonic generation experiment was Q-switchd Nd:YAG laser.

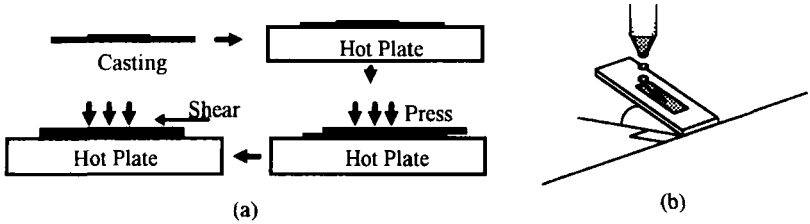

FIGURE 2 Schematic illustration of film preparation processes (a) thermal treatment (b) flow casting

RESULTS AND DISCUSSION

Fig. 2 shows schematic illustration of film preparation processes used in this study. During film preparation process, the orientation of the molecules were affected by the shear force given parallel to the substrate.

In the three kinds of carbazole polymer shown in Fig. 1, only polymer film (c) with an additional NLO chromophore in the side chain showed SHG activity prepared by above described methods. Fig. 3 shows the typical SHG signal of film made by the thermal treatment. It shows in-plane alignment of chromophore.

To study the thermal stability of the polar alignment, we measured SHG signal while warm up the film from the room themperature to a certain

temperature above T_g(°C). At the elevated temperathre, the relative SHG intensity, even above T_g, was about 70% of the pristine value. The film showed very stable alignment.

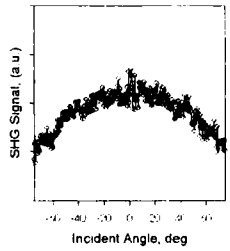

FIGURE 3 SHG signal from the polymer c (made by thermal treatment).

CONCLUSION

Spontaneous in-plane alignment of carbazole polymer was induced by thermal treatment and flow casting. The second harmonic generation studies indicated thermally stable polar alignment was achieved in the carbazole main-chain polymer with an additional NLO chromophore in the side chain.

Acknowledgments

This research was done at RIKEN and partly supported by Korea Science and Engineering Foundation.

References

[1.] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (Wiley, New York, 1991).
[2.] G. R. Meredith, J. G. Vandusen and D. J. Williams, *Macromolecules*. **15**, 1385 (1982).
[3.] I. R. Girling, P. V. Kolinsky, N. A. Cade, J. D. Earls and I. R. Peterson, *Opt. Commun.*, **55**, 289 (1985).
[4.] Y. Zhang, T. Wada, T. Aoyama, L. Wang and H. Sasabe, *Mol. Cryst. Liq. Cryst.*, **295**, 51 (1997).