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TRANSPORT BEHAVIOR ASSOCIATED WITH BATHOCHROMIC SHIFT IN Si AND Ge POLYMERS.

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Abstract . Time-of-flight drift mobility experiments have been carried out on poly(di-n-hexylsilylene) (PDHS) and poly(di-n-butylgermylene)(PDBG) over a wide range of temperature and electric field. A change in transport behavior in PDHS and PDBG associated with the conformational transitions which are responsible for the bathochromic shift in these polymers, is unambiguously demonstrated.

Keywords: Charge transport, sigma conjugated polymers, thermal transitions

BACKGROUND

The electronic spectra of polysilylenes and polygermylenes are dominated by intense transition attributed to a $\sigma\sigma^*$ transition.[1,2] Optical spectra of the corresponding oligomers are characterized by a molecular weight dependent shift of the absorption maximum similar to that observed in polyacetylene and other π- conjugated polymers.[3,4] Thus, the absorption wavelength is typically observed to increase with catenation but then to rapidly approach limiting value as the molecular weight increases.[5,6] For example, in aliphatic sidegroup containing polymers this saturation value occurs between 300 and 325 nm.[7] In the case of PDHS, however, the strong electronic absorption is found to depend critically on the thermal history of the specimen.[8] The dominant absorption in PDHS is observed at 310-320 nm, but only at temperatures above the specific transition temperature T_{Tr} ~315K. Below this temperature, the corresponding absorption is significantly redshifted into the 370-380 nm range. It has been sugested[8,9] that the long wavelength absorption observed below 315K is a consequence of conformational locking of the polysilylene chain into a trans configuration which is driven by crystallization of pendant linear alkyl groups. The highly ordered form of PDHS which appears at $T<T_{Tr}$ is called phase I. In the case of PDHS, spectroscopic and NMR measurements indicate that in phase I the n-hexyl sidegroups are packed in a regular array with their long axes oreinted nearly perpendicular to the silicon backbone which under these circumstances is in the all-trans planar zig zag conformation. Above T_{Tr}, PDHS is driven into a

conformationally disordered state referred to as phase II as a consequence of sidechain melting. The latter transition is fully reversible but the kinetics of the transition is molecular weight dependent and the relative proportion of the phases varies with thermal history. A similar thermochromic transition has been observed in poly(di-n-hexylgermylene)[10] but at considerably lower temperature, 262K. The spectral shift in PDHS has been associated with the changes of the dihedral angles.[8] It is therefore interesting to investigate whether properties such as electronic charge transport, clearly associated with elecronic states derived from the chain backbone[11], are changed as a consequence of the phase I - phase II transition.

RESULTS

The absorption spectra of phases I and II in PDHS at 370-380 nm and 315-320 nm, respectively, are shown in Fig 1c. The associated hole drift mobility data are presented in Fig 1a and diferential scanning calorimetry data are displayed in Fig 1b. Figs 1b and 1c together delineate three distinctly different thermal regimes in PDHS, namely: 1) the glassy state below Tg with its highly ordered side chains, and backbone locked in all trans (planar zig-zag) conformation, 2) the region between Tg and T_{Tr} where the sidechains remain in the ordered state while the backbone executes liquid - like motions, and, 3) the phase II where side chain melting has induced main chain reconformation into the helical form. Transport behavior of PDHS in regions 1 and 2 is similar to that in a number of glassy polymeric media.[12,13] Thus, when $T \sim Tg$, the apparent activation of mobility changes abruptly but the mobility itself does not exibit a simultaneous change. In addition, there is no associated change in the uv / vis spectra. This is to be contrasted with changes in drift mobility occuring in the vicinity of the sidechain melting transition, as illustrated in Fig 1a. Here, both mobility values and the temperature dependence of μ change abruptly. This change is clearly associated with the transition at $T = T_{Tr}$ shown in the DSC data. At $T > T_{Tr}$, PDHS exhibits a greatly enhanced temperature dependence of mobility. Extension of measurements to higher temperatures would have been interesting but the softened specimen films become difficult to handle in the Time-Of-Flight (TOF) experimental cell. If we presume that the transport in the disordered region above T_{Tr} is still activated, the extrapolated room temperature mobility would be $\sim 10^{-6}$ cm^2/Vs. Unfortunately, our spectral analysis indicates that rapid quenching of the molten films always produces substantial

reconversion of phase II to phase I. We were unable to devise any rapid quench procedure which would preserve the film in phase II below the transition temperature.

Figs 2a, b and c show data for PDBG reflecting behavior analogous in all respects to that illustrated in Fig1 a, b, c for PDHS. The bathochromic shift in PDBG reported here for the first time (Fig 2c) is approximately 26 nm (341 to 367nm) compared to ~ 65 nm in PDHS. The associated change in hole drift mobility in PDBG shown in Fig. 2a is also smaller but clearly visible. It is interesting to note that the silicon backbone analogue, poly(di-n-butyl-silylene), does not exhibit a comparable shift in absorption at least up to about 370K even though the DSC scan indicates a weak endotherm at ~ 340K.

In both cases the Figures 1 and 2 demonstrate that the onset of melting behavior in the DSC is accompanied by the onset of decrease of the hole drift mobility.

CONCLUSION

In PDHS and PDBG, a change in main chain conformation induced by side chain melting and simultaneously manifested in DSC and as a bathochromic shift in the electronic spectra, has in each case a clearly discernable impact on transport behavior. Nevertheless, the overall effect on transport in the vicinity of the transition is relatively small. Evidently, the rate limiting electron transfer process which could for example be an interchain hop is not significantly perturbed by the observed change in conformation and the associated change in the electronic structure (i.e. electronic states) of the polymer. The latter is in contrast to polymers where transport proceeds by hopping among pendant side groups such as carbazole in poly(n-vinylcarbazole)(PVK). In the case of PVK, small but systematic changes in the relative orientation of the carbazole groups are predicted to profoundly affect intermolecular wavefunction overlap[14] and, as a result, the rate of intermolecular charge transfer.

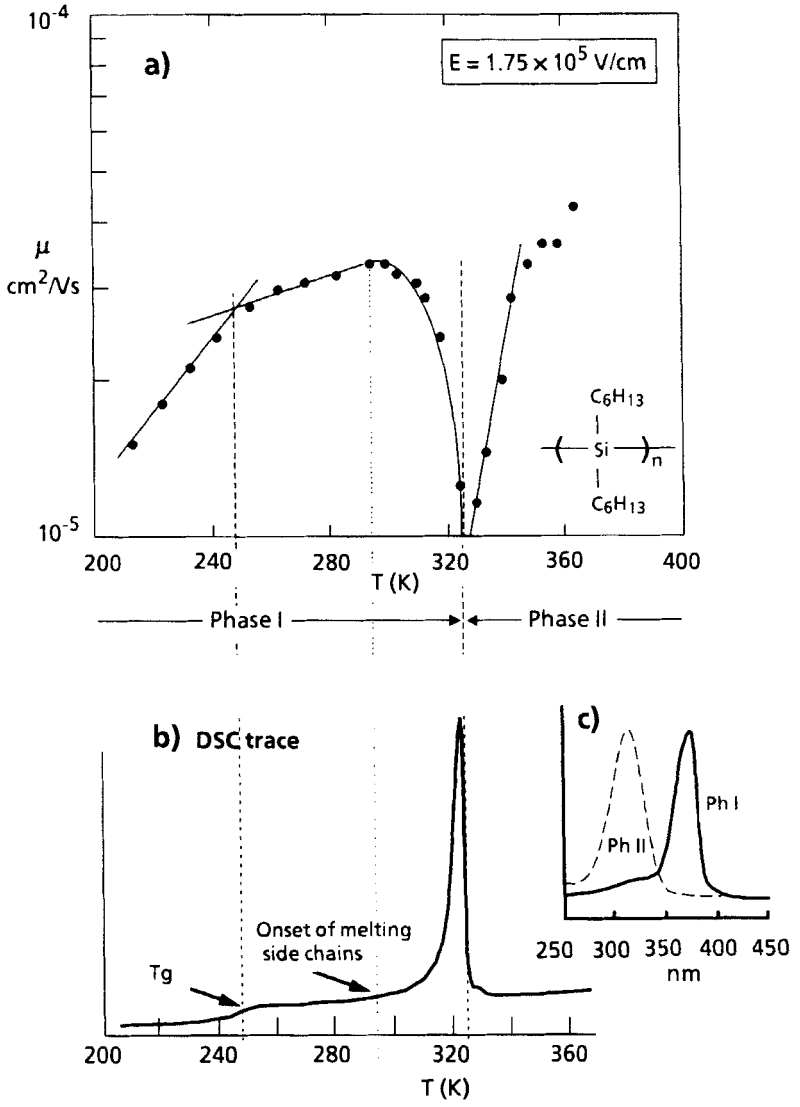

Fig. 1. a) Log hole drift mobility μ in PDHS vs temperature. Three distinct temperature regions are indicated.

b) DSC trace of PDHS plotted on the same temperature axis as a). Scanning rate 20 degrees / minute. Data collected during second heating cycle.

c) Absorption spectra of PDHS. Solid line: phase I, dashed line: phase II.

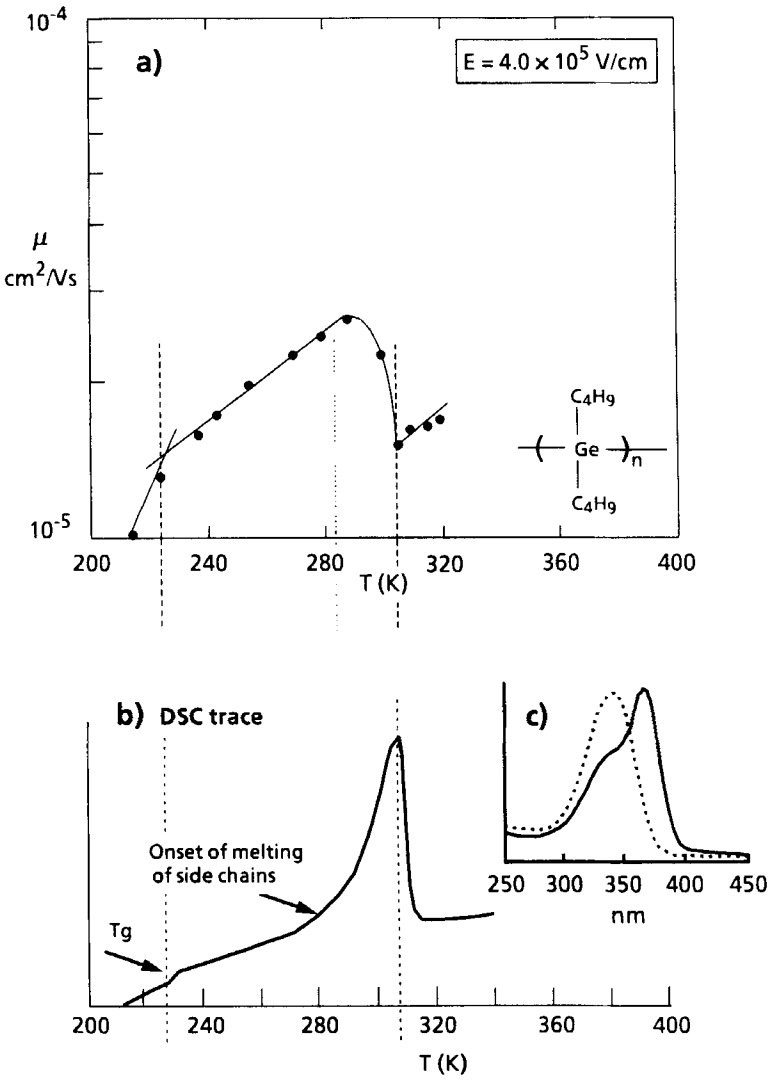

Fig. 2. a) Log hole drift mobility in PDBG vs temperature. Three distinct temperature regions are indicated.

b) DSC trace of PDBG plotted on the same temperature axis as a). Scanning rate 20 degrees / minute. Data collected during second heating cycle.

c) Absorption spectra of PDBG at $T < T_{Tr}$ (solid line) and $T > T_{Tr}$ (dashed line).

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