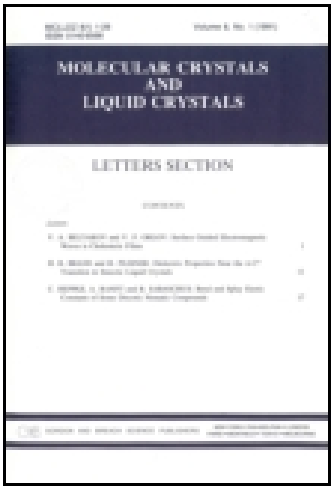

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Polymer Composite Based on DAST Submicron Crystals: Technology and Properties

J. A. Burunkova [a], I. Yu. Denisyuk [a] & M. I. Fokina [a]
[a] St.-Petersburg State University of Information Technologies, Mechanics and Optics, St.-Petersburg, Russia
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Polymer Composite Based on DAST Submicron Crystals: Technology and Properties

J. A. BURUNKOVA,* I. YU. DENISYUK, AND M. I. FOKINA

St.-Petersburg State University of Information Technologies, Mechanics and Optics, St.-Petersburg, Russia

We propose a new nonlinear optical material, a polymeric nanocomposite based on DAST submicron crystals (trans-4'-(dimethylamino)-N-methyl-4-stilbazolium tosylate). The method and the preparation conditions for films based on a mixture of polymer solutions and a DAST powder are studied. Polymer matrices of various types, solvent ratio for the pair DAST/polymer, and electrical poling conditions are investigated. Absorption and luminescence spectra and the second harmonic generation have confirmed the creation of red-form DAST nanocrystals in polymer films. The figure of merit for a resulting polymer film is approximately 400 times higher than that for $LiNbO_3$ at a wavelength of 1.32 microns.

Keywords Nonlinear optical materials; polymers; organic composite; electro-optical dye molecules

Introduction

In the last years, organic nonlinear optical materials with high second-order nonlinear susceptibilities are found many applications in various electro-optical devices such as optical waveguides or frequency modulators [1]. Three classes of electro-optical (EO) materials are used today: inorganic crystals (e.g., $LiNbO_3$), polymers or dendrimers doped with electro-optical dye molecules, and organic crystals with large EO coefficients. The recent investigations of materials such as nanocrystals in polymer materials that combine the properties of both organic crystals and polymer media are very promising. Only a few studies in this direction are known now [2, 3, 4]. In this paper, a new nonlinear optical material, a polymeric nanocomposite based on DAST submicron crystals (trans-4′-(dimethylamino)-N-methyl-4-stilbazolium tosylate, DAST), is proposed. This work is a continuation of our previous researches [5, 6]. As is known, DAST is a particularly interesting material for nonlinear optical (NLO) device applications due to its large EO coefficient and a low dielectric constant ($\varepsilon = 5.2$), giving rise to a high modulator figure of merit and the stability up to 250°C [7, 8]. According to data in [9], DAST exhibits the second-order NLO susceptibility $\chi^{(2)} = 2020 \pm 220$ pm/V at $\lambda = 1318$ nm and the electro-optical figure of merit $n_1{}^3\, r_{11} = (530 \pm 60)$ pm/V at $\lambda = 1313$ nm. The goal of our work was the creation of a polymeric material with high NLO characteristics on the basis of submicron DAST crystals.

*Address correspondence to J. A. Burunkova. E-mail: burunj@list.ru

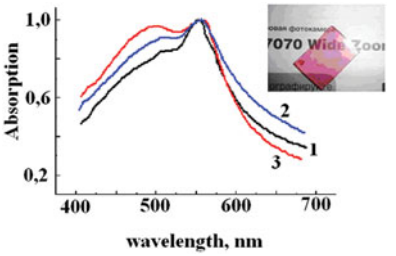

Figure 1. The absorption spectra of 4 wt.% DAST - PMMA (5 h, $T = 180^{\circ}$C). Films from solutions containing chloroform: *1*- 60 vol.%; *2* - 67 vol.%; *3* - 83 vol.%.

Materials and Methods

4-dimethylamino-N-methyl-stilbazolium tosylate (DAST) – Aldrich, No. 514160-5G; polymethylmethacrylate (PMMA) - Aldrich, No. 18,223-0, UV-cured acrylate bisphenol A glycerolate (BisA) - Aldrich, No. 41,116-7.

Films 2–4 μm in thickness were made by a Spin-Coater KW-4A centrifuge (Chemat Technology Inc.). The samples were examined on an optical microscope OLYMPUS STM6. The UV-Vis spectra were obtained on a Perkin-Elmer spectrophotometer 555, and the luminescence spectra were obtained on a MicroTime 100 PicoQuant device. The second harmonic generation (SHG) measurements were carried out with a Q-Switched Laser Systems (MPL-III series) laser operating at $\lambda = 1319$ nm. Second harmonic signals (660 nm) were measured by a light-to-voltage optical sensor TSL252R.

Results and Discussion

The peculiarity of this method is the simultaneous formation of both submicron DAST crystals and polymer matrices. The obtained DAST composites are transparent films with low scattering and bright red color (Fig. 1, inset).

The process of preparation of the acrylate DAST composite includes the following steps:

- preparation of DAST and polymer/monomer solutions;
- fabrication of thin DAST - polymer/monomer films on a centrifuge;
- thermal annealing;
- orientation of DAST nanocrystals by the electrical poling under heating.

Two methods of formation of a polymeric matrix are studied. It is worth noting that the way to produce the polymer matrix determines the mechanism of formation of submicron DAST crystals in synthesized composites.

In the first way, the polymeric matrix is produced from a PMMA solution. Nanocrystals are formed by the evaporation of solvents, the subsequent annealing of the composite, and the electrical poling under heating. In the second way, UV-cured acrylates were used. In this case, the resulting nanocomposite is more thermally stable. The DAST solubility in the monomer is higher than that in the resulting polymer. That is why (as we think) the DAST crystallization occurs during the UV-curing.

Thin polymeric films obtained by the first method were formed by the spin-coating from a PMMA -chloroform - methanol solution containing 2–12 wt.% DAST. As is known,

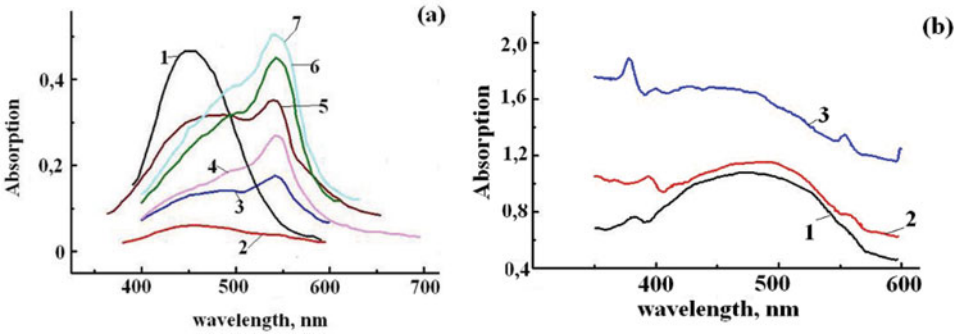

Figure 2. Thermal annealing: a) for 2 h at 180°C, PMMA - DAST wt.%: *1* - 10 wt.% before annealing; *2* - 2 wt.%; *3* - 4 wt.%; *4* - 6 wt.%; *5* - 8 wt.%; *6* - 10 wt.%; *7* - 12 wt.%; b) BisA - 10 wt.% DAST : *1* - before annealing; *2* - 2 h at 180°C; *3* - 5 h at 180°C.

the absorption spectra of the molecular form of DAST and the crystalline form have, respectively, a maximum absorption at 480 and 550 nm [10]. As seen from Fig. 1, the solvent ratio influences the rate of formation and the proportion of the crystalline form of DAST in the formed film.

As seen from Fig. 1, for the ratio of solvents $CHCl_3/CH_3OH$ equal to 3/2, the greatest share of the crystalline form of DAST in PMMA is generated. We have obtained samples of PMMA with the DAST concentration up to 12 wt.%.

The formation of DAST nanocrystals takes place simultaneously with the formation of a polymer matrix due to the evaporation of solvents. The DAST crystal nucleation occurs in the early stages of the solvent evaporation, followed by the growth of crystals. Conditions were chosen so that the sizes of crystals were in the submicron range. It is found that the heating at a definite high temperature for a certain time period is necessary for the formation of the red crystalline form of DAST. A clear peak of the red crystalline form of DAST in PMMA at a wavelength of 550 nm is observed, by starting from a concentration of 4 wt.% after the annealing at 180°C for 2 h (Fig. 2 *a*).

For materials based on UV-curable monomer BisA (Fig. 2 *b*), the maximum in the absorption spectrum of the red crystalline form of DAST is observed for concentrations starting from 10 wt.% after the annealing at 180°C for 5 h.

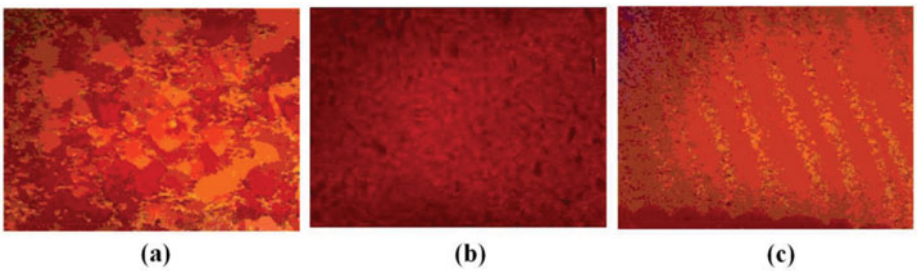

Figure 3. Photos of DAST/PMMA films after the thermal annealing. DAST concentration: *a* - 4 wt.%; *b* - 8 wt.%, *c* - 12 wt.%.

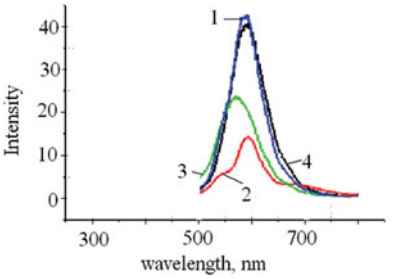

Figure 4. Luminescence spectra: *1* - PMMA/2 wt.% DAST; *2* - PMMA/4 wt.% DAST; *3* - BisA/5 wt.% DAST; *4* - BisA /10 wt.% DAST.

A nonuniform distribution of DAST in the composite is observed for concentrations less than 8 wt.% (Fig. 3). DAST is uniformly distributed in the nanocomposite volume for a concentration of 8 wt.%.

Two stripes different in the color intensity are observed at a concentration of 12 wt.% DAST in the nanocomposite (Fig. 3). One area is a material homogeneous in color and in structure, and the other has a low-intensity color and submicron-sized crystals.

As is well known, only one form of DAST crystals, namely the red crystalline form, has the ability to luminesce ($\lambda \approx 600$ nm) [10]. We have measured the luminescence spectra of the prepared samples (Fig. 4.) Intense luminescence in the region at 600 nm for DAST-Bis and DAST-PMMA films confirms the existence of the submicron red crystalline form of DAST crystals in polymer matrices.

A NLO material with orientational order on the basis of submicron DAST crystals of the red crystalline form in a polymer matrix was obtained by the electric poling using the corona method under heating. The 4 wt.% DAST-polymer composition was heated for 14.5 h at 150°C. This film after annealing was performed by the corona poling for 3 min at 125°C and then 60 min at 110°C. Then the polymer film was cooled down in a high electric field so that the alignment of electric dipoles was "frozen", and the macroscopic optical nonlinearity was achieved. To optimize the poling result, the effects of the variation of poling conditions such as the temperature, time, and pre-curing processes were investigated extensively in order to obtain the red crystalline form of DAST without damaging the polymer surface. As can be seen from Fig. 5, the peak at $\lambda = 550$ nm corresponding to the red crystalline form of DAST is observed after the annealing and the electric poling.

The second harmonic generation efficiency of the samples was measured and compared with that of the reference crystal $LiNbO_3$ 5 mm in thickness. The figure of merit of the polymer film was calculated and compared with that of the reference crystal $LiNbO_3$. The conversion efficiency is defined as the ratio of the average power of the second harmonic to the average power of the output emission. As is known, the emission intensity of the second harmonic is proportional to the squared intensity at the fundamental frequency and the square of the length of a nonlinear crystal,

$$I_{2\omega} = k(I_\omega)^2 l^2,$$

where k is the figure of merit of a nonlinear crystal depending on its nonlinear optical susceptibility, the emission frequency, and the refractive index, and l is the optical path length. The ratio of the figure of merits of the obtained polymer film (8 wt.% DAST/PMMA) and a crystal $LiNbO_3$ with regard for the ratio of their optical lengths was 400 at a wavelength

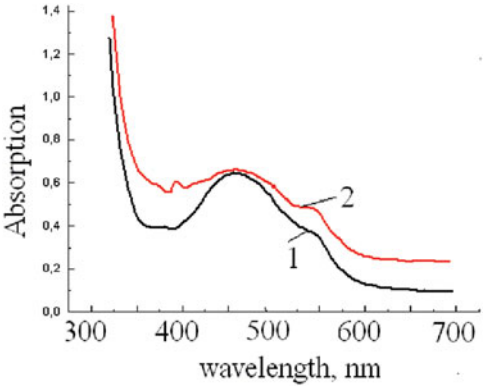

Figure 5. Absorption spectra of PMMA/4 wt.% DAST : *1* - before electrical poling; *2* - after electrical poling.

of 1.32 μm. Due to the facts that the second harmonic of DAST is located in the absorption region, where the refractive index is complex, and its exact value is unknown, we did not calculate the nonlinear optical coefficient of DAST at this wavelength.

Conclusions

We have established the conditions for the production of NLO polymer composites based on submicron crystals of DAST by means of the evaporation of a solvent from a supersaturated DAST/polymer solution. The formation of submicron crystals in the red crystalline form is confirmed by the absorption and luminescence spectra, as well as by the SHG in films. The ratio of the figure of merits for the polymer film (8 wt.% DAST/PMMA) and a crystal $LiNbO_3$, with regard for the ratio of their optical lengths was 400 at a wavelength of 1.32 μm.

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