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Electrochromism in an Organopolysilane

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ABSTRACT: This paper reports solid-state electrochromism observed in poly[(3,3,3-trifluoropropyl)-methylsilane-*co*-methylpropylsilane]. The UV absorption increases by ca. 50% at 3.1×10^8 V·m^{-1} accompanied by a 5-nm red shift of the λ_{max}. The response time is less than 100 ms. The absorption recovers when the electric field is removed. This electrochromic behavior is rationalized in terms of structural changes in the silicon chain, which is the first known example of electrochromism not involving an electrochemical reaction.

Introduction

Organopolysilanes are a family of functional polymers consisting of substituted silylene repeating units. These polymers have many interesting chemical, electrical, and optical properties arising from the Si−Si bonding.[1,2] For instance, β-silicon carbide is obtained either directly by pyrolysis[3] or through the formation of polycarbosilanes.[4] UV light irradiation causes chain scissions in the Si−Si backbone.[5] Volatile small fragments are also produced by the irradiation.[6] The σ electrons of the silicon chain are delocalized along the chain and form an energy band structure[7] called a σ-conjugation.[8] This characteristic of the electronic structure makes these polymers both photoconductive[9] and photoluminescent.[10] They are also electrically conductive when doped with AsF_5.[11] Based on these properties, they can be used in many applications, e.g., as precursors for silicon carbide ceramics,[3,4] photoresists,[12] photoreceptors for electrophotography,[13] and photoinitiators for vinyl polymerization.[14]

One fundamental characteristic of the silicon chain is the small energy difference between conformers and the low rotational barriers compared to carbon chains. Conformational energy calculations using empirical force field (EFF) methods indicate the energy difference between all-gauche (G) and all-trans (T) conformers is 0.09 kcal/mol[15] for tetrasilane and 0.7 kcal/mol[16] for pentasilane. Ab initio calculations for the parent (nonsubstituted) polysilane show a difference of 0.38 kcal/mol.[17] The rotational barrier for tetrasilane calculated by the ab initio method is 1.3−1.7 kcal/mol.[18] Experimentally, the value of 1.1−1.2 kcal/mol has been estimated for the rotational barrier in disilane.[19] These values are much smaller than those[20] observed for the corresponding carbon compounds. As for methyl-substituted polysilanes, the EFF method shows the energy difference between G and T conformers is 0.9 kcal/mol for permethylpentasilane.[16] The enthalpy change of the phase transition accompanied by a conformational change which occurs at 41 °C has been measured to be 5 kcal/mol for poly(di-*n*-hexylsilane) by differential scanning calorimetry (DSC).[21] These results suggest a small-energy difference between conformers, even for substituted polysilanes.

The low rotational barriers result in a flexible polymer chain, so that the conformation of the chain can readily be altered in response to external stresses. The change in conformation is often manifested in the UV absorption spectrum, since the electronic structure of organopolysilanes is sensitive to the conformation.[17,22] In fact, thermochromism has been observed at ambient temperatures in alkyl-substituted[1,2] and fluoroalkyl-substituted[23] polysilanes. The long-wavelength transition at 374 nm of poly(di-*n*-hexylsilane), for instance, decreases with increasing temperature, while the short-wavelength transition at 317 nm increases.[24] Through this process, the chain conformation changes from an ordered to a disordered structure.[25] Piezochromism has also been observed in this polymer.[26] As the pressure increases, the long-wavelength transition increases and the short one decreases.

We have been focusing on using electrical effects to induce the structural changes of the silicon chain. This can be caused by introducing polar side chains into the polymer. The polar side chain is oriented under an application of the electric field, and the side-chain orientation can distort the main-chain structure. A spectral change induced by the electric field is thus expected. Our preliminary study suggested such electrochromism in a fluoroalkyl-substituted polysilane-solid film.[27]

In this study, we investigate the electrochromism without electrochemical reactions in poly[(3,3,3-trifluoropropyl)methylsilane-*co*-methylpropylsilane] with 45 mol % of the monomer containing a polar fluoroalkyl side chain. A large electrochromic effect is expected for this particular polymer since it shows the largest thermochromism among the fluoroalkyl-substituted polysilane copolymers.[28]

Experimental Section

(1) Synthesis. The fluoroalkyl-substituted polysilane copolymer **[I]** was prepared from the two corresponding dichlorosilane monomers using sodium in decane at reflux for 5 h. The actual synthetic procedure is described elsewhere.[23,28] The molecular weight distribution was bimodal with M_w = 560 000 (14%) and 57 000 (86%), where M_w was the weight-average molecular weight. The composition was determined from the profile of gel permeation chromatogram monitored at 254 nm using tetrahydrofuran as the eluant.

$$\mathrm{FPrMeSiCl_2 + MePrSiCl_2 \xrightarrow[\text{decane}]{\text{Na}} -[(FPrMeSi)_{0.45}(MePrSi)_{0.55}]_n-}$$

$$\mathbf{I}\ (\mathrm{FPr{:}\ CF_3CH_2CH_2-})$$

(2) Measurement. A sandwich-type cell was used to measure the UV absorption spectrum (Scheme 1). The polymer was dissolved in toluene and spin-coated on a semitrans-

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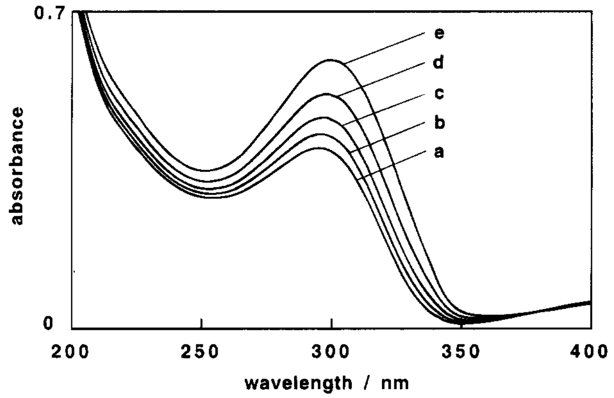
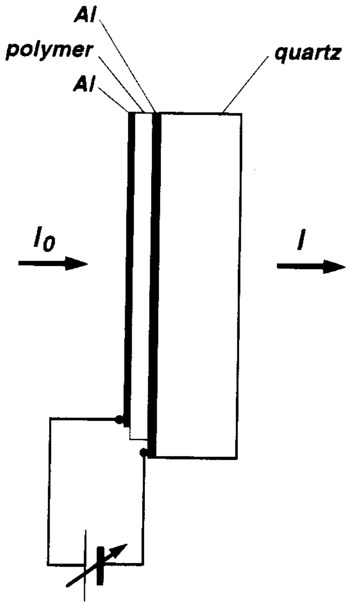


Figure 1. Electric field dependence of UV absorption spectra for **I** in a solid film: (a) 0, (b) 1.2 × 10^8, (c) 1.9 × 10^8, (d) 2.5 × 10^8, (e) 3.1 × 10^8 V·m^{-1}. Film thickness: 800 Å.

Scheme 1. Cell Structure



parent Al-bottom electrode vacuum-deposited on a quartz substrate (7 × 15 mm). A second semitransparent Al electrode was deposited on the film by vacuum deposition. The film thickness measured by the Stylus method (Tencor Instruments, ALPHA-STEP 200) was ca. 1000 Å.[29] The cell was mounted in a UV spectrometer (Hitachi U-3500), and the spectrum was measured while applying voltage between the top and bottom electrodes at room temperature in air.

Results

Electric field dependence of the UV absorption spectrum for **I** in the solid film is shown in Figure 1. The broad absorption around 400 nm is due to the interference from the cell structure. The characteristic UV absorption attributed to a $\sigma-\sigma^*$ transition in the silicon chain was observed with a maximum at 294 nm. As the applied electric field increased, the absorbance increased. The increase was ca. 50% at 3.1 × 10^8 V·m^{-1} accompanied by a 5-nm red shift of the λ_{max} (Figure 2). The spectral profile recovered when the electric field was removed.

The time response of the UV absorption for **I** monitored at 310 nm for repetitive application of various electric field strengths is shown in Figure 3. When the electric field was applied, the absorbance initially increased quickly within 100 ms followed by a more gradual rise. The same response was observed when the electric field was removed. The rise time of the initial quick response was limited by the time constant of the spectrometer used in this study. The actual rise time was expected to be shorter than 100 ms.

Discussion

The first question is whether electrochemical reactions are the reason for this electrochromic behavior. In general, both oxidation and reduction causes a red shift of the λ_{max}. For the present system, both positive and negative charges must be injected from the electrodes during the ionization. In other words, oxidation and reduction of the polymer takes place on each respective electrode. It should be noted that oxidation at the electrode is usually irreversible in organopolysilanes.[30] The present electrochromic behavior is, in contrast, reversible, which is inconsistent with ionization. In addition, the λ_{max} of the radical ions of organopolysilanes appears ca. 50-nm red-shifted from those for the neutral states.[31] The red shift of **I** is, however, 1 order of magnitude smaller than that. From these considerations, the above electrochromic behavior is not from an electrochemical reaction but rather from some physical effect caused by the electric field.

When the electric field is applied to the polymer film, the temperature may increase because of the conducting current. This could change the UV absorption spectrum since many organopolysilanes with alkyl side chains are well-known to exhibit thermochromic behavior, as described above. However, the thermochromic behavior for **I** shows a blue shift with increasing temperature.[28] This is inconsistent with the electrochromic behavior. The absorption maximum also decreases with increasing temperature,[28] which is contrary to the electrochromic behavior. Quantitatively, heat estimated from the conducting current raises the film temperature by ca. 0.1 °C during the rapid spectral change occurring within 100 ms.[32] This temperature increase is too small to cause the observed spectral changes. Therefore, the present electrochromic behavior does not originate from the heat caused by the conducting current.

Organopolysilanes have also been recognized as new types of one-dimensional semiconductors with wide band gaps of ca. 4 eV. An interband electronic transition from valence to conduction bands in the silicon chain has been predicted theoretically.[7] Experimental evidence of exciton formation has also been reported in several organopolysilanes.[33] Thus, the contribution of the electronic effects such as the Franz–Keldysh or Stark effects should be checked. Figure 4 shows the difference spectra of the UV absorption for **I** as a function of the electric field. The absorption at 0 V·m^{-1} is used as the base. The lack of oscillatory structure in the profile is inconsistent with those electronic effects.[33,34] In addition, the electric field dependence of the absorption is too large for the spectral change to originate from the Stark effect. The change in the absorbance due to the Stark effect for poly(di-*n*-hexylsilane), for instance, is only 0.1%.[33] No evidence of the Franz–Keldysh effect on organopolysilanes has been reported yet.

Furthermore, the present electrochromic behavior was not observed in the homopolymer poly(methylpropylsilane). This polymer has the limiting structure of **I** but does not have any polar side chains. The fact that the characteristic absorption for poly(methylpropylsi-

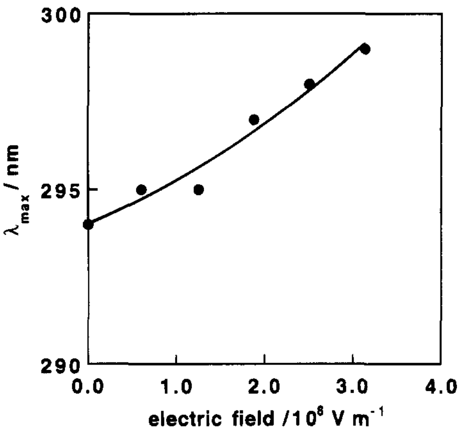


Figure 2. Electric field dependence of λ_{max} and absorbance at λ_{max} for **I** in a solid film.

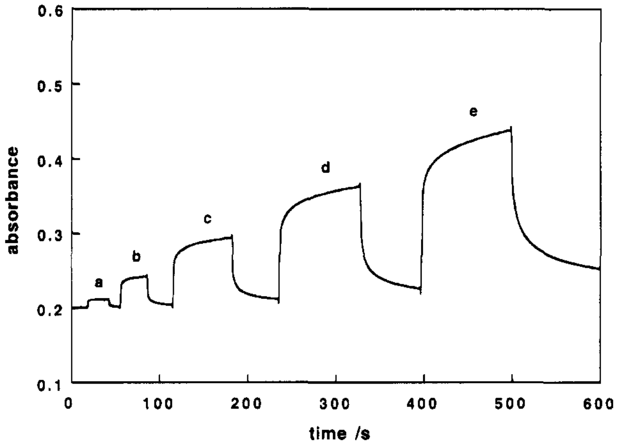


Figure 3. Time response of UV absorption of **I** in a solid film monitored at 310 nm for various electric fields: (a) 0.6 × 10^8, (b) 1.2 × 10^8, (c) 1.9 × 10^8, (d) 2.5 × 10^8, (e) 3.1 × 10^8 V·m^{-1}. Film thickness: 800 Å.

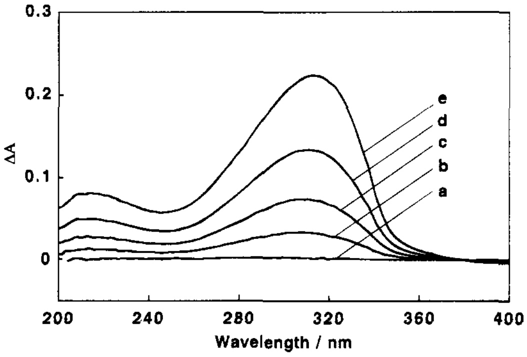


Figure 4. Difference spectra of UV absorption of **I** as a function of an electric field. The spectrum at 0 V·m^{-1} in Figure 1 is used as the base: (a) 0.6 × 10^8, (b) 1.2 × 10^8, (c) 1.9 × 10^8, (d) 2.5 × 10^8, (e) 3.1 × 10^8 V·m^{-1}.

lane) at room temperature is observed in the UV region (λ_{max} = 326 nm in solids)[23] similar to that for **I** suggests that both polymers basically have a similar electronic structure. If the present electrochromism is based on the above electrochemical, thermal, and electronic effects, similar spectral changes should be observed for the two polymers due to the similar electronic structure. The failure to observe rapid spectral changes from poly(methylpropylsilane) upon applying an electric field suggests that the change observed for **I** does not originate from those effects.

UV absorption of organopolysilanes along the chain is suggested to be larger than that in the direction perpendicular to the chain.[35,36] So, the UV absorption spectra must be changed by the orientation of the polymer chains. The electric field may cause the chain orientation if the polymers are in the liquid crystalline states. Alkyl-substituted polysilanes are shown to form liquid crystalline phases.[37−39] However, no first-order transitions suggesting their formation were observed for **I** in a DSC analysis from −75 to +75 °C. One should also pay attention to the response speed of the orientation. It is expected to be slow at room temperature compared to the present response within 100 ms. For instance, it takes 3 h for the formation of Williams domains even at the more elevated temperature of 275 °C in a thermotropic nematic polymer poly(ethylene terephthalate-*co*-1,4-benzoate).[40] Chain orientation may be possible in the solid when the side chains are polar, but the response will still be slower than that for the liquid crystalline state due to the higher viscosity. It is, thus, unlikely that the present spectral change originates from the orientation of the polymer chains.

In the present cell, a polymer is sandwiched between two electrodes, to which a large potential is applied. The attractive force between the electrodes can apply pressure to the polymer film. To evaluate such a piezochromic effect, a nonpolar polysilane with a large demonstrated piezochromic response, poly(di-*n*-hexylsilane), was examined under the conditions of the present experiment. No spectral changes on applying the electric field were observed for poly(di-*n*-hexylsilane), implying the present phenomenon is not the piezochromic response.

A characteristic of the molecular structure of **I** is the side chain with a large dipole moment based on the C−F bond. The glass transition temperature T_g determined by DSC analysis was −21 °C for **I**. When an electric field is applied to the dipoles above T_g, they are forced to be oriented along the electric field. This could slightly distort the structure of the main chain. The value of the energy from the external electric field can be estimated to be 1−2 kJ·mol^{-1}.[41] The rotational barrier for organopolysilanes is considered to be around 10 kJ·mol^{-1}, as mentioned above. Accordingly, distortion of the silicon chain induced by the side-chain orientation is energetically possible.

Changes in the chain structure should be reflected by the UV absorption spectra. The difference spectra in Figure 4 show that a new transition band at λ_{max} = 314 nm appears as the electric field increases. This suggests that formation of the corresponding component is promoted by the orientation of the side chain.

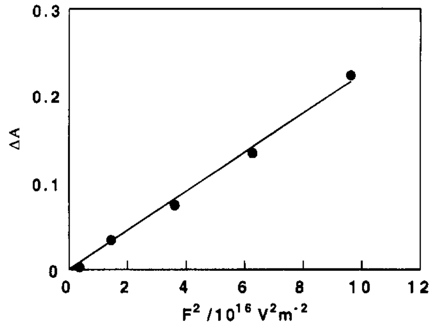


Figure 5. Absorption increase for **I** at 314 nm as a function of F^2.

The increment of the new component, Δn, is proportional to the density of the oriented side chains.[42] Thus,

$$\Delta n = 2\pi\alpha n_0 \int_0^{\pi} \exp(\mu F \cos\theta/kT) \sin\theta \, d\theta \qquad (1)$$

where a newly introduced parameter α represents the efficiency for the side chain to induce the distortion of the main chain. n_0 is the density of the polar side chains, μ is the dipole moment, F is the applied electric field, k is the Boltzmann constant, and T is the absolute temperature. The parameter θ is the polar angle between the dipole moment and the field direction. Performing the integration of (1) yields

$$\Delta n = 2\pi\alpha n_0 \{\exp(\mu F/kT) - \exp(-\mu F/kT)\}/(\mu F/kT) \qquad (2)$$

Employing the Taylor progression with a third-order approximation for (2) gives

$$\Delta n = 4\pi\alpha n_0 \{1 + (1/6)(\mu F/kT)^2\} \qquad (3)$$

Since the absorbance ΔA based on the new component is proportional to Δn, i.e., $\Delta A = \beta\Delta n$,

$$\Delta A = 4\pi\alpha\beta n_0 \{1 + (1/6)(\mu F/kT)^2\} \qquad (4)$$

where β is a parameter reflecting the cross section for absorption and film thickness. Equation 4 shows ΔA increases with the square of the electric field, i.e., $\Delta A \propto F^2$.

The measured ΔA for **I** at 314 nm as a function of F^2 is shown in Figure 5. The ΔA linearly increases with increasing F^2, which is consistent with the theoretical analysis. This might validate the suggestion that the electrochromic behavior originates from changes in the chain structure. A conformational change is a probable idea for the structural changes; however, it has been recently suggested[43] that the changes in the absorption from a silicon chain are related to the degree of the chain coiling. The absorption increases as the chain structure approaches the rod form. It might, therefore, be rather reasonable to conclude that the changes in either the conformation or macroscopic shape or both of the chain contribute to the present electrochromism. Further investigation is necessary to elucidate the operative mechanism.

Conclusion

We have observed electrochromism in a solid film of an organopolysilane containing a polar side chain. The response time was demonstrated to be less than 100 ms. We failed to explain the observation by electrochemical, thermal, and electronic effects. Explanations involving orientation of the polymer chains or a piezochromic effect caused by attractive forces between high potential electrodes also failed. Consequently, we conclude the phenomenon is best rationalized in terms of structural changes in the silicon chain induced by the side-chain orientation.

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is typical for organic polymers. The mass of the present film sandwiched by the electrodes is ca. 5 μg. The heat raises the temperature by 0.09 °C in 100 ms. This assumes all the heat contributes to the temperature rise without any thermal loss.

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