Macromol. Symp. **2004**, *212,* 461-466

Optical Spectroscopy of Polysilylene Films

Yevhen V. Demchenko,[1] *Josef Klimovič,**[1] *Stanislav Nešpůrek*[1,2]

[1] Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic
E-mail: klimovic@kmf.troja.mff.cuni.cz; Fax: (+420) 221 912 351
[2] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

Summary: Luminescence of poly[cyclohexyl(methyl)silylene] films was studied by time-resolved emission spectroscopy at temperatures from 15 K to 300 K. The main short-wavelength peak, shifted with rising temperature to lower energies, showed time features typical of an energy donor. Three weak emission centres were found in the visible spectral region. They decayed more slowly having the time features of an energy acceptor. The rise in temperature made both the energy transfer and extension of the effective σ-conjugation length more efficient. Model calculations of the chain conformation energy showed the close-to-all-trans and gauche helix minima for iso- and syndiotactic sequences and barriers between them.

Keywords: conjugated polymers; luminescence; molecular modeling; polysilylenes; time-resolved spectroscopy

Introduction

Polysilylenes are a linear arrangement of covalently bonded silicon atoms with interesting electronic structure and photophysical properties[1-3]. Optical spectra of polysilylenes with alkyl side groups reflect mainly the transitions between electronic states of the σ-conjugated system of the silicon main-chain atoms. If the side groups contain a π-electron system, the energy states contain a contribution of a mixture of π- and σ-orbitals. Experiments with oligomers shorter than 20 silicon atoms in solutions showed[2] that with rising number of chain atoms, both the absorption and luminescence spectral maxima related to the lowest electron transitions were shifted to the red and the luminescence lifetime shortened.

An important condition for an effective π-conjugation is the stiffness of the backbone of the macromolecule. An array of single-bonded silicon chain atoms in polysilylenes is

DOI: 10.1002/masy.200450858

different. Its conformation can change due to the possibility of rotation around the chain single bonds. Thus, the extent of σ-conjugation must be a function of both the length and the conformation state of the oligomer or polymer chain segments. This fact complicates the explanation of a number of experimental facts. For example, thermochromism of polysilylene solutions often observed during cooling was explained by temperature changes in the conformational preferences of the chains[1]. By conformation changes was also explained the considerable spectral red shift observed in stress-oriented polysilylene samples[1].

We report here the changes in luminescence spectra of poly[cyclohexyl(methyl)silylene], p(cHxMeSi), films caused by temperature changes in the region from 15 to 300 K. p(cHxMeSi) is structurally similar to the often studied poly[methyl(phenyl)silylene]. On the other hand, the electronic structure of p(cHxMeSi) is simpler because the alkyl side groups do not change the nature of the electronic states of the σ-conjugated system of silicon atoms. In the used temperature region, the polymer under study was deep in its glassy state and, thus, only small conformation changes could occur. The aim of this work is to find the influence of temperature on the conjugated system of p(cHxMeSi) under the condition that conformation changes are strongly limited.

Experimental

Poly[cyclohexyl(methyl)silylene], p(cHxMeSi), $T_g = 399$ K, was prepared by Wurtz coupling polymerization. Films were prepared from a toluene (UV spectroscopy grade) solution by casting on polished Cu substrates or UV quartz glasses, dried under toluene vapor and then in vacuum. Their thickness was around 10 μm for luminescence and less than 1 μm for absorption measurements. Samples were placed inside an optical refrigerator (Air Products Ltd.). Absorption was measured using a Hitachi 3000 spectrophotometer.

In emission studies, the samples were excited by the 311 nm nitrogen line of a pulse nanosecond lamp (Applied Photophysics Ltd.) selected with an absorption UV filter and interference filter (Hg313, Melles Griot), at 45° to the film surface. Luminescence was measured at 90° to the sample surface, analysed with a grating monochromator (Jobin-Yvon Model H.20 VIS), and detected with a cooled photomultiplier (Philips Model XP2254B) in the time-correlated single-photon counting regime. At every wavelength (usual bandpass 8 nm), the whole time dependence of the luminescence response was detected. By integration (computer summation) in the time period of the whole response curves, the total spectrum (equivalent of the stationary spectrum) was obtained. The spectrum was corrected for the spectral dependence of the sensitivity of the detection part of the spectrometer. The emission decay function was determined from the time-response curve of luminescence at a chosen wavelength and from the time shape of the scattered excitation pulse by computer deconvolution (Levenberg-Marquardt procedure).

Results

The conformation of the p(cHxMeSi) chain was modeled using commercial program *Cerius2* (Biosym Technologies, Inc.), with the force field based on the quantum mechanical calculations of Sun[4]. Segments of Si chains with Si atoms were constructed in the zig-zag (all-trans) conformation, the side groups being positioned in both the isotactic and syndiotactic sequence. All torsion angles around the chain Si-Si bonds were fixed at a certain value (of a set of angle values) and, by the minimization procedure, all the other space parameters were determined for the state of minimal intramolecular interaction energy of the segment at a chosen torsion angle. The results are seen in Figure 1.

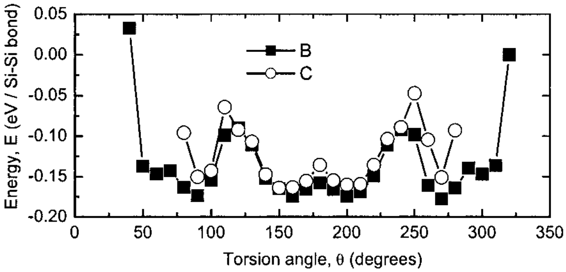

Figure 1. The conformation energy of isotactic and syndiotactic chain segments of p(cHxMeSi) as a function of the torsion angle of the Si-Si bonds.

Due to the bulky side-groups, the all-trans conformation is not exactly zig-zag but forms an open helix (torsion angle near 20°). The torsion angle dependence of conformation energy does not differ substantially between iso- and syndiotactic chains. The position and the energy of trans and gauche minima differ only little, the barrier between them is ca. 0.1 eV high. These results show that the intramolecular conformation energy determines the space arrangement of the chains only partly; a substantial role in this respect must play the intermolecular interactions.

UV absorption and photoluminescence parts of spectra of p(cHxMeSi) in toluene solution at room temperature are shown in Figure 2. The absorption spectrum corresponds well to the literature data: a strong narrow absorption peak with a maximum at 320 nm. The absorption spectrum of a p(cHxMeSi) film is almost the same.

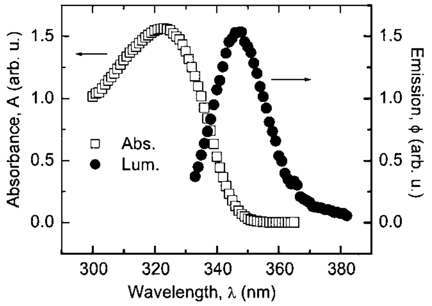

Figure 2. UV absorption and emission parts of the spectra of p(cHxMeSi) in a toluene solution at room temperature.

The photoluminescence of p(cHxMeSi) films consists of a strong narrow peak at 348 nm observed also in solution and of a broad very weak emission in the range from 380 to 550 nm. The intensity difference of the two emissions was so high that it was necessary to measure and analyze them separately.

The shapes of the short-wavelength emission peaks at different temperatures are plotted in Figure 3. It can be seen that the position of the peak maximum is influenced by temperature; it is shifted from approx. 3.6 eV at 45 K to 3.5 eV at 270 K. In the time-resolved spectra, no important differences in the shapes were detected. The luminescence decay measurements on films confirmed a rapid decay. For achieving satisfactory deconvolution, a sum of four exponentials was necessary to express the decay. The shape of the decay curves was typical of a donor of excitation energy in the presence of acceptors (the Foerster-type decay curve, see Ref.[5] for details). Within the frame of the Foerster model, the lifetime of the donor chromophores (conjugated parts of chains) without the presence of energy acceptors is around 0.6 ns (in the spectral band from 340 to 348 nm) at 15 K. By rising the temperature, the energy transfer becomes faster and the lifetime a little shorter. In a toluene solution at room temperature, this lifetime was close to 0.5 ns.

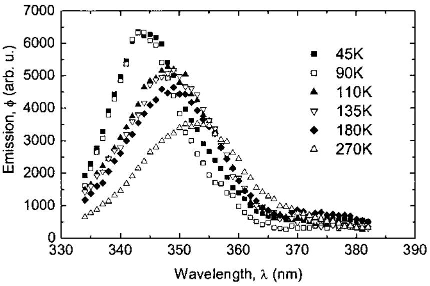

Figure 3. The total spectra of the short-wavelength strong emission peak of a p(cHxMeSi) film at different temperatures.

In Figure 4 is plotted the emission spectrum of p(cHxMeSi) film measured in the spectral region from 380 to 550 nm at 15 K. At this temperature, the intensity of the emission is sufficiently high and the shape of possible components is well expressed (raising the temperature the total intensity falls down).

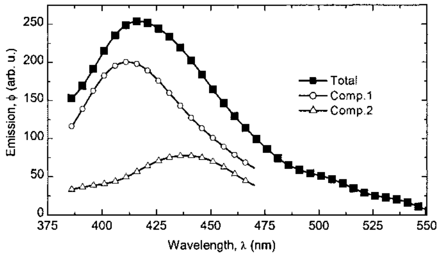

Figure 4. The total long-wavelength emission spectrum of p(cHxMeSi) films at 15 K and its components.

The time-resolved spectra showed a shift of the emission maximum towards lower energies with time. The analysis leads to the conclusion that the total spectrum consists of two major overlapping components with maxima at around 412 and 438 nm (which are also shown in Figure 4) and a weak additional band at around 500 nm. The long-wavelength luminescence decays much more slowly than the UV main band emission. The decay curves (measured in the 8-nm-broad region around 430 nm) were again complicated (satisfactory was deconvolution using a sum of several exponential functions was satisfactory). The shape of the decay curve was typical of an acceptor of excitation energy including a short initial period of rising intensity (cf. Ref.[5] for details). The lifetime of the excited state of acceptor(s) was found to be 5.9 ns at 15 K. On raising temperature, the intensity of this emission is strongly quenched. In toluene solution at room temperature, the intensity was too low to allow a detailed analysis.

Discussion and conclusions

The absorbing chromophores of the alkyl-substituted polysilylene films are mainly the segments of the Si chain regular in tacticity and conformation (very probably the gauche helices). Due to the proximity of other chain segments, the excitation can rapidly migrate through the film. The distribution of emitting conjugated segments can thus differ from that of absorbing species (this is a part of the observed Stokes shift). Excitation is also transferred to other centres emitting at lower energies. The rate of the energy transfer added to the rate of nonradiative and of fluorescence processes causes the observed rapid decay of the fluorescence. The observed red shift of the emission on heating the film above 90 K (Figure 3) can hardly be ascribed to the conformation changes (glassy state). It can be the result of the changes in the relaxation properties of the chain parts surrounding the emitting segment or of the lowering of the barriers between conjugated segments related to local irregularities in the conformation caused by rising chaotic thermal motion.

The time-resolved measurements of the weak broad visible emission of p(cHxMeSi) show that it consists of three components and that their emission decays much more slowly than that of the main short-wavelength emission. For the explanation of the sources of similar emission observed in other polysilylenes, a number of suggestions can be found in the literature including impurities, local chemical defects, triplet or excimer states, branching points or weakened Si–Si bonds. Our above-described experiments are not sufficient for their identification.

Acknowledgement

The authors wish to express their thanks to Mr. S. Zubarev for help with the model calculations and to the Computer Center of the Czech Technical University for access to the facilities. The financial support by grants No. 12/96/K of the Grant Agency of the Academy of Sciences of the Czech Republic, No. 202/01/0518 of the Grant Agency of the Czech Republic, and No. ME 440 of the Ministry of Education, Youth and Sports of the Czech Republic is gratefully appreciated.

[1] L.A. Harrah, J.M. Zeigler, *Macromolecules* **1987**, *20*, 601.

[2] Y. Kanemitsu, in: *"Photonic Polymer Systems"*, D.L. Wise, G.E. Wnek, D.J. Trantolo, T.M. Cooper, J.D. Gresser, Eds., M. Dekker, Inc., NewYork-Basel-Hong Kong 1998, pp.1-32.

[3] S. Nešpůrek, A. Eckhardt, *Polym. Adv. Technol.* **2001**, *12*, 427.

[4] H. Sun, *Macromolecules* **1995**, *28*, 701.

[5] J.B. Birks: *"Photophysics of Aromatic Molecules"*, Wiley-Interscience, London-N.Y.-Sydney-Toronto 1970, Chapter 11.