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Optical properties of ferroelectric Langmuir–Blodgett films impregnated with dye molecules

VLADIMIR B. ZAITSEV*, ALEXANDER N. NEVZOROV, GENNADY S. PLOTNIKOV

M. V. Lomonosov Moscow State University, Physics Department

Ferroelectric polymer films are very promising materials for modern microelectronics, molecular electronics and nonlinear optics. Langmuir–Blodgett films of poly vinylidene fluoride copolymer impregnated with organic dye molecules were studied experimentally. Ferroelectric films of this type undergo a phase transition at the Curie temperature. Fluorescence spectra of the structures were investigated. A strong influence of the phase transition onto the position and shape of the fluorescence spectrum was observed. A new effect of photosensitized shift of the Curie temperature was found. Besides the main ferroelectric transition, a low-temperature structural transition in super thin films was discovered for the first time by the optical method. Possible mechanisms of the effects observed are discussed.

Key words: *ferroelectric polymer film; structural transition; organic dye molecules; fluorescence; photosensitization*

1. Introduction

Ferroelectric polymer films are very promising materials for modern microelectronics, molecular electronics and nonlinear optics. Ferroelectric polymer poly (vinylidene fluoride) and its copolymers (deposited by spin coating with thickness from 0.6 to several microns) have been under intense study for about 30 years, providing fundamental data [1] and practical applications [2]. New interest to this material rose after extremely thin films of copolymer obtained built by Langmuir –Blodgett (LB) method. It was found [3] that the films save their ferroelectric properties down to thickness of about 4 nm. This technology can well provide very thin active dielectric films of controllable thickness.

Our interest in ferroelectric polymer films is inspired by the fact that they can provide a novel material with unusual optical properties when being impregnated with polar dye molecules. The use of a ferroelectric film as a matrix for the dye applies

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*Corresponding author, e-mail: vz@hofme.phys.msu.su.

a very strong local electric field to the molecules, causing the dye molecules orient inside the film. We studied fluorescence spectra of such structures. A new effect of photosensitized shift of the Curie temperature was found. Possible mechanisms of the observed effects are discussed.

In analogy with ferromagnetism, the main properties of ferroelectrics are: a spontaneous electrical polarization and possibility of polarization switching, as well as disappearance of polarization above the Curie temperature T_c. We found a strong influence of the ferroelectric phase transition on all optical parameters of the LB film of copolymer of vinylidene fluoride with trifluoroethylene P(VDF-TrFE) impregnated with a small quantity of organic dye Rhodamine G (RhG) molecules.

2. Experimental

Experiments were performed with copolymer of vinylidene fluoride with trifluoroethylene (VDF/TrFE = 70/30 mol %). The 40 and 10-monolayer thick films were deposited onto a glass surface by the Langmuir–Sheffer method. The thickness of one monolayer is about 0.4 – 0.5 nm, so the films obtained had the thickness of 16–20 nm and 4–5 nm, correspondingly. Dye molecules of Rhodamine G (RhG), as well as anthracene were embedded into specimens by the absorption from an ethanol solution after each LB monolayer deposition during the film growth or after the whole film deposition. The concentration of Rhodamine molecules in the film was controlled by the concentration of the solution, and was chosen to provide a high fluorescence signal and to avoid dimerization of dye molecules. Xenon lamp and monochromator or Argon laser were used to obtain the light of a proper wavelength for the dye excitation. Fluorescence spectrometer was used for the spectra recording.

3. Results and discussion

The wavelength of the fluorescence maximum of the 40 layers thick P(VDF-TrFE) film with RhG versus temperature is shown in Fig. 1a. A 20 nm “blue” shift of the spectrum was observed inside the temperature range of ~20 K around $T_c = 352$ K. The effect was dependent on the dye type.

Such a spectrum shift can be caused by several reasons. First, orientational relaxation of the dye molecules after excitation inside the polymer matrix can produce strong spectral shifts [4] at the temperatures, when the lifetime of molecule excited state τ becomes close to the time of orientational relaxation τ_r. However, corresponding temperatures for RhG are much lower than those in the study. Consequently, the shift of the fluorescence spectrum of RhG adsorbed on the test quartz sample was smaller than 1 nm in the temperature region studied. The change of steric interaction of dye molecules with the polymer matrix during ferroelectric phase transition could be the second origin the spectral shift. Possible effect of this change on the spectrum position was carefully estimated and proved to be negligibly small.

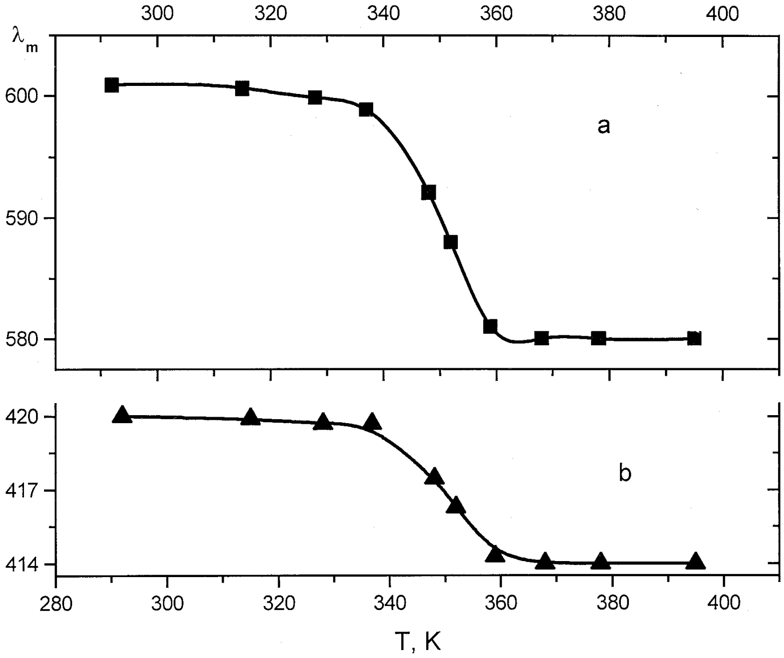

Fig. 1. Temperature dependences of the wavelength of the fluorescence maximum λ_m for RhG (a) and anthracene (b) in the 40-layer LB film of P(VDF-TrFE). Excitation wavelength 480 nm for RhG and 400 nm for anthracene

The most probable reason for the observed effect is the Stark shift of the electronic levels in the dye molecule [5] under the influence of changes of the surrounding local electric field. The change of the wave number ν associated with the field E_{loc} is given by the equation:

$$\Delta\nu \sim \frac{1}{hc}\left(\Delta\boldsymbol{\mu}\cdot\mathbf{E}_{\mathrm{loc}} + \frac{1}{2}\Delta\alpha E_{\mathrm{loc}}^{2}\right) \tag{1}$$

where $\Delta\boldsymbol{\mu}$ and $\Delta\alpha$ are the changes of the dipole moment and polarizability of the molecule in the electric field. High order of the LB film structure causes great value of the E_{loc} in the ferroelectric state. Our calculations based on the literature data for $\Delta\alpha$ and $\Delta\boldsymbol{\mu}$ give the value of $E_{\mathrm{loc}} \approx 4\times10^{9}$ V/m for the local electric field inside the LB film below T_c. The values of $\Delta\alpha$ and $\Delta\boldsymbol{\mu}$ for anthracene molecules are much lower, causing lower sensitivity to the electric field. The spectral shift for anthracene was about 6 nm (Fig. 1b).

During the optical measurements we have noticed that the temperature of the phase transition of the films differs from that obtained from the electrophysical and structural measurements of other authors. The Curie temperature obtained from the spectral data is about 20 K lower. This may be due to the non-radiative energy transfer from the dye molecules to the polymer chains. The dye molecule excited by a light quantum, has a possibility to discharge the energy through several channels: (1) luminescence; (2) non-radiative energy transfer to near adsorbed molecules through the Förster–Dexter induction-resonance mechanism; (3) intramolecular singlet-triplet transfer; (4) non-radiative electron energy transfer to the matrix; (5) electron-vibrational coupling (internal energy conversion to vibrational modes). The channels (4) and (5) can cause the energy transfer to the polymer chains either directly or via vibrational modes. In both cases it may be the reason of the shift of the Curie point to lower values. Photo-induced transitions in the adsorbed dye molecules are known to cause the shift of the semiconductor–metal phase transition in VO_2 to lower temperatures [6].

To prove our assumption, we carried out a special experiment. We have built a capacitor structure sputtering a metal (Sn) layer before the film deposition and on the surface of LB film with dye molecules. The temperature dependences of the capacitance of such a structure are shown in Fig. 2. As is seen from the picture, the capacitance has a local maximum at 378 K in the dark. This local maximum is unambiguously identified with the ferroelectric phase transition [3]. The local maximum of the capacitance shifts to 352 K when the sample is illuminated by the light of Argon laser for the dye excitation. A control experiment has proven that the direct heating of the sample by the Argon laser was lower than 1 K.

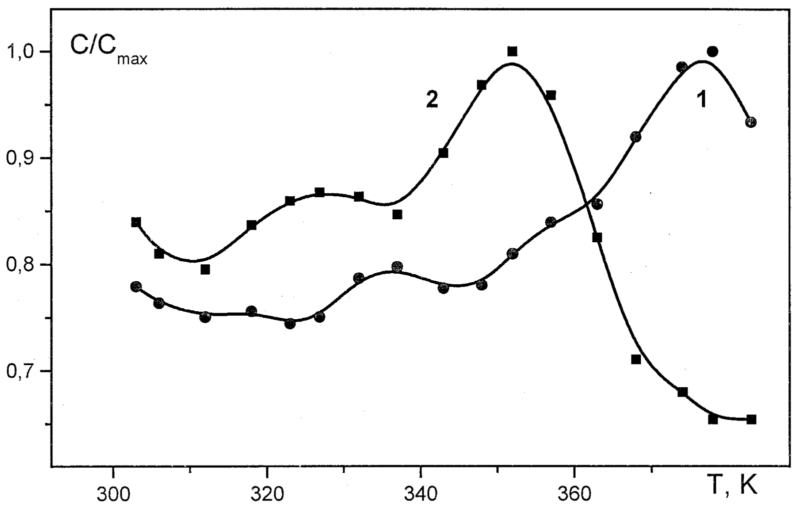

Fig. 2. Temperature dependences of the relative capacitance of the 40-layer LB film impregnated with the RhG dye molecules in the dark (1) and when illuminated at the wavelength of the RhG absorption (2)

The spectral maximum shifts were accompanied by strong changes of the band widths (Fig. 3). Despite different Stark shifts of the spectra for the RhG and anthracene, temperature dependences of their widths had completely the same trend. The width of the spectral line is the combined result of uniform and non-uniform broadening:

$$I = \int G(\nu, \nu_u) F(\nu, \nu_n) d\nu \tag{2}$$

where ν_u and $G(\nu, \nu_u)$ are the centre and the function of uniform broadening, and ν_n, $F(\nu, \nu_n)$ – of the non-uniform one. The uniform broadening depends on the temperature, as $G \sim T^k$, where k is a number from 2 to 3. It is smoothly growing from 4 to 8 nm in the temperature range studied for RhG.

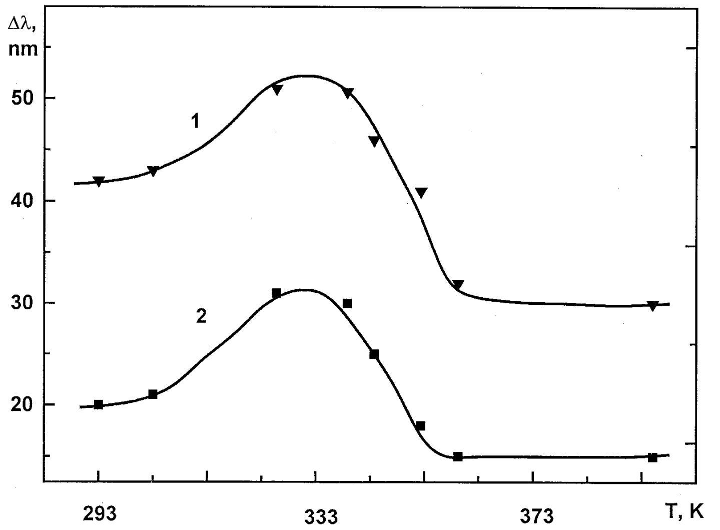

Fig. 3. Half width $\Delta\lambda$ of the fluorescence spectrum of RhG (1) and of anthracene (2) versus temperature in the 40-layer LB film of P(VDF-TrFE)

As is seen from Fig. 3, the spectrum width is almost constant at lower temperatures, and growing at temperatures approaching the Curie point. It reaches the maximum at the very beginning of the phase transition. Then the width of the spectrum diminishes to reach a constant value above 363 K. Since the uniform line width has to be slightly growing in the studied temperature region, this means that the temperature dependence of the spectrum width is determined by the non-uniform broadening, which is caused by the difference in the local field that influences neighbouring dye molecules [7]. The maximum non-uniform broadening is reached at lower temperatures than the Stark shift, because at the beginning of the phase transition the ferroelectric domains are breaking, the film structure starts to change and the heterogeneity of the fields is maximal. Taking into account the temperature growth of the uniform broadening, the non-uniform part of the spectrum half width decreases from about 40 nm at 293 K to 30 nm at 363 K, when the ferroelectric state of the film is completely destroyed. This fact acknowledges the understanding of the P(VDF-

TrFE) film structure at room temperature as “semi crystalline”, when crystal parts alternate with amorphous regions.

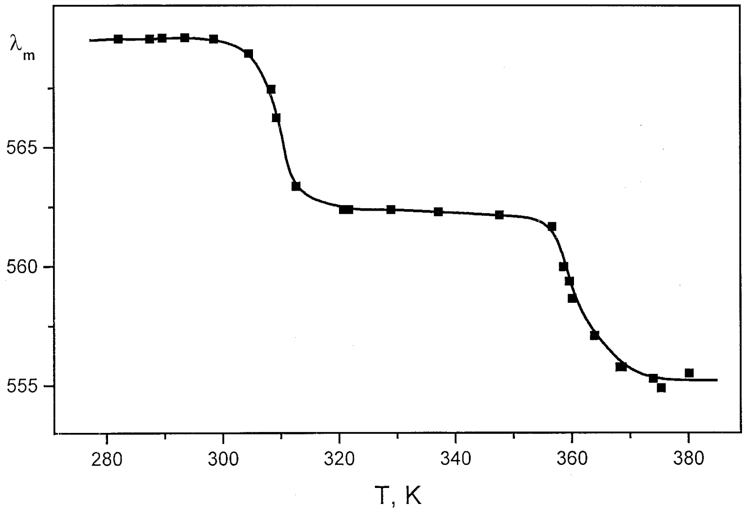

Fig. 4. Temperature dependence of the wavelength λ_m of the fluorescence maximum of RhG in the super thin (10 layers) LB film of P(VDF-TrFE)

Figure 4 shows the temperature dependence of the position of the fluorescence maximum of RhG inside the super thin copolymer film (10 layers). It is seen from Fig. 4 that the shift of the spectrum at T_c in the super thin films is analogous to that in the films of 40 layers. This confirms the existence of the ferroelectricity in the super thin LB films down to the thickness of 5 nm. Besides the main phase transition, the second strong shift of the spectrum at ~300 K was found in the super thin film. This shift can be caused by a structural transition, which is observed only in super thin LB film (<20 layers). This transition can occur because of the conversion of the thermodynamically nonstable film to more stable state with a slight raise of the temperature. The conversion can be observed when free energy of the film becomes comparable with the energy of the surface tension and of the film interaction with the substrate. We have found the increase of the capacitance of the film at the temperature region of this low temperature structural transition in analogy with [8].

4. Conclusions

The novel effect of the photosensitized shift of the ferroelectric phase transition temperature was found in Langmuir–Blodgett films of the vinylidene fluoride and trifluoroethylene copolymer impregnated with organic dye molecules. The work showed advantages of the method of luminescent dye probes for the study of thin polymer films which undergo structural transitions. This helps to accomplish one of the most important tasks of the surface and thin films science – the heterogeneity study. We have detected, by the optical method, the existence of a low-temperature structural transition in super thin films of P(VDF-TrFE) copolymer. We have also shown the influence of the ferroelectric phase transition in the thin LB P(VDF-TrFE) films impregnated with RhG molecules on the parameters of the fluorescence of the dopant. An extremely strong effect of the electric field in the film changing during the phase transition on the optical properties of the adsorbed molecules makes it possible to produce novel materials for micro- and molecular electronics, as well as for nonlinear optics. The possibility of the photosensitization of the phase transition in the material studied makes it especially interesting.

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