Radiation-Induced Conductivity in Poly(methylphenylsilylene) and Poly(di-*n*-hexylsilylene) Studied by Time-Resolved Microwave Conductivity

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ABSTRACT: The transient conductivity change resulting on nanosecond pulsed irradiation of poly(methylphenylsilylene) (PMPS) and poly(di-*n*-hexylsilylene) (PDHS) has been studied using the time-resolved microwave conductivity (TRMC) technique from nanoseconds to milliseconds after the pulse. The transients show a dispersive decay. In PMPS, where the hole is the major charge carrier, the mobility at room temperature appears to decrease with time from an initial value of at least 3×10^{-8} m^2/V·s on a nanosecond time scale to a value 1 order of magnitude less at milliseconds. In PDHS the initial radiation-induced conductivity per unit dose is 2 orders of magnitude larger than for PMPS at room temperature and corresponds to a charge carrier mobility of at least 1×10^{-5} m^2/V·s. The end-of-pulse conductivity decreases by a factor of 20 at the solid-to-mesophase transition.

Introduction

Polysilanes, catenated Si polymers, currently attract wide attention due to their intriguing electronic, optical, and charge transport properties.[1] The conformation-dependent σ-conjugation of the polymer backbone leads to intense UV absorptions in the solid state and in solution which are comparable with those of π-conjugated systems.[2] Based on their unique electronic properties, applications in microlithography,[3] electrophotography,[4] display fabrication,[5] and data storage[6] as well as nonlinear optics[7,8] have been proposed. Although polysilanes are insulators with relatively large band gaps in the pure state, photoconductivity with high quantum yields[9] and dark conductivity on doping[10] are observed.

Polysilanes with an amorphous structure such as poly(methylphenylsilylene) (PMPS) have been studied intensively with respect to their potential as polymeric materials for photoreceptors in electrophotography.[11–14] This interest is motivated by the hole drift mobilities on the order of 2×10^{-9}–2×10^{-8} m^2/V·s, which are among the highest reported for polymers. Values of this magnitude have been observed for various polysilanes on irradiation or on injection of charge carriers in time-of-flight (TOF) experiments. They have been confirmed by thermally stimulated current (TSC) measurements on thin films.[15,16] Hole transport was found to be nondispersive and thermally activated.[12–14] Carrier lifetimes were estimated to be several milliseconds.[17]

Charge transport in noncrystalline, catenated Si polymers has been explained in terms of thermally activated and field-assisted hole hopping between backbone-derived localized states, which are assumed to be all-trans chain segments separated by disordered regions.[11–14] This explanation is supported by the independence of charge transport on the nature of the side chains.[18] Similar mobilities have been observed for all polysilanes with nonsymmetric and nontactic structures.[19] Fluorescence experiments on poly(methylphenylsilylene) with two-photon excitation showed highly mobile excitons on a picosecond time scale. It has been suggested that these also move rapidly along the chains and frequently hop from chain to chain.[20]

In contrast to the atactic poly(methylphenylsilylene), symmetrical di-*n*-alkyl-substituted polysilanes form highly ordered crystalline structures.[21,22] At higher temperatures, columnar mesophases,[23] also termed "condis crystals"[24] are formed. So far, little information is available on the mobilities and lifetimes of charge carriers[18,25] in the crystalline solid and liquid crystalline phases of poly(di-*n*-alkylsilylene)s. Investigation of the influence of the phase transition on the charge transport properties of these materials is made difficult by contact problems, which are encountered when the materials transform from the solid into the liquid crystalline state[18] and vice versa.

The comparison of PMPS and poly(di-*n*-hexylsilylene) (PDHS) in the time-resolved microwave conductivity (TRMC) pulse radiolysis[26] study reported here was motivated by interest in the nature and the kinetics of charge transport in highly ordered crystalline polysilanes and the influence of the phase transition on their conductive properties. In contrast to dc conductivity methods, the TRMC technique is free from electrode contact problems and problems caused by microheterogeneities within the sample. In addition, pulse radiolysis results in close to uniform charge carrier formation throughout the sample for specimens up to several millimeters thick.[26,27]

Experimental Section

Poly(methylphenylsilylene) (PMPS) and poly(di-n-hexylsilylene) (PDHS) were synthesized by reacting the corresponding dichlorosilanes with a dispersion of sodium in a hydrocarbon solvent. The high molecular weight polymers were separated from the cyclic and linear low molecular weight byproducts by repeated reprecipitation. Details on the synthesis are described elsewhere.[28] Molecular weights were determined by gel-permeation chromatography, which was calibrated using polystyrene standards. The weight-average molecular weight (M_w) and dispersity (M_w/M_n) of the PMPS samples were 3×10^4 and 3.5 and those of the PDHS samples were 5.4×10^5 and 1.8.

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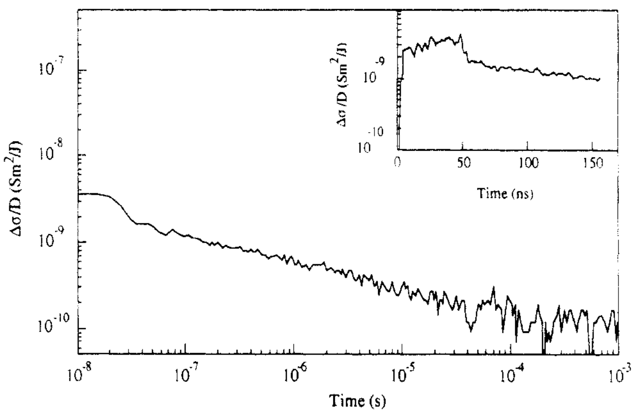

Figure 1. Dose-normalized, radiation-induced conductivity in PMPS at 20 °C obtained using a 50-ns, 2.6-A pulse of 3-MeV electrons. In the main figure, the data are displayed on a logarithmic time scale from 10 ns to 1 ms. In the inset, the data are displayed on a linear time scale over the first 150 ns from the beginning of the pulse.

The polymers were compressed by hand into a short-circuited piece of rectangular waveguide of cross section 7.1 × 3.55 mm². The length of the sample was approximately 10 mm. The fraction of bulk solid in the compressed sample could be calculated from the measured length and weight based on a density of 1 g/cm³ for the bulk material. This fraction was found to be 0.57 for the PMPS and 0.80 for the PDHS samples.

The samples were ionized by irradiation with nanosecond pulses of 3-MeV electrons from a van de Graaff accelerator. The integrated beam charge per pulse, Q (in nC), was monitored routinely. The energy deposition could be assumed to be uniform within the sample since the penetration depth of 3-MeV electrons in the materials is approximately 10 mm. This is almost 3 times the sample depth. The energy deposition per unit volume, D (in J/m³), was determined to be 580Q J/m³, using a thin-film radiochromic dosimeter (Far West Technology Nr92). The employed low linear energy-transfer (LET) high-energy electron radiation produces electron–hole (e–h$^+$) pairs by ionization with an average distance between events along the track of 1000 Å or more.[29]

Pulse widths of 2–50 ns and beam charges from 5 to 200 nC were used. The average concentration of e$^-$–h$^+$ pairs formed per pulse was on the order of 10 μM or less. Usually 4–16 single-pulse traces were averaged per measurement. No degradation of the samples, apparent either as a change of the signal height or as decay kinetics was observed to occur with accumulated irradiation.

Changes of the conductivity of a sample upon irradiation were monitored as changes in the microwave power reflected by the sample using the TRMC technique.[26,27,30] The microwave frequency band used was 26.5–40 GHz. Variations in the conductivity of 10^{-5} S/m could be readily measured. Changes in the output of the microwave detector diode were monitored using either a Tektronix 7912 digital oscilloscope or a tandem combination of a Tektronix 2205 oscilloscope (7A13 plug-in) and a Sony/Tektronix RTD 710 digitizer. Using the former, the response time was approximately 1 ns. The latter combination had a rise time of 5–10 ns but was capable of registering data using a pseudologarithmic time base. This allowed the recording of transient data from 10 ns to milliseconds using a single accelerator pulse.

Conductivity transients were usually monitored at several different microwave frequencies across the band. The absolute value of the conductivity change was determined from a calculated best fit to the data points. This procedure has been described fully elsewhere.[27,30]

Results and Discussion

Nanosecond pulsed irradiation of both PMPS and PDHS samples at room temperature results in readily measurable transient conductivity signals, as is shown in Figures 1 and 2. The temporal form and, in particular,

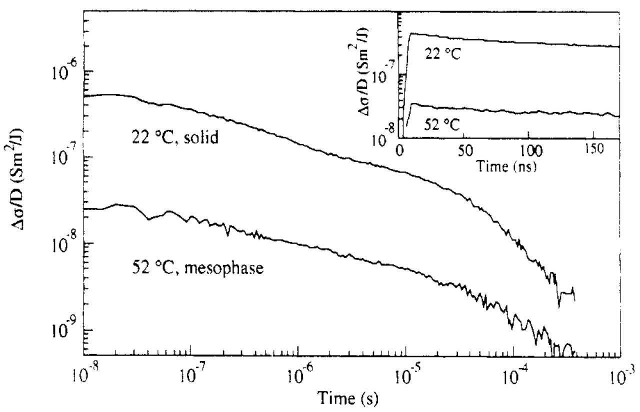

Figure 2. Dose-normalized, radiation-induced conductivity in the solid (22 °C) and liquid crystalline (52 °C) phases of PDHS obtained using a 10-ns, 2.6-A pulse of 3-MeV electrons. In the main figure, the data are displayed on a logarithmic time scale from 10 ns to 1 ms. In the inset, the data are displayed on a linear time scale over the first 170 ns from the beginning of the pulse.

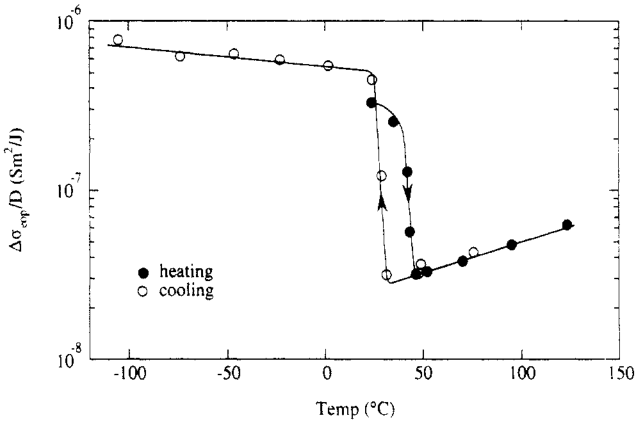

Figure 3. Temperature dependence of the end-of-pulse, dose-normalized, conductivity of pulse-irradiated PDHS. The filled circles are obtained on heating from room temperature and the open circles on subsequent cooling.

the magnitude of the dose-normalized conductivity, $\Delta\sigma/D$, are however quite different for the two materials.

In the case of PMPS, there is evidence of a very short-lived component which reaches a steady-state level during the pulse and decays very rapidly immediately following the pulse. The lifetime of this component is estimated to be close to or shorter than the time resolution of the measurements, which is approximately 1 ns. The initial rapid decay after the pulse gives way to a much more slowly decaying component which decreases gradually over a time scale extending to milliseconds. The decay kinetics of this component are disperse, i.e., nonmonoexponential.

The initial, i.e., nanosecond time scale, radiation-induced conductivity of PDHS, in the solid phase at room temperature, is approximately 2 orders of magnitude larger than that observed for PMPS. In addition, there is no evidence of a short-lived component for this material. Rather, the whole conductivity signal decays gradually over a time scale which extends to hundreds of microseconds.

A further difference between the two materials is that the conductivity of PDHS undergoes an abrupt decrease on heating by a factor of approximately 20 in the region of 40 °C, as shown in Figure 3. This is the same temperature at which the crystalline solid to mesophase transition is found to occur by differential scanning calorimetry and by X-ray diffraction.[1,21,23,31] This transition is accompanied by drastic changes in the backbone

σ-delocalization and thus in the electronic and optical properties related to the band-gap energy.[32] PMPS on the other hand displays only a continuous gradual increase in $\Delta\sigma/D$ with increasing temperature, in agreement with its amorphous character and lack of phase transitions.

Before discussing the results further, we consider the quantitative relationship between the radiation-induced conductivity transients observed and the properties of the mobile charge carriers formed.

Radiation-Induced Conductivity. A change in the real component of the microwave conductivity of an irradiated material resulting from the formation of mobile charge carriers is related to the mobility of the carriers, $\mu(+)$ and $\mu(-)$, and the concentration of charge carrier pairs present at time t, $N_p(t)$, by

$$\Delta\sigma(t) = e[\mu(+) + \mu(-)]N_p(t) \qquad (1)$$

In (1), e is the elementary charge and it is assumed, at least initially, that only one type each of positive and negative charge carriers with characteristic mobilities is present.

For an infinitely short pulse which results in an energy deposition in the material of D J/m^3, the initial concentration of electron–hole pairs would be

$$N_p(0) = D/eE_p \qquad (2)$$

In (2), the "pair-formation energy", E_p, is the average energy required to form one e^-–h^+ pair. From (1) and (2), the "initial" conductivity per unit dose, $\Delta\sigma(0)/D$, is then seen to be given by

$$\Delta\sigma(0)/D = [\mu(+) + \mu(-)]/E_p \qquad (3)$$

It is apparent from eq 3 that if E_p is known, the sum of the mobilities of the primary charge carriers can be determined from the measured value of $\Delta\sigma(0)/D$.

$$[\mu(+) + \mu(-)] = E_p\Delta\sigma(0)/D \qquad (4)$$

From measurements of e^-–h^+ formation on high-energy irradiation of several semiconductor materials, the following relationship between E_p and the band-gap energy, E_g, has been found to be a good approximation.[33]

$$E_p \approx 2.73E_g + 0.5 \qquad (5)$$

This relationship is found to give a good estimate of E_p even for large band-gap organic materials. For example, taking an extreme case, the band gap for condensed saturated hydrocarbons is estimated to be approximately 8 eV,[34] which would lead to an estimate of ca. 22 eV for E_p using (5). The values of E_p that have actually been determined from scavenging studies[35] in saturated hydrocarbon liquids all lie within the range 20–26 eV, i.e., close to the value predicted.

In the case of PMPS and poly(di-n-alkylsilylene)s, the band gap has been estimated to be 5.7 eV. This would result in an estimate of 16 eV for the pair formation energy using eq 5. In the case of PDHS, 88% of the energy will be initially deposited in the saturated hydrocarbon regions of the sample. A weighted average value of 21 eV for E_p for this material is therefore considered to be a good approximation. In reality, a finite pulse width is always used and it is possible that a fraction of the initially formed charge carriers may have recombined on a time scale shorter than or comparable with the pulse length. Therefore when considering the experimental "end-of-pulse" conductivity, $\Delta\sigma_{eop}$, we have to include a parameter W_{eop}, which is the survival probability of the charge carriers. To take this into account, eq 4 should be replaced by eq 6 for practical experiments.

$$[\mu(+) + \mu(-)] = E_p\Delta\sigma_{eop}/DW_{eop} \qquad (6)$$

Since W_{eop} is unity or less, the following inequality will always be valid.

$$[\mu(+) + \mu(-)] \geq E_p\Delta\sigma_{eop}/D \qquad (7)$$

The mobility determined using (7) and the experimental end-of-pulse conductivity value will therefore always represent a lower limit to the sum of the mobilities of the primary charge carriers, $\sum\mu_{min}$.

Even when measurements are made with nanosecond time resolution, it is possible that the initial charge carriers have already undergone a substantial change in either their concentration or their mobility within the duration of the pulse. The former effect is particularly prevalent in low dielectric constant materials where strong, long-range Coulomb forces can result in geminate recombination of e^-–h^+ pairs on a picosecond time scale.[35] For example, only approximately 3% of the initially formed pairs in saturated hydrocarbon media escapes geminate recombination at room temperature.

We hope in the future to be able to directly measure the escape probabilities for the present type of materials. Until then, it should be kept in mind that the actual mobilities of the charge carriers in the present systems determined from the end-of-pulse conductivity could be as much as 1–2 orders of magnitude larger than the "minimum" mobility values calculated using (7).

The gradual decrease of the conductivity on a time scale of nanoseconds or longer that is monitored in the present experiments can be ascribed to delayed recombination of those charge carrier pairs which have escaped initial, rapid geminate recombination, described by a change in $N_p(t)$.

A decrease with time in the radiation-induced conductivity can also result from a decrease in the mobility of the carriers. This can result from temporary or permanent localization of charge carriers at impurity sites or regions of low potential energy. The latter are expected to be particularly prevalent in amorphous and mixed-morphology, polymeric materials. This effect of the localization of the primary, mobile charge carriers can be taken into account by including in the conductivity expression (1) mobility relaxation functions, $F(t)$.

$$\Delta\sigma(t) = e[\mu(+)F(t)_+ + \mu(-)F(t)_-]N_p(t) \qquad (8)$$

At time zero, the functions $F(t)$ will be equal to 1. If subsequent localization of the primary electronic charge carriers results in the formation of completely immobile charged sites, then $F(t)$ will be simply the fraction of the mobile carriers still present at time t. If, however, there is a gradual deepening of the trapping sites occupied, as is thought to occur in many amorphous materials, $F(t)$ can be a more complex function which results in dispersive decay kinetics of the conductivity.

With the above considerations in mind, we return to the specific results for the two materials investigated.

Poly(methylphenylsilylene). Time-of-flight conductivity measurements on PMPS have shown that the hole is the major charge carrier in this material on a time scale of microseconds to milliseconds.[11–14,17] We therefore assign the long-lived conductivity transient in the present measurements to mobile holes. The carriers responsible for the rapidly decaying, in-pulse conductivity transient are probably excess electrons which are initially highly mobile but become localized in this amorphous material on a (sub)nanosecond time scale.

The TOF measurements on PMPS thin films have further shown that the mobility of holes is field strength dependent.[11-14,17,18] The "zero-field" mobility, i.e., the mobility for fully thermally equilibrated carriers obtained by extrapolation to zero field at room temperature is approximately 5×10^{-9} m^2/V·s. This increases close to linearly with the square root of the field strength up to a value of approximately 5×10^{-8} m^2/V·s at a field strength of 10^8 V/m.

The value of $\Sigma\mu_{\min}$ determined in the present work from the conductivity immediately following the rapid, after-pulse decay, is 3×10^{-8} m^2/V·s. This minimum value, which has been assigned above to the mobile hole, is much larger than the zero-field hole mobilities found in the TOF measurements. In the present work, the maximum electric field strength of the microwaves is only 3×10^3 V/m, which is even lower than the lowest field strengths used in the TOF measurements. The present measurements are therefore made under very close to zero-field conditions. In order to correlate the two types of measurement, it has to be concluded that the mobility of the hole decreases gradually with time subsequent to its formation. The lower mobility found in the TOF measurements could then be due to the time window of these measurements being situated at a later stage in the lifetime of the carriers.

The relevant time window in TOF measurements is the drift time, t_d, of charge carriers across the thickness, d, of the sample. For a well-defined mobility, t_d is related to the field strength E by

$$t_d = d/E\mu \tag{9}$$

Most TOF measurements[11-14,17,18] have been carried out on PMPS films approximately 10 μm thick with field strengths varying from 10^6 to 10^8 V/m. The drift times at the lowest field strengths would therefore be on the order of a few milliseconds for a mobility of ca. 5×10^{-9} m^2/V·s. At the highest field strengths, approaching 10^8 V/m, for which 1 order of magnitude larger mobility is found, the drift times would be reduced to only a few microseconds.

As can be seen from the transient in Figure 1, the conductivity signal in the present time-resolved measurements does in fact decay by close to 1 order of magnitude in going from microseconds to milliseconds. Part, at least, of the increase in the mobility of the hole with increasing field strength, as determined in TOF experiments, could therefore be a result simply of a shortening of the time window of the observations. The hole mobility that we would calculate on the basis of the conductivity signal remaining on a time scale of milliseconds is $\leq 2 \times 10^{-9}$ m^2/V·s. This is not in conflict with the zero-field value of ca. 5×10^{-9} m^2/V·s found in TOF experiments.

The present data can therefore be accommodated in a general scheme in which the hole mobility in PMPS is time dependent, as has been found for amorphous silicon.[36] Field effects on the hole mobility may then be ascribed either to a change in the time window of the measurements or to field-induced detrapping of charge carriers. The precise details of the process whereby the mobility relaxes, which presumably involves an increasing degree of interaction with the medium, will not be speculated on further here.

Poly(di-*n*-hexylsilylene). As mentioned above, the initial radiation-induced conductivity of PDHS at room temperature is more than 2 orders of magnitude larger than for PMPS. In addition, there is no indication of a rapidly decaying, (sub)nanosecond component as found for the latter compound. Rather the first half-life of the total conductivity is much longer than the pulse length, and the decay extends to several hundred microseconds. The value of $\Sigma\mu_{\min}$ determined from the end-of-pulse conductivity is 1×10^{-5} m^2/V·s. This is large for a polymeric material. The largest values that we have found for $\Sigma\mu_{\min}$ in other systems are, for example, 1.5×10^{-6} m^2/V·s in aligned ultrahigh molecular weight polyethylene[37] and ca. 5×10^{-7} m^2/V·s in a variety of polythiophene samples.

Unfortunately, we have no way of determining the sign of the charge of the major carrier in the present experiments. If, however, the mobility of the hole in PDHS at room temperature is only 3×10^{-9} m^2/V·s, as found in TOF measurements,[18] then we would be forced to conclude that the major charge carrier in the crystalline solid phase of PDHS must be the excess electron. That excess electrons have a much longer lifetime in the crystalline solid than in the amorphous PMPS would not be completely unexpected.

The fact that the solid phase of PDHS displays a strongly red-shifted UV absorption band compared with PMPS[10,22] has been taken to indicate that there are significant differences in the Si–Si bonding between the two compounds. Since the hole is considered to be localized on the Si backbone and its motion along the chain of Si atoms would be expected to be markedly dependent on the σ-bond conjugation, one might have predicted that its mobility would also be markedly different in the two materials. We feel therefore that it cannot be completely ruled out that the species responsible for the very high radiation-induced conductivity in solid PDHS is a highly mobile hole instead of the electron as suggested above.

The apparent conflict between the present observations of a very large mobility and the TOF measurements on PDHS[18] could be resolved if the hole is in fact initially highly mobile in solid PDHS but becomes localized on a time scale comparable with or shorter than the time scale of the TOF measurements.

From the data given in ref 18, we estimate the drift time in the TOF measurements at room temperature to be approximately 200 μs. As can be seen in Figure 2, the conductivity transient in PDHS decreases very rapidly in the time region of a few hundred microseconds. This could well be due to hole trapping leaving an effectively much less mobile positive charge center. However, we cannot rule out that the decrease is due to charge recombination.

Figure 3 shows the abrupt decrease in the end-of-pulse conductivity that occurs at approximately 40 °C. The decrease by a factor of approximately 20 yields a value which corresponds to $\Sigma\mu_{\min} \approx 5 \times 10^{-7}$ m^2/V·s. This dramatic change in the radiation-induced conductivity is found to be reversible on cooling, with a hysteresis of approximately 15 °C. The coincidence of the transition temperatures with those found for the phase transition between the solid and liquid crystalline phases of PDHS using DSC and X-ray diffraction techniques leaves no doubt that the phase change is the underlying cause of the drastic change in the radiation-induced conductivity. It is worth pointing out that even in the mesophase the end-of-pulse radiation-induced conductivity at nanosecond time scale is still 1 order of magnitude larger than that of the slowly decaying component in PMPS.

As mentioned above, the phase transition is accompanied by a large shift in the optical absorption band, which has been ascribed to a decrease in the σ-bond conjugation in the mesophase. This might be expected to result in a decrease in the hole mobility if the holes are indeed transported along the Si–Si backbone. In fact, an abrupt decrease in the hole mobility at the solid-to-liquid crystalline transition has been found in the TOF measurements in PDHS.[18]

We are continuing pulse radiolysis studies of a variety of alkyl-substituted polysilanes in order to gain a better insight into the factors influencing the charge carrier mobilities particular at close to the solid-to-mesophase transition. Pulse radiolysis dc conductivity studies are also planned in order to gain more definitive information about the nature of the charge carriers and their mobilities.

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