Dielectric Properties of Poly(methylphenylsilylene) under Humidity in the Kilohertz Range[1)]

Hiroshi AWANO,* Takayoshi IWAI,† and Hiroji OHIGASHI
Department of Materials Science and Engineering, Yamagata University, Jonan, Yonezawa 992
† Consumer Products Engineering Laboratory, Toshiba Corporation, Shinsugita-cho, Isogo-ku, Yokohama 235
(Received April 11, 1991)

Synopsis. The capacitance and dielectric loss tangent of poly(methylphenylsilylene) thin films were measured under various humidities over the frequency range 0.1—1000 kHz. In the high-humidity range, both the quantities increase with decreasing frequency. The existence of an anomalously low-frequency relaxation (lower than 0.1 kHz) is suggested in which the adsorbed water molecules are involved.

Although the electrical properties of organopolysilanes have become of great interest,[2)] few studies have been carried out on the dielectric properties. In the present work, thin films of poly(methylphenylsilylene) (PMPS) were prepared and their dielectric properties measured under various humidities. An anomalous relaxation of the adsorbed water molecules has been found.

PMPS was prepared by condensation polymerization of dichloromethylphenylsilane based on the Wurtz–Fittig reaction, and purified by reprecipitation from toluene with hexane. A toluene solution of the precipitate was washed several times. Gel permeation chromatography in THF resulted in $\overline{M}_n=9.07\times10^3$ and $\overline{M}_w/\overline{M}_n=1.75$ (reduced to polystyrene). The specimen used had a sandwich structure with a gas-permeating upper electrode. A PMPS thin film with a thickness of 2—3 μm was formed by casting on a glass substrate having a couple of Cr–Au thin-film lower electrodes with a thickness of ca. 100 nm. A gas-permeating Au thin film with a thickness of 30—40 nm was formed on the PMPS film by dc sputtering. Both the capacitance and dielectric loss tangent of the film were measured with a Yokogawa Hewlett-Packard 4192A LF impedance analyzer. The relative humidity was controlled using a Shin-ei SRH-1M humidity generator. Each measurement was carried out after the specimen had been kept standing under the desired temperature and humidity for at least 20 min.

Figure 1 shows the humidity dependence of the capacitance of PMPS at 25 °C. The humidity dependence varies remarkably with the frequency. When the humidity is increased from 10 to 90%, the capacitance doubles at 1 kHz, but it increases by a maximum of 2% at 100 kHz. Moreover, the hysteresis observed at low frequencies is not ignorable, suggesting that the adsorption and desorption of water molecules are somewhat slow. Figure 2 shows the humidity dependences of both the capacitance and the loss tangent of PMPS at 10 kHz. The extent to which these quantities vary with the relative humidity becomes greater as the temperature is raised.

In order to discuss the mechanism through which these dielectric properties vary with the humidity, it may be

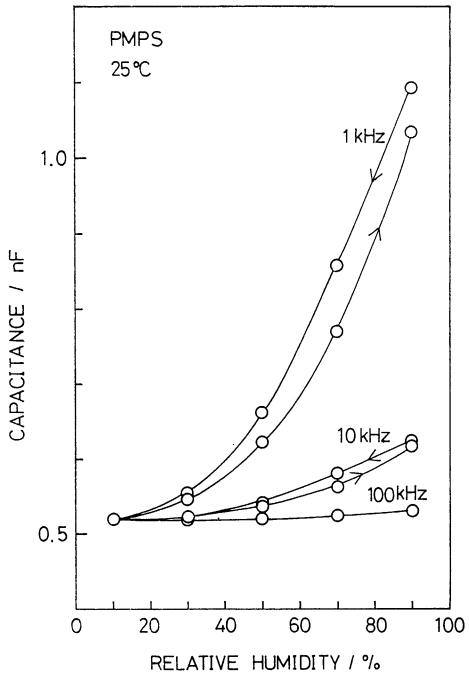

Fig. 1. Humidity dependence of the capacitance of a PMPS film at 25 °C.

convenient to use the absolute humidity or water vapor pressure rather than the relative humidity. Figure 3 shows plots of the capacitance and loss tangent against the logarithm of the water vapor pressure. Thus, as shown in the figure, all of the curves have almost the same shape, and the curves shift to the right with increasing temperature. If we regard these curves as being some kind of adsorption isotherm, the equilibrium constants of adsorption at 10 and 25 °C are greater by factors of 1.9 and 3.7, respectively, than at 40 °C. From these data, the enthalpy change of the adsorption of water has been estimated to be -32 kJ mol^{-1}. This value is near to the energy of hydrogen bonding of water ca. 40 kJ mol^{-1} (per water molecule).[3)] This suggests that the adsorption of water on a PMPS surface might involve the formation of small clusters, each of which comprises several water molecules.

Figure 4 shows the frequency dependence of both the capacitance and the loss tangent of PMPS at 25 °C in the humidity range 10 to 70%. Neither of the quantities vary with the frequency at low humidities, indicating that no relaxation exists in the kilohertz range, since the PMPS is in a glass state. At high humidities, on the

other hand, both the capacitance and loss tangent significantly increase with decreasing frequency, indicating the existence of relaxation in the lower frequency range.

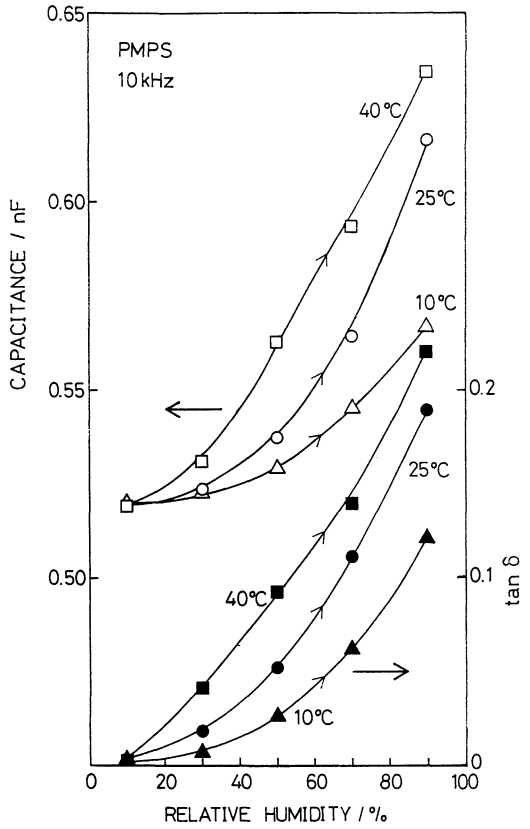

Fig. 2. Humidity dependence of both the capacitance and the dielectric loss tangent of a PMPS film at 10 kHz.

Relaxation in a range lower than kilohertz seems quite anomalous. It seems to be difficult to explain this phenomenon in terms of the usual state of water molecules. For example:

(a) Regarding ice, the relaxation time of Ice I has been reported to be about 0.2 ms.[4]

(b) Regarding the hydration of biopolymers, the rotational correlation time of water in hydrated collagen, from NMR studies, is 10^{-7} s at 25 °C.[5] From dielectric measurements, the fraction of water molecules is strongly bound to collagen with residence times on the order of 10^{-6} s.[6]

(c) In contrast to PMPS, polyimide has a capacitance that is almost invariant in the kilohertz range and a loss tangent that increases with increasing frequency above 10^5 Hz. The latter tendency becomes important as the humidity is increased.[7] This suggests that the relaxation time of the water molecules adsorbed on the polyimide is far shorter than 10^{-5} s.

Thus, a relaxation time of adsorbed water longer than 10^{-2} s is so anomalous. We can thus attribute such a long-term relaxation to hydrogen bonding between adsorbed water and the terminal hydroxyl groups of PMPS: the formation of hydrogen bonding would induce a large polarization in the glassy polymer, which can be related to long-term relaxation. The induction of polarization might involve sigma-conjugation in the silicon backbone of PMPS. We have obtained the following experimental result: the dielectric properties are almost independent of how many times the toluene solution containing PMPS has been washed with water after the synthesis of PMPS. The above result suggests that the contribution of some hydrophilic or ionic impurities to the dielectric properties must be minor. The long-range relaxation under humidity can therefore

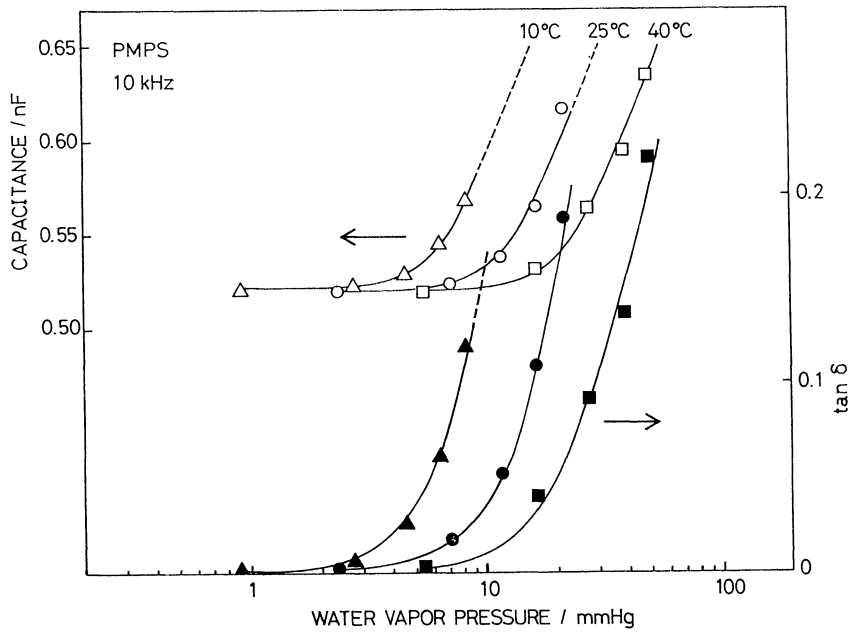

Fig. 3. Plots of the capacitance and the dielectric loss tangent of a PMPS film against the logarithm of water vapor pressure.

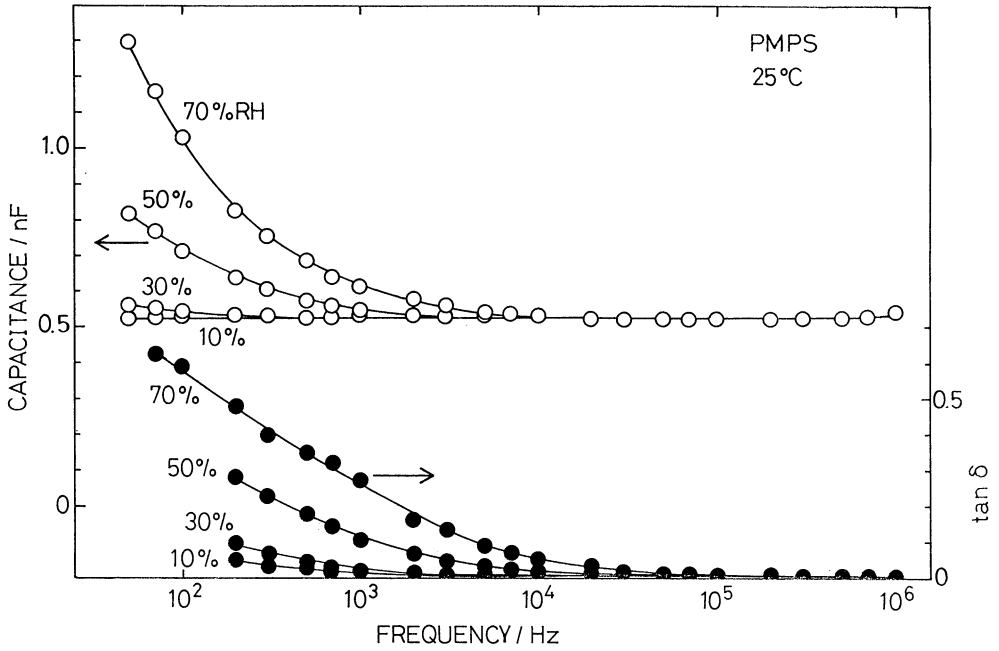

Fig. 4. Frequency dependence of both the capacitance and the dielectric loss tangent of a PMPS film at 25°C.

be attributed to hydrogen bonding between water and the terminal hydroxyl groups of PMPS, rather than to hydrophilic or ionic impurities.

The authors are grateful to Professor K. Ono of Tohoku University for valuable discussions.

References

1) Partially presented at the 39th Polymer Symposium of the Society of Polymer Science, Japan, Nagoya, October 1990.

2) As a review paper, R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca (1960), Chap. 12.

4) G. J. Wilson, R. K. Chan, D. W. Davidson, and E. Whalley, *J. Chem. Phys.*, **43**, 2384 (1965).

5) C. Migchelson and H. J. C. Berendsen, *J. Chem. Phys.*, **59**, 296 (1973).

6) J. R. Grigera, F. Vericat, K. Hallenga, and H. J. C. Berendsen, *Biopolymers*, **18**, 35 (1979).

7) T. Iwai, unpublished work.