

Anomalous optical and ESR properties of doped polydiethynylsilanes

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The optical, transport, and ESR properties of soluble conducting four-membered polydiethynylsilane heterocycles are described. The undoped one-dimensional gap is 2.0 eV in both films and solutions; no photoluminescence is observed. I₂ doping induces a single absorption band at ~1.05 eV in solutions and lightly doped films, but another at ~0.55 eV in heavily doped films. Both are correlated with strong ir-active vibrations associated with known lines in Raman scattering. The doping-induced ESR of the solutions is linear in the 1.05-eV peak, but only ~2% of the carriers yield an ESR, which is motionally narrowed. No light-induced ESR is detected. The results are discussed in relation to solitons, polarons, and bipolarons in a degenerate ground-state system.

Various (semi)conducting polymers, notably polyacetylene (CH)_x, polydiacetylene (PDA), polyaniline, and polythiophene (PT)-type five-membered polyheterocycles, have been studied extensively,¹ due to novel physical properties² and promise in synthetic-metal, energy-storage, and nonlinear-optical (NLO) applications.³ The existence of solitons in the degenerate-ground-state *trans*-polyacetylene [*t*-(CH)_x], and polarons and bipolarons in nondegenerate systems is now well established.² To date, the doping-induced optical absorption signature of solitons has been accepted to be a single absorption band at or below midgap ($E_g/2$). Those of bipolarons and polarons are accepted to be two bands peaking at ω_1 and ω_2 , where $\omega_1 + \omega_2 \leq E_g$, and three bands peaking at ω_1 , ω_2 , and ω_3 , where $\omega_1 + \omega_2 = \omega_3$, respectively.² Among the charged excitations, only polarons have a spin.

This paper describes anomalous doping-induced optical and ESR results on novel conducting poly(diethynylsilanes) (PDES); the strong ultrafast NLO response of these polymers has recently been described by Wong *et al.*⁴ In solution, only a single I₂-doping-induced absorption band is observed peaking at $E_g/2$ (1.05 eV), but an additional band appears in films at ~0.55 eV. Both absorption bands are correlated with strong ir active vibrations. The very slight doping-induced ESR is apparently motionally narrowed. Self-consistent *ab initio* Hartree-Fock (HF) calculations indicate that the splitting between the two dimerizations of the system is less than ~4 meV, i.e., the idealized system has an essentially degenerate ground state.⁵ The results are discussed not only in terms of electronic excitations in nearly degenerate polymers but also within the framework of degenerate-ground-state diatomic (AB)_x polymers.⁶

$R_2Si(C\equiv CH)_2$ monomers, where R=phenyl (Ph),

methyl (Me), butyl (Bu), or hexyl (Hex), were polymerized by MoCl₅ or WCl₆ catalysis.^{7,8} Weight-average molecular weights ranged from ~100 000 (~450 monomers/chain) with Ph to values in excess of 2×10^5 , or ~1500 (~1200 monomers/chain, with Bu (Hex) substituents. The polymers are soluble in various organic solvents, easily cast into films, and apparently quite stable in air. Detailed ¹³C and ²⁹Si NMR measurements indicate the structure shown in Fig. 1(a).⁹ Acyclic segments probably disrupt the chain conjugation,¹⁰ but since only ~75% of the monomers become cyclic when polymerized via WCl₆, it is suspected that one or two acyclic units do not disrupt the conjugation.

The two isomers of the cyclic segments⁵ are drawn in Fig. 1(b). The absence of a solvatochromic effect,⁷ the strong dispersion in resonant Raman scattering, and the relatively low conductivity (~0.1 S/cm) of the heavily I₂-doped films (see below) is consistent with a relatively short average conjugation length.

dc conductivity measurements on pristine films cast from solution yielded $10^{-9} \leq \sigma \leq 10^{-7}$ S/cm. Roughly 3-wt.% I₂ [one I₃⁻ group per 67 Bu₂Si(C≡CH)₂ monomers] are absorbed during ~1 min exposure to ~1 torr I₂ vapor, whereupon σ increases to ~10⁻² S/cm. The iodine content increases to ~6 wt.% following 1 h exposure, and σ increases to ~0.1 S/cm. The I₂ doping is reversible.

The undoped PDES display interband transitions peaking at 2.1 eV with an onset at 1.9 eV; we thus estimate the one-dimensional (1D) gap to be 2.0 eV. Only a single absorption band at 1.05 eV ($\approx E_g/2$) is observed in a dilute CHCl₃ solution at up to 50-wt.% I₂ doping [Fig. 2(c)]. It grows at the expense of interband transitions. The optical response of films to I₂ (or AsF₅) doping [Fig. 2(b)] is

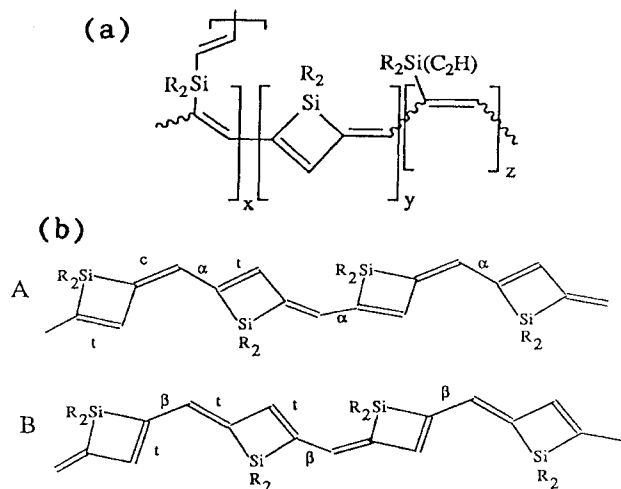


FIG. 1. (a) The structure of polydiethynylsilanes (PDES), as determined by Parbhoo *et al.* (Ref. 9). When polymerized via MoCl_5 (WCl_6), $\sim 42\%$ ($\sim 75\%$) of the monomers are cyclic. (b) The two apparently degenerate dimerizations of the cyclic segments shown in (a) (Ref. 5).

strikingly different from that of the solutions. While light (< 1 wt.%) doping induces only the high-energy (HE) band at 1.05 eV as in solutions, heavier doping induces a second low-energy (LE) band peaking at ~ 0.55 eV. The LE band is more intense at the highest doping levels (~ 6 -wt.% I_2), but decreases more rapidly as the I_2 evolves out of the film. Indeed, the intensity of the LE band is proportional to the square of the HE band in the Bu_2 PDES and to the fourth power of the HE band in the Hex_2 PDES.

The doping efficiency of I_2 in dilute solutions of Bu_2 PDES in benzene and acetonitrile (ACN) decreases from $\sim 25\%$ at 10-wt.% I_2 to $\sim 10\%$ at 50-wt.% I_2 .¹¹ If it is similar in CHCl_3 , this would correspond to one I_3 in ~ 80 monomers at 10-wt.% I_2 , and one I_3 in ~ 40 monomers at 50-wt.% I_2 . A 10% doping efficiency at 50-wt.% I_2 in solution would then be similar to the maximal level of ~ 6 wt.% observed in the films.

The injection of mobile charge carriers onto the chains is also evident from the ir active vibrational modes induced by I_2 or AsF_5 doping (Fig. 3).

A typical room-temperature X-band ESR spectrum of pristine undoped films and solutions is shown in Fig. 4(a). The g value is 2.003; the derivative peak-to-peak linewidth ΔH_{pp} is ~ 10 G, and its integrated intensity in both films and solutions yields ~ 1 spin per ~ 14000 monomers. The ~ 3.6 G linewidth of deuterated samples [Fig. 4(b)] is sharply lower, indicating that the hyperfine interaction with neighboring protons dominates the linewidth. I_2 doping increases the (doubly integrated) ESR intensity by up to a factor of ~ 8 . ΔH_{pp} initially decreases to 3.4 G in hydrogenated and 2.9 G in deuterated films [Fig. 4(c)], but only to 7 G in 40-wt.% I_2 in solutions of hydrogenated $[(\text{HC}\equiv\text{C})_2\text{SiBu}_2]_x$ in benzene. Heavier doping slightly increases ΔH_{pp} to 3.2 G in the deuterated films. Its dependence on T , broadening to 4.9 G at 7.5 K [Fig. 4(d)], suggests motional narrowing¹² with an activation

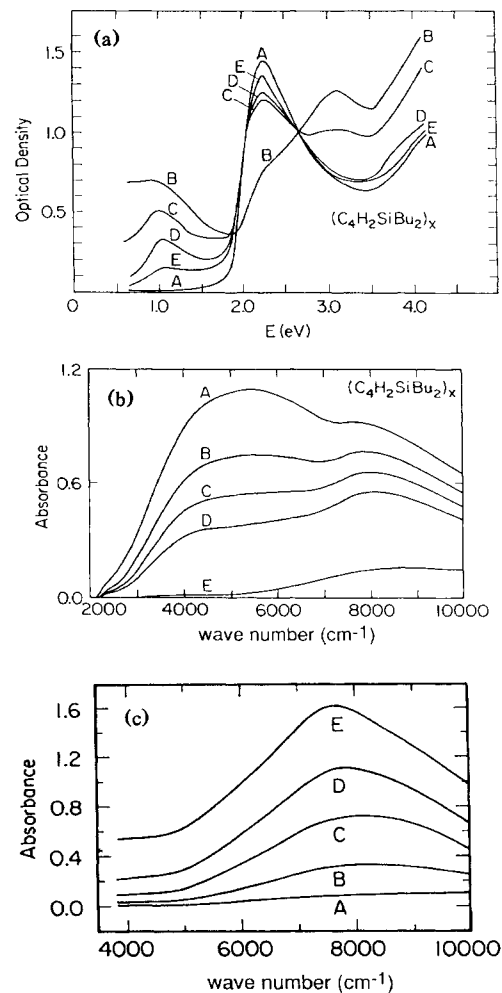


FIG. 2. (a) The optical absorption of $[(\text{HC}\equiv\text{C})_2\text{SiBu}_2]_x$ films, during evolution of I_2 , after exposure to ~ 1 -torr I_2 for 15 min. A, undoped; B, after 4 min; C, 25 min; D, 65 min; E, 210 min. (b) Similar to (a): A, after 5 min; B, 18 min; C, 26 min; D, 40 min; E, 110 min. (c) I_2 doping-induced absorption of dilute solution of the same PDES in CHCl_3 .

energy of ~ 3.7 meV, contrasting sharply with poly(3-hexylthiophene) solutions, where the linewidth *increases* (to ~ 16 G upon 50-wt.% I_2 doping). The weaker narrowing effect in solutions relative to films suggests that interchain hopping contributes significantly to the motional narrowing.

As described above, at the highest doping level there is one I_3 in ~ 40 monomers, but only one spin in ~ 1800 monomers. Yet the relation between the ESR spin density and the integrated intensity of the 1.05-eV band, during I_2 doping of benzene solutions of $[(\text{HC}\equiv\text{C})_2\text{SiBu}_2]_x$ is linear. Thus, $\sim 98\%$ of the carriers are spinless, independent of the doping level.

The intensity of the light-induced ESR (LESER) is comparable to the dark ESR. Yet the kinetics of the formation and decay of the LESER are slow (several minutes to several hours) at room temperature, and slow down further upon cooling. They thus indicate that the LESER is due to metastable defect formation, rather than intrinsic

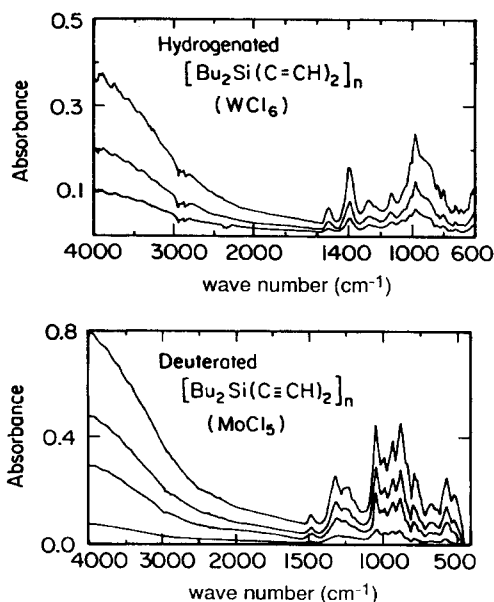


FIG. 3. The I_2 doping-induced infrared active vibration modes in PDES films. The observed peaks are directly related to resonance Raman modes (see Ref. 13).

photogenerated carriers. The absence of any double modulation LESR signal confirms this conclusion.¹³ It thus appears that similarly to the doping-induced ESR, almost all of the photogenerated excitations are spinless.¹⁴

Interpretation of the observed results in terms of conventional solitons, polarons, or bipolarons is problematic: (i) Charged solitons should not yield a doping-induced

ESR, nor two optical absorption bands (Fig. 2) in either films or solutions. (ii) Polarons should yield a much stronger ESR and three absorption bands.^{2,15} (iii) If most of the polarons decay into bipolarons two doping-induced subgap bands should be observed even in solution. (iv) If the polarons decay into bipolarons only by interchain hopping, and are thus absent from dilute solutions, then the two bipolaron bands observed in the films should depend similarly on the doping level.

In light of the foregoing problematic results, we note that they bear a striking *qualitative* resemblance to $t-(CH)_x$: (i) There is only a single absorption band, at midgap, in solution. As in $t-(CH)_x$, the (ii) photoluminescence, (iii) LESR, and (iv) doping-induced ESR are very weak. (v) The results of *ab initio* HF calculations indicate that the idealized system is essentially degenerate. It is therefore believed that the primary doping-induced excitations are spinless charged solitons. Yet if the degeneracy is slightly lifted (by ≤ 4 meV), then one would expect that doping would induce both polarons and solitons.

An alternative picture may involve the lifting of the degeneracy in short conjugated segments (i.e., chain-end effects). In such a case, the longer ground-state degenerate segments would support solitons, and the shorter segments would yield bipolarons or two overlapping solitons.¹⁶ The coincidence of the upper bipolaron transition at 1.0 eV with the soliton transition would then be very intriguing. This picture, however, does not account for the absence of nondegenerate ground-state segments in solution, unless the carriers can overcome the barriers between the short segments in solution.

The near degeneracy of the two dimerizations shown in

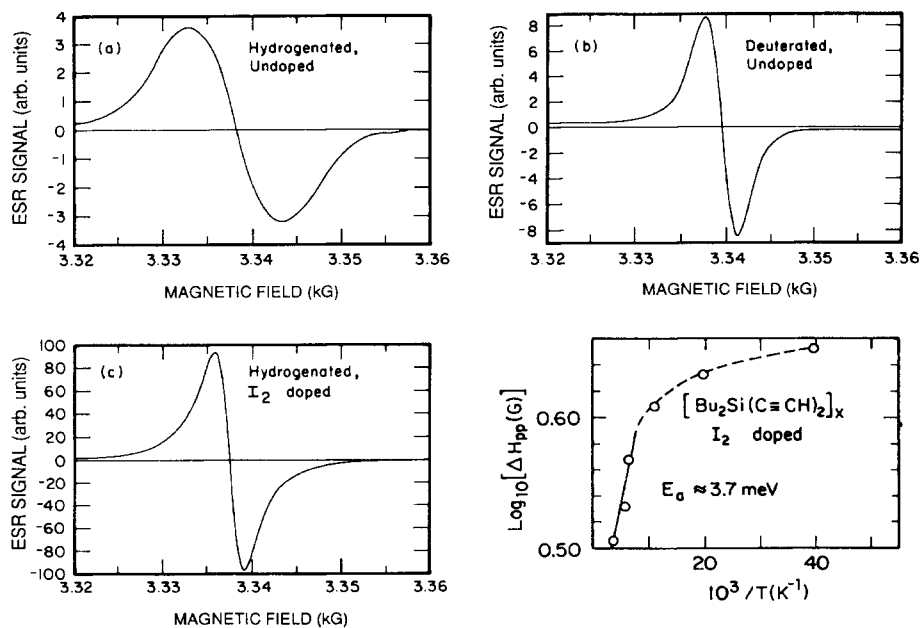


FIG. 4. (a) Room-temperature X-band ESR of pristine undoped hydrogenated PDES films and solutions. (b) ESR of deuterated films and solutions under similar conditions. (c) ESR of hydrogenated films following 3–5-wt. % I_2 doping. (d) The logarithm of the linewidth of hydrogenated films vs $1/T$, indicating a motionally narrowed ESR (see Ref. 12).

Fig. 1 (to within ~ 4 meV) is surprising in view of the fact that in one form, all of the C=C double bonds are *trans*-like, whereas in the other they alternate between endocyclic *trans*-like and exocyclic *cis*-like bonds. Since alternate C atoms of the backbone are bonded to Si, the on-site lattice potential α of the C p orbitals is expected to alternate in a manner similar to the hypothetical degenerate-ground-state diatomic $(AB)_x$ polymer.⁵ The elementary excitations of such a system are two solitons S_A and S_B centered on the A and B atoms, respectively. Their levels are at $\pm \alpha$ relative to midgap, respectively.⁴ In the lowest overall neutral configuration, S_A is empty, and S_B is doubly occupied. They are thus spinless, but carry fractional charges $Q_A = (1-f)e$, $Q_B = -(1-f)e$, where $0 \leq f \leq 1$. However, the value of α in the PDES may be small, possibly due to nearly identical A and B species. The S_A and S_B levels would consequently be unresolved. Thus the relevance of the degenerate-ground-state $(AB)_x$ diatomic polymer may be marginal.

In summary, the anomalous doping-induced optical absorption in the electronic and ir spectral range and the ESR of PDES films and solutions were described and discussed. The behavior is believed to result from generation of solitons in degenerate ground-state segments consisting of four-membered polyheterocycles attached to a vinylene unit. The striking anomalies are not clearly understood but may involve interchain excitations or a lifting of the degeneracy in short segments.

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