N.I. OSTAPENKO,[1] Y.V. OSTAPENKO,[1] O.A. KERITA [1, 2]

[1] Institute of Physics, Nat. Acad. of Sci. of Ukraine
 *(46, Nauky Prosp., Kyiv 03028, Ukraine; e-mail: ostap@iop.kiev.ua)*
[2] National Technical University of Ukraine "Kiev Politechnic Institute"
 *(37, Prosp. Peremogy, Kyiv 03056, Ukraine)*

# FORMATION OF THE LIQUID-CRYSTALLINE PHASE IN POLY(DI-n-HEXYLSILANE)

*We studied the formation of the liquid-crystalline (LC) phase in a poly(di-n-hexylsilane) (PDHS) film at the heating above the thermochromic transition temperature and its evolution, when the samples are cooled to room temperature. For this purpose, we measured the absorption (293–413 K) and luminescence (5 K) spectra depending on the annealing temperature, annealing modes, film thickness, and molecular weight of the polymer. It is shown that the formation of two LC phases at the heating of the film is associated with the appearance and a transformation of the positions and the intensities of two new absorption bands in the region of gauche-conformation, as well as the appearance of two bands in the region of trans-conformation of the cooled film. It is assumed that the formation of two LC phases is due to the existence of two absorption centers, which correspond to different distributions of the segment lengths in neat polymer. It is shown that, in the polymers with three different lengths of a Si-backbone (18, 50 and 180 nm), the LC phase reliably appears only in the polymer with the length of the Si-backbone of about 50 nm. We associate the appearance of new wide bands in the absorption spectrum of the annealed PDHS film after the cooling to room temperature with the defect states related to residual phenomena arising after the transition of the thermally treated film from the LC state to trans-conformation.*

*K e y w o r d s:* poly(di-n-hexylsilane), optical spectra, heating, *trans-* and *gauche*-conformation, liquid-crystalline (LC) phase.

## 1. Introduction

A lot of photo-physical properties of silicone polymers (polysilanes) are related to the delocalization of electronic excitations on the segments of a polymeric chain [1], which consist of silicon atoms and organic molecules as side groups. As a result, the strong absorption in the UV range, strong dependence of the electron transition energy on the conformation of a polymeric chain, phenomenon of thermochromism, and high mobility of charge carriers in these polymers are observed. The high mobility of charge carriers determines the use of polysilanes as transport [2] and luminescence [3] layers in organic electroluminescent devices. Orienting the polymeric chains increases significantly their photoconductive characteristics [4], which stimulates the study of the processes of orientation and organization in these polymers.

Poly(di-n-hexylsilane) (PDHS) is one of the most studied polysilanes. This polymer is characterized by the order-disorder thermochromic transition [5] above the phase transition temperature $T = 315$ K. In the disordered phase, the polymeric chains become free to move due to the disorientation of side groups [6]. Disordering the polymeric chains results in a significant change in the absorption spectrum of PDHS films. Namely, the absorption band of *trans*-conformation shifts toward shorter wavelengths by about 50 nm, which indicates the sensitivity of the polymer to large conformational changes of its fragments and to the orderliness of its structure.

The study of the diffraction of X-rays and electrons confirmed that the PDHS polymeric chain has *trans*-conformation below the phase transition temperature and transits in *gauche*-conformation above it, which is accompanied by the spontaneous appearance of the liquid crystal (LC) phase [7]. The presence of the LC phase in thermally treated polymeric films is also confirmed by the optical texture observed by the studies

of PDHS films at $T = 353$ K on a polarizing optical microscope [8–10]. Then the similar results were obtained for a number of polysilanes [11–13]. The existence of the LC phase was confirmed by a twofold increase in the birefringence of PDHS films cooled to room temperature after the heating, as well as by the orientation of the nematic LC deposited on the PDHS film arising after the heating [10]. The anomalous thermochromic behavior of the absorption spectra of poly (di-n-octylsilane) was studied in [14].

In this paper, we used the methods of optical spectroscopy to study changes in the conformation and the organization of PDHS films, resulting in their transition from *trans*-conformation into *gauche*-conformation, and to form the LC phase by heating the polymer above the phase transition temperature, as well as the reverse transition at the cooling of samples down to room temperature. For this purpose, we measured the absorption (at 293–413 K) and luminescence spectra (at 5 K) depending on the annealing temperature, annealing modes, film thickness, and molecular weight of the polymer.

## 2. Experimental

PDHS films were obtained by casting a solution of the polymer in toluene on a rotating substrate made of fused quartz with the subsequent drying at room temperature. We investigated the absorption and luminescence spectra of the PDHS films with different molecular weights ($M_{wi} = 53600$, 21000, and 219000; $i = 1$–3). The lenght of the Si-backbones are 18, 15, and 180 nm in this case corresponding. The absorption spectra were measured on a spectroscopic-computing complex KSVU-23 in the temperature interval 293–413 K. The heating of samples was carried out in two modes. In the first case, the sample temperature was changed in this temperature interval. For this purpose, the tested samples were placed in an oven located on the optical axis of the device. The absorption spectra were recorded during the heating, by starting from room temperature. The sample heated to a certain temperature was cooled to room temperature, and then the absorption spectrum was recorded. In the second case, the temperature of a sample was stabilized at $T = 318$ K, and the spectra were recorded in 10 min for one hour. Then the sample was cooled to the room temperature, and its absorption spectrum was recorded.
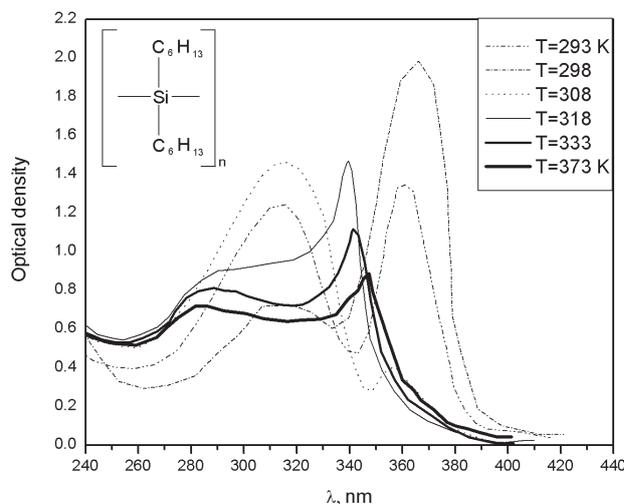


**Fig. 1.** Temperature dependence of the absorption spectra of PDHS films ($M_{w1}$) at the heating in the interval 293–373 K. Inset shows the PDHS structural formula

The luminescence spectra at $T = 5$ K were registered by a spectrograph DFS-13 combined with an optical helium cryostat. The luminescence of the samples was excited by light at the wavelength $\lambda_{\mathrm{ex}} = 313$ nm.

## 3. Experimental Results

Figure 1 shows the temperature dependence of the absorption spectra of PDHS films ($M_{w1}$) under the heating in the temperature interval 293–373 K. As is known, the absorption spectrum of PDHS films at 293 K consists of two bands with maxima at 365 nm (*trans*-conformation) and 316 nm (*gauche*-conformation) [1]. Let us consider the dynamics of the band corresponding to *trans*-conformation, as the temperature increases in the interval 293–308 K. In Fig. 1, we can see that, as the temperature increases, the band shifts to shorter wavelengths. At 308 K, its maximum is equal to 356 nm. Then, as the film is heated to the phase transition temperature, it transits from *trans*- into *gauche*-conformation. It would be natural to expect that the absorption spectrum will contain only the *gauche*-conformation band at 316 nm. But we see in Fig. 1 that even a small increase in the temperature above the phase transition one leads to the appearance of two new bands instead one band: the narrow band with maximum at 337 nm and with long-wave wing tightened to 380 nm and the broad band with maximum at ∼287 nm. The further
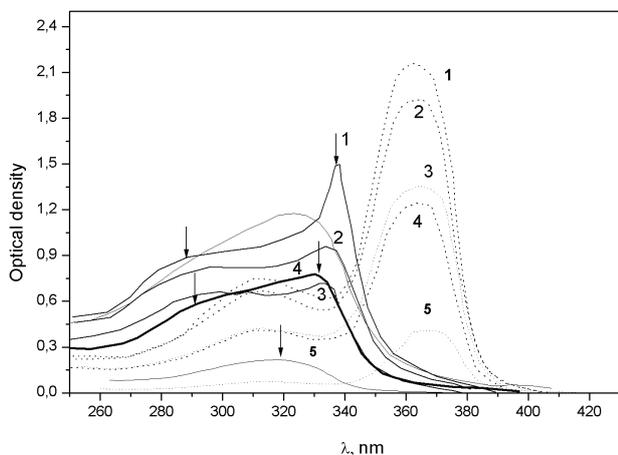
**Fig. 2.** Thickness dependence of the absorption spectra of a PDHS film at 293 K (dotted line) and at 318 K (solid line). Arrows indicate the maxima of new bands at 337 and 287 nm with decreasing the film thickness. Numbers show the spectra of the same thickness
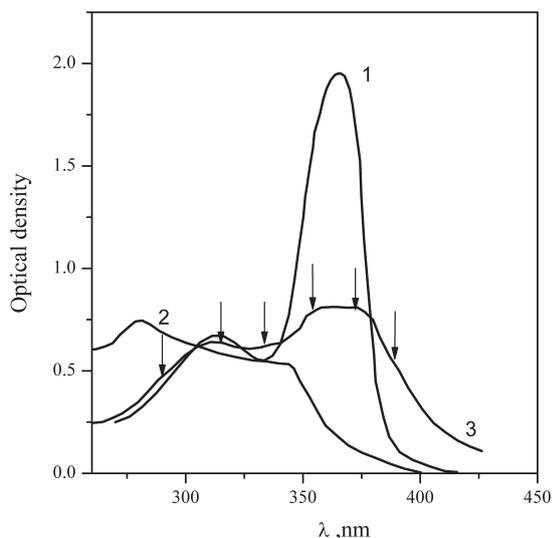


**Fig. 3.** Absorption spectra of a PDHS film: *1* – as-prepared at 293 K, *2* – after the heating to 398 K; *3* – after the heating to 398 K and the consequent cooling to 293 K. Arrows indicate the new bands arisen in the absorption spectra of films cooled to 293 K after the preliminary heating

increase in the temperature to 373 K leads to a shift of these bands by ~7 nm in opposite directions. The bands at 337 and 287 nm are shifted, respectively, to the red and blue sides. As the temperature increases, the intensities of both bands decrease, but the intensity of the band at 287 nm decreases less than that

of the 337 nm band. Note that the distance between these new absorption bands is equal to the distance between the absorption bands of *trans*- and *gauche*-conformations in neat polymer at room temperature.

The appearance of two new absorption bands of *gauche*-conformation, as well as a similar change in their evolution can be obtained without heating the sample to high temperatures, but only maintaining its temperature a little higher than the phase transition temperature (318 K) for about an hour.

We assume that the emergence of two new bands in the absorption spectrum can be associated with the formation of two LC phases in the polymeric PDHS film. The appearance of two new absorption bands (at 337 and 287 nm), their position, and the intensity of the absorption spectra of a PDHS film during its heating above the phase transition temperature strongly depend on the thickness of the studied film (Fig. 2). The bands are reliably observed in the absorption spectrum of the films with optical density $D > 1$ (thickness is about 600 nm) and are not seen in thinner films, e.g., in those with optical density $D \sim 0.4$. As the thickness of films decreases, the long-wave band maximum is shifted to shorter wavelengths by about 8 nm (Fig. 2). The short-wave band maximum is shifted to longer wavelengths. However, the intrinsic mechanisms of the displacements of both bands are different: the shift of the short-wave band is smaller at large thicknesses of films and increases, as the film thickness decreases.

At the cooling of a film down to room temperature for a day after the preliminary annealing, there are several new bands in the region of *gauche*-conformation in the absorption spectrum of films (Fig. 3): weak bands near 287, 312, and 343 nm. In the region of *trans*-conformation, we observe two bands with maxima of the same intensity at 356 and 374 nm instead of a single band with maximum at 365 nm, as well as the shoulder at 385 nm with a very lengthy long-wave edge up to 425 nm (Fig. 3, curve *3*). The significant difference is observed during the cooling of samples aged at a temperature above the phase transition temperature to room temperature. In this case, the short-wave band of *trans*-conformation is much more intense than the long-wave one.

In the luminescence spectrum ($T = 5$ K, $\lambda_{ex} = 313$ nm) of the PDHS films ($M_{w1}$) cooled after the heating, there is one band at 375 nm with a wave-
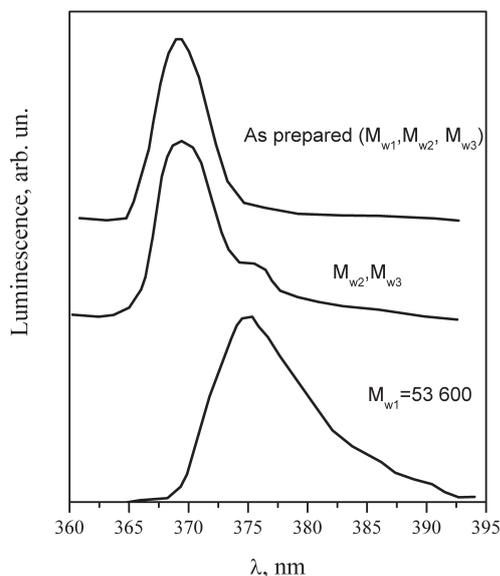
**Fig. 4.** Luminescence spectra of as-prepared PDHS films and thermally treated films with different molecular weights $M_{wi}$ cooled down to room temperature ($T = 5$ K, $\lambda_{\mathrm{ex}} = 313$ nm)

length edge tightened to 425 nm. It is shifted relative to the exciton band in the luminescence spectrum of the original sample to longer wavelengths by 4 nm (Fig. 4).

The dependence of the absorption spectrum of PDHS films ($M_{w1}$) on the number of heating cycles is given in Fig. 5. Figure 5 shows that, as the number of heating cycles increases, the band at 287 nm in *gauche*-conformation becomes more intense, than the band at 337 nm. As the temperature increases further, their intensities decrease, and the maxima of both bands are shifted to longer wavelengths. It should be emphasized that, at the cooling of a repeatedly heated sample to room temperature, it is clearly seen that the band of *trans*-conformation consists also of two bands with maxima at 356 and 375 nm. Moreover, the blue band becomes more intense than the red one, as the number of heating cycles increases.

The studies have shown that the formation of LC phases in the polymer depends significantly on the molecular weight. The temperature dependences of the absorption spectra of PDHS films ($M_{w2}$) in the interval from 293 to 373 K in the first and second heating cycles are shown in Figs. 6 and 7, respectively. It is seen from Fig. 6 that, in this case, the appearance of LC phases is much more complicated. With
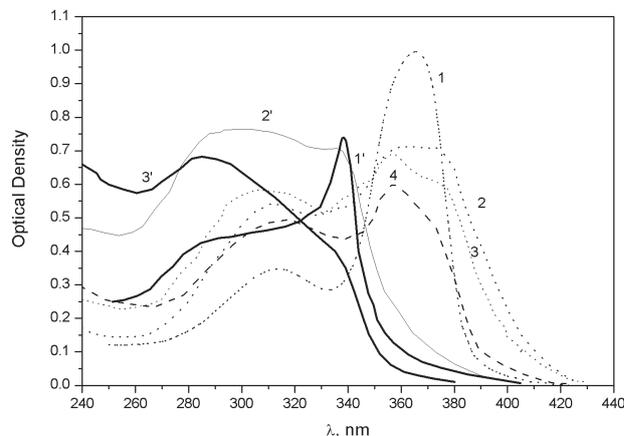


**Fig. 5.** Dependence of the absorption spectra of a PDHS film ($M_{w1}$) on the number of thermal cycles at 318 K (*1, 2, 3, 4*). Dashed lines indicate the absorption spectra: *1* – as-prepared film, *2, 3, 4* – the film cooled down to room temperature after the first, second, and third cycles
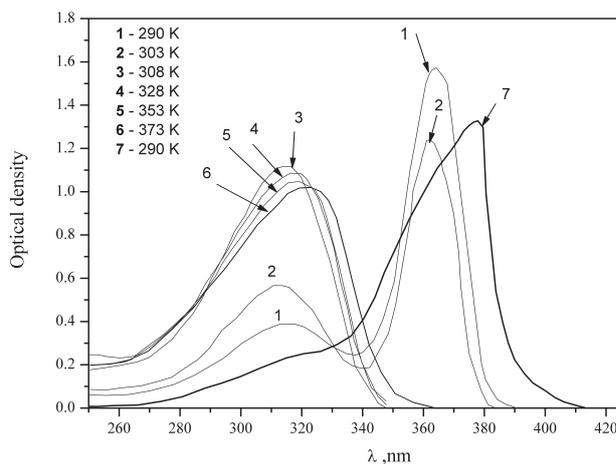


**Fig. 6.** Temperature dependence of the PDHS absorption spectra with $M_{w2}$ at the first heating from 293 to 373 K

increasing the temperature, we observe only a slight shift of the 316 nm band to longer wavelengths, which arrives at 323 nm at 373 K. The second band does not appear at all. The LC phase appears only after the reheating at a higher temperature $\sim$343 K (Fig. 7). The temperature dependence of the absorption spectrum of PDHS films ($M_{w3}$) during the heating from 293 to 413 K is given in Fig. 8. It can be seen that the appearance of LC phases becomes complicated, and they are observed only at a higher temperature ($\sim$343 K) than that for the polymer with $M_{w1}$. In
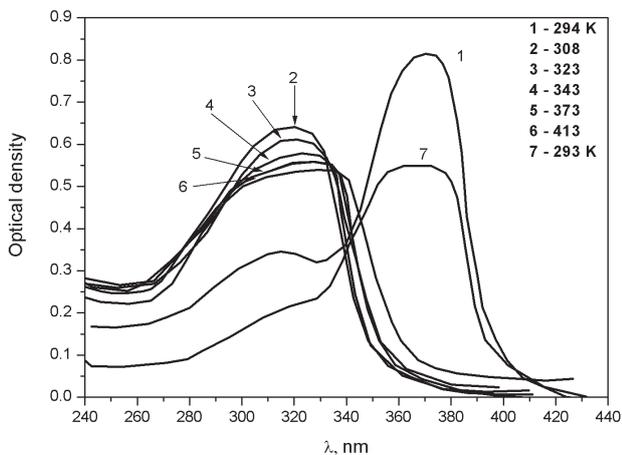
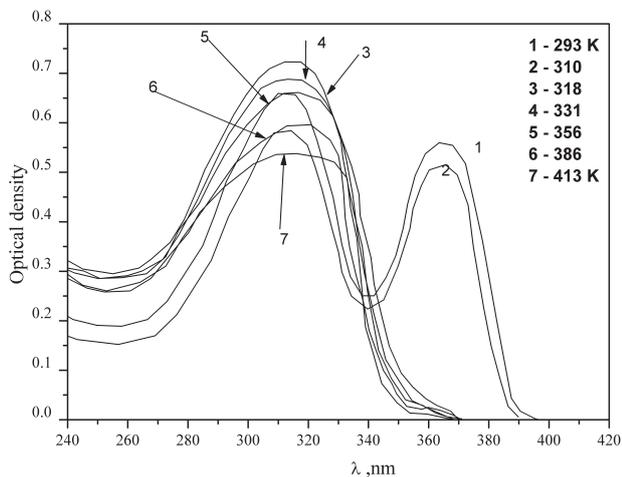**Fig. 7.** Temperature dependence of the PDHS absorption spectra with $M_{w2}$ at the second thermal cycle



**Fig. 8.** Temperature dependence of the PDHS absorption spectra with $M_{w3}$ at the heating from 293 to 413 K
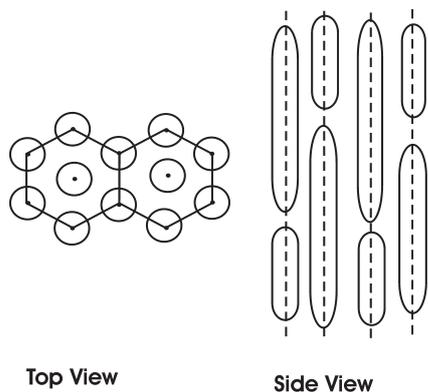


**Top View**      **Side View**

**Fig. 9.** Representation of the structure proposed for a PDHS film after the thermal treatment [7]

the luminescence spectrum ($T = 5$ K, $\lambda_{\mathrm{ex}} = 313$ nm) of PDHS films ($M_{w2}$ and $M_{w3}$) cooled after the heating, a weak long-wavelength band (Fig. 4) appears at $\lambda = 375$ nm in addition to the exciton band in the spectrum of the original sample at 371 nm.

## 4. Discussion of Results

We associate the appearance of two new absorption bands at 337 nm and 287 nm in the region of the band of *gauche*-conformation of the PDHS polymer with the formation of two LC phases at the heating of the film above the thermochromic transition temperature (Fig. 1). The spontaneous formation of LC phases in the PDHS polymer at these temperatures was indicated by studies of the diffraction of X-rays and electrons [7]. It was shown that the polymeric chains are oriented in this case in the form of cylinders in the hexagonal lattice (Fig. 9). The existence of the LC phase in PDHS was also confirmed by the observation of an optical texture on the surface of an annealed film, which is characteristic of the classical ordered structure of liquid crystals [8–10].

We may assume that the intramolecular disordering of side groups results in the allowedness of the motions of polymeric chains leading to an increase of the intermolecular interaction between adjacent polymeric chains. This can cause an enhancement of the orientation degree of adjacent polymeric chains and their ordering in the form of cylinders in the hexagonal lattice (Fig. 9). Thus, the heating of a polymeric film above the phase transition temperature initiates the spontaneous transition of the polymer in the LC phase. The LC phases appear, when the polymer is in *gauche*-conformation. Therefore, the formation of these phases and their variation with the temperature can be observed by the appearance of new specific features in their absorption spectra, namely in the region of the band of *gauche*-conformation. The study of the absorption spectra of PDHS films at the heating in the temperature interval 293–373 K confirms this assumption (Fig. 1). Indeed, Fig. 1 demonstrates the appearance of two new bands in the region of *gauche*-conformation in the absorption spectrum of a heated sample instead of a single band at 316 nm in the absorption spectrum of the initial sample at room temperature. The co-existence of these new bands in the absorption spectrum of PDHS at 337 and 287 nm up to a temperature of 423 K agrees with the bire-

fringence revealed by PDHS films at the heating of the polymer above the phase transition temperature, i.e., in the temperature interval 315–523 K [6]. It was shown that the birefringence decreases at the heating of the PDHS film, but does not vanish up to very high temperatures.

It is essential that the new bands shift to opposite sides. The displacement of the long-wave band (337 nm) to the long-wave side testifies, apparently, to a decrease of the distance between adjacent polymeric chains due to an increase of the intermolecular interaction between them. This result can be related, apparently, to an increase of the arrangement density of polymeric chains, which coincides with the data obtained in studies of the diffraction of X-rays. Since the new bands in *gauche*-conformation shift in different sides, we may assume that the LC phases are located at different distances from the substrate surface and are related to two types of ordering of polymeric chains with different lengths of segments (short and long), respectively. It should be emphasized that the study of optical spectra testifies to the appearance of two LC phases in the polymer, as distinct from the results of studies of the diffraction of X-rays [7], where a single LC phase was observed.

It is known that the absorption spectrum of the polymer is a superposition of segments with various lengths. The study of the absorption spectrum of the polymer at a low temperature ($T = 2$ K) showed that the absorption band at 365 nm (*trans*-conformation) become asymmetric, as the temperature decreases [15]. It was assumed that it consists of two bands (361 and 366 nm) that correspond to two different spatially separated absorption centers which have different distributions of the segment lengths of the polymer chain, i.e., with different collections of short and long segments, respectively. The presence of two types of absorptive packings can be traced at the heating of the film in the interval 293–308 K (Fig. 1). This is indicated by a shift of the band of *trans*-conformation at 365 nm to the short-wave side, as the temperature grows, to 356 nm at $T = 308$ K. Indeed, with increasing the temperature, the relatively long segments are disordered in the first place. Therefore, the absorption band at 365 nm that corresponds to the absorption of shorter segments is clearly seen. We assume that these two states in *trans*-conformation are the reason for the formation of two LC phases. The formation of these phases from relatively long and short segments of polymeric chains is supported by the fact that the distance between the bands at 287 and 337 nm is equal to the distance between the absorption bands of *trans*- and *gauche*-conformations in the spectrum of as-prepared films. The contribution of each of these LC phases can be changed, by varying the number of thermal cycles and the thickness of films.

As the number of heating cycles increases, the short-wave bands in the region of *gauche*- and *trans*-conformations become more intense than the corresponding long-wave bands (Fig. 5). This testifies to an increase of the degree of energy disordering of the polymer after the repeated heating.

It is known that if the film thickness decreases to less than 20 nm, the polymer Si-backbone disorders, and the extensive organization of polymeric chains is hindered [16]. This implies that the formation of LC phases must become complicated with decreasing the film thickness, which is observed in experiments (Fig. 2)

If the appearance of two new absorption bands in an annealed sample is related to two types of centers with different distributions of segment lengths of a polymeric chain, then, at its cooling, we would expect the presence of two bands instead of the single one of *trans*-conformation at 365 nm. It follows from Fig. 3 that, indeed, the absorption spectrum of the cooled sample contains two bands at 356 and 375 nm instead of the single one of *trans*-conformation at 365 nm.

At the formation of an LC phase, the polymeric chains orient relative to one another, which leads, apparently, to an increase of the concentration of long segments of a polymeric chain. Hence, while the polymeric PDHS film is cooled down to room temperature after the heating above the phase transition temperature, the length of segments of a polymeric chain should increase. Respectively, the excitation delocalization region should spread. This must cause a shift of the long-wave absorption band of *trans*-conformation of an annealed film to the long-wave side relative to the initial position. In the absorption spectrum of a film cooled down to room temperature after the heating (Fig. 3), we observe, indeed, the appearance of a band with maximum at 375 nm. This band is shifted by 10 nm to the long-wave side relative to the band in the absorption spectrum of the initial film, whose position and intensity depend on the annealing temperature and the annealing modes.

The additional conformation of the presence of oriented structures in *trans*-conformation of PDHS after its preliminary annealing is given by the appearance of the long-wave band in the luminescence spectrum of such sample ($M_{w1}$, $T = 5$ K), which is shifted to the long-wave side by 4 nm relative to the exciton band in the luminescence spectrum of the initial sample (Fig. 4). A significant broadening of this luminescence band as compared with the exciton band confirms the existence of defects in this polymer (Fig. 4). Indeed, as the temperature of the film decreases down to room temperature, the defect states related to the residual phenomena at the transformation of the polymer from the LC phase into *trans*-conformation must appear in the polymer. The bands at 287 and 343 nm in the region of *gauche*-conformation and the shoulder at 385 nm in the region of *trans*-conformation are related, apparently, to transitions in such defect states (Fig. 3). These defect states are related, apparently, to the formation of clusters in the polymer due to the intermolecular interaction of adjacent polymeric chains.

The studies showed that the formation of LC phases in a polymer depends essentially on its molecular weight and, respectively, the length of the Si-backbone. The studies of the adsorption (Fig. 1) and luminescence (Fig. 4) spectra indicate that the LC phases are formed most reliably in the polymer with $M_{w2}$ (the Si-backbone length is about 50 nm). In the polymers with less, $M_{w2}$, and large, $M_{w3}$, molecular weights, the formation of LC phases is hampered (Figs. 4, 6, and 8). These phases arise only at the repeated heating of films (Fig. 7) or at a higher temperature (Fig. 8). Since the formation of LC phases occurs at the heating above the phase transition temperature as a result of the orientation and the ordering of polymeric chains, the length of polymeric chains is significant for a reliable manifestation of these processes. The polymers with long Si-backbone (180 nm) require, apparently, higher temperatures for their motion and orientation. In the case of polymers with small lengths of a Si-backbone (18 nm), their organization due to a rather free motion is too complicated, which is observed in experiments.

## 5. Conclusion

By methods of optical spectroscopy, we have studied the process of formation of two LC phases in PDHS films, which was initiated by their heating above the thermochromic transition temperature. The manifestation of two LC phases is connected with the observation of two new bands in the region of the absorption band of *gauche*-conformation. It is assumed that the formation of two absorption centers corresponds to the different distributions of segments in a neat sample. The formation of LC phases is also related to the appearance of defect bands in the absorption spectra of annealed samples cooled down to room temperature. The defect states are, apparently, cluster structures that are formed as a result of the intermolecular interaction of adjacent polymeric chains.

The orientation of polymer chains arisen at the formation of the LC phase is related to the shifts of the absorption band of *trans*-conformation and the appropriate luminescence band in the spectra of annealed films to longer wavelengths.

1. R.D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1989).
2. H. Suzuki, H. Meyer, S. Hoshino, and D. Haarer, J. Appl. Phys. **78**, 2684 (1995).
3. A. Sharma, M. Katiyar, Deepak, S. Seki, and S. Tagawa, Appl. Phys. Lett. **8**, 143511 (2006).
4. Y. Nakayama, K. Hirooka, and R. West, Solid State Communic. **100**, 759 (1996).
5. R.D. Miller, D. Hofer, J. Rabolt, and G.N. Fickes, J. Am. Chem. Soc. **107**, 2172 (1985).
6. J.F. Rabolt, D. Hofer, R.D. Miller, and G.N. Fickes, Macromolecules **19**, 611 (1986).
7. A.J. Lovinger, F.C. Schilling, F.A. Bovey, and J.M. Zeigler, Macromolecules **19**, 2657 (1986).
8. P. Weber, D. Guillon, A. Skoulios, and R.D. Miller, J. Phys. France **50**, 793 (1989).
9. P. Weber, D. Guillon, A. Skoulios, and R.D. Miller, Liq. Crystals **8**, 825 (1990).
10. N. Ostapenko, V. Zaika, S. Suto, and A. Watanabe, Proc. of SPIE **5122**, 157 (2003).
11. E.K. Karikari, A.J. Greso, B.L. Farmer, R.D. Miller, and J.F. Rabolt, Macromolecules **26**, 3937 (1993).
12. J. Watanabe, H. Kamee, and M. Fujiki, J. Polymer **33**, 495 (2001).
13. T. Asuke and R. West, Macromolecules **24**, 343 (1991).
14. T. Kanai, H. Ishibashi, Y. Hayashi, K. Oka, T. Dohmaru, T. Ogawa, S. Furukawa, and R. West, J. of Polym. Sci. B. Polym. Phys. **39**, 1085 (2001).
15. M. Shimizu, S. Suto, T. Goto, A. Watanabe, and M. Matsuda, Phys. Rev. B. **58**, 5032 (2001).
16. M.M. Destopoulou, D.R. Miller, J.F. Rabolt, and C.W. Frank, J. of Polym. Sci. B. Polym. Phys. **34**, 2335 (1998).

*Н.І. Остапенко, Ю.В. Остапенко, О.О. Керіта*

ФОРМУВАННЯ РІДКО-КРИСТАЛІЧНОЇ
ФАЗИ В ПОЛІ(Ді-н-ГЕКСИЛСИЛАНІ)

Р е з ю м е

Вивчено формування рідко-кристалічної (РК) фази в плів-
ках полі(ді-н-гексилсилані) (ПДГС) при температурі вище
температури термохромного переходу, а також її еволюцію
при охолодженні зразків до кімнатної температури. З цією
метою досліджені спектри поглинання (293–413 K) і люмі-
несценції (5 K) залежно від температури та режимів від-
палу, товщини плівки і молекулярної маси полімеру. По-
казано, що формування двох РК фаз при нагріванні плів-
ки пов'язано з появою і трансформацією положення і ін-
тенсивностей двох нових смуг поглинання в області гош-
конформації, а також з появою двох смуг в області транс-
конформації охолодженої плівки. Передбачається, що фор-
мування двох РК фаз пов'язано з існуванням двох центрів
поглинання, які відповідають різним розподілам сегментів
по довжині в полімерному ланцюгу. Показано, що в полі-
мерах з трьома різними довжинами полімерного ланцюга
(18, 50 і 180 нм) РК фаза надійно спостерігається тільки в
полімері з довжиною Si-ланцюга 50 нм. Ми пов'язуємо по-
яву нових широких смуг в спектрі поглинання відпаленої
плівки ПДГС з дефектами, які відповідають залишковим
станам, що виникають після переходу термічно обробленої
плівки від РК стану до транс-конформації.