# Thermal Hysteresis in UV Absorption of Polysilane Films

*T. Dohmaru and K. Oka*
*Research Institute for Advanced Science and Technology, Osaka Prefecture University*
*Sakai, Osaka/Japan*
*T. Nakamura and H. Naito*
*College of Engineering, Osaka Prefecture University*
*Sakai, Osaka/Japan*

## Abstract

UV absorption spectra of poly(methylphenylsilane) films were measured at varying temperatures from 25°C to 200°C and a new thermal hysteresis in UV absorption of the polysilane films was observed. Once a polysilane film was annealed above its glass transition temperature, its UV absorption spectrum greatly and irreversibly changed. In other words, the absorption spectrum intrinsic to a particular polysilane film is obtained only after it is annealed above its $T_g$. This thermal hysteresis is discussed in relation to the changes in the micrtoscopic free spaces and in the hole transport characteristics between the annealed and non-annealed polysilane films. We concluded that after a polysilane film is annealed above its $T_g$, there occurs an irreversible re-distribution of the σ-conjugated domains in a way as to increase their average size.

## Introduction

Organic polysilanes have been extensively studied because of their high hole drift mobilities of *ca*. $10^{-4}$ $cm^2/Vs$.[1-5] It is generally accepted that hole transport in polysilanes occurs by hopping through σ-conjugated domains developed along their silicon main-chains. Since σ-conjugated domains are considered as chromophores for UV absorption of polysilanes, extensive studies[1] have been carried out on the UV characteristics of polysilanes in relation to their microscopic main-chain structures.

In this paper, we report the detailed thermochromic behabior of poly(methylphenylsilane) films between 25°C and 200°C and discuss the results in terms of the change in the average size of the σ-conjugated domains caused by the thermal motion of the main-chains. The thermal change in the microscopic free spaces in poly(methylphenylsilane) films were also measured by positron annihilation life-time spectroscopy. We will also discuss the hole transport characteristics of poly(methylphenylsilane) based on these two results.

## Experimental

Poly(methylphenylsilane) was synthesized by means of the Wurtz coupling reaction of methylphenyldichlorosilane with sodium metal and purified by repeated fractional precipitations.[6,7] The weight average molecular weight of the polysilane (MW) was 226,000 with dispersity of 2.3.

Poly(methylphenylsilane) was coated on a quartz plate by a bar-coater from its toluene solution of extremely low concentration and dried for 1 hour at room temperature and for 2 hours at 80°C. Then the polysilane-coated substrate was put in an optical probe connected to a photon counter (UNISOKU PCS-400) with an optical fiber. The optical probe was put in an electric oven, and UV absorption was measured at varying temperatures from room temperature to 200°C. The rate of heating and cooling was 1°C /min. The glass transition temperature of this sample was measured as 118°C by a DSC (Rigaku DSC8230D).

The microscopic free spaces in polysilane films were measured by means of positron annihilation life-time spectroscopy using the conventional fast-fast coincidence system. $^{22}$NaCl was employed as a radioactive source and the source was enveloped by a piece of Kapton film with thickness of 25 μm. Poly(methylphenylsilane) was casted on pure iron substrates from its toluene solution. The source ($^{22}$NaCl enveloped by a piece of Kapton film) was sandwiched by two polysilane/Fe samples and placed on a sample holder equipped with a wolfram heater, and then the holder was inserted into a glass vessel, through which $N_2$ gas was kept flowing during the measurements. The range of temperatures was from 25°C to 180°C and the rate of both heating and cooling was 1°C/min. The life-time spectra were computer-fitted by using "POSITRONFIT" in the PATFIT-88 program of Kirkegaard et al.[8]

Samples for the drift mobility measurements were of a sandwich type of Au/polysilane film (*ca*. 12 μm)/bisazo compound (*ca*. 1 μm)/Al/PET film. Poly(methylphenyl-silane) was coated by a bar-coater from its toluene solution, and dried in the same manner as the samples for UV measurements. Then the polysilane film was annealed at 130°C for 6 hours in vacuum. The rate of heating and cooling was 1°C/min. The hole drift mobilities were

measured by means of the conventional Time-of-Flight (TOF) technique.

## Results and Discussion

### UV Absorption

Figure 1 shows temperature dependences of (a) the UV absorption maximum ($\lambda_{max}$) ascribed to σ-σ* transition in a poly(methylphenylsilane) film and (b) the absorbance at the $\lambda_{max}$ during heating, cooling and the second heating cycles between 25°C and 200°C at a rate of 1°C/min.

It is noted that both $\lambda_{max}$ and the absorbance in the first heating step quite differ from those in the fisrt cooling step and the second heating step. This large hysteresis is explained as follows. The as-prepared polysilane film retains considerable amount of strain which is built-in during the evapolation of the solvent. The built-in strain may be completely relaxed by heating up to 200°C beyond $T_g$ (118°C). Thus the first cooling step and the second heating step are free from the effect of the in-born strain and may exibit the intrinsic temperature dependences of the respective absorption parameters. We will discuss this "intrinsic" spectral change in terms of the change in size and number of the chromophores (σ-conjugated domains) caused by the thermal motions of the silicon main-chains. With increasing temperatures from 25°C to 125°C (close to $T_g$), $\lambda_{max}$ increases and the absorbance is invariant, while from 125°C to 200°C $\lambda_{max}$ is constant and the absorbance decreases.

This result is rather difficult to explain only by the conformational change of the main-chains most often observed in the conventional thermochromism of poly-silanes.[1] Generally, as the temperature increases, the conformation of the main-chains changes toward more disordered form resulting in the blue shift in $\lambda_{max}$. However, Fig. l(a) shows the opposite trend.

We propose an alternative model to explain the result. In the temperature range below $T_g$, the re-distribution of the σ-conjugation along the main-chains occurs according to the thermal motion of the main-chains. With increasing temperatures, the average size of the σ-conjugated domains becomes bigger ($\lambda_{max}$ increases) and their numbers decrease. The absorbance became larger by the bigger domains and became smaller by the smaller numbers of the domains: the net effect on the absorbance was almost zero. In the temperature range above $T_g$, the conformational change comes into play by the easier motion of the main-chains, inducing both $\lambda_{max}$ and the absorbance to decrease. We propose that there occurs the thermal re-distribution of the σ-conjugation along the main-chains in the whole range of the temperatures adopted in this study.

### Microscopic Free Space

Since the σ-conjugated domains are formed along the silicon backbones, the spatial disposition of the domains is determined by the relative positions of the individual polymer chains. Thus the information on the microscopic inner structure of a polysilane film is particularly important for the better understanding of the UV absorption and therefore of the hole transport characteristics.
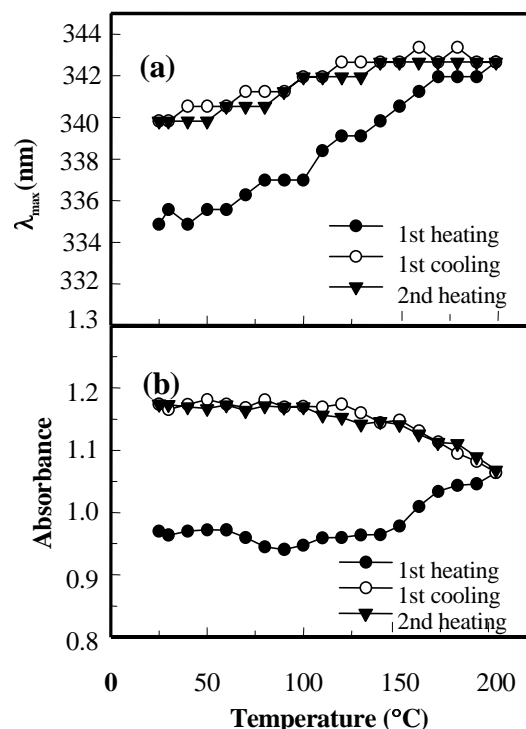


*Figure 1. Temperature dependences of (a) $\lambda_{max}$ and (b) the absorbance at $\lambda_{max}$ in a poly(methylphenylsilane) film*

Figure 2 shows temperature dependences of (a) ortho-positronium life-times and (b) their relative intensities for a poly(methylphenylsilane) film in the same heating and cooling cycles as in Fig. 1. Thermal hysteresis is again clearly observed in both the life-time and the relative intensity. Once the polysilane film was annealed above $T_g$, it revealed the thermal response of the life-time and the relative intensity "intrinsic" to poly(methylphenylsilane). The average radius of the free spaces can be calculated according to the semi-empirical equations (1) and (2).[9]

$$\tau = 0.5 \{1 - R/R0 + sin(2\pi R/R0)/2\pi\}^{-1} \tag{1}$$

$$R = R0 - \Delta R \quad (\Delta R = 0.166 \ nm) \tag{2}$$

where τ is a life-time of a positron or a positronium and R is the free volume radius (FVR).

Figure 2 shows firstly that the room-temperature FVR of the as-prepared film calculated from eqs. (1) and (2) is 3.1A and considerably larger than that (2.8A) of the film annealed at temperatures above $T_g$. Secondly the intrinsic FVR monotonously increased and the numbers of the free spaces (corresponding to the relative intensity) slightly decreased with increasing temperatures. This result may simply be explained by the thermal expansion of the film.

The combiation of the results of Fig. 1 and Fig. 2 allows us to give more detailed description of the thermal change intrinsic to the poly(methylphenylsilane). As the tempera-ture increases from room temperature, the thermal expansion occurs and the free volume spaces keep increasing, resulting in easier motion of the silicon

backbones. According to the movement of the badkbone chains the re-distribution of the σ-conjugation along the backnone chains constantly occurs. In this process, the average size of the σ-conjugated domains grows bigger with increasing temperatures at the expense of the numbers of the σ-conjugated domains.
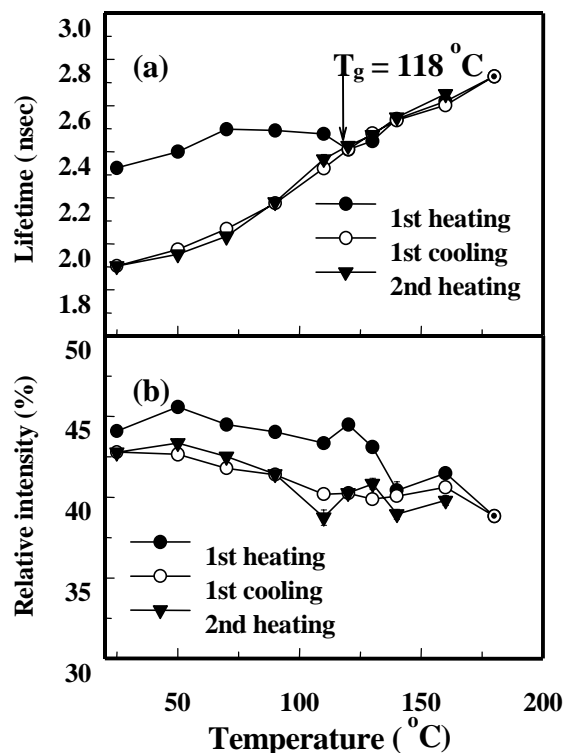


*Figure 2. Temperature dependences of (a) ortho-positronium life-times and (b) the relative intensities in a poly(methylphenylsilane) film*

### Hole Transport Characteristics

As described in the preceeding sections, we found that the as-prepared poly(methylphenylsilane) film retains considerable amount of built-in strain and has larger free spaces and smaller numbers of σ-conjugated domains of smaller size than those of the film annealed at temperatures above $T_g$. On the basis of these results, we proceeded to study the effect of annealing upon hole transport characteristics.

Figure 3 shows electric-field dependences of the hole drift mobilities at 293K for the as-prepared film and the annealed film. The two values at each electric field do not change much, but the slope for the annealed sample is slightly but discernibly smaller than that for the as-prepated one, demonstrating that there appears an influence of annealing in hole transport properties in poly(methyl-phenylsilane). The temperature dependences were studied as shown in Fig. 4 and deconvoluted in the framework of the disorder formalism by Bässler et al.[10-12] expressed as in eq. 3.

$$\mu=\mu_0 exp\{-(2\sigma/3kT)^2\}exp[C\{(\sigma/kT)^2-\Sigma^2\}F^{1/2}] \ (\Sigma>1.5) \qquad (3)$$

where $\mu_0$ is the prefactor mobility of a hypothetical crystalline structure (with no disorder), σ is the energy width of Gaussian distribution of hopping sites, Σ is the degree of the positional disorder of hopping sites, F is the electric field and C is a constant.
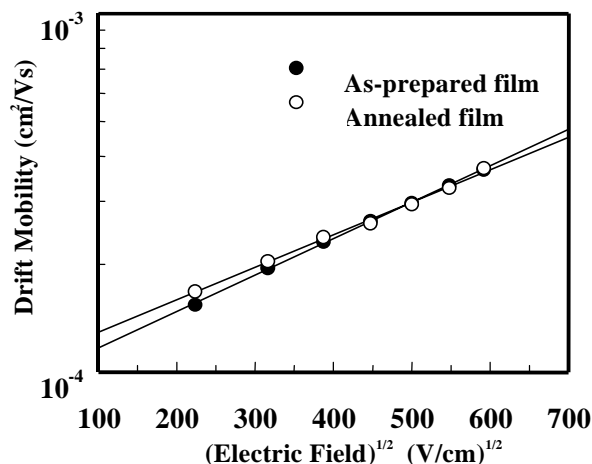


*Figure 3. Electric-field dependences of the hole drift mobilities at 293 K for the as-prepared and the annealed poly (methylphenyl-silane) films*

Table 1 summarizes the obtained disorder parameters, together with $\lambda_{max}$ and the absorbance from Fig. 1, and the average free volume radius (FVR) from Fig. 2.

**Table 1. The Disorder Papametes, $\lambda_{Max}$, the Absorbance and FVR for the As-Prepared and the Annealed Poly(Methylphenylsilane) Films**

| Film | $10^2\mu_0$/cm/ Vs | σ/meV | Σ | $\lambda_{max}$/nm | Abs. | FVR/A |
|------|------|------|------|------|------|------|
| As-prep. | 2.7 | 90 | 2.3 | 335 | 0.98 | 3.1 |
| Annealed | 3.4 | 92 | 2.5 | 340 | 1.18 | 2.8 |

Table 1 shows that both Σ, σ values for the annealed film are all slightly larger than those for the as-prepared film. These changes, at first, seemed rather unexpected considering the smaller FVR for the annealed film indicating the shorter average distance between the main-chains. But the key factor in this case is the size and the number of the σ-conjugated domains whose information is most dirctly obtained by the absorption parameters shown in Table 1. Upon annealing both $\lambda_{max}$ and the absorbance become larger due to the relaxation from the in-born strain which may correspond to the heterogeneous distribution of the space sizes suggested by the measured FVR. Thus in the annealed film, there are various sizes of σ-conjugated domains leading to the larger positional disorder (Σ) and the largr enegetic dosorder (σ). The small increase in $\mu_0$ value for the annealed film shows that the bigger spaces in the as-

prepared film are not homogenously positioned but rather aligned in the direction perpendicular to the film surface because the solvent evapolates and leaves space in this direction. Reversibly, the densities of the σ-conjugated domains are smaller in the perpendicular direction.

The change in the hole transport characteristics between the as-prepared and the annealed poly(methyl-phenylsilane) films was successfully explained on the basis of the thermal hysteresis of UV absorption combined with the information on the thermal change in the microscopic free spaces.
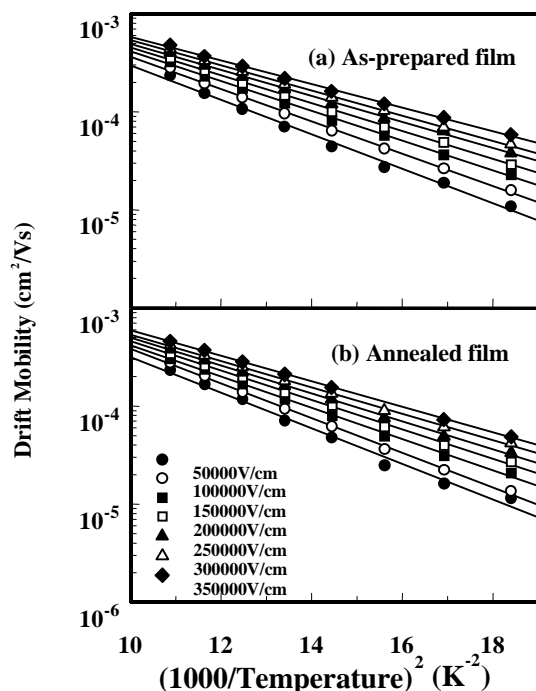


*Figure 4. Temperature dependences of the hole drift mobilities for (a) the as-prepared and (b) the annealed poly(mehylphenylsilane) films plotted against the reciprocal of the square temperature parametric in electric fields*

## Summary

The thermal change of the UV absorption and the microscopic space of poly(methyphenylsilane) films were measured and found that the intrinsic thermal changes in these physical properties were obtained only after the films were annealed above their $T_g$.

## References

1. R. D. Miller and J. Michl, *Chem. Rev.* **89**, 1359 (1989).
2. R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, *Phys. Rev. B* **35**, 2818 (1987).
3. M. A.Abkowitz, F. E. Knier, H.-J. Yuh, R. J. Weagley, and M. Stolka, *Solid State Commun.* **62**, 547 (1987).
4. M. Stolka, H.-J. Yuh, K. McGrane, and D. M. Pai, *J. Polym. Sci., Polym. Chem.* **25**, 823 (1987).
5. M. A. Abkowitz, M. J. Rice, and M. Stolka, *Phil. Mag. B*, **61**, 25 (1990).
6. T. Nakamura, K. Oka, H. Naito, M. Okuda, Y. Nakayama, and T. Dohmaru, *Solid State Commun.* **101**, 503 (1997).
7. T. Nakamura, K. Oka, F. Hori, R. Oshima, H. Naito, and T. Dohmaru, *J. Imag. Sci. Tech.*, **42**, 371 (1998).
8. P. Kirkegaard, M. Eldrup, O. E. Mogensen, and N. J. Pedersen, *Comp. Phys. Commun.* **23**, 307 (1981).
9. H. Nakanishi and Y. C. Jean, in Positron and Positronium Chemistry, edited by D. M. Schrader and Y. C. Jean (Elsevier, Amsterdam, 1988).
10. H. Bässler, *Phys. Stat. Sol.* **B107**, 9 (1981).
11. H. Bässler, Phil. Mag. B **50**, 347 (1984).
12. P. M. Borsenberger, L. Pautmeier, and H. Bässler, *J. Chem. Phys.* **94**, 5447 (1991).

## Biography

Dr. Takaaki Dohmaru graduated from Osaka Prefecture University in 1964. He is now a professor of the Research Institute for Advanced Science and Technology, Osaka Prefecture Univeristy. His current interest is in carrier transport in organic photoconductors, especially in organic polysilanes, and their application to electrophotography. He is a member of the Chemical Society of Japan, the Japan Society of Applied Physics, the Imagiang Society of Japan, and the Society of Imaging Science and Technology.