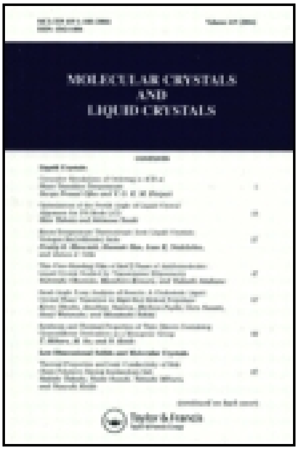

Molecular Crystals and Liquid Crystals

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

Molecular Organic Crystals Dast and Pom in the Form of a Thin Crystalline Film and a Nanocrystal-The New Promising Medium for NLO Application

Igor Yu. Denisyuk [a] & Julia E. Burunkova [a]

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

Version of record first published: 22 Sep 2010

To cite this article: Igor Yu. Denisyuk & Julia E. Burunkova (2007): Molecular Organic Crystals Dast and Pom in the Form of a Thin Crystalline Film and a Nanocrystal-The New Promising Medium for NLO Application, Molecular Crystals and Liquid Crystals, 467:1, 213-226

To link to this article: http://dx.doi.org/10.1080/15421400701223993

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 213–226, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701223993

Molecular Organic Crystals Dast and Pom in the Form of a Thin Crystalline Film and a Nanocrystal–The New Promising Medium for NLO Application

Igor Yu. Denisyuk
Julia E. Burunkova
Saint-Petersburg State University of Information Technologies, Mechanics, and Optics; Saint-Petersburg, Russia

We investigate the process of synthesis of the "red" crystalline form of DAST nanocrystals both by the precipitation and impregnation methods. We developed the impregnation method of the preparation of DAST nanocrystals in a UV-cured matrix based on the specific intermolecular interaction between DAST and polymer molecules in a supersaturated methanol solution. The method allows one to produce a highly concentrated (up to 30%) nanocrystal-filled transparent composition. The nanocomposite is suitable to produce photonics structures by the soft lithography method. The formation of an anisotropic nanocomposite by use of the oriented polymeric matrix is investigated. The second-harmonic generation in very thin (about 1 micron) layers confirms the high nonlinear susceptibility of this material.

Keywords: electro-optics; molecular crystal; nanocrystals; non-linear optics

INTRODUCTION

The new promising materials based on well-known organic and inorganic substances in the nanocrystalline state introduced into a polymeric matrix now widely investigated. Polymer–nanoparticle

---

The work was made under the support of RFBR Project # 05-02-08048 "Investigation of electro-optic nanostructures with high hyperpolarizability based on the dense packing of nanocrystals in a polymer matrix for the use in microwave optoelectronic elements"; RFBR Project # 06-02-27233, and Project of Russian Federal Agency of Education # 1.3.06 "Investigation of the process of formation of non-linear properties under the transformation from the molecular to nanocrystalline state of organic crystals".

Address correspondence to Igor Yu. Denisyuk, St. Petersburg State University of Information Technologies, Mechanics, and Optics, 14 Sablinskaya Str., Saint-Petersburg, 197101, Russia. E-mail: denisiuk@mail.ifmo.ru

composite materials derived from several components have attracted the interest of number researchers due to their synergistic and hybrid properties. Being in a solution or bulk, these materials offer unique mechanical [1], electrical [2], optical [3], and thermal properties [4] that are induced by the physical presence of nanoparticles, the interaction of the polymer with nanoparticles, and the state of dispersion [5–7].

As compared to traditional additives, one advantage of nanoparticles, as polymer additives, consists in that the loading requirements are quite low. Microsized particles used as reinforcing agents scatter light, thus reducing light transmittance and optical clarity. The efficient nanoparticle dispersion combined with the good polymer–particle interfacial adhesion eliminates scattering and allows the exciting possibility to develop strong, but transparent films and coatings. Shear-induced structural changes in the fluids containing anisotropic species are often encountered in polymer solutions in liquid crystalline materials, block copolymer melts, and particle solutions. A large body of literature exists on the behavior of inorganic particle slurries and solutions, as well as polymer solutions. However, a little is known about polymer–nanoparticle systems based on organic nanoparticles and especially on molecular nanocrystals in polymers. The investigation of a method of synthesis of molecular nanocrystals and especially molecular nanocrystals with strong nonlinear proprieties was the aim of this work.

THE SOURCE OF NONLINEARITY IN MOLECULAR CRYSTALS

An applied electric field perturbs the electron distribution of a material affecting the transit of light through the material. The result is an electric-field-dependent change in the index of refraction of the material and a phase shift of light. For a significant perturbation of light (e.g., a phase shift by a half-wavelength) to be realized with the application of small applied voltages, the electrons of a material must be weakly confined by nuclei (i.e., the electrons must be highly polarizable). For organic materials, electrons are much less tightly bound by nuclei than *U*-electrons, as is easily understood from considering their relative position with respect to nuclei. Thus, more than 2 decades ago, electron organic materials were identified as promising candidates for nonlinear optical applications. The requirement of the presence of easily polarizable electrons in a material will result in large dipole moments of molecules. Under the crystallization of organic molecules with large dipole moments, they tend to arrange

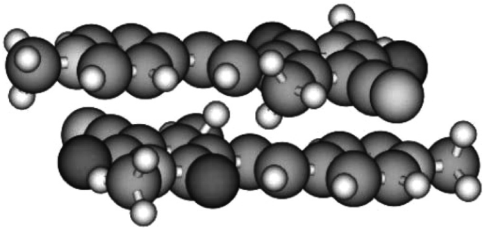

FIGURE 1 Formation of a pair on the aggregation of Disperse Red dye at high concentrations.

into the pairs as “head to tail”. The resulting dipole moment of these pairs will be close to zero as long as the dipole moments of initial molecules will compensate one another. All the well-known chromophores tend to form aggregates from the pairs at high concentrations, and the aggregate hyperpolarizability goes to zero. The formation of aggregates begins at a concentration of 20–25 vol.%. For example, in Figure 1, we show the arrangement of well-known Disperse Red dye into pairs at its high concentration in a polymer.

According to this consider mostly part of chromophores in nanocrystalline state have no practical use, because they lose hyperpolarizability as result on formation of nanocrystals. For the preparation of nanocrystals with nonzero second-order hyperpolarizability, one needs to overcome the dipole–dipole interaction by any larger forces, usually by the forces of chemical bonding. In molecular crystals with nonzero hyperpolarizability, two requirements are satisfied: (1) they are made of highly polarizable molecules, the so-called conjugated molecules, where highly delocalized p-electrons can easily move between electron donor and electron acceptor groups on the opposite sides of a molecule, inducing the molecular charge transfer, (2) molecules are adequately packed to build up a noncentrosymmetric crystal structure that provides the nonvanishing second-order nonlinear coefficients [8,9].

There is a small group of substances satisfying these requirements (below, the molecular crystal abbreviation and the nature of forces overcoming the dipole–dipole interaction are indicated):

–POM (3-Methyl-4-Nitropyridine N-oxide), chiral molecules

–NPP, the hydrogen bonding between certain parts of molecules resulting in the rotation of molecules in one direction [10]

–merocyanine dye contains a co-crystallizer that forms hydrogen bonds with a dye molecule, and they rotate in one direction (Fig. 2) [11].

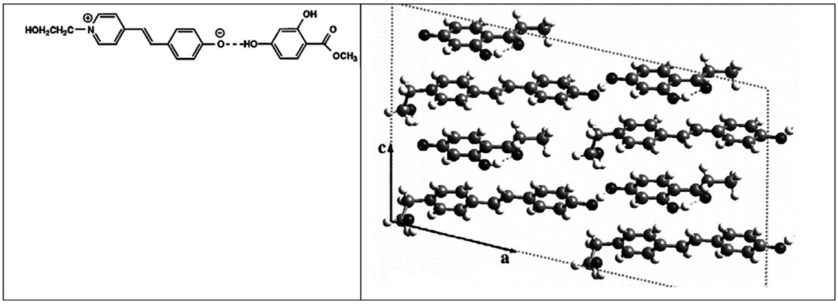

FIGURE 2 Hydrogen bonding between a molecule of merocyanine dye and a co-crystallizer (a-left), the crystalline lattice of the molecular crystal with a co-crystallizer (b-right).

–for the last decade, new efficient methods are developed and applied to some molecular crystals, DAST being most well-known of them. These substances are organic anion dyes having anion and cation parts. The ionic forces between these parts are mostly powerful and overcome the dipole–dipole interaction easily [12,13].

With regard for the aim of this work – the preparation of NLO nanocrystals – we note that the large surface of a nanomaterial will result in a decrease of the crystalline order and requires to use more powerful forces making the noncentrosymmetric crystalline lattice, as compared with a large bulk crystal. So, we use DAST molecular crystals in our experiments as a material having the largest crystal-forming forces.

MATERIALS AND EXPERIMENT

There are different organic substances that can form molecular crystals. Its common feature is a poor or slow crystallization. So, the preparation of nanocrystals by the simple precipitation method similarly to the methods used for inorganic nanocrystals is difficult, and the result is not evident. However, there is a group of organic substances (phthalocyanines) having very low solubility in most solvents, which allows one to use the precipitation method used for the preparation of well-known inorganic nanocrystals. In the first part of this work, we investigate the main processes of the formation of molecular nanocrystals with the use of phthalocyanine as a model system. Next, by a similar technique, we will synthesize some nonlinear organic molecular nanocrystals (DAST, POM). We propose and check experimentally a new promising method of the preparation of NLO molecular nanocrystals in a polymeric matrix based on the specific interaction between polymeric molecules and molecular crystals in a supersaturated solution. This method is similar to the impregnation method.

As initial materials for the preparation of molecular nanocrystals, we used materials from Aldrich of about 99% purity. Phthalocyanine – Mg phthalocyanine (Aldrich number #402737), abbreviation Mg-Pc; nonlinear molecular crystals 4-dimethylamino-*N*-methyl-stilbazolium tosylate (DAST), (Aldrich number #514160), 3-Methyl-4-Nitropyridine N-oxide (POM), (Aldrich number #370061). To realize the impregnation process, we used a mixture of polymerized acrylic UV curable monomers having acid groups in one component. As solvents, we used isopropyl alcohol, toluene, acetone, diethylamine with a purity of 99%, and distillated water.

For the measurement of absorption spectra, we used an UV-VIS spectrophotometer Perkin – Elmer, model 555 UV-Vis (198–900 nm). For the measurement of the second-harmonic generation, we applied a Nd-YAG laser with pulses of 10 mJ in power and 7 ns in duration and a microscope with CCD camera to register the SH generation.

A MODEL PHTHALOCYANINE SYSTEM

The preparation of nanocrystals was made similarly to the synthesis of Mg-Pc nanocrystals described in our works [14–16].

The Mg-Pc–polycarbonate nanocomposite was prepared by the following method: A saturated molecular solution of Mg-Pc in diethylamine + 10% alcohol as crystallization agent was precipitated by water that does not dissolve Mg-Pc. Thus, we formed a colloidal solution of Mg-Pc nanocrystals having an X form of aggregation, which was evidenced by a long-wavelength band with maximum around 840 nm that appeared in the absorption spectrum. When a solution of polycarbonate in chloroform was poured into this solution, molecules of the polymer were adsorbed on dye nanocrystals, by stabilizing them. When an appreciable quantity of water was added to the solution, the nanocomposite precipitated. It was then separated and dried.

The comparison of the absorption spectra of synthesized nanocrystals with the spectra of the well-known bulk crystals [17] in the same crystalline form has shown their identity (Fig. 3).

So, we can suppose that the crystalline structure of Mg-Pc nanocrystals is similar to that of bulk crystals, and their proprieties are similar too.

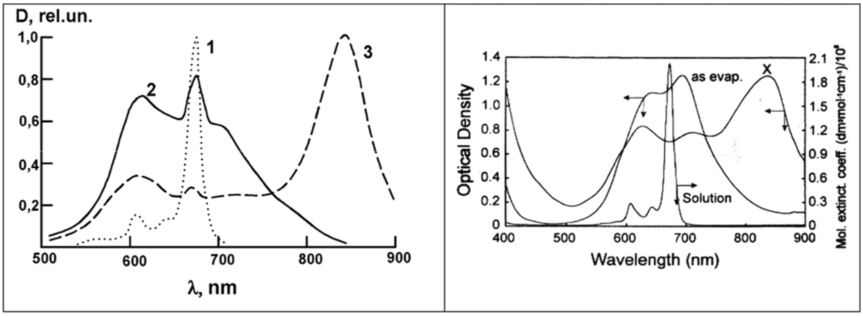

FIGURE 3 Comparison of the spectra of nanocrystals (left) and bulk crystals (right). 1 – molecular form, 2 – beta-form, 3 – X-form.

We measured the sizes of Mg-Pc nanocrystals by a modified dynamic light scattering method. The changes of the sizes of nanoparticles after the precipitation are shown in Table 1 [18].

The sizes of Mg-Pc nanoparticles are fixed, depend on the crystalline form, and do not depend on the time passed after the precipitation, which is not usual for nanocrystals. The comparison of the sizes of nanoparticles with the literature data on the crystalline cell size of Mg-Pc according to work [17] allows us to suppose that Mg-Pc nanocrystals compose one cell of the crystalline lattice (Fig. 4). The identity of the absorption spectra of nano- and bulk crystals with so different sizes can be explained by a small intermolecular interaction in organic substances in comparison with that in inorganic ones. As a result, the interaction between two planes of the crystalline lattice is enough strong to obtain the lattice of a bulk crystal, i.e., the interaction at distances further than the nearest molecular layer in a crystal is small.

We investigated the transformation of Mg-Pc nanoparticles for some time interval after the precipitation [16]. If we do not add the crystallization agent – alcohol, Mg Pc nanocrystals in the beta form will be firstly formed. If alcohol is added later on, the crystalline beta form will turn to the X-form during some time. Figure 5 show a change

TABLE 1 The Sizes of Nanoparticles for Different Crystalline Forms After the Precipitation

No.	Crystalline form	Solvent	Size (nm)
1	β-form after precipitation	water	1.93–2.1
2	X-form after precipitation	toluene	2.41
3	X-form in 24 hours after precipitation	toluene	2.51

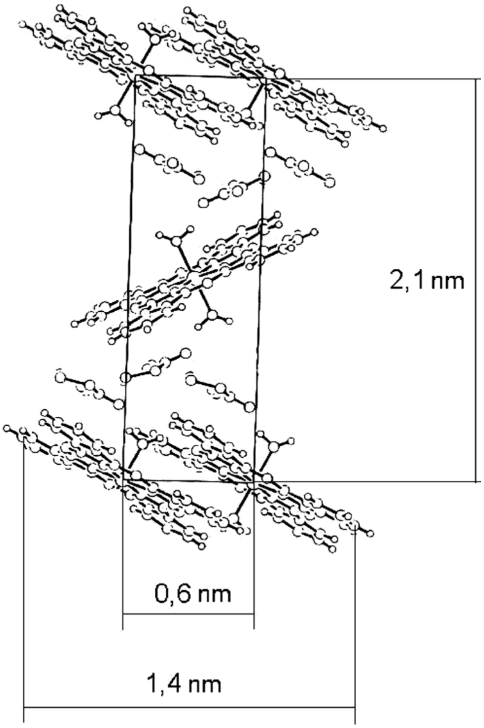

FIGURE 4 Cell of the crystalline lattice of Mg-phthalocyanine bulk crystals.

of the absorption spectra of a colloidal solution of nanoparticles in one day after the precipitation. We see a fast change of the spectrum which is impossible in a bulk crystal. As a result, the usual X-crystalline modification is formed after about 2 days. At a heating up to 150 C, the inverse process of transformation from the X to beta form of Mg-Pc occurs.

The preparation of a nanocomposite from nanoparticles and the polymeric matrix can be made by common precipitation according to the method described in our work [19] and by mixing the colloidal solution of nanoparticles with surface active polymer and then making a layer by the spin coating technique. If we need to obtain a polymer-free layer from nanoparticles, we can apply the electrostatic deposition method [20]. The deposition of nanoparticles from a colloidal solution was carried out in a laboratory device containing a cell, in which a colloidal solution of Mg-Pc nanoparticles in toluene was placed. The electrodes were two glass plates with a conductive ITO coating. A dc supply voltage was applied to the electrodes. Since the small Mg-Pc

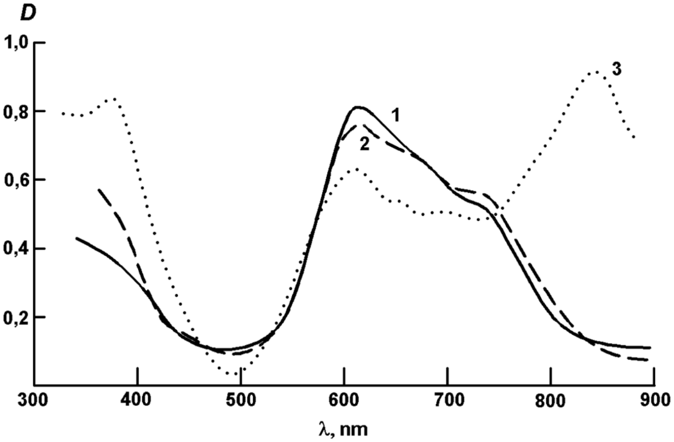

FIGURE 5 Transformation of the absorption spectra of Mg-Pc nanocrystals after the precipitation. Time after the precipitation: 1–10 min, 2–4 hours, 3–1 day.

nanoparticles diffuse as they undergo Brownian motion, the volume of the colloidal solution included between the electrodes is constantly replenished by nanoparticles from the surrounding volume of the flask, and the entire volume of the colloid is used to create the layer. The gap between the electrodes was determined by Teflon spacers and was varied from 3 to 5 mm. The deposition of a Mg-Pc layer from nanoparticles takes place during ten minutes with the formation of a transparent homogenous layer consisting of many nanoparticles sticked together.

Thus, molecular crystals in the nanocrystalline state have crystalline lattice and properties of similar to those of bulk crystals. The size effects, at least for Mg-Pc, are almost absent. Unlike the bulk crystals, the phase transformation in nanocrystals is possible at room temperature and runs fast. There are few methods of the introduction of nanocrystals into a polymeric matrix and the deposition of transparent polymer-like films from them. In this case, it is possible to deposit a film from nanoparticles without polymer.

NONLINEAR MOLECULAR CRYSTALS IN THE NANOCRYSTALLINE STATE

By using the technique considered above for the model phthalocyanine system, we made the experiments on the preparation of nonlinear molecular nanocrystals, DAST. DAST has important difference from phthalocyanine dye. First, DAST is aromatic anionic dye with large dipole moment. Therefore, it can be dissolved in most of solvents: e.g., water, toluene, and alcohol. We were faced with large difficulties to apply the precipitation method, since there are almost no liquids that cannot dissolve it. Because of a large dipole moment, DAST is hygroscopic, so all reactives should be water-free. The complicated molecule of DAST exists in many different crystalline forms, but only the "red" form has high NLO proprieties.

For the precipitation method, we choose isopropyl alcohol as a solvent and decaline as a non-solvent. DAST was dissolved in water-free isopropyl alcohol (10% solution in 1 ml). As a surfactant carboxylic amine was used in the same solution, and then the solution was poured out in 100 ml of decaline. At once after the precipitation, a red colloidal solution was formed. The spectrum is shown in Figure 6. For comparison, in the same figure, the spectrum of the "red" crystalline form of a bulk DAST crystal is shown according to [21].

The results show that molecular DAST is formed first on the precipitation. The spectrum, curve 1, is equivalent to the well-known spectrum of a DAST molecular solution. Then, during one hour, the transformation of the molecular form of nanoparticles to the "red" crystalline form occurs: curves 2–4. Depending on the non-solvent used in the precipitation, this transformation takes part differently. At the use of decaline, the transformation takes part completely and faster (1). At the use of dodecane, the transformation is not complete (2). This effect is similar to the transformation of Mg-Pc nanoparticles from the beta to X-form described above and is possible for the nanosized state only.

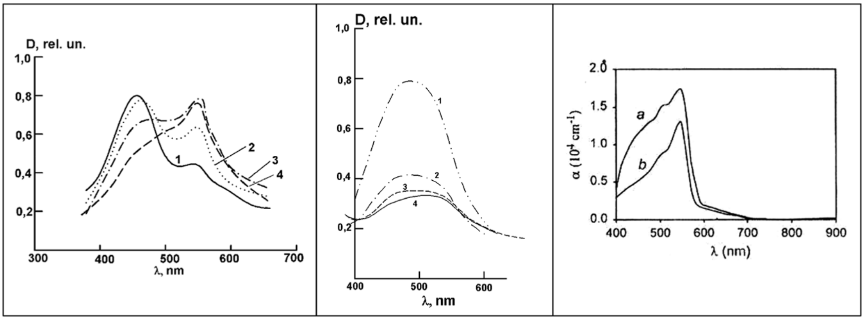

FIGURE 6 Spectra of DAST nanoparticles. The precipitation by using the different non-solvents: 1 – decaline, 2 – dodecane, 3 – absorption spectrum of a bulk crystal (for comparison). Curves 1–0 min, 2–2 min, 3–30 min, 4–60 min.

Similar experiments were made with POM at the use decaline as a non-solvent. The colloidal dispersion of nanoparticles was obtained, but the absence of noticeable extrema do not allow identifying it with bulk crystalline forms. At the same time, the bulk crystalline forms of POM are less known in comparison with those of DAST. The sediments of the "red" crystalline form of DAST and POM were tested for the SH generation by the "powder test" under irradiation by a Nd-YAG laser. The green light emission prove the second-harmonic generation from these materials.

As a result, we can conclude that it is possible to synthesize some molecular crystals in the nano-sized state. The needed crystalline modification can be obtained with the use of a suitable crystallization agent. The main defect of the precipitation method is a small reaction yield of the process and large expenses of a non-solvent.

HIGH-CONCENTRATION DAST NANOCOMPOSITE MADE BY THE IMPREGNATION METHOD

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

The method is as follows: as an initial substance, we used a supersaturated solution of DAST in methanol prepared by dissolution at 50 C and cooling up to 45 C. The polymer plate prepared by UV-polymerization of the mixture contains one component with acid group heated up to 45 C. We place it into a beaker with a hot solution of DAST. The cross-linked composition of the polymer matrix allows one to form gel in hot methanol, but it cannot be dissolved in it. After the treatment of the polymer in the solution during 2–5 hours, the red polymer plate was taken away and dried at once. At drying, methanol goes away and keeps the solid polymeric matrix colored by nanocrystals. In Figure 6, we show the view of a DAST nanocomposite and the luminescent spectra of nanocrystals and the well-known molecular and "red" crystalline forms (for comparison).

There are two questions:

1. What form of DAST was obtained?
2. What concentration of DAST nanocrystals is in the polymer?

A high DAST concentration in the polymer matrix after the impregnation makes difficulties for the measurement of absorption spectra

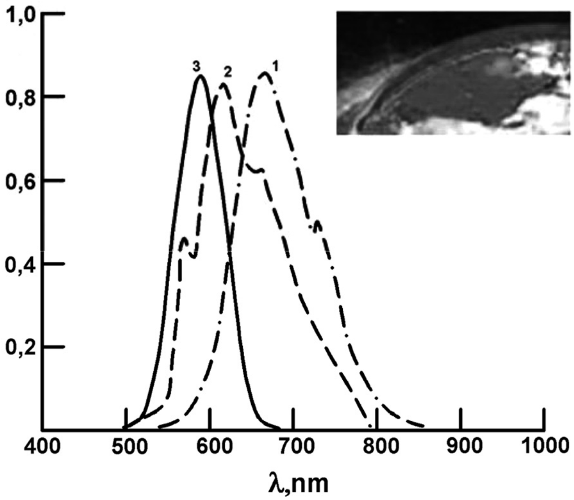

FIGURE 7 Photoluminescence spectrum of nanocomposite (1); for comparison (2) - DAST bulk crystal in the "red" form; (3) molecular form. The photo of the DAST nanocomposite (above).

because of a too high optical density. For this reason, we measured the photoluminescence of the obtained material. The comparison of the photoluminescence spectra of nanocrystals with the well-known spectra of molecular and various crystalline forms prove that we obtained a crystalline form with a large red shift in comparison with the spectrum of the molecular form (Fig. 7). The volumetric concentration of DAST nanocrystals in the polymeric matrix was determined by light extinction in a thin polymer film with nanocrystals and its comparison with the well-known light extinction in a bulk crystal. The calculations give a value of 20–30 vol.%.

Another important process is the orientation of nanocrystals in one direction, which is important for electro-optic applications.

Contrary to chromophores, the orientation of nanocrystals was not investigated. The method of orientation in an electric field, which is well-known for chromophores, is not effective 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 to be melted. We investigated a method of orientation based on accomplishing the impregnation process with the use of (1) a one-directional mechanical stretch of the polymeric film; (2) a polymeric cylinder polymerized in one direction. The photos of nanocomposites prepared in a polymer

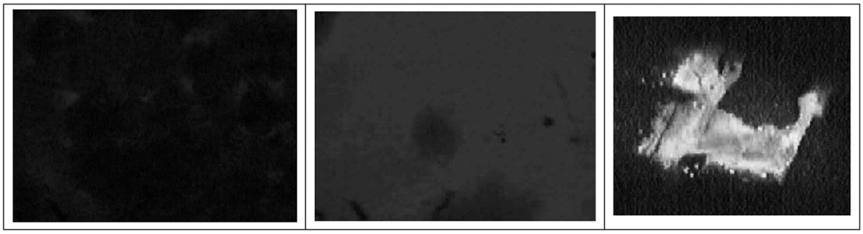

FIGURE 8 Photos of nanocomposites prepared in a polymer film stretched previously and the second-harmonic generation from it (left – without polarizer; middle – with cross polarizer; right – the SH generation from a film).

film stretched previously and the second-harmonic generation from the film are shown in Figure 8. In Figure 9, we present the same results obtained with the use of a polymeric cylinder obtained by the one-directional polymerization in the active glass substrate for the impregnation.

A possible explanation of the anisotropy formation effect can be as follows: On a one-directional distortion of the polymeric structure, a polymeric chain will stretch in one direction as well. Under the impregnation, the nanocrystals having large dipole moment will be directed by polymer chains. After drying, the previously dissolved nanocrystals become oriented according to the direction of the polymeric matrix.

The creation of anisotropic nanocomposites can be realized at least in two ways. Both methods are used a previously treated polymeric matrix, in which a nanocomposite is formed during the impregnation process. Now the uniformity of the oriented field is not good, but we have made only the first stage of the work.

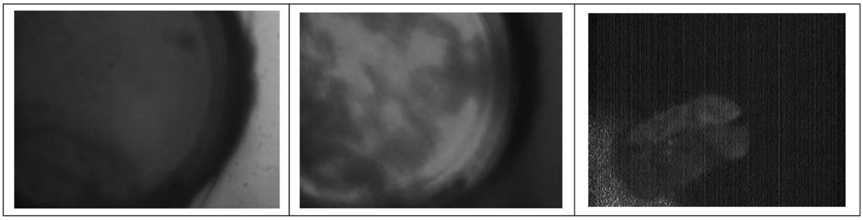

FIGURE 9 Photos of nanocomposites prepared in a polymeric cylinder polymerized in one direction previously and the second-harmonic generation from it (left – without polarizer; middle-with cross polarizer; right – the SH generation from the cylinder).

CONCLUSIONS

1. Nanocomposites on the basis of molecular nanocrystals in a polymeric matrix are new promising optical materials having plasticity similar to that of a polymer and physical properties similar to those of bulk crystals.
2. It is possible to prepare high-concentration nanocomposite with NLO properties. Moreover, materials keep transparency and are suitable for optical applications. The developed method of preparation of nanocomposites is based on the impregnation process. The method allows one to obtain a highly concentrated (30 vol%), oriented NLO nanocomposite material.
3. Two methods of orientation of nanocomposite are investigated. They are based on a preliminary orientation of the polymeric matrix in any manner and next on the execution of the impregnation process with the use of this oriented matrix.
4. The molecular crystal DAST in the form of a nanocrystalline film is a new good processable material with high second-harmonic generation.

REFERENCES

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

[2] Chapman, R. & Mulvaney, P. (2001). *Chem. Phys. Lett*, *62*, 349–358.

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

[4] Yoon, P. J., Fornes, T. D., & Paul, D. R. (2002). *Polymer*, *43*, 6727.

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

[6] Lu, Changli, Cui, Zhanchen, Li, Zuo, Yang, Bai, & Shen, Jiacong. (2003). *J. Mater. Chem.*, *13*, 526.

[7] Luckham, P. F. & Rossi, S. (1999). *Adv. Coll. Interface Sci*, *82*, 43.

[8] Chemla, D. S. & Zyss, J. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: New York.

[9] Follonier, S., Bosshard, Ch., Meier, U., Knopfle, G., Serbutoviez, C., Pan, F., & Gunter, P. (1997). *J. Opt. Soc. Am. B*, *14*, 3.

[10] Bosshard, Ch., Sutter, K., Pretre, Ph., Hulliger, J., Florsheimer, M., Kaatz, P., & Gunter, P. (1995). *Organic Nonlinear Optical Materials*, Gordon and Breach: Basel.

[11] Wong, Man Shing, Pan, Feng, Bosch, Martin, Spreiter, Rolf, Bosshard, Christian, & Gunter, Peter. (1998). *J. Opt. Soc. Am. B*, *15*, 426.

[12] Aakero, C. B., Hitchcock, P. B., Moyle, B. D., & Seddon, K. R. (1989). *J. Chem. Soc., Chem. Commun.*, 1856.

[13] Aakero, C. B., Hitchcock, P. B., & Seddon, K. R. (1992). *J. Chem. Soc., Chem. Commun.*, 553.

[14] Akimov, I. A., Denisyuk, I. Yu., & Meshkov, A. M. (1994). *Opt. Spektrosk.*, *77*, 954.

[15] Akimov, I. A., Denisyuk, I. Yu., Meshkov, A. M., & Gorelova, A. V. (2003). *Journal of Optical Technology*, *70*(2), 67.

[16] Denisyuk, I. Yu. & Kamanina, N. V. (2004). *Opt. Spektrosk.*, *96*, 269.

[17] Endo, A., Matsumoto, S., & Mizuguchi, J. (1999). *J. Phys. Chem. A*, *103*, 8193.

[18] Butyanov, S. V., Burunkova, Yu. E., Denisyuk, & I. Yu. (2005). *Scientific Technical Bulletin of St.Petersburg State University of Information Technologies, Mechanics and Optics*, *22*, 188, Saint Petersburg.

[19] Denisyuk, I. Yu. & Meshkov, A. M. (2001). *J. Opt. Technol*, *68*(11), 841.

[20] Denisyuk, I. Yu. & Kamanina, N. V. (2004). *J. Opt. Technol.*, *71*, 3.

[21] Bhowmik, Achintya K., Xu, Jianjun, & Thakur, Mrinal. (1999). *Appl. Phys. Lett.*, *75*(21), 3291.