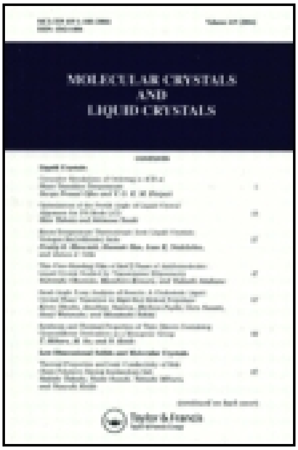


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Investigation of Technology and Property of NLO Crystals and Nanocomposites Based on Dast (4-Dimethylamino-N-Methyl-Stilbazolium Tosylate)

J. A. Burunkova [a] & I. Yu. Denisuk [a]

[a] State University of Information Technologies, Mechanics, and Optics, Saint-Petersburg, Russia

To cite this article: J. A. Burunkova & I. Yu. Denisuk (2008): Investigation of Technology and Property of NLO Crystals and Nanocomposites Based on Dast (4-Dimethylamino-N-Methyl-Stilbazolium Tosylate), Molecular Crystals and Liquid Crystals, 496:1, 322-331

To link to this article: http://dx.doi.org/10.1080/15421400802451931

Mol. Cryst. Liq. Cryst., Vol. 496, pp. 322–331, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802451931

Investigation of Technology and Property of NLO Crystals and Nanocomposites Based on Dast (4-Dimethylamino-*N*-Methyl-Stilbazolium Tosylate)

J. A. Burunkova and I. Yu. Denisuk
State University of Information Technologies, Mechanics, and Optics,
Saint-Petersburg, Russia

We study the technology and property of NLO materials based on DAST (4-dimethylamino-N-methyl-stilbazolium tosylate): namely, a monocrystal, nanocrystals, and polymeric nanocomposites. These materials are very promising because their high nonlinear coefficients higher than that of traditional LiNbO3. We have considered the methods of preparation and the modifications of DAST nanocrystals under the synthesis conditions in solutions. The modifications of DAST crystals are determined by the type of solvents, precipitation conditions, and the used surfactant. The obtained nanocrystals are mixed with polymers, and homogeneous transparent films are fabricated.

Keywords: nanocomposite; nanocrystal; NLO materials

INTRODUCTION

At the present time, nanostructured materials present a new promising way to obtain new homogenous materials with unique mechanical [1], electrical [2], optical [3] and thermal [4–5] properties combined of those of a polymer matrix and crystals such that it is impossible to obtain them by any other manner.

A lot of literature on inorganic particles embedded into a polymeric matrix exist. However, a little is known about polymer-nanoparticle systems based on organic nanoparticles and especially about molecular nanocrystals manifesting nonlinear properties in polymers. The investigation of the method of synthesis of molecular nanocrystals,

Address correspondence to J. A. Burunkova, State University of Information Technologies, Mechanics, and Optics 49, Kronverskii Str, Saint-Petersburg 197101, Russia. E-mail: burunj@list.ru

the preparation of a nanocomposite by mixing it with a polymer, and the formation of its anisotropy is the aim of this work.

We used two techniques for the preparation of nanocrystals and nanocomposites: the liquid precipitation technique based on the precipitation of a solution of nonlinear molecules by a precipitator in the presence of a surfactant and the method based on the impregnation of a surface active polymer matrix by a hot solution of nonlinear molecules. The current work is a sequel of our previous work in this field [6,7].

MATERIALS AND CONDITIONS OF EXPERIMENTS

As initial materials for the preparation of molecular nanocrystals, we took nonlinear molecular crystals 4-dimethylamino-*N*-methyl-stilbazolium tosylate (DAST). To realize the impregnation process, we used a polymerized acrylic UV curable monomer having acid groups.

The second harmonic generation was used as a control express method of NLO properties. For the measurement of SHG, we used a Nd-YAG laser (a pulse power of 10 mJ, 7 ns) and a microscope with a CCD camera for registering the SH generation. SHG can be observed only on thin films (2–5 μm), because this wavelength ($\lambda = 532$ nm) lies in the absorption band of DAST. If we would take films with thicknesses more than 10 μm, we will observe only the radiation in the DAST luminescence band. But this information is enough for a qualitative assessment of nonlinear properties of compositions.

For the measurement of absorption spectra, we used a UV-Vis spectrophotometer Perkin–Elmer, model 555. The photoluminescence measurements were performed on a laboratory setup based on a LED laser source for the photoluminescence activation and a Vis-IR sensor with a monochromator to measure the luminescence.

EXPERIMENTAL SECTION AND DISCUSSION

DAST crystals demonstrate a large nonlinear susceptibility (by 20 times better than that of $LiNbO_3$ and by 150–1000 times better than that of KH_2PO_2 crystals). There are several DAST forms. Only the red-form shows nonlinear properties. Its maximum absorption is observed at $\lambda = 550$ nm [8], whereas the molecular absorption is maximum at $\lambda = 480$ nm [9].

We applied the methods of fabrication of nanocrystals based on the precipitation from a solution with surfactant. A most part of nonlinear molecular crystals have high dipole moments, so they can be dissolved in plenty of polar solvents including water. As we investigated, the solvate environment influence the formation of DAST nanocrystals. That is, the type of DAST crystallization is determined by solvents (isopropanol, ethanol), precipitants (decaline, dodecane), and the surfactant (dodecylamine).

Preparation of nanocrystals was made as follows: a DAST solution was poured out in precipitators (dodecane, decaline). The surfactant was added to the solution at different stages. After the precipitation, a transparent solution without light scattering was formed in all cases. Then the color of the solution changed with the course of time, which proves the formation of DAST nanoparticles at the precipitation.

We obtain colloidal nanoparticles by the precipitation of a 0.1 ml DAST/acetone solution in 10 ml dodecane without surfactant (way 1). The absorption spectrum of these particles was similar to that of molecular absorption (Fig. 1, curve 1). But it changed during 2 h, and a feebly visible maximum at 520 nm had appeared. This can be explained by the formation of DAST quasicrystals.

Preparation of DAST nanocrystals by the precipitation by decaline (way 2). The process was made similar to that described above (way 1), but we now used a 0.1 ml saturated DAST/isopropanol solution in 10 ml of decaline. The spectra of the precipitate are shown in Figure 2.

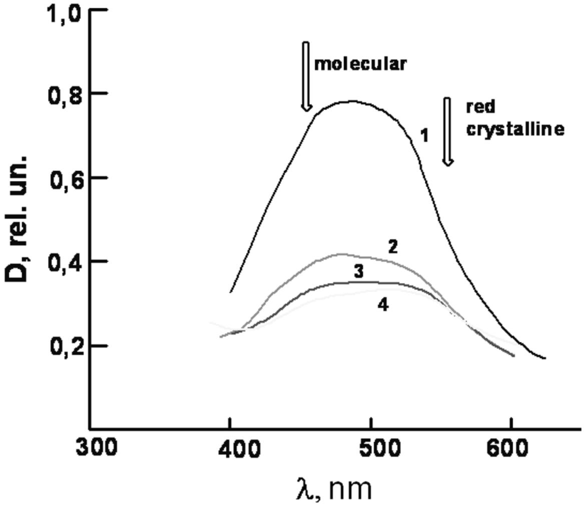
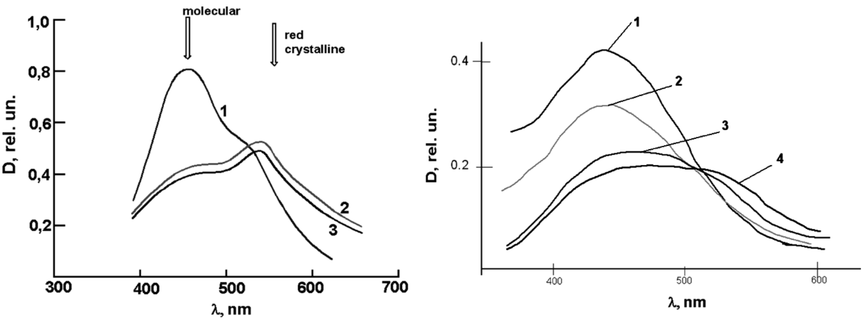


FIGURE 1 Absorption spectrum of a colloid (the precipitation of DAST by dodecane): (1) after the precipitation (molecular absorption with the maximum at $\lambda = 480$ nm), (2) after 10 min, (3) after 60 min, (4) after 120 min (maximum absorption at 520–530 nm).



(a) (b)

FIGURE 2 Absorption spectrum of a colloid: (a) precipitation of DAST/isopropanol in decaline (1) at once after the precipitation, (2) 10 min, (3) 20 min min later; (b) precipitation of DAST/isopropanol/water in decaline (1) 2 min, (2) 50 min, (3) 1 h 20 min, (4) 2 h 30 min later.

With the use of decaline, DAST nanoparticles are formed at once as in the previous case. After that, they transit into the crystalline state. The absorption spectrum of the formed modification of DAST corresponds to that of its "red" crystalline form. The obtained nanocrystals precipitate rather rapidly, which can be explained by its growth with the formation of micro-sized particles. To decelerate the process of growth, we use dodecilamine as a surfactant.

If we add the surfactant to a DAST solution in alcohol, a molecular solution of DAST is formed at the precipitation (way 3). As DAST is insoluble in decaline, we think that, in this case, a complex of DAST with dodecilamine is formed, which allows agglomerates to precipitate.

(Way 4) The precipitation in decaline in the presence of the surfactant added to decaline (Fig. 3); 0.01 ml of dodecylamine/isopropanol was added to decaline (the molar ratio DAST:dodecilamine = 1:1). In this case, the colloid was stable, but it was intermediate between the molecular and "red" crystalline forms and is not changed during the storage for two days.

There occurs the stabilization of a colloid by joining the surfactant, which results in the stabilization of its crystalline state as well.

(Way 5) Precipitation in decaline, when the surfactant is added to the colloid immediately after the precipitation. The synthesis process is accomplished like that in way 4, but the surfactant was added at once after the precipitation (the molar ratio of DAST:dodecilamine = 1:1). In this case, the colloid was stable and transparent and changed rapidly from the molecular to the "red" crystalline form (Fig. 4). The

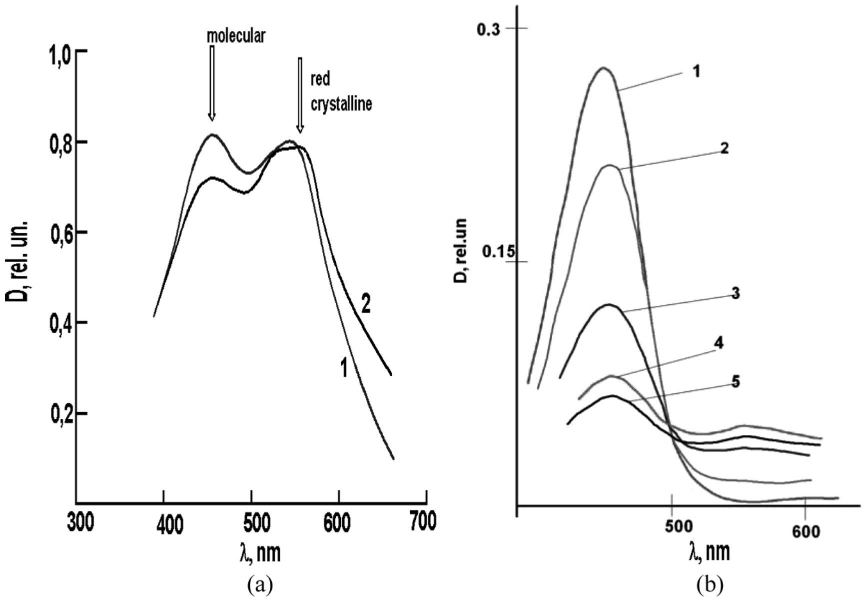


FIGURE 3 Absorption spectrum of a colloid: (a) precipitation of DAST/isopropanol in decaline + dodecilamine (1) at once after the precipitation, (2) 8–20 min later; (b) precipitation of DAST/isopropanol/water in decaline + dodecilamine (1) 1 min, (2) 20 min, (3) 32 min, (4) 1 h 10 min, (5) 2 h 15 min later.

transformation of the colloid took place almost completely according to the absorption spectra.

After the precipitation, we observed the molecular absorption maximum at $\lambda = 480\,\text{nm}$ and almost no crystalline maximum (Fig. 4, curve 1). During the storage, the colloid is transformed essentially from the molecular to the red crystalline aggregation. This nanocrystalline colloidal solution was stable during 24 h with no turbidity. After 2 days, nanocrystals are settling-out. They can be dispersed repeatedly in decaline or in UV-curable non-polar monomers with same absorption spectra.

We have study the influence of water on the formation of DAST nanoparticles during the precipitation (Figs. 2a, 2b, 3a, 3b). In decaline, DAST molecular forms were stabilized by water from the isopropanol solution. At first, the precipitation from DAST molecular forms was observed. The maximum absorption band ($\lambda = 460\,\text{nm}$) was decreased. After some time interval, crystalline DAST states began to form ($\lambda = 550\,\text{nm}$).

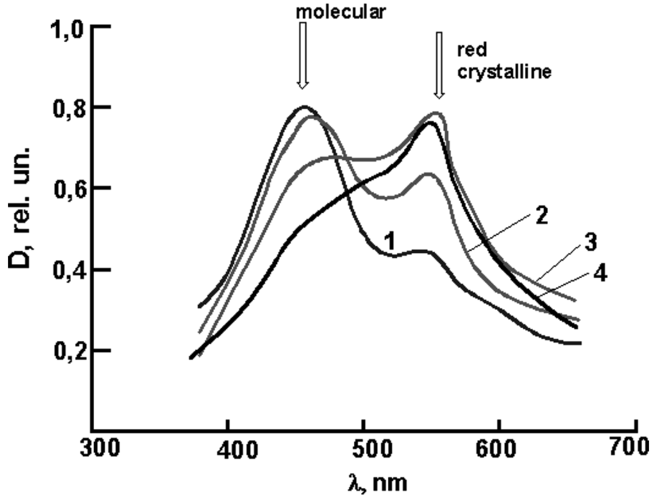


FIGURE 4 Absorption spectrum of a colloid (precipitation of DAST in decaline); dodecilamine was added after the precipitation immediately. Time after the precipitation: 1–10 sec; 2–2 min; 3–30 min; 4–60 min.

To obtain a solid nanocomposite film, the sediment of DAST nanocrystals was dispersed in a mixture of non-polar acrylic monomers and then polymerized by UV light in the region of 360–380 nm. Thus, a solid nanocomposite was obtained. The intense SH generation proves strong nonlinear properties of such a nanocomposite.

It is worth noting that the developed method of preparation of DAST nanocrystals in decaline by the precipitation is difficult, and the reaction yield of this process is small. Moreover, large amounts of a precipitator are needed for the precipitation.

In order to overcome these obstacles, we have investigated another method based on a specific intermolecular interaction between DAST and polymer molecules in a supersaturated methanol solution. This method is a variant of a large group of methods based on the impregnation of a polymeric matrix by a dye hot solution.

The method allows the formation and stabilization of a NLO nanocomposite in the UV-cured matrix. We observe that DAST molecules diffuse into the surface-active gel matrix in a supersaturated solution at $T = 45\text{–}50^{\circ}\mathrm{C}$. The fixation of DAST molecules in the polymeric matrix takes place due to both the specific interaction of DAST with acid groups of a polymer and the formation of nanocrystals during the evaporation of a solvent (methanol) from a limited volume.

The highest reached concentration of DAST nanocrystals was 30 wt %. The concentration was determined by measuring the extinction coefficient of a thin film with DAST nanocrystals.

The photo of a nanocomposition film on the glass substrate is shown in Figure 5. The photoluminescence spectra of such a nanomaterial essentially is shifted to the red region relatively to both the molecular spectrum and the spectrum of the red crystalline form.

We have detected a spontaneous anisotropy of nanocomposition films. This phenomenon is observed under stretching the polymeric matrix (up to the break point), which is accompanied by the orientation of DAST nanocrystals in the matrix.

The method of orientation in an electric field, which is well known for chromophores, is not efficient because of a larger mass of nanocrystals in comparison with that of chromophores. At the same time, this method is suitable for melted polymers only. On the contrary, our polymer matrix is cross-linked and cannot be melted.

In view of the above-presented results, we performed the first experiments on the creation of anisotropic nanocompositions. We investigated a method of orientation based on the process of impregnation with the use of a uniaxially stretched polymeric film.

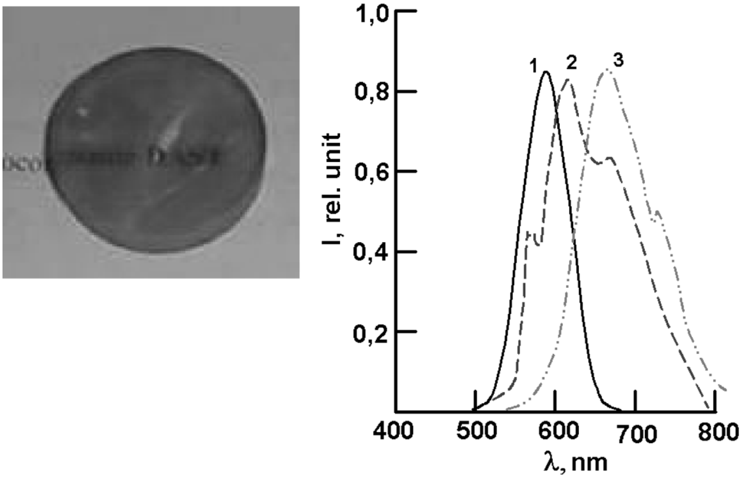


FIGURE 5 Photo of a nanocomposition film on the glass substrate and the photoluminescence spectra (1) molecular form of DAST (literature data), (2)-photoluminescence spectrum of a DAST monocrystal in the "red" form, (3)-nanocomposite.

FIGURE 6 Second harmonic generation in an anisotropic film (1 × 1 mm).

The observed spontaneous anisotropy is probably caused by a tension of the polymeric matrix. Therefore, we applied the method of preliminary uniaxial deformation of the matrix and the subsequent growth of nanocrystals to create the anisotropy of a film. The obtained film of a nanocomposite looked like a red isotropic film with birefringence on its turn at crossed polarizers. We observed the generation of the second harmonic of small separate regions of an anisotropic film of 5 μm in thickness (Fig. 6). A possible explanation of the anisotropy formation effect can be as follows. On a uniaxial stretching of the polymeric structure, polymeric chains are elongated in a single direction as well. Under the impregnation, the nanocrystals with large dipole moment are positioned along polymer chains. After drying, the previously dissolved nanocrystals become oriented according to the stretching direction of the polymeric matrix.

Hence, the creation of anisotropic nanocomposites can be realized with the use of a previously treated polymeric matrix, in which nanocrystals are formed during the impregnation process. Now the uniformity of oriented films is not so good, but we have made only the first stage of the work.

While investigating the impregnation process, we find the effect of growing of a thin crystalline film of DAST under the same conditions as in the preparation of nanocrystals (in a polymeric nanocomposition). If the impregnation proceeds a longer time, a polymer film cannot form a gel because it is cross-linked. On the surface of a polymer, thin red monocrystals with a size of about 2 × 2 × 0.01 mm are formed. The detailed description of the method is given in [10]. The photo of such a crystal and its photoluminescence spectrum are shown in Figure 7.

Its photoluminescence spectrum shows that we have obtained a thin crystalline film with properties similar to those of a well-known bulk DAST crystal, but with small thickness.

We made a light modulator based on thin DAST crystals [11]. Because of a high value of the electro-optical coefficient, this modulator works at a very low electric field strength. The modulation depth of about 50% was obtained at 0.7 V/μm only! For the distance between electrodes of about 2 μm, it is possible to construct a low-voltage electro-optic modulator with a 1.5-V driving voltage only. Planar DAST have the high NLO and EO coefficients. Its figure of merit is 400–700 pm/V.

The same crystals are used as a terahertz emitter and show a strong efficiency (1 μW of THz emission at a 50-mW IR laser pumping).

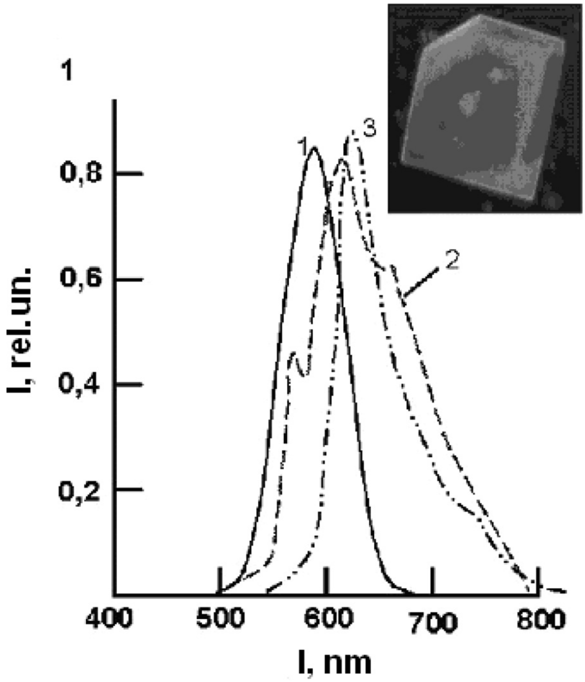


FIGURE 7 View of a DAST thin crystalline film and its photoluminescence spectrum (3). For comparison, the spectra of a crystal in the molecular state (1) and a "red" bulk crystal (2) are given.

CONCLUSIONS

We have developed a method of synthesis of NLO DAST nanocrystals by their precipitation. The crystalline state of DAST nanoparticles depend essentially on the nature of the solvate environment. Under some conditions, it is possible to induce a fast transition of nanoparticles from one to another state. We have found the conditions needed to get the "red" crystalline form of DAST nanocrystals which is stable and suitable for the mixing with a UV-curable monomer blend with the formation of a homogenous transparent nanocomposite. It is possible to prepare a high-concentration polymeric nanocomposite (30 vol %) with NLO properties. The materials are transparent and suitable for optical applications. The method is based on the process of impregnation. The methods of NLO nanocomposite orientation based on a preliminary orientation of the polymeric matrix and the subsequent impregnation are investigated.

DAST nanocrystalline thin films present a new well processable material allowing the second-harmonic generation. Thin crystalline films of DAST grown in the surface active polymer are used as a material for low-voltage light modulators. The same crystals are used as a terahertz emitter and show a high efficiency (1 μW of THz emission at a 50-mW IR laser pumping).

REFERENCES

[1] Krishnamoorti, R. & Vaia, R. A. (2002). *Polymer Nanocomposites*, ACS: Washington, DC, 804.

[2] Chapman, R. & Mulvaney, P. (2001). *Chem. Phys. Lett.*, *62*, 349.

[3] Wilson, O., Wilson, G. J., & Mulvaney, P. (2002). *Adv. Mater*, *14*, 1000.

[4] Yoon, P. J., Fornes, T. D., & Paul, D. R. (2002). *Polymer*, *3*, 6727.

[5] Decker, C. & Zahouily, K. (2002). *Radiation Phys. and Chem.*, *63*, 3.

[6] Denisyuk, I. Yu. & Burunkova, J. E. (2007). *Mol. Cryst. Liq. Cryst.*, *467*, 213.

[7] Denisyuk, I. Yu. & Burunkova, J. E. (2007). *Ukr. J. Phys.*, *52*, 407.

[8] (a) Luckham, P. F. & Rossi, S. (1999). *Adv. Coll. Interface Sci.*, *82*, 43. (b) Bhowmik, A. K., Xu, J., & Thakur, M. (1999). *Appl. Phys. Lett.*, *75*, 3291.

[9] Follonier, S., Fierz, M., Biaggio, I., & Meier, U. (2002). *J. Opt. Soc. Am. B*, *19*, 1990.

[10] Denisyuk, I. Yu., Burunkova, J. E., & Smirnova, T. V. (2007). *J. of Optical Techn.*, *74*, 63.

[11] Denisyuk, I. Yu., Burunkova, J. E., & Verzin, I. A. presented at Kharkiv Nanotechnology Assembly-2007, Ukraine, Kharkiv, April 23–27, 2007.