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

Eletric-Field-Induced Orientation of Polar Organic Microcrystals with Different Crystal Sizes Dispersed in Liquid as a Novel Optical Devices

Satoru Okazoe [a], Satoshi Fujita [a], Hitoshi Kasai [a], Shuji Okada [a], Hidetoshi Oikawa [a] & Hachiro Nakanishi [a]

[a] Institute for Chemical Reaction Science, Tohoku University Katahira 2-1-1, Aoba-ku, Sendai, 980-8577, JAPAN

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 11-17
Reprints available directly from the publisher
Photocopying permitted by license only

Electric-Field-Induced Orientation of Polar Organic Microcrystals with Different Crystal Sizes Dispersed in Liquid as a Novel Optical Devices

SATORU OKAZOE, SATOSHI FUJITA, HITOSHI KASAI, SHUJI OKADA, HIDETOSHI OIKAWA and HACHIRO NAKANISHI

Institute for Chemical Reaction Science, Tohoku University Katahira 2-1-1, Aoba-ku, Sendai 980-8577, JAPAN

DAST microcrystals with different crystal sizes, 250 nm to 600 nm, were prepared successfully by adding a special polymer in the inverse reprepicitation method. The relative changes in absorbance between applied and unapplied electric field were found to be approximately proportional to the crystal sizes. The applied electric field was ca. 300 V/ cm and remarkably low, compared with ordinary liquid crystal systems. This result reflects that DAST microcrystal has huge dipole moment, which depended on crystal size, and the dispersion system is regarded as a new concept of "Liquid-and-Crystal".

Keywords: microcrystals; reprepicitation method; DAST; dipole moment; size dependence; liquid-and-crystal system

INTRODUCTION

Microcrystals may occupy an intermediate phase between bulk crystal and single molecule, and have been extensively investigated so far[1-7].

These researches are the important subjects from the view points of basis and applications in material science and technology. Thus, novel crystal structure, unconventional optical and electronic properties, improvement of catalysis and medical action etc. are of much interest. Instead of the preparation techniques such as vacuum deposition for inorganic microcrystals, we have recently established "reprepicitation method" for fabricating "organic microcrystals" such as perylene, polydiacetylene, and ionic organic chromophores, and have reported the size dependence of their optical properties[8-10]. The most striking characteristic of this fabrication method is that organic microcrystals prepared are stably dispersed in a liquid. If microcrystals have a dipole moment and could respond sensitively to an applied electric field, the dispersion system would be converted from optically isotropic and random state to anisotropic and oriented state, which may induce the changes of the transmittance and refractive index. Actually, we have confirmed that the absorbance of DAST (4'-dimethylamino-*N*-methylstilbazolium *p*-benzeneslfonate) microcrystals dispersion liquid could be changed by applying much low electric field below at 300 V/cm[11], and proposed a new concept of "liquid-and-crystal" system, not being liquid crystal. DAST bulk crystal is one of the most promising material for second order nonlinear optics. In the present article, we succeeded in controlling crystal sizes of DAST microcrystals for the first time, and will discuss the crystal size dependence of their response to an applied electric field.

EXPERIMENTAL

DAST used in the present study was synthesized by reference to the literature[12]. DAST microcrystal dispersion was prepared by the "inverse reprepicitation method" as described elsewhere[8-11]. A 100 μl of ethanol solution of DAST (5.0 mM) and DTMAC (n-dodecyltrimethylanmonium chloride) (5.0mM) was injected into vigorously stirred decalin (10ml) containing poly (ester acrylate) (Acryldic A1381, DIC, Inc.). The crystal sizes were controlled by the amount of added polymer : 0 wt% to 0.5 wt%. The crystal sizes and the shape were evaluated by DLS (Otsuka Electronics, DLS-7000) and

SEM (Hitachi, S-900). DAST microcrystals dispersion liquid was poured into the quarts cell equipped with the two ITO glass electrodes. The direction of applied electric field was fixed to be perpendicular to an incident light to measure visible absorption spectra at room temperature (Shimazu UV-240 spectrometer).

RESULTS AND DISCUSSION

Figure 1 shows the relationship between crystal sizes of DAST microcrystals and the amount of added polymer.

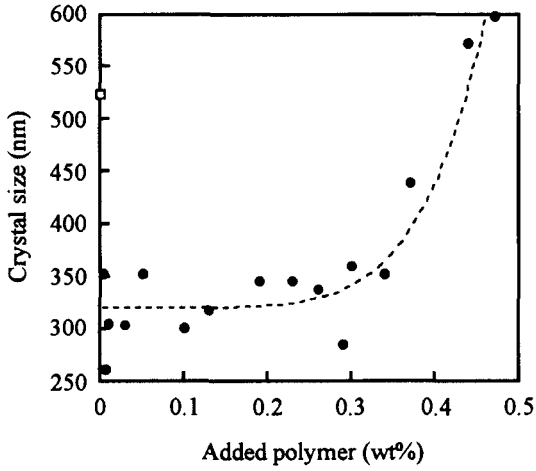

FIGURE 1. Relationship between crystal size and the amount of added Acryldic A1381polymer. The symbol □ indicates the crystal size of DAST microcrystal prepared without adding polymer.

In Figure 1, the crystal size was about 500 nm at 0 wt%, i. e. without adding polymer, and decreased drastically by adding the much small amount of polymer at below 0.3 wt%. But, the crystal size increased gradually at above 0.3 wt%. This may be attribute to partial adsorption of added polymer on the surface of DAST microcrystals.

Although the crystal size became smaller by adding the polymer, Figure 1 shows some scatter. So, some of the DAST microcrystals

with the suitable crystal sizes were actually chosen to perform the following electric-induced-orientation experiment.

Figure 2 shows the SEM photograph of DAST microcrystals. The crystal size was about 400 nm, which agreed with the result measured by DLS measurement.

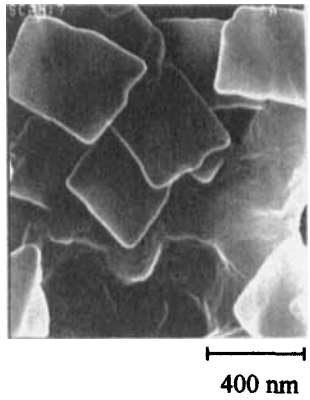

FIGURE 2. SEM photograph of DAST microcrystals, which was prepared at 6.0×10^{-3} wt% of the added polymer.

The shape seemed to be plate-like, which is similar to the shape of SHG active DAST bulk crystal. In fact, the DAST microcrystals were confirmed to be SHG active by the powder test[12].

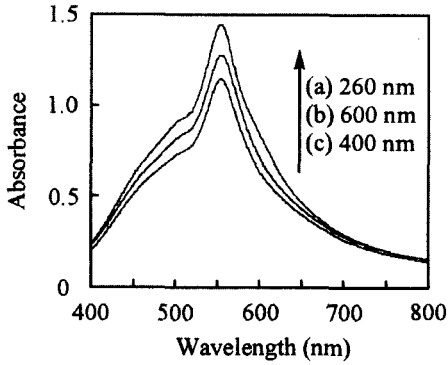

FIGURE 3. Visible absorption spectra of DAST microcrystals dispersion : (a) 260 nm ; (b) 600nm ; (c) 400 nm. The crystal sizes were controlled by the amount of added polymer.

Figure 3 shows the typical visible absorption spectra of DAST microcrystals dispersion liquid. The absorption maximum wavelength (λ_{max}) was around 550 nm, which was not influenced essentially by the crystal size.

The relative changes of absorbance at λ_{max} of DAST microcrystals dispersion under applied electric field (130 V / cm) was shown in Figure 4.

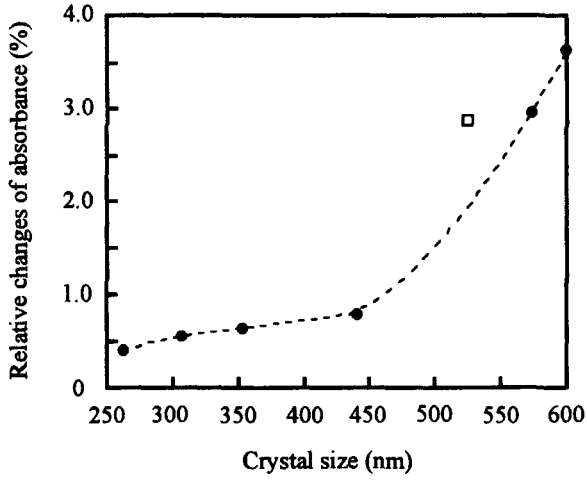

FIGURE 4. Relationship between crystal size and relative changes of absorbance. The symbol □ indicates the relation for DAST microcrystals prepared without adding polymer.

The relative changes of absorbance monotonously increased with the crystal size. This result implies that the magnitude of dipole moment of DAST microcrystals is roughly proportional to their crystal sizes, although the tendency for the increments turned significantly at around 450 nm in crystal size. This value can be regarded as a kind of threshold, depending on applied electric field. In fact, the increment in absorbance was slight at below 300 nm in crystal size at 130 V / cm of applied electric field, owing to thermal fluctuation and small dipole.

We found the interesting phenomenon in the time course of absorbance changes.

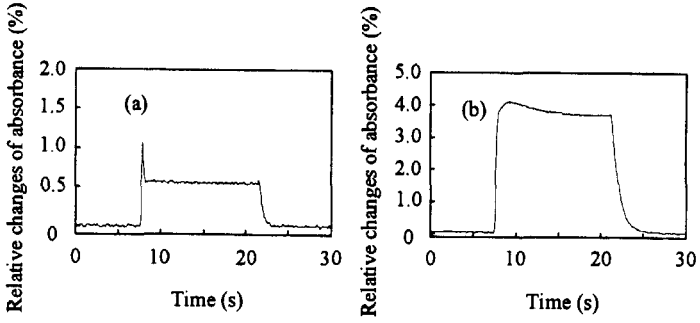

FIGURE 5. Time-course of relative changes in adsorbance. The crystal sizes were (a) 300 nm and (b) 600 nm. The applied electric field was 130 V / cm.

As shown in Figure 5, just after applying electric field (130 V / cm), the over-shoot phenomenon in absorbance changes was observed evidently at 300 nm in crystal size, while the absorbance change at 600 nm in crystal size was relaxed gradually to some extent with an elapsed time. Probably, not only crystal size and applied electric field but also visco-elastic effects from the surrounding polymers may be responsible for these results.

DAST microcrystals with large crystal size are easily oriented by applying much low electric field, owing to huge dipole moment, but the response rate and the dispersion stability are not so good. This tendency is in obviously conflict with each other. It is actually necessary to add a polymer in order to control the crystal size and to improve the stability of the microcrystal dispersions. we are new investigating the optimum crystal size as the "liquid-and-crystal" devices.

ACKNOWLEDGMENTS

The authors are grateful to Dainippon Ink and Chemicals, Inc. for providing us "Acryldic A1381" used in the present study.

References

[1] R. Kubo, *J. Phys. Soc. Jpn.,* **17**, 975 (1962).
[2] P. Buffat and J.P. Borel, *Phys. Rev. A.*, **13**, 2287 (1976).
[3] L.E. Brus, *J. Chem. Phys.*, **80**, 4403 (1984).
[4] S. Iijima and T. Ichihashi, *Jpn. J. Appl. Phys.*, **24**, L125 (1985).
[5] E. Hanamura, *Phys. Rev. B.*, **37**, 1273 (1988).
[6] W.M. Gelbart, A. Ben-Shaul, *J. Phys. Chem.*, **100,** 13169 (1996).
[7] G. Zhang and M. Liu, *J. Mater. Sci.*, **34**, 3213 (1999).
[8] H. Kasai, H.S. Nalwa, H. Oikawa, H. Matsuda, N. Minami, A. Kakuta, K. Ono. A. Mukoh and H. Nakanishi, *Jpn. J. Appl. Phys.,* **31**, L1132 (1992).
[9] H. Katagi, H. Kasai, S. Okada, H. Oikawa, K. Komatsu, H. Matsuda, Z. Liu and H. Nakanishi, *Jpn. J. appl. Phys.*, **35**, L1364 (1996).
[10] H. Oikawa, H. Kasai, H. Kamatani, H.S. Nalwa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh and H. nakanishi, Chem. Func. Dyes, **2**, 755 (1993).
[11] S. Fujita, H. Kasai, S. Okada, H. Oikawa, T. Fukuda, H. Matsuda, Sukant K. Tripathy and H Nakanishi, *Jpn. J. Appl. Phys.*, **38**, L659 (1999).
[12] H. Nakanishi, H. Matsuda, S. Okada and M. Kato, *MRS Int. Mtg. Adv. Mater.,* **1**, 97 (1989).