# Mobilities of Charge Carriers in Dendrite and Linear Oligogermanes by Flash Photolysis Time-resolved Microwave Conductivity Technique

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The photoconductive properties of a series of oligogermanes with dendrite or linear skeleton have been studied by flash photolysis time-resolved conductivity (FP-TRMC) technique. The values of mobility ($\Sigma\mu$) and photocarrier generation yield ($\phi$) have been discussed as a function of $C_{60}$ concentration. The $\phi\Sigma\mu$ values in the order of $10^{-4}$ to $10^{-3}$ cm$^2$/Vs were observed for the oligogermanes upon exposure to 532, 355, and 193 nm light. The intrinsic value of mobility in the derivatives was also estimated without contribution from the additives, suggesting the presence of a highly conducting path along the Ge backbones of not only linear oligogermanes but also hyper-branched germanium dendrites.

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Polymers containing group 14 elements such as silicon and germanium in their backbone have been a subject of considerable interest nowadays. Oligo and polygermanes have been extensively studied on their photochemical reaction dynamics, charged radical species, photodegradation, and ionization potentials.[1–4] However, the study of photogeneration of charge carriers and their transport properties is very limited in oligo or polygermanes compared with those of the corresponding silicon compounds.[5,6] Essential role of branching structures has been reported in the silicon analogs as the localization centers of charge carriers, leading to the degradation of charge-carrier mobility in the materials.[6] This suggests apparently that the backbone branching introduced randomly into the linear chain acts as "defects" of carrier-transport properties, however the intrinsic nature of the ordered hyper-branching structures in germanium dendrites is still in concern. The flash photolysis time-resolved microwave conductivity (FP-TRMC) technique having nanosecond time resolution enables us to obtain the intramolecular mobility of charge carriers on conjugated molecules.[7,8] An electrode less TRMC is the best technique to perform a direct measurement of charge-carrier mobility which is free from boundary perturbations, impurities, etc. In this paper, FP-TRMC experiments were carried out for fullerene-doped oligogermane (PG) films and the intrinsic intramolecular mobility was evaluated.

Thin films of PGs were prepared by casting solutions containing both PGs and the dopant (in *o*-dichlorobenzene) on quartz plates at ca. 1 μm thick. Molecular weights of PGs are summarized in Table 1 ($M$w/$M$n < 1.3 for linear compounds). The nanosecond laser pulses from both excimer and Nd: YAG lasers have been used as an excitation sources. The transient photoconductivity ($\Delta\sigma$) of the polymer film is related to the reflected microwave power ($\Delta$Pr/Pr) and $\phi\Sigma\mu$, the product of photocarrier generation yield ($\phi$) and sum of the mobilities of charge carriers ($\Sigma\mu$).[7,8] All the above experiments were carried out at room temperature. Absorbed photon density was calibrated based on UV–vis spectra of the films which showed significant contribution from $C_{60}$ at 532 nm and from PGs at 355 nm, respectively.

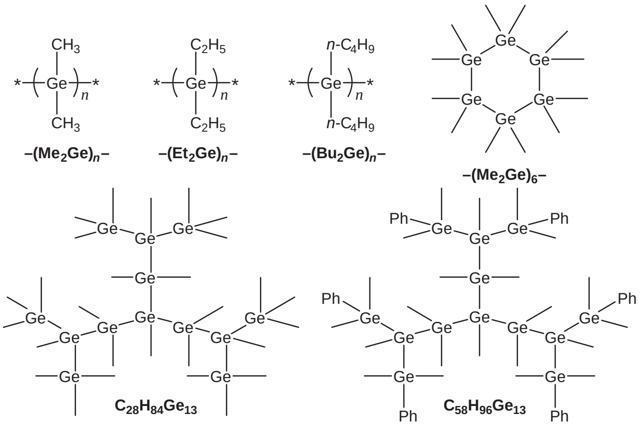

**Figure 1.** Chemical structures of oligogermanes used.

The primary molecular structures of the linear, cyclic, and dendrite PGs are given in Figure 1. Values of $\phi\Sigma\mu$ in the PG films doped with $C_{60}$ ($C_{60}$: 11 mol % relative to PG concentration) under an excitation at 532, 355, and 193 nm are presented in Table 1. The first ionization potentials of PGs have been reported as 5.31–5.95 eV.[4] Thus excitation at 193 nm (6.39 eV) would produce ion pairs directly on polymers, leaving negligible effect of $C_{60}$ for charge-transfer process. The maximum $\phi\Sigma\mu$ values upon exposure to 193 nm are due to the result of direct polaron formation on polymer molecules without interference of any other process, giving the higher $\phi$ values than those in the other excitation light sources. The mechanism of charge carrier generation in polymer sample is very different under an excitation at 532 and 355 nm. On exposure to 532 nm (2.32 eV) holes are created when electrons are transferred from PGs to $C_{60}$ molecules. Because of the high intersystem-crossing efficiency of $C_{60}$ with the fast rate constant ($1.1 \times 10^9$ s$^{-1}$),[3] the electron transfer reaction is most preferable between ground state of PGs and triplet excited state of $C_{60}$ ($^3C_{60}{}^*$) as represented by the following equation,

$$^3C_{60}{}^* + PG \rightarrow C_{60}{}^{\bullet -} + PG^{\bullet +}. \qquad (1)$$

**Table 1.** Values of $\phi\Sigma\mu$ in oligogermane film samples doped with 11.6 mol % of $C_{60}$ under an excitation at 532, 355, and 193 nm

| Compound | $M$w | $\phi\Sigma\mu$ ($\times10^{-4}$ cm$^2$/Vs) | | |
|---|---|---|---|---|
| | | at 532 nm | at 355 nm | at 193 nm |
| $-(Me_2Ge)_n-$ | 1050 | 4.2 | 5.8 | 67 |
| $-(Et_2Ge)_n-$ | 1630 | 16 | 18.5 | 55 |
| $-(Bu_2Ge)_n-$ | 3900 | 2.0 | 2.9 | 42 |
| $(Me_2Ge)_6$ | 616 | 3.7 | 4.7 | 43 |
| $C_{58}H_{96}Ge_{13}$ | 1737 | 2.0 | 3.1 | 26 |
| $C_{28}H_{84}Ge_{13}$ | 1365 | 1.4 | 2.0 | 55 |

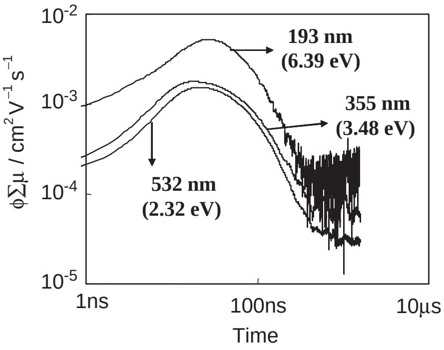

**Figure 2.** TRMC conductivity transients for a $C_{60}$ (11.6 mol %)-doped –$(Et_2Ge)_n$– film under an excitation at 193, 355, and 532 nm.

Upon exposure to 355 nm, the $\phi\Sigma\mu$ values obtained for PGs are slightly higher than those under 532 nm excitation. This may be due to the contribution from the photoionization via $^1PG^*$, because the photon energy of 355 nm (3.48 eV) is equivalent to the band edge of exciton transition of PGs.

The $\phi\Sigma\mu$ values of the dendrites ($C_{58}H_{96}Ge_{13}$ and $C_{28}H_{84}Ge_{13}$) are almost competitive with those in the linear PGs except for –$(Et_2Ge)_n$–. Although the branching structures in the $\sigma$-conjugated linear chain caused drastic decrease of charge carrier mobility (ca. $10^{-4}$ cm²/Vs in linear → ca. $10^{-6}$ cm²/Vs in 10% branching),[6,9] no significant decrease is observed in the $\phi\Sigma\mu$ value of PG dendrites. This is strongly suggestive that the intramolecular charge-carrier mobility is competitive in linear and dendrite PGs. The hyperbranching structures of the dendrites show no considerable effect of charge localization because of their highly ordered and symmetric structures. Among all PGs, the highest $\phi\Sigma\mu$ value is obtained for –$(Et_2Ge)_n$– under excitation at 355 or 532 nm, and the observed TRMC traces are shown in Figure 2. The identical traces are observed under both 355 and 532 nm excitations, however the trace decays apparently faster upon exposure to 193 nm.

Radical cations of PGs produced by the reaction (1) have been well known to exhibit a strong transient optical absorption band at near UV regions with high extinction coefficients ($\varepsilon^{\bullet+}$).[9–12] The transient optical kinetic traces were also observed for $(–(Et_2Ge)_n–)^{\bullet+}$ at 370–390 nm, and the traces show good correspondence with the TRMC traces within the entire time range from ns to μs. The observed values of optical density ($\Delta_{OD}$) attributed to the radical cations gave the yield of reaction (1): $\phi$ based on the values of $\varepsilon^{\bullet+}$ as follows;

$$\phi = A\Delta_{OD}/d\varepsilon^{\bullet+}N, \qquad (2)$$

where $A$, $d$, and $N$ are Avogadro's number, thickness of the film, and the number of photons absorbed in an unit volume, respectively. The values of $\varepsilon^{\bullet+}$ of symmetrically dialkyl-substituted polygermanes and polysilanes were reported to be 4.5–5.5 × $10^4$ M$^{-1}$ cm$^{-1}$,[9–12] thus the highest limit of $\phi$ value in the –$(Et_2Ge)_n$– and $C_{60}$ mixture system ($C_{60}$: 11.6 mol %) is estimated as 3.3 and 1.0% under 193 and 532 nm excitations, respectively.

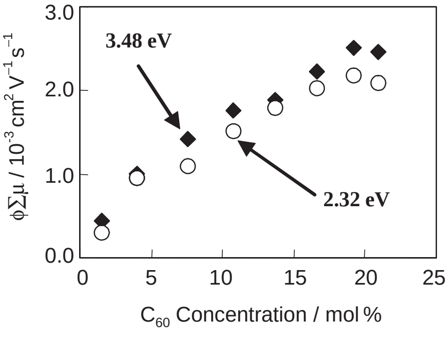

**Figure 3.** Dependence of $\phi\Sigma\mu$ values on $C_{60}$ concentration (mol %) in a –$(Et_2Ge)_n$– polymer film.

Figure 3 shows the dependence of $\phi\Sigma\mu$ values as a function of fullerene concentrations in –$(Et_2Ge)_n$– film upon exposure to 532 and 355 nm. The $\phi\Sigma\mu$ values increases gradually with fullerene concentration and saturated at higher fullerene concentration (ca. 20 mol %). The increase is attributed mainly to the following factors: (1) changes in the dipole moment of the film (2) an increase in $\phi$ due to aggregation of $C_{60}$, and (3) a contribution from $\mu^-$ of the electrons trapped in $C_{60}$ aggregates. The decrease in the total dielectric constant due to $C_{60}$ doping (with a low dipole moment) often causes an increase in the mobility. The contribution of $\mu^-$ towards $\Sigma\mu$ ($\mu^+ + \mu^-$) may lead to the higher $\phi\Sigma\mu$ value due to increasing number of trapped electrons at $C_{60}$ aggregates.[13] The extrapolation of the concentration dependence gives the $\phi\mu$ value of positive charges on –$(Et_2Ge)_n$– molecules as $\phi\mu^+ = 4.8 \times 10^{-4}$ cm²/Vs. According to the value of $\phi$ estimated by Eq. 2, the intrinsic intramolecular mobility of positive charges is derived as $\mu^+ > 4.8 \times 10^{-2}$ cm²/Vs. This is consistent with the value of the "isolated single-chain mobility" along Si chains in polysilane derivatives: silicon analogs of PG.[8] However, conventional direct-current (DC) techniques, such as time-of-flight measurement, gave two orders of magnitude lower values of $\mu^+$ as ca. $10^{-4}$ cm²/Vs. In the DC techniques, the charge-carrier motion is affected by trapping sites (impurity, domain boundary, defects, etc.) as they move over a long distance. This is the case giving the lower values estimated by the conventional techniques, thus the potentials of germanium skeleton in the PG compounds would be very high as positive charge conductors.

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