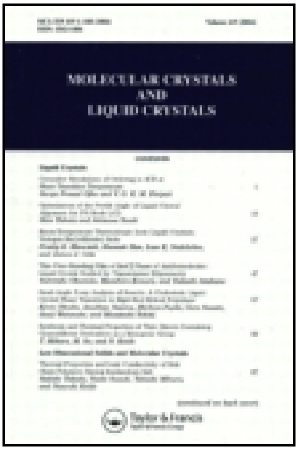

Molecular Crystals and Liquid Crystals

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Molecular conformation and orientation of silicon organic photoconductor films

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MOLECULAR CONFORMATION AND ORIENTATION OF SILICON ORGANIC PHOTOCONDUCTOR FILMS

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The conformational state and orientation of the films of poly(di-n-hexylsilane) (PDHS) were investigated in dependence on their annealing at the temperature over the temperature of the phase transition with the use of absorption (20–140)°C and luminescence (5K) spectra. The appearance of two new bands in the absorption spectra of the polymer in the region of the gauche conformation is explained with the formation of liquid crystal phase. The alignment of the PDHS backbones was confirmed by the study of orientation of liquid crystal on the surface of the annealed polymer film. Increasing orientational order and defects created during the cooling of the polymer film result in appearance of several new bands in the films absorption spectra after their cooling down to the room temperature.

Keywords: polysilanes; liquid crystal phase; conformation

INTRODUCTION

The use of polysilanes as hole transport layers in light emitting devices stimulates studies of polymer chain orientation and state of chain organization in these polymers, as far as they play essential role in determining properties of these polymers [1,2]. Poly(di-n-hexylsilane) (PDHS) is one of the most investigated polysilanes. In this polymer there is a phase transition of the order-disorder type ($T_c = 42°C$) [3]. The polymer chain of PDHS is in trans conformation below T_c and above this temperature the gauche conformer

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arises. Absorption peak of PDHS is observed at 365 nm below T_c and another peak appears at 316 nm above T_c. This essential shift of the absorption spectrum [3] is an evidence for the significant sensitivity of the polymer properties to the conformational changes and ordering of polymer fragments. It was found from the X-rays diffraction measurements that liquid crystal (LC) mesophase spontaneously appears in PDHS at temperatures above T_c [4]. The LC structure of PDHS was also confirmed by studying of the polymer films at $T = 80°C$ with the use of the polarization optical microscope [5].

In this work, we study formation of the LC phase in the PDHS and its evolution under variation of the temperature and film thickness, as well as the changes in conformation and orientation of the PDHS films at cooling the system down from 180°C to the room temperature. The methods of investigations include the study of absorption (20–180°C) and luminescence (5 K) spectra and the birefringence of the film before and after its thermal treatment. At present, we know only one work where the authors investigate the abnormal thermochromic behavior in the absorption spectra of poly(di-n-oktyl)silane [6].

EXPERIMENTAL

We used PDHS with molecular weight $M_w = 51{,}000$ and with distribution $M_w/M_n = 1.37$. The films were spin-coated from toluene solution onto quartz glass substrates. The absorption spectra of the PDHS film were recorded with the use of KSVU-23 spectrometer. The temperature dependence of absorption spectra of the PDHS films has been measured at continuous heating in the 20–180°C temperature range as well as after subsequent cooling down to room temperature. Photoluminescence (PL) spectra at $T = 5K$ were measured with the use of Hitachi fluorescence spectrophotometer. Excitation was performed by monochromatic ($\lambda_{exc} = 313$ nm) light from a 250 Wt xenon lamp. For the study of orientation of PDHS films, which arises after thermal treatment, we made two cells. The cells were based on PDHS substrates and LC was filled in these cells. In one of them, nematic liquid crystal E-7 (Merck) was disposed onto the surface of the initial film. In the second, liquid crystal was disposed onto the polymer immediately after its thermal treatment at 80°C during 40 min. In addition, we studied the birefringence of the films before and after thermal treatment of the films. In this case we used a transmission ellipsometry technique [7].

RESULTS AND DISCUSSION

In Figure 1 we present the temperature dependence of PDHS films absorption spectra at continuous heating in the temperature range of

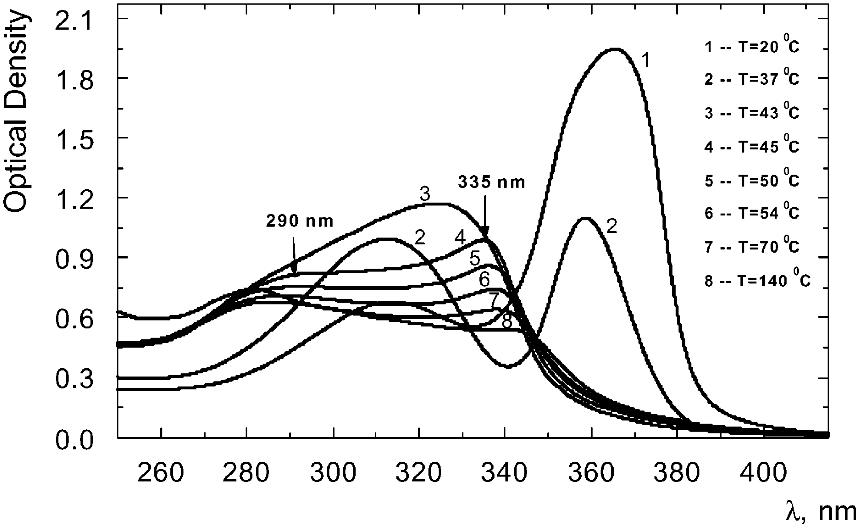

FIGURE 1 Temperature dependence of PDHS film UV absorption spectra at continuos heating in the range of 20–140°C.

(20–140)°C. The absorption spectrum of PDHS film at 20°C consists of two bands with maximum, respectively, at 365 nm (trans conformation) and 316 nm (gauche conformation). It is known [3], that at the heating of this films to the T_c, the polymers transfer from the trans conformation to the gauche one. In this case, the 316 nm band should dominate in the absorption spectrum. One can see from Figure 1 that in our case we have significant changes in the region of the 316 nm band. Even small heating over the phase transition temperature leads to the appearance of two new bands instead of the 316 nm band. Namely, there arise a band with a maximum at ~335 nm and a band with a maximum at ~290 nm. The further increase in the temperature of the film up to 140°C leads to changes in both the intensities and shifts of these bands. The intensity of each band with a temperature increasing behaves in a different manner: the intensity of the 335 nm band decreases, as well as the band 290 nm up to 140°C, which increases at further heating. The direction of shift of these bands is opposite to each other. The 335 nm band shifts towards the long-wavelength side, whereas the other one at 290 nm towards the short-wavelengths, both by 10 nm.

The appearance of two new absorption bands (335 and 290 nm), their positions, as well as their intensities in absorption spectra of PDHS film at continuous heating up to temperatures above the phase transition temperature strongly depend on the thickness of the film under study. These bands can be reliably detected in the absorption spectra of the films having optical density higher then 1, and they are not observed at all in the thin films, for example, in the films with optical density less than 0.4. When the film thickness decreases, the 335 nm band is shifted towards short-wavelengths by 9 nm and its intensity decreases (Fig. 2). The maximum of the blue band undergoes essentially smaller shift to the long wavelengths.

After cooling the film down to the room temperature and keeping it for one day after the preliminary annealing, several bands are observed in the absorption spectrum of the film. We have two new bands at 275 nm and at 342 nm in the region of the gauche conformation, and three new bands at 356, 374 nm, and 385 nm with a rather overextended long-wavelength wing (up to 425 nm) in the region of the trans conformation (Fig. 3). It should be emphasized, that the maximum of the band at 385 nm depends on the time storage of the sample at room temperature.

One should note that the birefringence of the annealed PDHS film, measured at room temperature, increases in two times as compared with the corresponding value for the initial sample.

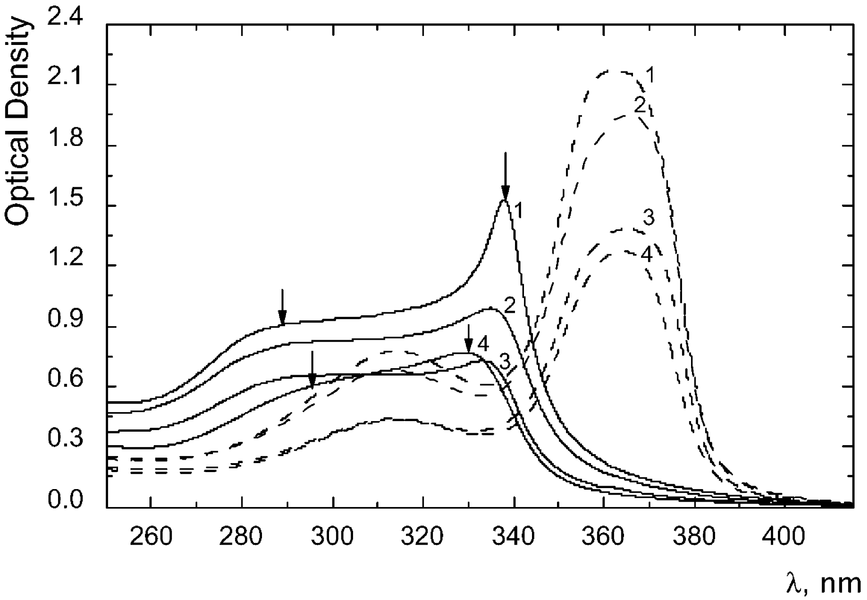

FIGURE 2 Dependence of the PDHS absorption spectra on the film thickness (dotted line corresponds to 20°C and solid line corresponds to 45°C). Thickness of the films decreases as the curve number increases. Arrows indicate maxima of the bands.

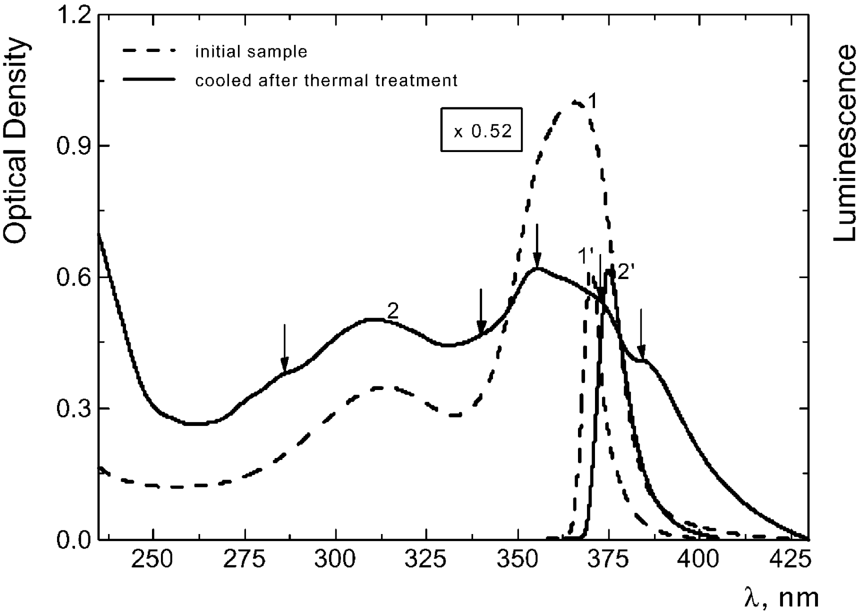

FIGURE 3 Absorption (1, 2) and luminescence (1′, 2′) spectra of initial sample (dotted line) and sample cooled to the room temperature after thermal treatment at 140°C (solid line). Arrows indicate the new bands in the absorption spectra of the cooled films.

In the luminescence spectrum ($T = 5\,K$, $\lambda_{exc} = 313\,nm$) of the cooled PDHS film, after continuous heating up to 140°C, arises a single band with $\lambda = 375\,nm$, shifted by 4 nm towards the long-wavelength side with respect to the luminescence band of the initial sample ($\lambda = 371\,nm$) (Fig. 3). The half-widths of these two bands differ from each other in two times, having the 375 nm band broader.

The orientation behaviour of the PDHS films after annealing was studied by the investigation of the alignment of nematic liquid crystal (E-7) in the symetric cell with thin films of the polymer as orienting layers. We found that the homeotropic orientation of the liquid crystal appeared only when the films had been preliminary annealed at 80°C for 40 min. The orientation of the liquid crystal was observed to be stable during several weeks. In the case of nonannealed films the multidomain texture of the liquid crystal appeared.

We associate the appearance of two new absorption bands at 335 nm and 290 nm (Fig. 1) with the formation of the liquid crystal phase in the polymer. It was supposed that the intermolecular interaction of polymer chains leads to the increase of both the alignment of neighbouring polymer

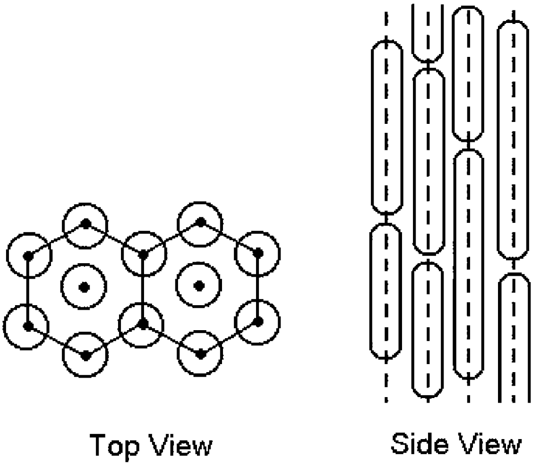

FIGURE 4 Pictorial representation of the structure proposed in [4] for the PDHS.

chains relative to each other and their packing as well as to the formation of LC phase in the polymer (Fig. 4). This is in good agreement with a presence of these bands in the spectra corresponding to temperatures up to 180°C as well as with the birefringence of PDHS films, observed in this temperature range [5]. The formation of the liquid crystal phase in the polymer, i.e., the appearance of oriented structures, is confirmed by the study of the alignment of the liquid crystal, placed on the polymer surface immediately after its keeping at the temperatures at which the liquid crystal phase should arise. We have shown that in this case we observe a homeotropic orientation of the liquid crystal. This orientation is conserved for a long time after cooling the sample down to the room temperature. This allows us to conclude that the orientation of the liquid crystal appears due to the orientation of the polymer after its keeping at the temperatures above the phase transition.

The appearance dynamics of the 335 nm band and its temperature behavior are qualitatively similar to the formation of the LC phase and its changes studied by X-ray diffraction. We assume, that the shift of this band towards the long-wavelength direction is probably an evidence for the decrease of the distance between the polymer chains due to the increase of the packing of neighboring polymer chains. The fact that the direction of the shift of new absorption bands (335 and 290 nm) is opposite allows one to consider their belonging to two different phases, located at different distances from the substrate. One can even suppose that formation of LC structures, based on two type segments with different lengths, is thermodynamically favorable.

The liquid crystal phase arises in polymer at temperatures above the phase transition due to the orientation and packing of neighboring polymer chains [5] (Fig. 4). When the temperature of the film decreases down to the room temperature, PDHS transfers to the trans-conformation, and defect states should arise in the polymer, which is connected with residual phenomena during this transformation of the film into the trans-conformation. The band with maximum at 342 nm in the region of the gauche conformation and with maximum at 385 nm in the region of trans-conformation are probably caused by such defect structures. These defects are probably caused by the formation of clusters in the polymer due to the intermolecular interactions of neighboring polymer chains. In the luminescence spectrum, this defect (385 nm) is not observed at all, probably due to the weak energy transfer in one-dimensional systems in the direction perpendicular to the polymer chain. The broadening of this luminescence band, compared to the one of the initial sample, confirms the defect structure of annealed samples.

It follows from the X ray investigations [4] that, at cooling of the PHDS polymer film down to the room temperature after preliminary annealing, the segment length of the polymer chain in the trans conformation increases, i.e., increases the length of the excitation delocalization. This process should lead to some shifts of the absorption band of the trans conformation towards the long-wavelength side in the absorption spectrum of the film (Fig. 3). Experimentally, it is really arisen a more long-wavelength absorption band with a maximum at 374 nm, whose position depends on the temperature and the regime of thermal treatment. The presence of more oriented structure in trans conformation of PDHS film after preliminary annealing is indicated by the appearance of the new luminescence band ($T = 5$ K), red shifted with respect to the luminescence band of the initial film by 4 nm (Fig. 4).

One more evidence of the orientational order increasing in PDHS at room temperature after annealing is a twice increase of the birefringence of the film in this case, as compared with the value obtained at room temperature for the initial sample. The polarization studies of PDHS films on the azobenzene oriented substrate [8] also showed that subsequent cooling of this sample down to the room temperature after annealing results in the increased orientational order. The same effect is obtained when the molecules of some liquid crystals are incorporated into the polymer [9].

CONCLUSION

By the methods of optical spectroscopy we have studied the appearance and genesis of the LC phase in PDHS films under their continuous heating above the temperature of phase transition as well as changes in their conformation and orientation at cooling the system down to room temperature. We have shown that the transitions from the phase with dominating trans-conformation to gauche-conformation one and vice versa are accompanied by prominent changes in conformation and organization of PDHS films. We assume that the appearance of new bands in the region of gauche-conformers at temperatures above the temperature of phase transition is associated with the formation of the LC phase. This agrees with the presence of birefringence in the PDHS films at these temperatures and with the observed orientation of E-7 liquid crystal disposed on the annealed sample of PDHS.

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