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Electronic structure of poly(dihexylgermane): A comparison with poly(dihexylsilane)

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One-photon and two-photon absorption and photoluminescence spectra have been investigated for thin films of poly(dihexylgermane) (PDHG) for a comparison with those of its Si-backbone analog, poly(dihexylsilane) (PDHS), with similar *trans*-planar backbones. The electronic structures of *trans*-planar PDHG and PDHS have been shown to resemble each other, including the energy positions of the $^1B_{1u}$ and ^1A_g exciton transitions, which is not in accord with a prediction by band-structure calculations. A significant difference of the exciton absorption peak in Si and Ge backbones is seen only for the *gauchelike* disordered conformation.

Polygermanes, Ge-based polymers with organic substituents, are a type of polymer that possesses σ-electron conjugated backbones like their Si analogs, polysilanes.[1,2] Recently, polygermanes have been found to show photoelectronic properties similar to those of polysilanes, such as photoconductivity[3] and a third-order nonlinear optical property.[4] Interesting correlations are also predicted from calculated band structures of polygermanes[5] and polysilanes:[6,7] Polygermanes with the *trans*-planar conformation have a direct band gap similar to the case of *trans*-polysilanes; yet the predicted band-gap value is considerably smaller than that of polysilanes, e.g., 3.31 and 3.89 eV for $(\mathrm{GeH}_2)_n$ and $(\mathrm{SiH}_2)_n$, respectively.[5] On this basis the possible existence of one-dimensional superlattice structures, such as ordered Si-Ge sequences of copolymers, has been suggested.[5] Such ordered Si-Ge block polymers have recently been synthesized chemically,[8] although the properties inherent in these superlattice structures remain to be clarified. To date the electronic structure of the polygermanes has been little studied as compared with that of the polysilanes.

In this paper, we report results of spectroscopic investigations on the electronic structure of a polygermane, poly(dihexylgermane) (PDHG), with a *trans*-planar conformation of the Ge backbones. Polarized absorption spectra of highly oriented films of PDHG have been measured up to 10 eV using synchrotron radiation (SR). The spectra have been compared with those of polysilanes (PDHS) with the same (dihexyl) sidegroups and also with the band-structure calculations. Furthermore, two-photon absorption spectra were measured to detect parity-forbidden exciton states in both polymers. The *trans*-planar backbones of PDHG and PDHS have been known to turn into the *gauche*-containing disordered forms upon the phase transition.[9,10] A significant difference between the electronic structures of PDHG and PDHS has been found for the *gauchelike* disordered form of the backbones.

PDHG and PDHS were synthesized with a previously reported method.[11,12] A molecular weight (M_W) measured using the polystyrene standard was 5.69×10^4 for PDHG and 2.44×10^5 for PDHS. Thin films of these polymers were spin-coated on the fused quartz plates from a heptane solution and allowed to stand overnight at room temperature after annealing at 380 K. For vacuum ultraviolet spectroscopy, LiF plates were used as substrates because of their transparency up to 11 eV. Films spin-coated on the LiF substrates were then rubbed gently along one direction with wiping paper to align the direction of the polymer backbones. The oriented films are highly anisotropic as proved by polarized absorption spectra (*vide infra*). Absorption spectra of the oriented films with light polarizations nearly parallel and perpendicular to the backbones were measured using polarized synchrotron radiation (SR) at the Synchrotron Radiation Laboratory (UV-SOR), The Institute for Molecular Science (Okazaki). The conformation of the thin films was changed by controlling and adjusting the temperature of the substrates.

For the measurements of photoluminescence, 308-nm light of an excimer laser (4.0 eV) was used as an exciting source. Two-photon absorption spectra were measured by monitoring the intensities of two-photon-induced luminescence as a function of twice the exciting photon energy. A pulse dye laser driven by a XeCl excimer laser was utilized as an exciting light source. At several photon energies, the intensity of the two-photon-induced luminescence was confirmed to be precisely proportional to the square of the exciting laser intensity.

First, to see the overall features in the electronic structures of polygermanes, we show in Fig. 1 polarized absorption spectra of an oriented PDHG film at 77 K in the photon-energy region of 2–10 eV, together with results for similarly obtained PDHS films[13] (indicated by dashed lines). In general, carbon σ-σ^* transitions due to the alkyl substituents attached to the Ge or Si backbones show a threshold of absorption around 8 eV.[14,15] Therefore, the four peaks, *F*, *A*, *B*, and *C*, as observed below 8 eV, are ascribable to electronic transitions inherent in the *trans*-planar Ge (Si) backbones of polygermanes (polysi-

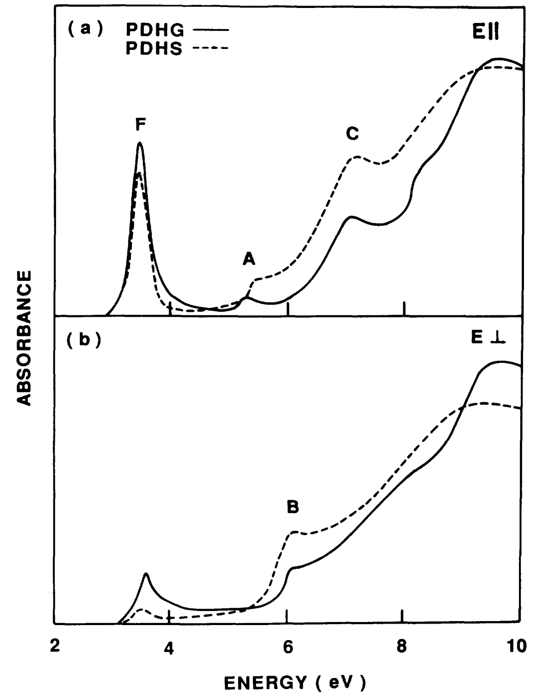

FIG. 1. Polarized absorption spectra of highly oriented films of *trans*-planar PDHG (solid line) and PDHS (dashed line) at 77 K.

lanes). At a first glance, one may notice that spectral features are very similar in PDHG and PDHS: Peaks *F*, *A*, and *C* are polarized parallel to the backbone, while peak *B* is polarized perpendicular to the backbones. The polarization characteristics and energy positions of these peaks of PDHG are quite similar, as listed in Table I, to those of PDHS, except for the energy position of peak *A*.

These characteristic four transitions in PDHG may be assigned in a similar manner to the case of PDHS. We have previously compared in detail the observed polarized spectra in PDHS with the calculated absorption spectra and band structure.[13] According to the calculated band structure,[6,7] the σ_p-electron-related valence band is composed of two (upper and lower) branches which are folded at the Brillouin-zone edge and show a different symmetry. The lowest-lying transition *F* is attributed to the transition between the highest valence band (upper σ_p band) and the lowest conduction band. More precisely, the absorption band *F* should be assigned to the $\mathbf{k}=0$ exciton associated with those band-to-band transitions as discussed later. The transition *A* (∥) and *B* (⊥) have been assigned to the transition to one branch of the σ^* conduction band from the upper and lower branch of the σ_p valence band, respectively (for details, see Figs. 2 and 3 in Ref. 13). On the other hand, the transition *C* (polarized parallel to the backbone) may be assigned to the transition between the lower σ_p valence band and highest-lying branch of the σ^* conduction band, as discussed in detail in Ref. 13. Therefore, the energy distance between the lowest (*F*) and highest (*C*) transitions with parallel polarizations can be an approximate measure for the sum of the dispersion widths of the σ-related valence and conduction bands, or equivalently for the width of the joint density states of the σ-related bands. The observed separation (ca. 4.0 eV) indicates a significant delocalization of σ electrons in PDHG as well as in PDHS. The common spectral features in PDHS and PDHG indicate that the electronic structures or band structures quantitatively resemble each other over a wide energy range up to 8 eV.

TABLE I. Comparison of energies of optical transitions in PDHG and PDHS with the *trans*-planar conformation.

Transition	*F*	*A*	*B*	*C*
Polarization	∥	∥	⊥	∥
PDHG (eV)	3.3	5.3	6.2	7.3
PDHS (eV)	3.4	5.5	6.2	7.3

Qualitatively similar band structures for polysilanes and polygermanes with the *trans*-planar backbones have been shown by Takeda and Shiraishi,[5] using $(SiH_2)_n$ and $(GeH_2)_n$ as model systems. According to their calculations, however, the band gaps are predicted to be 3.89 eV for $(SiH_2)_n$ and 3.31 eV $(GeH_2)_n$ and show a significant difference for polysilanes and polygermanes. Judging from the good coincidence of the observed transition energies, not only for the lowest transition *F* but also for the other higher-lying transitions, it is reasonable to consider that the bond structures (bond lengths, bond angles, etc.) in PDHG differ significantly from those of PDHS and that the near degeneracy between their electronic parameters, e.g., transfer integrals and orbital hybridizations in both the polymers, is fortuitous. In other words, the bond-structure relaxation in PDHG appears to cancel the difference in energy positions of atomic (Ge and Si) orbitals.

In the following, we focus on the lower-lying excitonic transitions in PDHG and compare them with those in PDHS. Figure 2 shows three spectra near the absorption edge in thin films of PDHG and PDHS at 77 K: ordi-

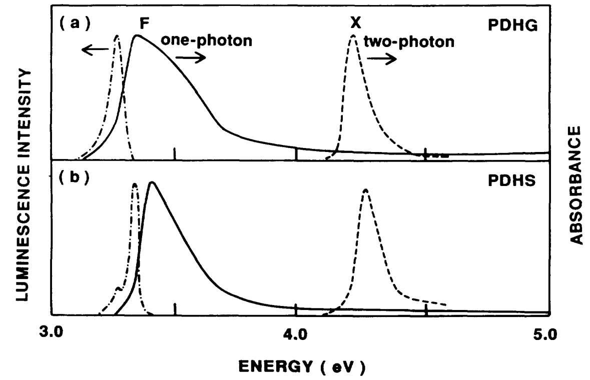

FIG. 2. Ordinary one-photon absorption (solid lines), photoluminescene (dashed-dotted lines), and two-photon absorption (dashed lines) spectra in thin films of PDHG and PDHS with the *trans*-planar conformation at 77 K.

nary (one-photon) absorption and photoluminescence spectra as well as two-photon absorption spectra which can probe the symmetry-forbidden exciton state. The two-photon absorption spectrum of PDHS is in good agreement with the previously reported one.[16,17] Even in such an expanded photon-energy scale as shown in Fig. 2, PDHG and PDHS surprisingly resemble each other in spectral features in these three kinds of spectrum.

The one-photon absorption band F has been assigned to the lowest singlet exciton ($^1B_{1u}$),[18,19] whose internal wave function (envelope function) is expected to extend along the backbone. The spectral width of the absorption band is partly due to coupling with lattice dynamics, but mostly due to inhomogeneous broadening. A broader shape of the absorption spectrum in PDHG than that in PDHS may be simply ascribed to the less-ordered conformation of the Ge backbones in PDHG films. The $^1B_{1u}$ exciton shows a radiative recombination, giving rise to a sharp resonance luminescence at 3.29 eV in PDHG and at 3.36 eV in PDHS. A very small Stokes shift for the photoluminescence of the exciton may signal relatively weak exciton-lattice interaction as compared with the exciton band dispersion in the *trans*-planar Ge chains as well as in the Si chains. This is, however, rather unusual in one-dimensional electronic systems, which often show a largely Stokes-shifted broad luminescence band, or otherwise (in most cases) remain nonluminescent due to nonradiative decay processes arising from the strong electron-lattice interaction.

As seen in Fig. 2, the two-photon absorption spectrum in PDHG shows a sharp peak (denoted as X) as well as the one-photon spectrum. It is remarkable that the two-photon absorption band shows quite a common feature both in the peak energy (4.22 eV for PDHG and 4.27 eV for PDHS at 77 K) and in the spectral shape for PDHG and PDHS. The two-photon transition X should have the symmetry of ^1A_g in the D_{2h} backbones of PDHG and PDHS. In our previous studies on the electroabsorption[18,20] and two-photon absorption[19] spectra in various polysilanes, the band X has been assigned to the first excited state of the one-dimensional (1D) Wannier exciton on the backbones. In the case in which an electron-hole pair is confined in one dimension, the internal wave functions of the exciton states show an alternating series of even and odd parity, analogous to the problem of the 1D hydrogen atom.[21] Our interpretation for the exciton spectra of polysilanes is that the $^1B_{1u}(F)$ and $^1A_g(X)$ excitons are the $\mathbf{k}=0$ ground and first excited states of such a 1D Wannier exciton series. Nearly identical excitonic structures for PDHG and PDHS, including the parity-forbidden (^1A_g) state, indicate again the nearly degenerate electronic parameters in both the polymers.

In contrast with the very similar electronic structures in *trans*-planar PDHG and PDHS, a considerable difference is observed in electronic spectra for the *gauche*-containing disordered conformations of the backbones above the phase-transition temperature. We show in Fig. 3 a comparison of the absorption spectra in PDHG and PDHS for (a) *trans*-planar and (b) disordered forms. The spectra for the *trans*-planar conformation were measured at 77 K well below the phase-transition temperature [286 K for PDHG (Ref. 9) and 316 K for PDHS (Ref. 10)], while the spectra for the disordered conformation were measured at 295 K for PDHG and 320 K for PDHS. As already may be evident in Fig. 2, the energies of the $^1B_{1u}$ exciton peaks are nearly degenerate for the *trans*-planar PDHG and PDHS. By contrast, the absorption peak for the disordered conformation is observed around 3.65 eV in PDHG, at a considerably lower energy than the peak position (4.00 eV) in PDHS. Since the disordered conformation contains the *gauchelike* component, the exciton energy may differ in polysilanes and polygermanes with the *gauche*-based conformation. However, the energy differences (ca. 0.35 eV) of the absorption peak in the disordered PDHG and PDHS chains is still within a reasonable range reflecting the atomic-energy parameters in Si and Ge. A smaller but similar difference (ca. 0.22 eV) in the lowest absorption peak energy is also observed for single PDHG and PDHS chains in solution,[11] in which the backbone conformations show coil-like disorder.

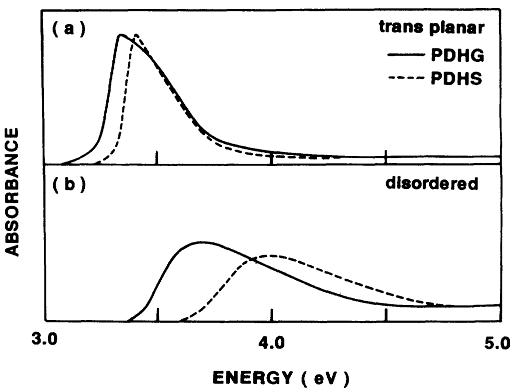

FIG. 3. Comparison of ordinary absorption spectra of PDHG (solid line) and PDHS (dashed line) films for (a) *trans*-planar and (b) disordered conformations.

In summary, we have spectroscopically investigated and compared the electronic structures of PDHG and PDHS. The electronic structure of PDHG with the *trans*-planar conformation has been demonstrated to be quantitatively similar to that of PDHS. Polarized absorption spectra of oriented films of PDHG show a large delocalization of σ electrons along the polymer backbone, as observed previously in PDHS. An appreciable difference between the exciton spectra in PDHG and PDHS was observed only for the *gauchelike* disordered conformation above the phase-transition temperature. As far as the *trans*-planar conformation of the polymer backbones is concerned, quantum-well fabrication for the exciton seems to be difficult by use of the superlattice structures of Si-Ge copolymers because of their nearly degenerate excitonic parameters. However, the *gauche*-based backbone structures in which we have observed an appreciable difference of exciton energies in polysilanes and polygermanes might make possible the construction of such quantum wells.

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