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Increase of polymeric chain conjugation length in UV irradiated monolayer of hydroxyalkadiynyl *N*-arylcarbamate derivative

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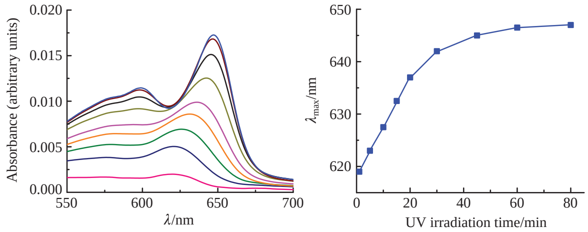
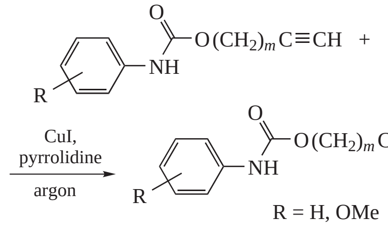
Photopolymerization of Langmuir–Schaefer monolayers of 12-hydroxy-7,9-dodecadiyn-1-yl *N*-(4-methoxyphenyl)carbamate molecules under long-term UV irradiation provided the new polymer material. The observed blue phase polymer absorption band shift (~30 nm) to the longer wavelengths during the sample UV irradiation corresponds to a continuous increase of the polymeric chain conjugation length. The morphology of monolayers was determined by the scanning electron microscopy.



Conjugated polymers based on various diacetylene derivatives are characterized by a notable light absorption in the visible range of the spectrum. The amazing chromatic and electronic properties of polydiacetylenes have opened the way for their wide practical applications, such as sensors, detectors, electronic circuit components, *etc*.[1] The conversion of diacetylene (DA) into polydiacetylene (PDA) occurs due to the solid-state topochemical polymerization reaction. Colorless crystals or films transform into the intensely colored objects under an external impact, *e.g*., electron beam, UV, γ- or X-ray radiation.[2,3] A red, purple or blue phase of the PDA with an absorption band in the region of 520, 575 or 620 nm, respectively, is formed upon such exposure.[4–7] Changes in the PDA phase may occur during an interaction of samples with chemical or biological objects,[8,9] due to the temperature change,[10,11] external pressure applied to the sample[12] or optical irradiation.[13] In such cases, the most common color transitions of polymer from the blue phase to the purple or red ones takes place. Note that such transitions were mainly observed for PDAs of diacetylene acid derivatives, while the polymerization products of DA alcohol derivatives usually displayed red phase PDAs.[14,15]

We have recently studied the spectroscopic and structural properties of a number of unsymmetrical hydroxyalkadiynyl *N*-arylcarbamate derivatives.[7,16,17] The general synthetical approach to thsese compounds is shown in Scheme 1.[7]



Scheme 1

It was shown that the result of DA film photopolymerization (*i.e*., PDA phase type) for such substances mainly depends on the values of m and n. To obtain the blue phase film of PDA that was not previously observed for any other DA alcohol derivative, it was necessary to introduce the methoxy substituent (see Scheme 1) in a molecule and to maintain the value of $n = 2$, and that of $m = 4$ or 5. However, the stability of obtained blue polymer was not satisfactory for $m = 4$. Redistribution in the intensities of excitonic and vibronic absorption bands were observed upon increasing UV irradiation time. The blue phase of PDA could be transformed into the purple one under prolonged UV irradiation. A stable blue polymer film with an absorption band in the region of 620–630 nm and a constant ratio between the excitonic and vibronic peak amplitudes was obtained for a diyne with $m = 5$. This indicated that an increase in the m value improved the polymer film characteristics. Note that the color of PDA with carbamate group depends on the conjugation length in the polymer chain. It reaches 30 or more conjugated monomer units in the blue phase PDA (λ_{max} = 620–650 nm).[5] Thus, the absorption bands of polymers with $m = 4$ and 5 appear in the initial region of the spectrum, peculiar for the blue phase PDA, wherein the conjugation chain length is about 30 units. One may assume that the blue phase of PDA with a longer conjugation length in the polymer chain (when λ_{max} ~ 650 nm) can be achieved by raising the m value.

The aim of this study was therefore to prepare thin film samples and to study the spectral and structural characteristics of monolayer films of the new compound, 12-hydroxy-7,9-dodecadiyn-1-yl *N*-(4-methoxyphenyl)carbamate (see Scheme 1, R = OMe, $m = 6$, $n = 2$).[†]

[†] 12-Hydroxy-7,9-dodecadiyn-1-yl *N*-(4-methoxyphenyl)carbamate was synthesized according to procedure reported earlier.[7] Chloroform (analytical grade, Merck) was used for the preparation of DA solutions (0.25 mM). A KSV LB 5000 System 2 (KSV Ltd., Finland) was used for the Langmuir

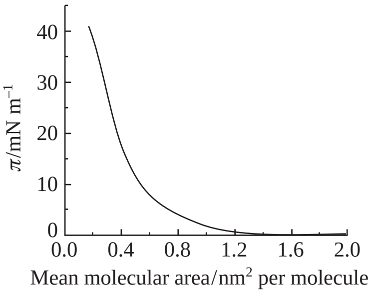


Figure 1 π–*A* isotherm of diyne monolayer measured at room temperature.

The surface pressure–mean molecular area (π–A) isotherm of diyne molecules at the air/water interface is shown in Figure 1. The onset of surface pressure in the layer appeared at ~1.2 nm^2 per molecule. Upon the monolayer compression, the molecules lying horizontally on the water surface began to rise and form a film with a predominant orientation of the molecules inside it. The condensed state isotherm of the monolayer with a limit area per molecule of ~0.6 nm^2 was thus measured.

The monolayers of diyne molecules were transferred onto quartz substrates by horizontal lifting method. The polymerization process in the formed films was studied by the absorption spectra measurements depending on the time of UV irradiation. The samples of monomer molecules did not absorb the visible light. Under the UV irradiation, the absorbance in the visible region of the spectrum appeared due to the monolayer photopolymerization [Figure 2(*a*)]. The excitonic band with a maximum at 618 nm and vibronic band at 570 nm appeared after a short-time UV irradiation. It corresponded to the transition of diyne monolayer into the blue phase PDA film. The amplitude of absorption signal gradually increased and reached its maximum value after the UV exposure for 80 min. At the same time, the peak of the excitonic absorption band shifted from its initial value of 618 nm to 648 nm [Figure 2(*b*)]. We can assume that in this case, the initial structural organization of molecules in the monolayer was the most preferable for the transition of monomers to the blue phase PDA film with the maximum conjugation length of polymeric chains. The excitonic absorption band shift of blue phase PDA by 30 nm during photopolymerization was the largest among all the compounds studied by our team.[16] It is well known that the optical spectra of PDA depend on many factors,[1] which makes it difficult to correctly estimate the relative effective conjugation lengths for any two PDAs. Due to the small structural difference in the molecules with the values m = 6 and m = 5, such parameters as the planarity of the skeleton, the coupling efficiency of side groups, and others, can be considered fairly identical. Thus, a comparative evaluation of the effective chain conjugation lengths of these polymers seems quite possible. The addition of one methylene group in the hydrophobic part of diyne molecule (m = 5 + 1) allowed us to obtain the blue phase PDA film with the longest conjugation length of the polymeric chains.

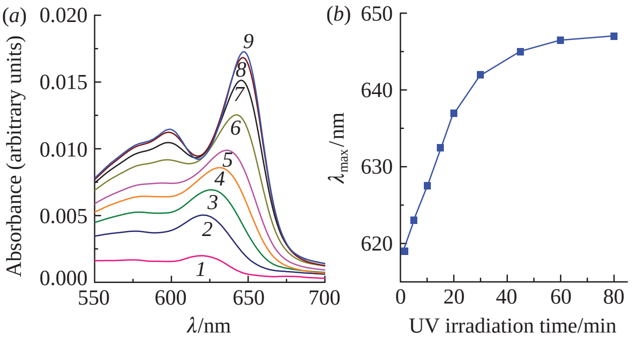


Figure 2 (*a*) Absorption spectra of LS diyne monolayer and (*b*) shift of the excitonic band peak of sample *vs*. UV irradiation time: (*1*) 1, (*2*) 5, (*3*) 10, (*4*) 15, (*5*) 20, (*6*) 30, (*7*) 45, (*8*) 60 and (*9*) 80 min.

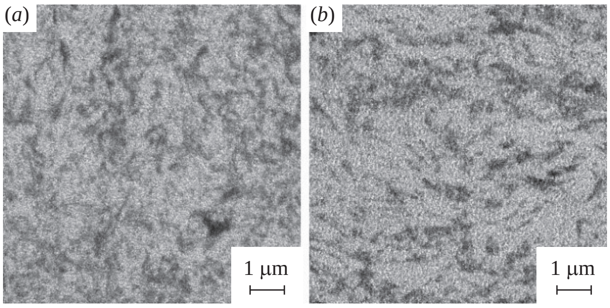


Figure 3 SEM images of LS films on silicon substrates (*a*) before and (*b*) after UV irradiation for 60 min.

Probably, the obtained compound is the best choice for the design of blue phase PDA films with the longest conjugation length. There are no reported data on compounds with m = 7 or 8. However, the monolayer films of compounds with m = 9 polymerized into unstable purple phase PDA.[7]

The spectroscopic data of samples are in agreement with the results of their structural studies. SEM images of the compound monolayer film before UV irradiation [Figure 3(*a*)] and after 60 min of irradiation [Figure 3(*b*)] suggest that after photopolymerization of the monolayer, the state of the film structure remained fairly stable. The film images demonstrated a relatively homogeneous coating of silicon substrates surfaces. It is also important to note that the exceptional resistance to unusually long-time exposure to UV light irradiation proves the high structural organization of prepared films.

The obtained new compound with the unique optical and structural characteristics can be used in the design of thin-film devices for applications in the molecular electronics, functioning on the principles of photoinduced charge separation and transfer process.

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monolayer creation, the compression isotherm measurement and transferring the films on solid substrates by Langmuir–Schaefer (LS) or Langmuir–Blodgett (LB) methods. Purified water (Milli-Q system, Millipore) was used as the subphase. The water temperature was set to 20 °C. The barrier speed was 3 mm min^{-1}. Langmuir films were transferred onto quartz substrates with 5 LB layers of octadecylamine (ODA) by LS method for spectroscopic measurements. The samples for structural studies were prepared by LS method on polished silicon wafers without additional hydrophobization of the substrates. The deposition surface pressures of the monolayers onto solid substrates were 24 and 25 mN m^{-1} for diyne and ODA, respectively. The DA films on solid substrates were polymerized by UV light irradiation with a low-pressure mercury lamp (λ_{max} = 254 nm) with a radiating power of 30 W from the distance of about 25 cm. The absorption spectra of the samples were measured by a Perkin Elmer Lambda 950 (USA) spectrophotometer. The surface morphology of the films on silicon substrates was studied before and after photopolymerization by scanning electron microscope (SEM) with a field emission cathode Scios (FEI, USA) in high resolution mode (Optiplan) at a reduced accelerating voltage of 1 kV using the Everhart–Thornley detector.

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