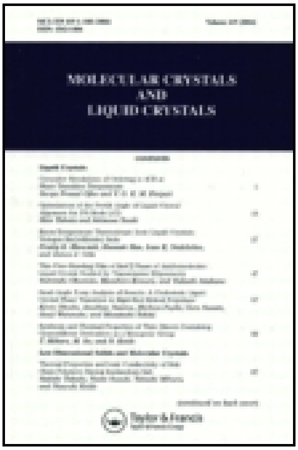

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Conformation Dependence of Electronic Structures in Polysilanes

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To cite this article: Hiroaki Tachibana , Yasujiro Kawabata , Yutaka Moritomo , Shin-Ya Koshihara , Yoshinori Tokura & Robert D. Miller (1992): Conformation Dependence of Electronic Structures in Polysilanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 65-70

To link to this article: http://dx.doi.org/10.1080/10587259208046878

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 65–70
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Printed in the United States of America

CONFORMATION DEPENDENCE OF ELECTRONIC STRUCTURES IN POLYSILANES

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Abstract Optical spectra (ordinary absorption, photoluminescence, electro-absorption, and two-photon absorption spectra) have been investigated for thin films of polysilanes with a variety of backbone conformations such as trans planar, alternating trans-gauche, helical, and disordered forms. The results observed have revealed new features of one-dimensional exciton states characteristic of each conformation of the polymer backbone.

INTRODUCTION

Polysilanes are σ-electron conjugated Si-polymers associated with a direct gap for the band-to-band transition.[1] The backbones of polysilanes take a variety of conformations such as trans planar, alternating trans-gauche, 7/3 helical, and disordered forms, depending on alkyl-substitutes attached to the polymer backbones (Fig.1). Optical properties of polysilanes (absorption, luminescence, and nonlinear optical susceptibility, etc.) are significantly affected by the conformation structures of the backbones.

In this paper, we have spectroscopically investigated the conformation dependence of exciton structures in solid films of poly(dihexylsilane) (PDHS), poly(ditetradecylsilane) (PDTDS), and poly(dibutylsilane) (PDBS), which show trans planar, alternating trans-gauche (TGTG'), and 7/3 helical conformations, respectively.

RESULTS AND DISCUSSION

Alkyl-substitutes polysilanes, PDHS, PDTDS, and PDBS were synthesized by the method described previously.[2] Photoluminescence (PL) spectra were measured by photo-excitation at 4.0 eV using a high-pressure mercury lamp. For the measurement of electro-absorption (EA) spectra, sinusoidal electric field (f=1 kHz) was applied along the normal of the films and the modulated signals were detected at a frequency of 2f with a lock-in amplifier. Two-photon absorption spectra were recorded monitoring the intensity of the PL as a function of twice the photon energy of the exciting laser pulse.

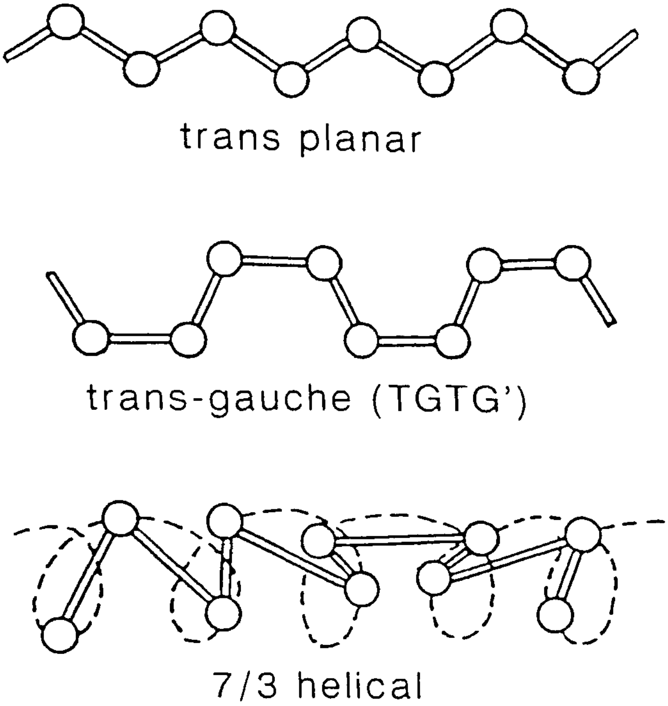

FIGURE 1. Backbone conformation of polysilanes

Figure 2 shows ordinary absorption (OA) spectra for thin films of PDHS, PDTDS, and PDBS and their changes upon thermally induced conformational transitions from the regular backbones to disordered ones. PL spectra of the ordered conformations of these three polysilanes are also shown in Fig. 2. OA spectra show the intense peaks due to the lowest singlet exciton transitions; at 3.4 eV for PDHS with the trans planar backbone, at 3.7 eV for PDTDS with the alternating trans-gauche one (TGTG'), and at 4.0 eV for PDBS with the 7/3 helical one. By contrast, the OA spectra are very similar in disordered conformations of these three

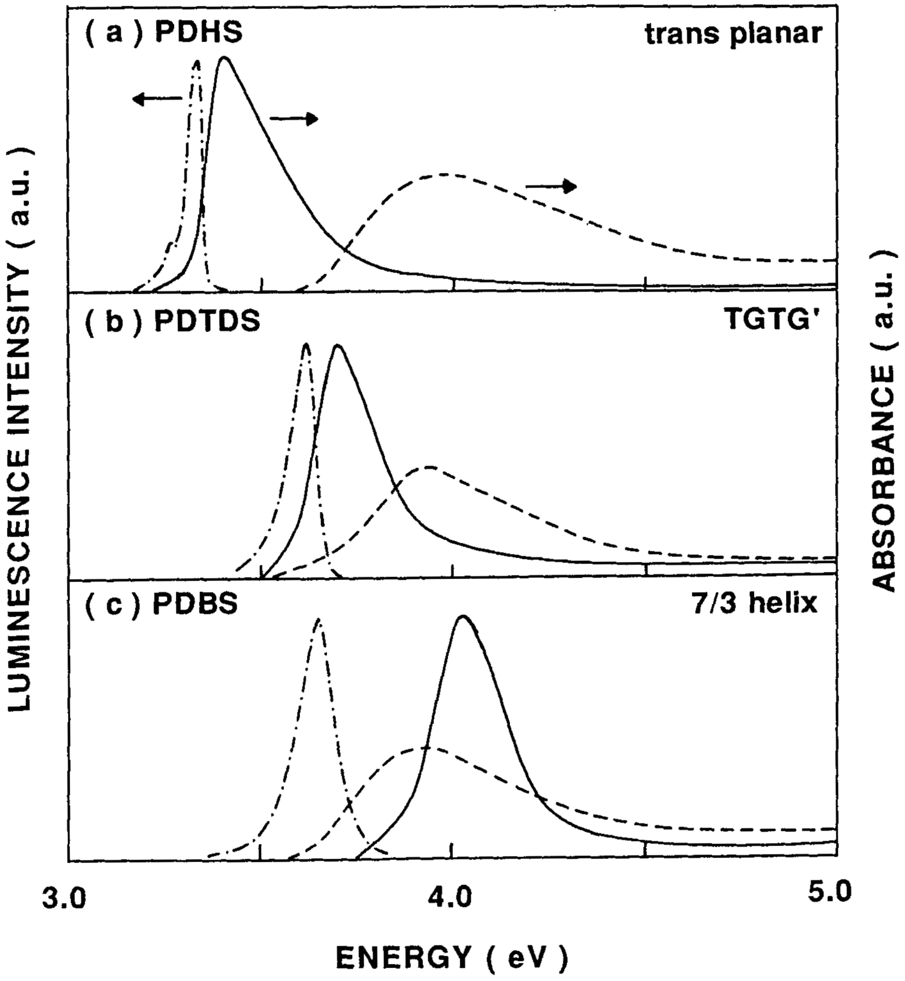

FIGURE 2. Ordinary absorption (—) and photoluminescence (—·—) spectra; (a) trans planar PDHS, (b) trans-gauche PDTDS, and (c) 7/3 helical PDBS. A dashed line represents absorption spectra of each conformation after phase transition.

polysilanes above the critical temperature for the phase transition.

For the trans planar and TGTG' conformations, the lowest singlet exciton bands shift to high energy (3.9 eV) and the spectral profiles become broader upon the phase transition, signaling a decrease in the delocalization of σ–electrons along the polymer backbone. PL peaks of the trans planar and TGTG' conformations are positioned at the nearly same energy of the OA peaks with no Stokes shift. Such a resonance emission implies a weak exciton–lattice interaction in polysilanes which is rather exceptional among the conjugated polymers.

On the other hand, the spectral features in PDBS films with 7/3 helical backbones appear to differ from the above cases: the lowest exciton band in the 7/3 helical conformation was observed to shift to lower energy upon the phase transition to the disordered form. Furthermore, an apparent Stokes shift is observed in PL spectra of the 7/3 helical conformation, but the PL peak shows up in edge of the low–energy tail of the OA peak around 3.6 eV. Such features are often observed in semiconductors and molecular crystals showing indirect gap. In the case of the 7/3 helical forms, therefore, the indirect exciton is considered to be located in the lower energy region (3.6–3.7 eV) below the direct exciton (4.0 eV) which shows up as the OA peak.

EA and two–photon spectra in thin films of polysilanes with the three conformations in comparison with their OA peaks are shown in Fig.3. EA spectra provide important information not only about optically allowed states but also about forbidden ones (two–photon excited states).[3,4] EA signals (F) are observed in the same energy region of OA peaks due to the lowest singlet excitons and are well reproduced by the calculated first energy–derivative curve of the OA spectra. This indicates the Stark shift of the resonance energy of the lowest singlet exciton in the external field. The EA peak (X) activated by the external electric field is observed in the higher energy region above the peak F. The energy of the peak X is consistent with that of two–photon absorption band[5,6] and the energy difference between the one–photon and two–photon absorption was nearly constant (ca. 0.9–1.0 eV) despite the change in backbone conformations. The band F and X can be assigned to the ground and first excited states of the one–dimensional (1D) excitons.[3,6] The EA signal (X) due to first excited state shows the energy–derivative–like features of the two–photon absorption spectrum. An additional EA structures indicated by an arrow is observed in the higher energy side of the EA signal X. The origin of this band may be related to second excited states of the 1D exciton or band–to–band transitions.

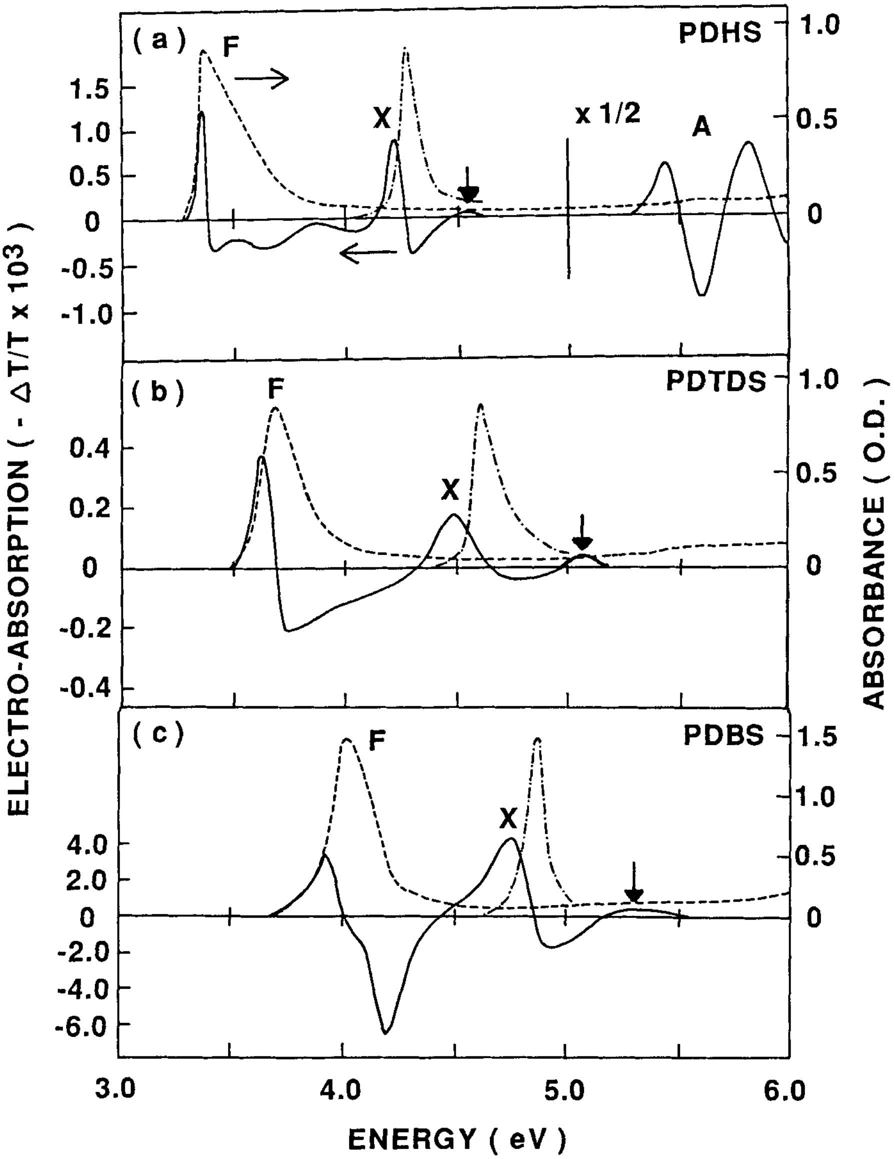

FIGURE 3. Ordinary absorption (- - -), electro-absorption (——), and two-photon absorption (-·-) spectra; (a) trans planar PDHS, (b) trans-gauche PDTDS, and (c) 7/3 helical PDBS.

In addition to these excited states, the strong EA signal (A) and two-photon absorption band[7] are observed around 5.5 eV in PDHS films with the trans planar conformation. The EA signal is very sensitive to the backbone conformation and disappear upon the order-disorder phase transition, indicating that the transition is characteristic of the extended trans planar conformation of polysilanes. The origin of this band A has been proposed to be the higher-lying excited state with the character of two-electron excitation like the bi-exciton state.[3,7] These strong two-photon exciton bands (X and A) may play an important role in the third-order nonlinear optical process.

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