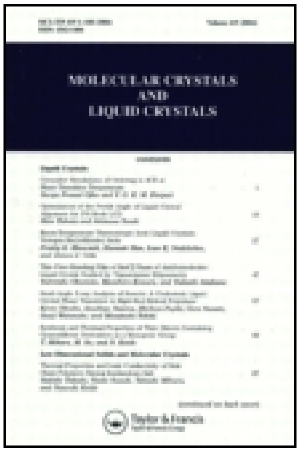

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# Electronic Transport in Si and Ge Backbone Polymers—Effect of Thermal Transitions

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# ELECTRONIC TRANSPORT IN Si AND Ge BACKBONE POLYMERS - EFFECT OF THERMAL TRANSITIONS

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Abstract. Time-of-Flight hole drift mobility measurements have been carried out on representative aromatic and aliphatic pendant group containing silicon and germanium backbone polymers over a wide range of electric field and temperature. The temperature range is broad enough in each case to incorporate the region of glassy solidification. For the specific case of poly(di-n-hexylsilylene), experiments have been extended to incorporate the side chain melting phenomenon identified with the bathochromic shift in the polymer. Mobility changes associated with this transition are analyzed. Specific features observed in Si and Ge backbone polymers, which appear to be a general characteristic of a wide range of disordered solids, are highlighted.

## INTRODUCTION

High molecular weight silicon backbone polymers, polysilylenes, are receiving considerable attention because of their unusual non-linear[1] optical, photostructural and photoelectronic properties.[2] These linear $\sigma$- bonded Si polymers can contain a variety of carbon based pendant groups, which provide these materials with certain properties that are characteristic of analogous carbon-chain vinyl polymers such as high dielectric strength, flexibility and toughness of films, etc. The inherent sensitivity of some polysilylenes to u.v. radiation-induced chain scission makes them attractive for use as photoresists.[2] These polymers are distinguished from plasma deposited organosilanes by quasi one-dimentional network topology, absence of silicon-hydrogen bonds and "dangling bond" defects, and by their stoichiometric composition. Films of these polymers are transparent, colorless, and typically amorphous or semicrystalline. On the other hand, key optical and electrical properties of these polymers have been found to differ significantly from analogous carbon based $\sigma$-bonded polymers like polyethylene, resembling rather more closely the fully $\pi$-conjugated systems like polyacetylene and its analogues. Electronic spectral investigations[3,4] indicated that the lowest lying electronic transitions (near visible UV band-gaps) involved sigma electrons delocalized along uninterrupted runs of Si or Ge atoms on the polymer backbone. The precise extent of this delocalization and its possible manifestation in transport behavior, provoked early scientific interest. In the present paper transport behavior of these polymers is described at and above their respective regions of glassy solidification and in the glassified state well below $T_g$. Transport phenomena associated with thermostructural transitions are delineated. Comparisons are made with other glassy systems.

## EXPERIMENTAL

The synthesis of polysilylenes and polygermylenes by modified Wurtz polycondensation of corresponding dialkyl or aryl-alkyl silicon or germanium dichlorides with sodium is described elsewhere[5,6]. The average molecular weight ($M_w$) exceeded 200,000. Thin films of these polymers (typically 8-25 µm) were prepared by solution coating either directly on aluminum substrates with a thin surface layer of Al oxide or on a naturally oxidized Al substrate overcoated with a ~0.5 µm thick film of a-Se or $As_2Se_3$. The top electrodes were vacuum-deposited semi-transparent gold or aluminum. The small-signal current mode TOF transients were induced by transport of holes injected from either a-Se or a-$As_2Se_3$ photoelectrodes excited by attenuated subnanosecond pulses from a $N_2$ pumped dye laser. Alternatively, the films were intrinsically excited by pulses of 337 nm light, strongly absorbed by the polymer. Both methods produced identical results. Polymers used in these studies were poly(methylphenylsilylene) (PMPS), poly(di-n-butylsilylene) (PDBS), poly(di-n-hexylsilylene) (PDHS) and poly(di-n-butylgermylene) (PDBG). Structures of these polymers are depicted in Fig. 1.

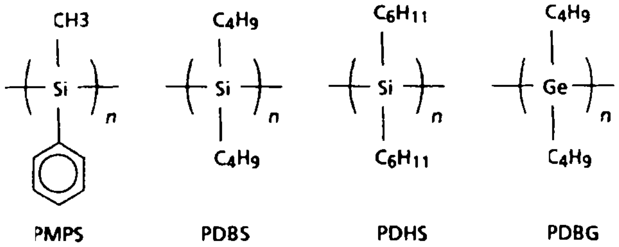


*Figure 1.* Structures of polymers under investigation.

## RESULTS AND DISCUSSION

### T<Tg:

Well below the temperature range of glassy solidification Si and Ge polymers exhibit a convoluted pattern of electric field and temperature

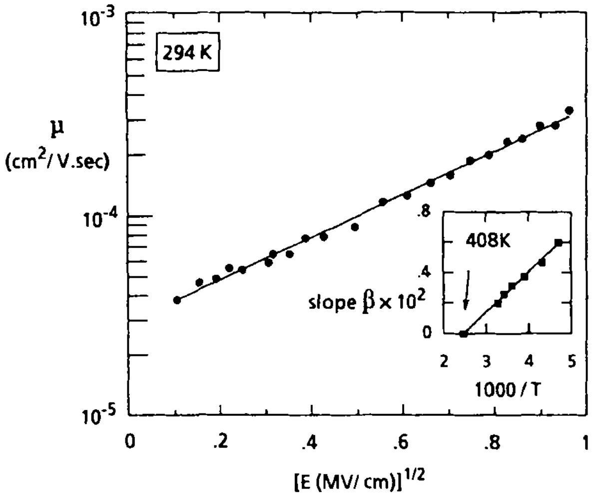


*Figure 2.* Log $\mu$ vs. $E^{1/2}$ for PMPS. Slope of plot depends on temperature as shown in insert.

dependence.[7] This behavior is fully deconvoluted in Figs. 2 and 3 for the case of PMPS. This deconvolution procedure, when also applied to other glassy solids (i.e., poly(N-vinylcarbazole) (PVK), molecularly doped polymers (MDP), Se:As alloys, etc.), reveals certain striking commonalities.[8] Thus drift mobilities in glasses are field dependent as shown in Fig. 1, but the gradient of this dependence varies with temperature as shown in the insert, decreasing as Tg is approached from below. Fig. 2 shows that drift mobilities are typically

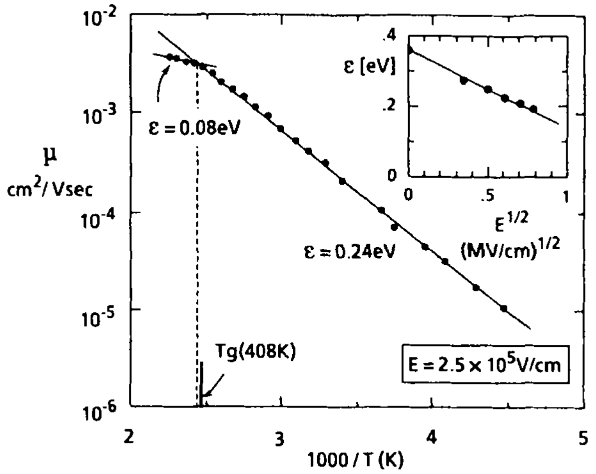
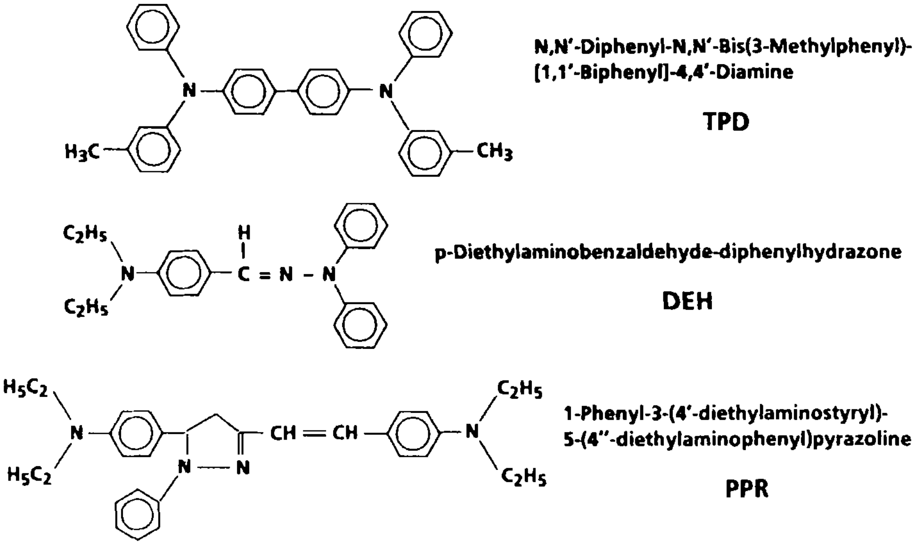


*Figure 3.* Arrhenius plot of $\mu$ in PMPS. Activation energy $\varepsilon$ is field dependent as shown in insert.



**N,N'-Diphenyl-N,N'-Bis(3-Methylphenyl)-[1,1'-Biphenyl]-4,4'-Diamine**

**TPD**

**p-Diethylaminobenzaldehyde-diphenylhydrazone**

**DEH**

**1-Phenyl-3-(4'-diethylaminostyryl)-5-(4"-diethylaminophenyl)pyrazoline**

**PPR**

*Figure 4.* Dopant molecules.

activated with a field dependent activation often exhibiting a square root dependence as shown in the insert. The associated constant of proportionality $\beta$ is typically less than the calculated one-dimentional Poole-Frenkel factor $\beta_{PF}$,

$$\beta_{PF} = (e^3/\pi\varepsilon_0\varepsilon)^{1/2} \qquad (1)$$

where e is the electronic charge and $\varepsilon$ the relative dielectric constant (for PMPS). The experimental $\beta$ is 0.215 meV/(V/cm)$^{1/2}$ vs. $\beta_{PF} = 0.453$ meV/(V/cm)$^{1/2}$). The overall behavior illustrated in Figs. 2 and 3 suggests that hole drift mobility in PMPS can be represented by an equation first proposed by Gill for PVK[9] namely

$$\mu = \mu_0 \exp\{-(\varepsilon_0 - \beta E^{1/2}) / KT_{eff}\} \qquad (2)$$

where $1/T_{eff} = 1/T - 1/T_0$. In the case of PMPS, $T_0 \sim 416K$, $\varepsilon_0 = 0.36$ eV, $\mu_0 = 4 \times 10^{-3}$ cm$^2$/Vsec and the experimental $\beta = 0.215$ meV/(V/cm)$^{1/2}$.

*Dopant induced effects: Trap controlled hopping.* Doping PMPS with the transport active molecules shown in Fig. 4 results in a reduction of $\mu$, of up to several orders of magnitude[10], as shown in Fig. 5. At a given concentration of dopant molecules, $\mu$ scales with the oxidation potential of the respective

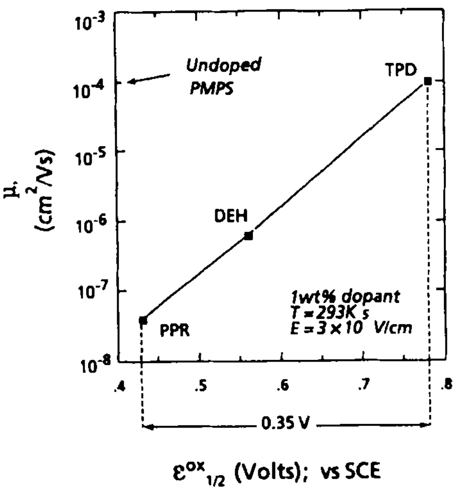


*Figure 5.* Hole drift mobility μ in PMPS doped with 1 wt.-% of dopant molecules plotted vs. oxidation potential $\varepsilon^{1/2}_{ox}$ of dopant molecules.

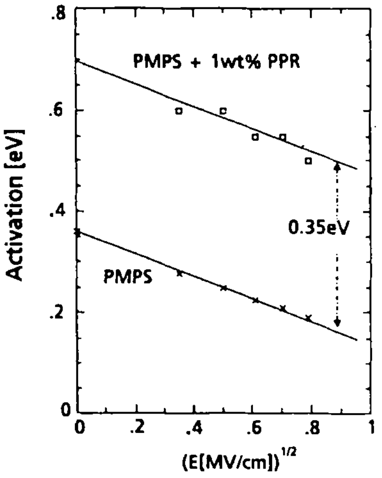


*Figure 6.* Activation energies of μ vs. $E^{1/2}$ for PMPS and PMPS doped with 1 wt.-% PPR. The difference in activation energies corresponds to the difference in $\varepsilon^{1/2}_{ox}$.

dopant $\varepsilon^{1/2}_{ox}$. The strongest effect is seen with PPR ($\varepsilon^{1/2}_{ox} = 0.43V$). On the other hand, TPD ($\varepsilon^{1/2}_{ox} = 0.78V$, estimated to be the same as PMPS) does not affect μ in PMPS. The difference in activation energies of transport between undoped and PPR-doped PMPS (0.35 eV, Fig. 6) corresponds to the difference in the energy levels of the transport states in PMPS and the dopant molecule illustrated in Fig. 7, or the difference of the oxidation potentials. Doping with electron donors which themselves are hole transporting augments the hole mobility in PMPS to levels which depend on the donor strength of the dopant. Doping studies thus provide means of characterizing relative energy levels of hole transport states.

The insulating character of PMPS doped with electron donors is retained. Doping with strong electron acceptors on the other hand is known to render polysilylenes highly conducting (conductivities σ near 0.5 $\Omega^{-1}cm^{-1}$ have been observed).[11]

### $T \geqq Tg$:

The behavior displayed in Fig. 3 for PMPS as temperature is increased from below into the glass transition region is also observed in PDBS, PDHS, and PDBG. Figure 8 shows that during both rate and step heating and cooling of PDBS films at fixed electric field E, an abrupt change in the effective transport activation occurs in the vicinity of the glass transition. To within

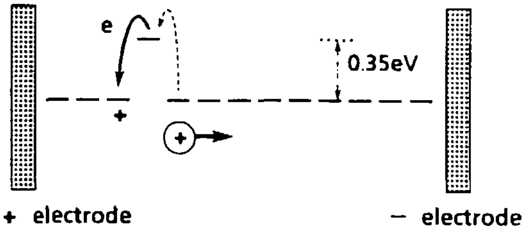


*Figure 7.* Schematic diagram illustrating trap controlled hopping for the case of trap located 0.35 eV above the transport states.

experimentally set limits, hysteresis behavior in mobility is not observed below $T_g$ in Si and Ge polymers. Similar results have been noted earlier in studies on other polymers and in molecular dispersions in glassy hosts.[12] A similar change in the temperature dependence of electron transport above $T_g$ has been observed in an a-Se:As alloy.[13] Photoelectronic behavior of chalcogenide alloys associated with thermal cycling through the glass transition has been analyzed in detail in a series of earlier publications.[13] In chalcogenides, rate heating and cooling in the vicinity of $T_g$, induced pronounced hysteresis in mobility behavior below $T_g$, as illustrated in Fig. 9. Relaxation of mobility hysteresis parallels thermostructural relaxation. Because mobility in Se based chalcogenides is shallow trap controlled, and because mobility activation does not exhibit hysteresis, the thermal history

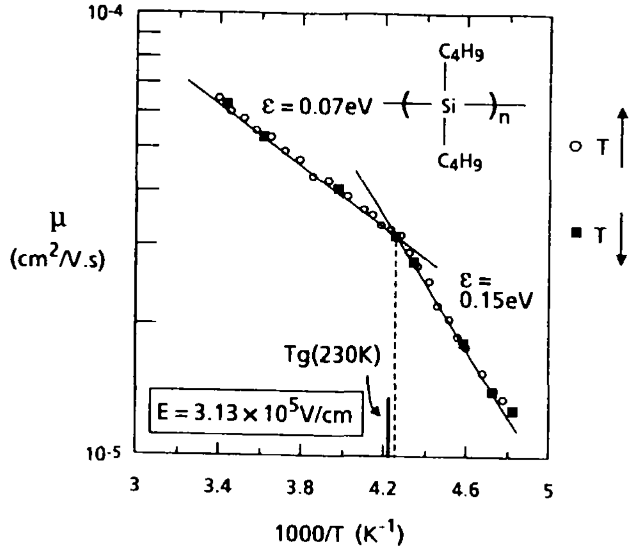


*Figure 8.* Arrhenius diagram of μ in PDBS over a temperature range containing Tg.

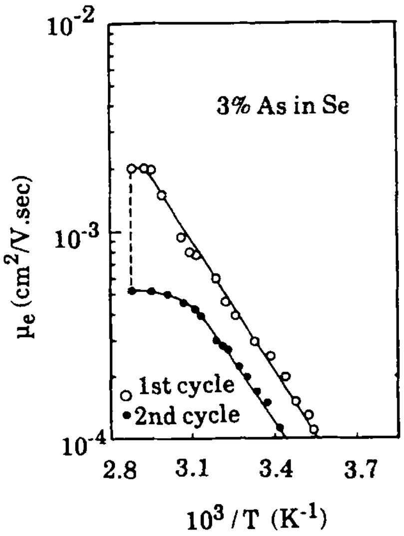


*Figure 9.* Arrhenius plots of electron drift mobility in Se-As alloy with 3% As. Open circles: 1st heating cycle of a specimen annealed for >1000 hours. Filled circles: Specimen cooled and the heating cycle repeated immediately after. Note pronounced hysteresis.

induced mobility fluctuations are associated with systematic variation in the population of shallow traps, whose position in the gap remains fixed. The traps in chalcogenides behave as thermodynamic defects. Their population is a function of the structural state of the glass. The comparison illustrated in Figs. 8 and 9 serves to distinguish two processes: (*1*) A change in the temperature dependence of effective transport activation, evidently observed in a wide range of glassy solids. The activation energy change itself exhibits no hysteresis and may, therefore, be directly associated with the unfreezing of liquid-like molecular excitation in the melt above $T_g$ - a generalized phenomenon. (*2*) Pronounced thermal memory effects below $T_g$ which appear to be a feature peculiar to systems like the Se rich chalcogenides where transport is controlled by thermodynamic defects. At a given temperature, the defects in the glassy state of these systems are always in the process of relaxing toward the quasi equilibrium (melt extrapolated) population they would have at that temperature.

*Mobility which decreases with field: PDBG above $T_g$.* Fig. 2 illustrates the temperature dependence of the slope of ln μ vs. $E^{1/2}$ plots in PMPS. The slope becomes zero at 408K, which in this case is in the temperature range of glassy

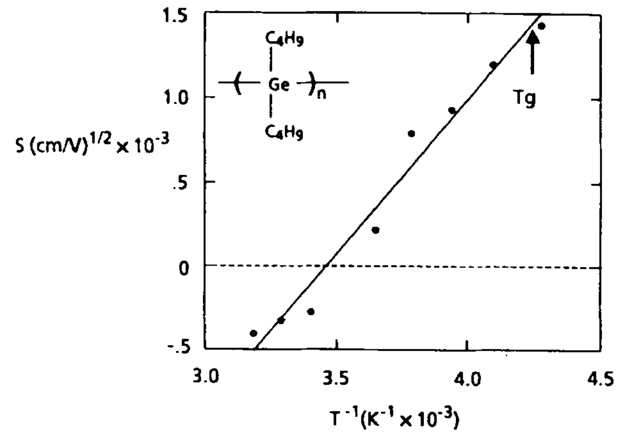


*Figure 10.* Plots analogous to insert in Fig 2 derived for PDBG.

solidification. Fig. 10 is a plot analogous to the insert in Fig. 2 derived from drift mobility data on PDBG. An arrow denotes $T_g$ (~230K) on the temperature scale. At the highest experimental temperatures which are well above $T_g$, the slope has evolved through zero at approximately 290K to negative values. Recently, qualitatively similar behavior was reported by Peled and Schein[14] for the molecularly doped polymer, DEASP in polycarbonate.. The latter observations were made at low concentrations of the small molecule and in the restricted temperature range $T_g < T < T_0$ where $T_0$ is the temperature shift parameter in Gills equation (2). It was suggested that for DEASP Gill's equation in fact remained valid for temperature $T > T_0$ (with the same set of phenomenological parameters). For the present case of PDBG, however, the use of Gill's equation with the same parameters below and above $T_g$ cannot describe the data. In neither case are the underlying microscopics of these interesting newly identified phenomena adequately understood.

*Effect on mobility of conformational transition in PDHS.* Polysilylenes with aliphatic pendant groups are characterized by an intense absorption which is variously attributed to a $\sigma\sigma^*$ or a $\sigma 3d\pi_{Si\text{-}Si}$ transition. These transitions are molecular weight dependent, which is reminiscent of polyacetylene and other π- conjugated polymers.[15] The absorption wavelength initially increases with catenation, but rapidly approaches a limiting value as the number of silicon atoms in the chain increases.[16] In polysilylenes with aliphatic pendant groups this limiting value is typically between 300 and 325 nm.[17] It was recently reported that solid films of poly(di-n-hexysilylene)

(PDHS)[18], exhibit the expected electronic absorption at 310-320 nm but only above a specific transition temperature $T_{Tr}$. Below the transition temperature $T_{Tr}$, the absorption is shifted to a considerably longer wavelength, near 370-380 nm. For PDHS, this transition temperature is ~315K. It was proposed that the long-wavelength absorption at $T < T_{Tr}$ is the result of conformational locking of the polysilylene chain into a specific configuration caused by crystallization of pendant linear alkyl groups.[18,19] The more ordered form of films at $T < T_{Tr}$ is referred to as phase I. Spectroscopic and NMR studies show that in this phase the n-hexyl sidegroups are packed in a regular array with their long axes nearly perpendicular to that of the silicon backbone and the Si backbone has all-trans planar zig-zag conformation rather than the expected helical conformation.[18-21] Above the transition temperature, this polysilylene is in a conformationally disordered (albeit not completely amorphous) state[19,21,22] which is referred to as phase II. "Melting" of the sidegroup aggregates, at $T_{Tr}$, relaxes the structure and allows formation of some gauche links in the backbone.[23] The phase transition is completely reversible, even though the kinetics of the phase transformation is molecular weight dependent and the relative proportion of phases I and II depends on the annealing and thermal history.

An association of the change in the spectrum with changes in the dihedral angles of the silicon backbone has been suggested.[18] The $\sigma_{Si\text{-}Si}$ orbital shifts and corresponding changes in the electronic spectra caused by changes of the dihedral angle between neighboring σ bonds were actually shown to occur in short chain substituted silane catenates.[24] In view of the recently published studies it is reasonable to expect that conditions leading to changes of the dihedral angles between interacting σ bonds from the equilibrium "normal" solution values will lead to changes not only in spectral characteristics but also other electronic properties of the polymer.

Since charge transport states in polysilylenes are backbone derived and since the electronic states of the backbone are altered during the observed phase I - phase II transition, it is of interest to elucidate the effect of the transition on the charge transport behavior.

The phases I and II of PDHS are well characterized by the absorption peaks at 370-380 nm and 315-320 nm, respectively, as shown in Fig. 11. The hole drift mobility data displayed in Fig. 12 are organized into three regions corresponding to three distinctly different conformational states of PDHS: *(1)* the ordered (w.r.t. side chains) glassy state below $T_g$, *(2)* the ordered region between $T_g$ and $T_{Tr}$ and *(3)* the disordered (w.r.t. the side chains) phase II above $T_{Tr}$. Behavior of PDHS in the glassification region is similar to the

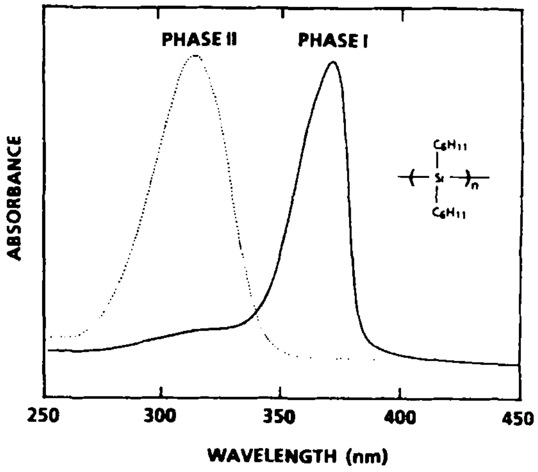


*Figure 11.* UV spectra of Phase I and Phase II PDHS.

behavior near $T_g$ described in Fig. 8 for PDBS. In the case of $T \sim T_g$, mobility activation changes abruptly but mobility does not simultaneously exhibit a step change and there is no corresponding charge in the near visible u.v. spectra. It is clear however, from Fig. 12, that both mobility values and the temperature dependence of mobility change abruptly at $T_{Tr}$, a region in PDHS that is characterized by the dramatic change in electronic spectra as illustrated in Fig. 11. It appears that the hole drift mobility initially decreases with temperature from the onset of the melting of side chains. The phase II material is then characterized by a greatly enhanced temperature dependence of mobility. Unfortunately, at these temperatures the softened specimen becomes difficult to handle in the experimental cell, limiting our ability to extend measurements to even higher temperatures. If the mobility in the pure phase II region is assumed to be activated, then the room temperature mobility value that would result if phase II structure could be completely preserved by quick quenching, would extrapolate to approximately $10^{-6}$ cm$^2$/volt sec. Our spectral analysis indicates however that dry ice quenching results in rapid and substantial reconversion of phase II to phase I. In fact, all of our attempts to rapidly quench phase II materials lead at best to films which are an admix of phase I and phase II material as characterized by u.v.-vis spectroscopy.

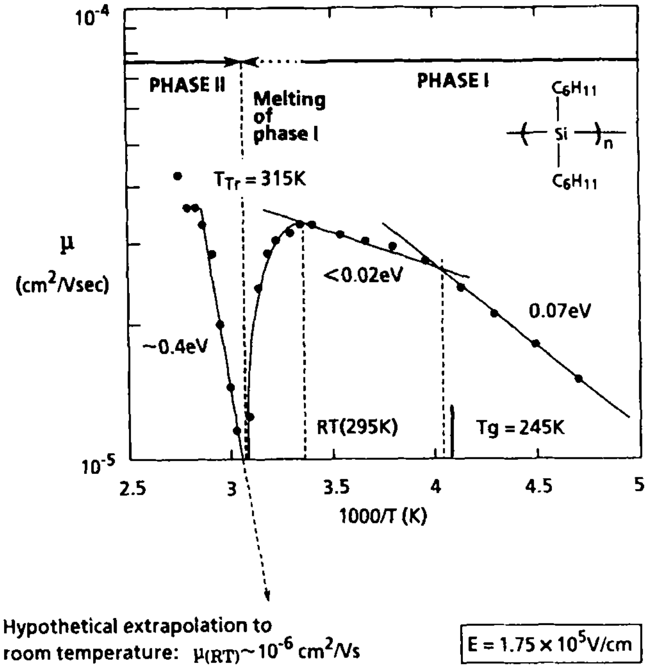


*Figure 12.* Arrhenius plot of μ in PDHS through a tempeature range encompassing Tg (245K) and a side chain melting induced transition $T_{Tr}$ at 325K. Respective activation energies are indicated.

## SUMMARY AND CONCLUSIONS

(1) Temperature and field dependence of hole drift mobility has been studied in representative aromatic and aliphatic side group containing silicon and germanium backbone polymers. Deconvolution of the experimental data reveals a pattern of behavior common to a wide group of disordered systems including polymers with pendant transport-active groups, molecularly doped polymers and even amorphous selenium. A mechanism of field - assisted thermal release from transport - controlling localized states is apparently common to a wide range of disordered solids.

(2) Doping effect of transport-active molecules with oxidation potential $\varepsilon^{1/2}_{ox}$ lower than that of the host PMPS, has been clearly demonstrated. The analysis of the data indicates that the underlying mechanism is that of trap controlled hopping.

(3) An abrupt decrease in activation energy in the vicinity of $T_g$ has been observed in PMPS, PDBS, PDHS and PDBG. Virtually identical behavior was reported earlier in both molecularly doped polymers and polymers with

pendant transport active groups. Similar effect has been reported in a Se-As alloy with 3% As. The change in activation energy is not accompanied by a step change in mobility itself, neither is it associated with temperature induced change in electronic spectra. It is suggested that the observed behavior is associated with molecular dynamics, e.g. spectrum of relaxation rates, rather than with any change in static structure.

(4) In PDHS, a change in the static structure manifested in a bathochromic shift in electronic spectra has been identified with a change in main chain conformation. An abrupt change in μ and and its apparent activation have now been clearly identified with this phenomenon. It appears that μ in the disordered phase II - if extrapolated to low temperatures - is significantly lower than μ associated with the more ordered phase I material.

Studies comparing phase transformation in PDHS, which is caused by side group crystallization, with phase transformation caused by main chain crystallization in poly(methyl-n-propylsilylene) are currently in progress.

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