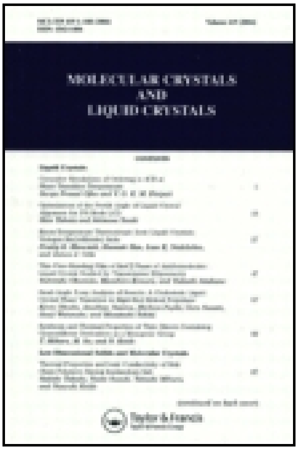

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoluminescence Study of Photodegradation of Polysilanes

Yu. Skryshevski [a], N. Ostapenko [a], A. Kadashchuk [a], A. Vakhnin [a] & S. Suto [b]

[a] Institute of Physics, NASU, Prosp., Nauki 46, 252022, Kiev, Ukraine

[b] Department of Physics, Tohoku University, Sendai, 980-8578, Japan

Version of record first published: 24 Sep 2006

To cite this article: Yu. Skryshevski, N. Ostapenko, A. Kadashchuk, A. Vakhnin & S. Suto (2001): Photoluminescence Study of Photodegradation of Polysilanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 361:1, 37-42

To link to this article: http://dx.doi.org/10.1080/10587250108025715

Mol. Cryst. and Liq. Cryst., 2001, Vol. 361, pp. 37-42
Reprints available directly from the publisher
Photocopying permitted by license only

Photoluminescence Study of Photodegradation of Polysilanes

YU. SKRYSHEVSKI[a], N. OSTAPENKO[a], A. KADASHCHUK[a],
A. VAKHNIN[a] and S. SUTO[b]

[a]*Institute of Physics, NASU, Prosp. Nauki 46, 252022, Kiev, Ukraine and*
[b]*Department of Physics, Tohoku University, Sendai 980–8578, Japan*

Photodegradation in poly(methylphenylsilane) (PMPS) and poly(di-n-hexylsilane) (PDHS) films was studied by absorption and luminescence spectroscopy at T=295 and 5 K as function of wavelength, λ_{irr}, and duration of UV-irradiation, t_{irr}. It was shown that irradiation at longer wavelengths results in the scission of the longest segments of the polymer chain, while the short-wavelength irradiation leads to the scission of both the short and the long segments. This is due to competing processes of scission of short segments and energy transfer to long segments. The conformational transformation of polymer chain of irradiated PDHS from trans-conformation into helix-conformation has been found.

Keywords: poly(methylphenylsilane); poly(dihexylsilane); trans-helix chain conformation; luminescence; absorption spectra; photoscission

INTRODUCTION

The σ-σ* transition absorption band of polysilanes (PS) lies in the near UV region. It is known [1-2] that UV irradiation of PS at T=295 K leads to the photoscission of Si-Si bonds. The observation of the progressive blue shift in the maximum of the σ-σ* absorption band suggested that the polymer molecular weight was being reduced [1,2]. It was supposed [3,4] that in PS there is an energy transfer to the longest segments and photochemical events occur in these segments. On the other hand, the rise time of transient absorption signals assigned to a radical is close to the lifetime of exciton luminescence in PS [4,5]. Therefore, one might assume that the scission of Si-Si bond and the transfer of the excitation to the longest segments are competitive processes. To prove the above suggestions the dynamics of the excited state and photodegradation of PDHS and PMPS films as function of λ_{irr} and t_{irr} were investigated by measuring and analyzing absorption (T=295 K) and luminescence (T=5 and 295 K) spectra.

EXPERIMENTAL

The 1 μm thick PMPS and PDHS films were prepared from toluene solution by casting onto quartz substrates. Absorption and luminescence spectra of PS films were obtained using KSVU-23 and SDL-1 spectrometers, respectively. Excitation and photodegradation of the films were performed by the light from Hg lamp using filters for selection of λ_{irr}.

RESULTS AND DISCUSSION

Absorption spectrum of PDHS films at 295 K consists of two bands at 375 nm (trans-conformation) and 317 nm (helix-conformation) (Fig.1, curve 1). Luminescence spectrum at T=5 K excited at λ_{ex}=313 nm consists of a sharp exciton band at λ=371 nm and a weak structureless shoulder at λ=400-600 nm (Fig.2, curve 1). The PMPSi films show σ-σ* absorption band at 337 and π-π* band at 275 nm at T=295 K (Fig.3, curve 1). The luminescence spectrum of PMPS at T=5 K (λ_{ex}=313 nm) (Fig.4, curve1) consists of exciton band at λ_{max}=350 nm and a broad

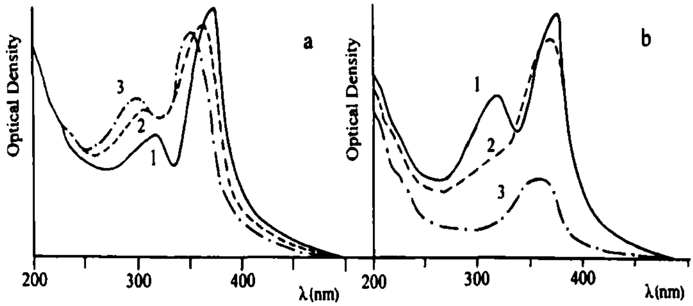

FIGURE 1 Absorption spectra of PDHS films vs. irradiation time at T=295 K with: a) λ_{irr}=405 nm, t_{irr}=0, 3 and 15 minutes (curve 1, 2 and 3, respectively); b) λ_{irr}=265 nm, t_{irr}=0, 3 and 6 minutes (curve 1, 2 and 3, respectively).

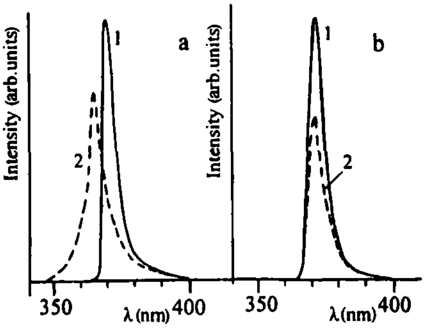

FIGURE 2 Luminescence spectra of PDHS films (λ_{ex}=313 nm, T=5 K) after irradiation at T=295 K with: a) λ_{irr}=405 nm, t_{irr}=0 and 60 minutes (curve 1 and 2, respectively); b) λ_{irr}=265 nm, t_{irr}=0 and 60 minutes (curve 1 and 2, respectively).

band at λ_{max}=415 nm which was assigned to the emission from a charge-transfer state [6]. After irradiation of PS films with the light in λ_{irr}=265-405 nm region at T=295 K, irreversible changes occur in their absorption spectra. The shape and maximum of the exciton band strongly depend on λ_{irr}. These changes intensify with increasing t_{irr}.

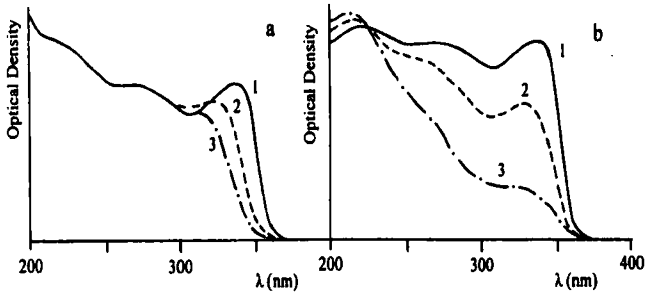

FIGURE 3 Absorption spectra of PMPS films vs. irradiation time at T=295 K with: a) λ_{irr}=365 nm, t_{irr}=0, 3 and 50 minutes (curve 1, 2 and 3, respectively); b) λ_{irr}=265 nm, t_{irr}=0, 10 and 30 minutes (curve 1, 2 and 3, respectively).

Decrease of absorption at the red edge of σ-σ* band and its blue shift by 25-30 nm occur for PMPS and PDHS films after irradiation with λ_{irr}=405 and λ_{irr}=365 nm (at the red edge of the σ-σ* absorption band) (Fig.1a, curve 2, 3 and Fig.3a, curve 2, 3). Similar change was also seen in the luminescence spectrum where decrease of the exciton band intensity and a blue shift were found (Fig.2a, curve 2 and Fig.4a, curve 2, 3). Thus, the observed spectral changes can be related to the selective scission of the longest segments. It should be noted that the changes related to conformational transformations in polymer chain were found in the absorption spectra of PDHS films irradiated with λ_{irr}=405 and 365 nm light. As one can see from Fig.1a (curve 1, 3), such irradiation results not only in decrease of absorption at 375 nm, but also in increase of the intensity and a blue shift of the absorption band at 317 nm. Thus, short segments formed after scission of the long segments in the trans-conformation partially transform into the helix conformation. It was found that the decrease of the entire σ-σ* absorption band of PMPS, as well as the decrease of both absorption bands of PDHS after irradiation at λ_{irr}=313 nm, is caused by the scission of both long and short segments. This results in small blue shift of exciton luminescence band of PS. This is also proved by similar decrease of the both absorption bands of PS films under irradiation with λ_{irr}=265 nm, i.e. at the blue edge of the absorption band of PDHS helix-conformation and near the maximum of the π-π* band of PMPS (Fig.1b, curves 2, 3 and Fig.3b, curves 2, 3). There is no shift of exciton luminescence bands of PDHS (Fig.2b, curve 2) and PMPS (Fig.4b, curves 2,3) while their intensities decrease.

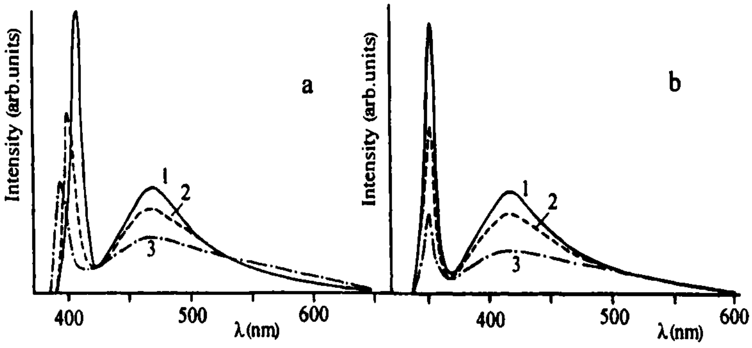

FIGURE 4 Luminescence spectra of PDHS films (λ_{ex}=313 nm, T=5 K) after irradiation at T=295 K and t_{irr}=0, 5 and 60 minutes (curve 1, 2 and 3,respectively) with: a) λ_{irr}=365 nm; b) λ_{irr}=265 nm.

Therefore, we can conclude that after the irradiation of the films with λ_{irr}=265 nm the degradation of the short rather than the long segments occurs mainly. The essential result is as follows. Irradiation of PS films with all used λ_{irr} causes changes in absorption spectra that can be assigned to the selective scission of long or short segments. However, the changes in their luminescence spectra weaken when λ_{irr} decreases from 405 to 265 nm. Since the luminescence occurs from the longest segments, we assume that irradiation at 313 and 265 nm leads to the selective scission of short segments that competes with the process of energy transfer to the longer ones.

It was found that photodegradation of PS films occurs even at T=5 K at large light exposures. It correlates well with hole-burning observed in the spectra of PDHS films at T=1.4 K [4]. Besides, the luminescence band of the defect at λ=377 nm, which was earlier assigned to the vibronic replica [7], was clearly observed after λ_{irr}=365 nm irradiation. Intensity of this band is almost 50 times smaller than the intensity of exciton band. This band was not observed when shorter λ_{irr} was used. The intensity of this band increases tenfold when the sample is irradiated with unfiltered UV-radiation of Hg lamp at T=5K for 15 min. At the same time, intensity of the exciton band decreases and a slight blue shift (~1 nm) is observed. The defect band disappears after irradiation with λ_{irr}=313 nm light at T=295 K (60 min) and it is not observed after repeated irradiation at T=5 K. This implies that this band is connected to the conformational defects of polymer chain which are formed during polymer irradiation within its absorption band (trans-conformation) at T=5 K and destroyed after irradiation at T=295 K.

References

[1] R.D. Miller, J. Michl. *Chem. Rev.* **89**, 1359 (1989).

[2] M. Sawodny, J. Stumpe, W. Knoll. *J. Appl. Phys.* **69**, 1927 (1991).

[3] H.P. Trommsdorf, J.M. Zeigler and R.M. Hochstrasser. *Chem. Phys. Lett.* **154**, 463 (1989).

[4] J.R.G. Thorne, S.T. Repinec, S.A. Abrash, J.M. Zeigler and R.M. Hochstrasser. *Chem. Phys.* **146**, 315 (1990).

[5] Y. Ohsako, J.R.G. Thorne, C.M. Phyllips, J.M. Zeigler and R.M. Hochstrasser. *J. Phys. Chem.* **93**, 4408 (1989).

[6] O. Ito, M. Terazima, T. Azumi, N. Matsumoto, K. Takeda and M. Fujino. *Macromolecules* **22**, 1718 (1989).

[7] A. Tilgner, H.P. Trommsdorf, J.M. Zeigler and R.M. Hochstrasser. *J. Chem. Phys.* **96**, 781 (1992).