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High stability of a blue phase polymer based on a diacetylene alcohol derivative

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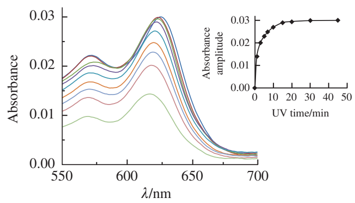
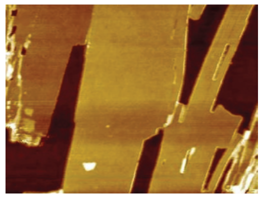
The effect of prolonged UV irradiation and high temperature on a blue phase polymer film prepared by the Langmuir–Schaefer method based on 11-hydroxyundeca-6,8-diyn-1-yl *N*-(4-methoxyphenyl)carbamate was evaluated. The high stability of the polymer under extreme external influences was revealed. The transition of a monolayer to a bilayer with increasing surface pressure during the Langmuir layer formation was confirmed by atomic force microscopy.





Polydiacetylenes (PDAs) are the products of the solid-state topochemical polymerization of diacetylene derivatives.[1] Polymerization can occur under UV light or γ irradiation, the heating of monomer thin films (or crystals), and mechanical stresses.[2,3] For many years, PDAs have found practical applications in medicine, production of chemical and biological sensors, molecular electronics and nonlinear optics[4–7] due to their unique optical, mechanical and electrical properties[2–5,8] and advances in the chemical synthesis of new diacetylene derivatives with predetermined properties. In particular, such compounds include the derivatives of unsymmetrical hydroxyalkadiynyl *N*-arylcarbamates.[9–12] The Langmuir–Blodgett (LB) and Langmuir-Schaefer (LS) methods for the preparation of thin film samples[13] make it possible to obtain structurally ordered mono- and multilayer films on different solid substrates.

Recently, we reported the LS and LB preparation and the structural (AFM and SEM) and optical characterization of the films of diynylic *N*-arylcarbamate alcohol derivatives.[11,12] It was shown that the result of photopolymerization under UV irradiation depended on the numbers of methylene groups (CH_2) in hydrophobic (*m*) and hydrophilic (*n*) parts of test molecules. The red, purple and blue phase polymeric films were prepared uder variation of these parameters and the presence of a MeO group or a hydrogen atom at the aryl substituent.[11] Under UV irradiation, the monomer films of molecules with $m = 4$ or 5 and $n = 2$ transformed into a blue phase polymeric film, and the absorption intensity of the polymer at ~620 nm increased as the sample exposure time was raised to 20 min.[12] The structures of Langmuir, LS or LB monolayers were more homogeneous if the MeO group rather than a hydrogen atom was at the aryl substituent of the molecule. Among the diynylic *N*-arylcarbamates, $MeOC_6H_4NH(C{=}O)O(CH_2)_5(C{\equiv}C)_2(CH_2)_2OH$, below referred to as DA7, was chosen as the most promising material for detailed studies of its optical, thermal and structural characteristics.[†,12]

The aim of this work was to study the properties of diyne DA7 LS films at an elevated temperature (180 °C) under UV irradiation (for 45 min).

The absorption spectra measurements started immediately after transferring the film on a quartz substrate and then repeated after UV irradiation at regular time intervals from 30 s to 45 min. The absorption band position corresponded to the blue phase of PDA, and the signal amplitude continued to increase during UV irradiation. In that connection, the questions arose: how will the film behave with a further increase in the UV irradiation dose? Will there be a transition of a blue polymer in a state with a shorter conjugation length of the polymer chains (purple or red phase),[11,14] or the polymer will be simply disorganized? Note that the same effects could result at a high environment temperature.

Before the UV irradiation, the DA films had no absorbance in the visible range, demonstrating the presence of monomer molecules in a film only. This pointed out to the efficiency of the polypropylene filters used to remove small polymer amounts formed during the storage of the compound after its synthesis. At the same time, several absorption peaks typical of diynylic carbamates at 220–280 nm were observed. Under the UV irradia-

† A solution of DA7 in chloroform (analytical grade, Merck) was passed through a polypropylene filter (0.2 μm) before use to avoid the presence of PDA particles and spread over the water subphase surface (Milli-Q) of the trough KSV 5000 LB System 2 (KSV Ltd.). The subphase temperature was 19 °C. The diyne concentration in solution was 0.1 mM. The speed of the trough barriers during monolayer compression and π–A isotherm measurement was 2.25 $cm^2\ min^{-1}$. The monolayer transfer on a solid substrate (quartz for optical measurements or Si for structural studies), pretreated by a standard method,[13] was carried out by horizontal dipping (LS) at a surface pressure of 35 $mN\ m^{-1}$. Each quartz substrate was previously covered with five LB layers of octadecylamine (99% purity, Sigma) for a reliable transfer of diyne monolayer. The DA films on solid substrates were polymerized using a 30 W low-pressure mercury lamp (λ_{max} = 254 nm). The distance between the source of UV irradiation and the sample surface was 25 cm. The visible absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer before and after UV irradiation. To study the topography of the samples, an NTEGRA Prima atomic-force microscope (NT-MDT) in intermittent contact mode fashion was applied. The topographic structure images were obtained at 25 °C using silicon cantilevers with a nominal tip radius of 10 nm (NSG01, NT-MDT). The scan rate was 0.39 Hz. The SPIPTM program (Image Metrology) was used for image analysis.

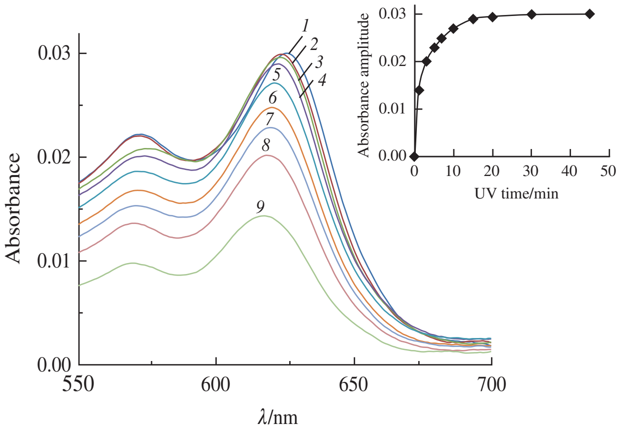


Figure 1 Absorption spectra of the compound LS monolayer and absorption amplitudes (in the inset) at different UV irradiation times: (*1*) 45, (*2*) 30, (*3*) 20, (*4*) 15, (*5*) 10, (*6*) 7, (*7*) 5, (*8*) 3, (*9*) 1 min.

tion of monomer films, a band due to the formation of blue phase polymer (~618 nm) based on an diacetylene alcohol derivative appeared in the absorption spectrum (Figure 1). After irradiation for 20 min, the absorption band shape and signal amplitude were consistent with data obtained earlier.[12] A further increase of UV irradiation time to 30 and 45 min did not lead to the destruction of the polymer film, but demonstrated the saturation of absorption (inset in Figure 1) and further streamlining of the polymer film structure. The latter was confirmed by the exciton absorption band maximum shift from 618 to 627 nm as a result of UV irradiation. Such stability of a single-layer blue phase PDA film, obtained from diyne alcohol derivative, to the excessive dose of UV irradiation was observed for the first time. Note that the re-measurement of the polymerized samples absorption spectra at room temperature after storage for more than six months showed the stability of optical characteristics of diyne DA7 polymer films.

To study the effect of temperature on a sample, the film of monomers was pre-polymerized by UV light for 30 min. The measurements were conducted at 85, 120 and 180 °C. An increase in the temperature of a diyne DA7 polymer film up to 120 °C led to a slight shift of the absorption band towards shorter wavelengths and a small decrease of the signal amplitude (Figure 2). However, the absorption spectrum of the film measured at room temperature a day after heat exposure showed the complete coincidence of absorption maximum positions and amplitudes with those of the spectrum of this sample measured before the experiment with temperature increasing. This indicated the complete recovery of structural and optical parameters of the sample after cooling to room temperature (see Figure 2). To determine the

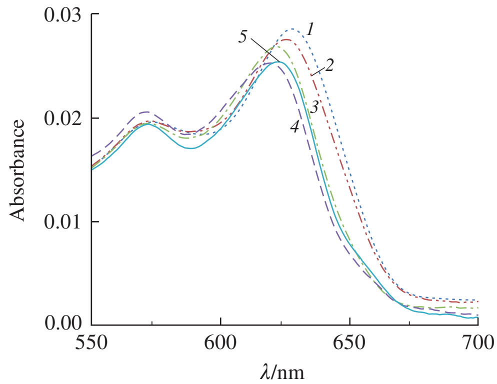


Figure 2 Changes in the absorption spectrum of PDA LS layer with temperature: (*1*) 22 (before heating), (*2*) 85, (*3*) 120, (*4*) 180 °C and (*5*) spectrum measured at room temperature after 24 h.

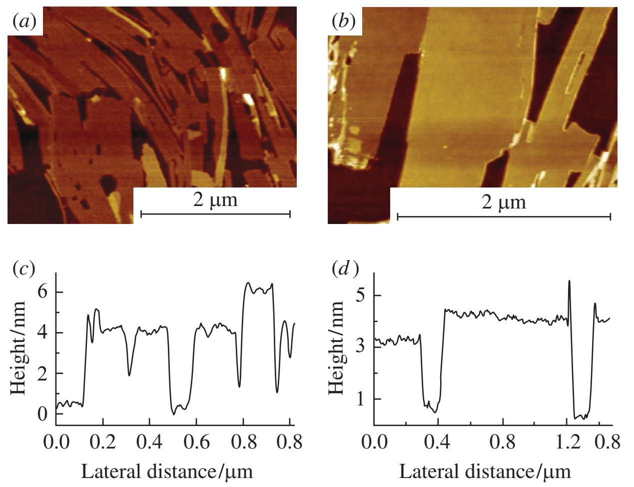


Figure 3 (*a*, *b*) AFM images and (*c*, *d*) corresponding line profiles over a substrate-film border of DA (*a*, *c*) and PDA (*b*,*d*).

possible limit of the thermal effect on LS polymer film, the temperature was increased up to 180 °C. In this case, the polymer absorption band maximum (excitonic) shifted from ~627 nm (at 22 °C) to 618 nm (at 180 °C) due to a slight decrease in the conjugation length of the polymer chains and some minor disordering of the film structure. The absorption signal amplitude decreased by ~15%. Measurements made at room temperature 24 h after the polymer thermal exposure revealed a small shift of the absorption spectrum to longer wavelengths without significant absorption changes (Figure 2, curve *5*). Thus, despite the sample temperature increased up to 180 °C, the PDA film remained in a state of blue phase polymer.

The structure of diyne DA7 films on silicon substrates prepared at a surface pressure of 28 mN m^{-1} in monolayer was reported.[12] The optical absorption of the blue polymer monolayer film after 20 min UV irradiation was a half of that found in this study. According to AFM measurements,[12] the LS film thickness was ~1.6 nm. The cause of this discrepancy in the absorption values was identified in a careful study of the Langmuir monolayer compression isotherm on a water subphase surface.[12] A small decrease in the isotherm slope was found, when the surface pressure was greater than 30 mN m^{-1}. In this work, the films were transferred on solid substrates at 35 mN m^{-1}. Thus, at this surface pressure, the bilayer film could be organized on a water subphase surface. To verify this assumption, the single layer samples were prepared on Si plates at a surface pressure of 35 mN m^{-1}. Figure 3 shows the AFM topographic images of the films on silicon substrate surfaces and film profiles in a state of monomers [see Figure 3(*a*,*c*)] and polymers (after 20 min UV irradiation) [see Figure 3(*b*,*d*)]. The thickness of the film transferred at 35 mN m^{-1} was approximately twice as high (~3.5 nm) as that determined for the monolayer transferred onto the substrate at 28 mN m^{-1}.[12]

Summarizing the spectral and thermal data, we can conclude that the blue phase polymer films prepared from an unsymmetrical 11-hydroxyundeca-6,8-diyn-1-yl *N*-(4-methoxyphenyl)carbamate with five and two methylene groups in the hydrophobic and hydrophilic moieties of the molecules, respectively, are exceptionally stable. Films with such properties can find applications in the molecular photovoltaic devices together with donor–acceptor dyad molecules.[15,16]

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