

Glassy dynamics in thin films of polystyrene

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Glassy dynamics was investigated for thin films of atactic polystyrene by complex electric capacitance measurements using dielectric relaxation spectroscopy. During the isothermal aging process the real part of the electric capacitance increased with time, whereas the imaginary part decreased with time. It follows that the aging time dependences of real and imaginary parts of the electric capacitance were primarily associated with change in volume (film thickness) and dielectric permittivity, respectively. Further, dielectric permittivity showed memory and rejuvenation effects in a similar manner to those observed for poly(methyl methacrylate) thin films. On the other hand, volume did not show a strong rejuvenation effect.

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I. INTRODUCTION

Amorphous materials show a glass transition as the temperature decreases in the liquid state. Throughout the glass transition, the molecular mobility due to the α process is frozen and the material transforms into a glassy state. Polymeric glass shows structural changes during the aging process, even below the glass transition temperature T_g . Corresponding physical changes are observed with these structural changes [1–3]. These changes are known as physical aging, and are related to the glassy dynamics. This is regarded as an important property characteristic of disordered materials including; polymer glasses [4–6], spin glasses [7,8], and other disordered systems [9–11].

In our previous papers [5,6], the glassy states of poly(methyl methacrylate) (PMMA) show a decrease in both the real and imaginary parts of the complex dielectric constant with increasing time during the isothermal aging process. The glassy states show memory and rejuvenation phenomena for thermal treatment of a constant rate mode and of a temperature cycling mode, as shown below. In the constant rate mode, the temperature changes from high temperature above T_g to an aging temperature, at which the sample is aged isothermally and the dielectric susceptibility decreases with increasing aging time during the process. This decrease in dielectric susceptibility is associated with the relaxation of the system into the equilibrium states. The change to the equilibrium is called aging. Then, the temperature subsequently decreases from the isothermal aging temperature to room temperature at a constant rate. A comparison of the value of the dielectric susceptibility at room temperature after the isothermal aging to that without isothermal aging, revealed that the values were in good agreement. This suggests that the decrease in dielectric susceptibility induced by the isothermal aging is totally compensated during the cooling process from the isothermal aging temperature to room temperature. This change in dielectric susceptibility has the

opposite direction compared to the change due to the aging. Therefore, the change in dielectric susceptibility induced during the cooling process after the isothermal aging is called rejuvenation, and hence the system is rejuvenated as far as the dielectric response is concerned. However, during the subsequent heating process from room temperature, the dielectric susceptibility deviates from the value observed during the cooling process without isothermal aging, and shows a maximum deviation just above the aging temperature as if the sample remembered the isothermal aging it experienced during the preceding cooling process. This behavior is called memory effect and it suggests that the thermal history is maintained as a memory.

In the case of amorphous polymers, it is well known that the density of the polymers increases due to the isothermal aging below T_g , and this density change is maintained even at room temperature [1]. On the other hand, there is no rejuvenation for the density. This finding appears to be inconsistent with the fact that the dielectric ac susceptibility shows rejuvenation. Herein, we investigate the aging behavior of thin films of atactic polystyrene (a-PS) using electric capacitance measurements in order to elucidate the nature of the glassy dynamics in polymer glasses.

II. EXPERIMENT

Thin films of atactic polystyrene (a-PS) with two different thicknesses, 14 nm and 284 nm, were prepared by spin coating from a toluene solution of a-PS on an aluminum (Al) deposited glass substrate. The thickness was controlled by changing the concentration of solution. The samples of a-PS used in this study were purchased from Aldrich Co., Ltd. ($M_w=1.8 \times 10^6$, $M_w/M_n=1.03$). After annealing at 70 °C under vacuum for 2 days to remove solvents, Al was again vacuum deposited to serve as an upper electrode. Several heating cycles through and above a bulk value of T_g were carried out before the capacitance measurements were taken for the relaxed as-spun films in order to obtain reproducible results. The values of T_g in the thin films with $d=14$ nm and 284 nm were 350 K and 368 K, respectively. The thickness

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was evaluated from the value of the electric capacitance at 293 K for the as-prepared films before measurements in the same manner previously reported [12,13].

The T_g of the two thin films differs by about 18 K. According to the recent report on T_g of thin films of polystyrene, the effect of oxidation can be a possible origin of the reduction of T_g [14]. However, we performed T_g measurements for each thin film several times and confirmed that the reduction of T_g is not due to the oxidation effect in the present case.

Capacitance measurements were carried out using an LCR meter (HP4284A) for the frequency $f=1$ kHz during the cooling and heating processes between 380 K and 273 K at a rate of 1 K/min as well as during isothermal aging at various aging temperatures T_a ($=315$ K– 351 K). The complex electric capacitance of the sample condenser C^* ($\equiv C' - iC''$) was measured as a function of temperature T and aging time t_w . The value of C^* was converted into the dynamic (complex) dielectric constant ϵ^* ($\equiv \epsilon' - i\epsilon''$) by dividing the $C^*(T)$ by the geometrical capacitance $C_0(T_0)$ at a standard temperature T_0 . The value of C^* is given by the relation $C^* = \epsilon^* \epsilon_0 \frac{S}{d}$ and $C_0 = \epsilon_0 \frac{S}{d}$, where ϵ_0 is the permittivity in vacuum, S is the area of the electrode, and d is film thickness. For evaluation of ϵ^* and C_0 , we use the thickness d which is determined at $T_0=293$ K and $S=8 \times 10^{-6}$ m².

III. RESULTS AND DISCUSSION

A. Aging dynamics

Figure 1 shows the change in the real and imaginary parts of the complex electric capacitance for a-PS films with $d=284$ nm and $f=1$ kHz. The temperature of the sample was changed as follows: After several temperature cycles in order to stabilize the measurements, the temperature changed from 380 K to 273 K (cooling process, dotted line) and then from 273 K to 380 K (heating process, solid line). The data obtained for the cooling and heating processes are used as a reference data. The sample was cooled from 380 K to 340 K ($\equiv T_a$), the temperature was maintained at T_a for 20 h, and then the sample was again cooled down to 273 K after isothermal aging (open circles). Finally, the sample was again heated from 273 K to 380 K (open triangles).

In Fig. 1(a), the reference data shows that the real part of the electric capacitance C' is a decreasing function of temperature and the slope of C' with respect to temperature gradually changed around 365 K. Thus, there is a difference between the heating and cooling processes. This gradual change corresponds to the glass transition. Furthermore, from the data for the subsequent cooling process including isothermal aging, C' was observed to increase with aging time during isothermal aging at T_a . In this case, the value of C' increased by 0.3% for isothermal aging at 340 K for 20 h.

Contrary to C' , the imaginary part of the electric capacitance C'' was an increasing function of temperature during the cooling and heating processes at a constant rate. Above 380 K a decrease in the peak was expected due to the α process. Further, during the isothermal aging process at 340 K, C'' was observed to decrease with increasing aging time.

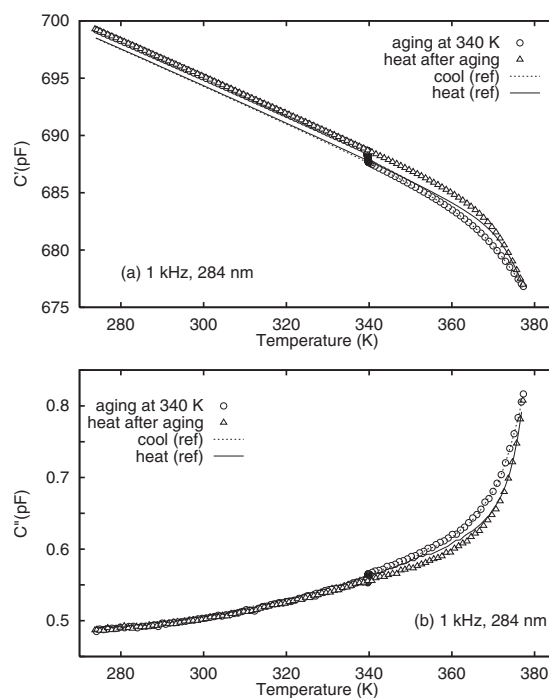


FIG. 1. Temperature change in (a) the real part of electric capacitance C' and (b) the imaginary part C'' for a-PS films with thickness of 284 nm for frequency 1 kHz. Temperature changes between 380 K and 273 K including isothermal aging at 340 K.

The change in C'' for aging at 340 K for 20 h was about 0.2 pF, which corresponds to a decrease by 3%. This fraction was an order of magnitude larger than the increase in C' for the same aging process.

Figure 2 shows the temperature dependence of the complex electric capacitance in thin films of a-PS with $d=14$ nm. In this case, a similar result was obtained for the temperature dependence of C' and C'' as that for $d=284$ nm. For thin films, the absolute value of C^* is enhanced. The change in C' is more distinct due to the smaller slope of C' with respect to T . Furthermore, the scatter of data in C' is reduced due to the larger geometrical capacitance. The slight increase in C' above 375 K was due to the existence of the α process. In the case of $d=14$ nm, the amount of the change in C' and C'' are 0.1% and 3% for the isothermal aging at 340 K for 20 h, respectively.

This suggests that during the isothermal aging process of a-PS, C' increases with aging time, whereas C'' decreases with aging time. It is important to note that both C' and C'' decrease with increasing aging time for the isothermal aging in poly(methyl methacrylate) [4,12,13]. It is also reported in the literature that the real part of complex electric capacitances (dielectric constants) decreases with increasing aging time for polycarbonate [15] and poly(ethylene terephthalate) [16]. The observed increase in C' in a-PS is different from the decrease observed commonly for other polymeric systems.

Figure 3 shows the aging time dependence of C' and C'' during isothermal aging at various temperatures T_a (between 321.3 K and 350.8 K) for $d=14$ nm. The values $\Delta C'(t_w)$ and $\Delta C''(t_w)$ are defined by $\Delta C'(t_w) = C'(t_w) - C'(0)$ and

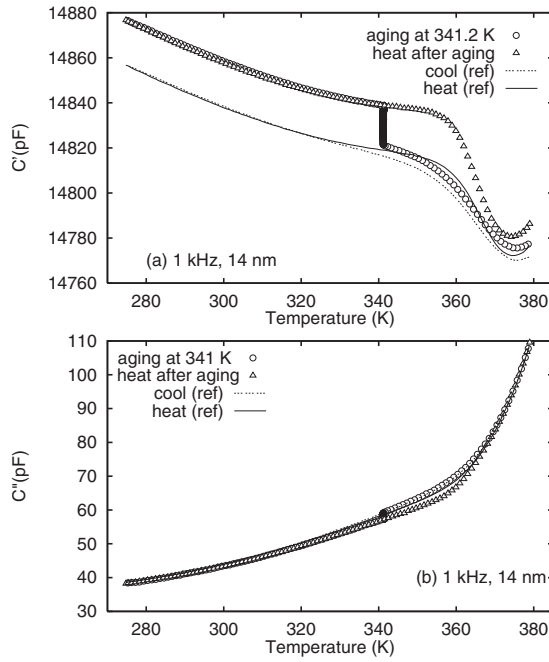


FIG. 2. Temperature change in (a) the real part of electric capacitance C' and (b) the imaginary part C'' for a-PS films with thickness of 14 nm for frequency 1 kHz. Temperature changes between 380 K and 273 K including isothermal aging at 340 K.

$\Delta C''(t_w) = C''(t_w) - C''(0)$, and the time $t_w = 0$ is the initial time at which the temperature of the sample reaches the aging temperature. In Fig. 3(a), the value $\Delta C'$ increases monotonically with aging time and the value $\Delta C'$ at 20 h decreases with decreasing aging temperature. In Fig. 3(b), it is found that $\Delta C''$ decreases with increasing aging time and the absolute value of $\Delta C''$ at 20 h decreases with decreasing T_a between 341.2 K and 321.3 K. The relaxation behavior of C'' for isothermal aging at $T_a = 350.8$ K appears to be slightly different from that at other T_a 's lower than 350.8 K.

B. Change in volume and dielectric permittivity

A possible explanation for the observed dependence of C' and C'' on the aging time during isothermal aging is provided in this section. The real and imaginary parts of the complex electric capacitance are given as follows:

$$C'(\omega, T, t) = [\epsilon_\infty(T, t) + \epsilon'_{\text{disp}}(\omega, T, t)]C_0(T, t), \quad (1)$$

$$C''(\omega, T, t) = \epsilon''_{\text{disp}}(\omega, T, t)C_0(T, t), \quad (2)$$

where ϵ_∞ is the dielectric constant at the high frequency limit, and ϵ'_{disp} and ϵ''_{disp} are frequency-dependent contributions to the dielectric constant due to the orientational polarization associated with molecular motions. The following relations can be derived: $\epsilon' = \epsilon'_{\text{disp}} + \epsilon_\infty$ and $\epsilon'' = \epsilon''_{\text{disp}}$. In the case of a-PS, the polarity is very weak, therefore; $\epsilon'_{\text{disp}} \ll \epsilon_\infty$ is expected. Thus, Eq. (1) can be approximately rewritten as

$$C'(\omega, T, t) \approx \epsilon_\infty(T, t)C_0(T, t). \quad (3)$$

For an isothermal aging process, the density is expected to increase with aging time, and hence the film thickness d

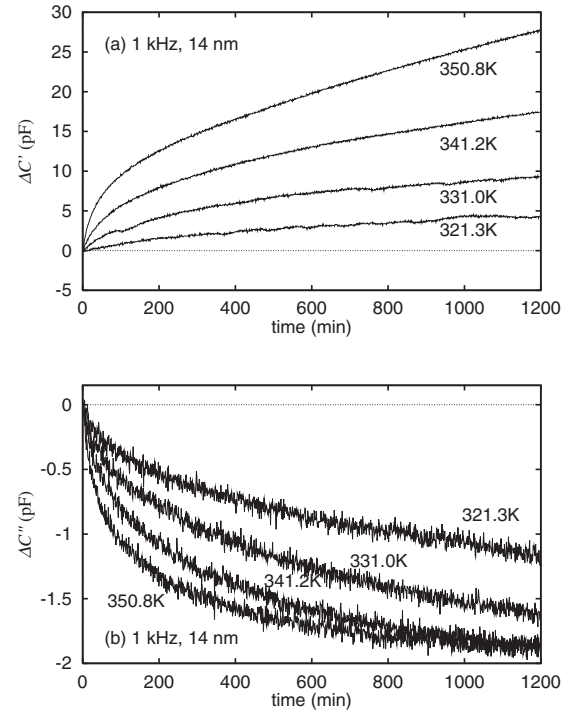


FIG. 3. Aging time dependence of the deviation $\Delta C'$ ($\Delta C''$) of $C'(t)$ [$C''(t)$] from the initial values $C'(0)$ [$C''(0)$] for various aging temperatures for thin films of a-PS with film thickness of 14 nm for $f = 1$ kHz. The aging temperatures are 350.8 K, 341.2 K, 331.0 K, and 321.3 K.

decreases on the condition that the area of the film remains constant. Therefore, this density change causes an increase in C' according to the following rate:

$$\frac{1}{C'} \frac{\partial C'}{\partial t} = -(\eta + 1) \frac{1}{d} \frac{\partial d}{\partial t}, \quad (4)$$

where η is a constant and its value is almost equal to 1 for a-PS [12]. Equation (4) suggests that the decrease in film thickness increases C' for isothermal aging.

Figure 4 shows the temperature change in the inverse of C' observed during the constant rate mode. The vertical axis approximately corresponds to the volume of this system if the area remains constant. Therefore, in Fig. 4 a temperature dependence of the volume characteristic of amorphous polymers can be observed. As the sample is cooled down from a high temperature to a lower one through T_g , the initial liquid state changes to a glassy state (Glass 1) and then the glassy state is converted into a second glassy state (Glass 2) during an isothermal aging. This temperature dependence of volume can typically be measured using dilatometric measurements for amorphous polymers.

On the other hand, Eq. (2) shows that C'' includes two different contributions from ϵ''_{disp} and C_0 . For the isothermal aging, C_0 is expected to increase with aging time, because the density increases, i.e., the film thickness decreases, as shown above. Therefore, the decrease in C'' with aging time suggests that the imaginary part of dielectric constant, ϵ''_{disp} , decreases with aging time and that its contribution can over-

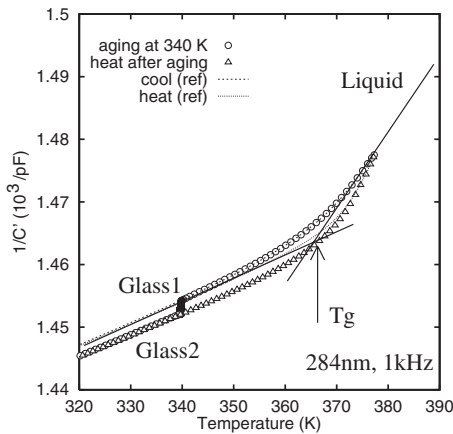


FIG. 4. Temperature dependence of the inverse of C' for a constant rate mode observed at 1 kHz for a-PS with thickness of 284 nm. The vertical axis approximately corresponds to the volume V .

come the contribution from the increase in C_0 . For PMMA, which has a strong polar group in the chain, it has been reported that both real and imaginary parts of the dielectric constant decrease with aging time during the isothermal aging process [4,6].

The results observed in a-PS can be explained as follows: for the isothermal aging process, the decrease in film thickness is observed as the increase in C' , whereas the decrease in the imaginary component of dielectric permittivity is observed as a decrease in C'' . Therefore, the present measurement on the electric capacitance of a-PS will provide information on the change in volume and dielectric permittivity simultaneously for the same sample during the isothermal aging process.

C. Volume relaxation during isothermal aging

As discussed in the preceding section, the real part of the complex electric capacitance changes with aging time in accordance with the volume change. Figure 5 shows the aging time dependence of C' relative to the value of $C'(0)$ for thin films with $d=284$ nm. The horizontal axis is the logarithm

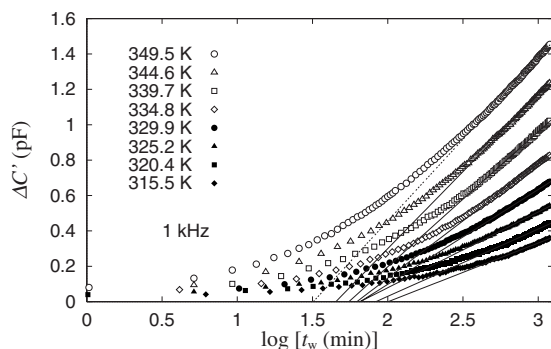


FIG. 5. Time evolution of the deviation $\Delta C'$ observed at various aging temperatures for a-PS thin films with $d=284$ nm. The frequency of the applied electric field is 1 kHz. The horizontal axis is the logarithm to the base 10 of aging time.

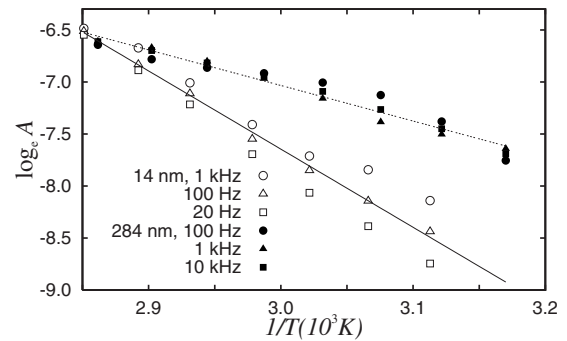


FIG. 6. Dependence of the logarithm of the coefficient A on $1/T$ for various frequencies and thicknesses. The values of f are 20 Hz, 100 Hz, and 1 kHz, and the values of d are 14 nm and 284 nm.

of aging time. Figure 5 clearly shows that $\Delta C'$ increases with the logarithmic law with respect to the aging time for the long time region. Further, there is no tendency to saturate in this time region. We evaluate the slope of this aging time dependence using the following equation:

$$\Delta C'(t_w) = \tilde{A} \log_{10} t_w + B \quad (\text{for large } t_w). \quad (5)$$

Here, from the value of \tilde{A} , the aging rate of the volume, A , for thin films of a-PS can be evaluated as follows:

$$A = \frac{\tilde{A}}{C'(0)} = \frac{1}{C'(0)} \frac{d\Delta C'}{d \log_{10} t_w}, \quad (6)$$

where for a given frequency $C'(0)$ is the value of C' at the time at which the temperature reaches the aging temperature. Figure 6 shows the temperature dependence of A for thin films with two different thicknesses $d=14$ nm and 284 nm. In the present temperature range, the aging rate A was found to be larger in $d=284$ nm than in $d=14$ nm. In this figure, it is clear that the rate A increases with increasing aging temperature and obeys the Arrhenius law, $A=A_0 \exp(-U/k_B T)$, where k_B is the Boltzmann constant, U is the activation energy, and A_0 is a constant.

It should be discussed what is the molecular origin associated with the volume change during the aging process. Below T_g there should be no contribution due to the α process, and hence it can be expected that the β process should be the most probable candidate for the molecular origin for the physical aging. However, in the literature the activation energy for the β process in atactic polystyrene was estimated to be 38 kcal/mol [17] or 30 kcal/mol [18], which are larger than the activation energy evaluated from the temperature dependence of the aging rate A . Therefore, the present result cannot be regarded as an evidence that the β process is directly associated to the physical aging, although the α process can be excluded from the candidate for molecular origin for the physical aging. Probably, the β process is indirectly related to the volume change during the physical aging process.

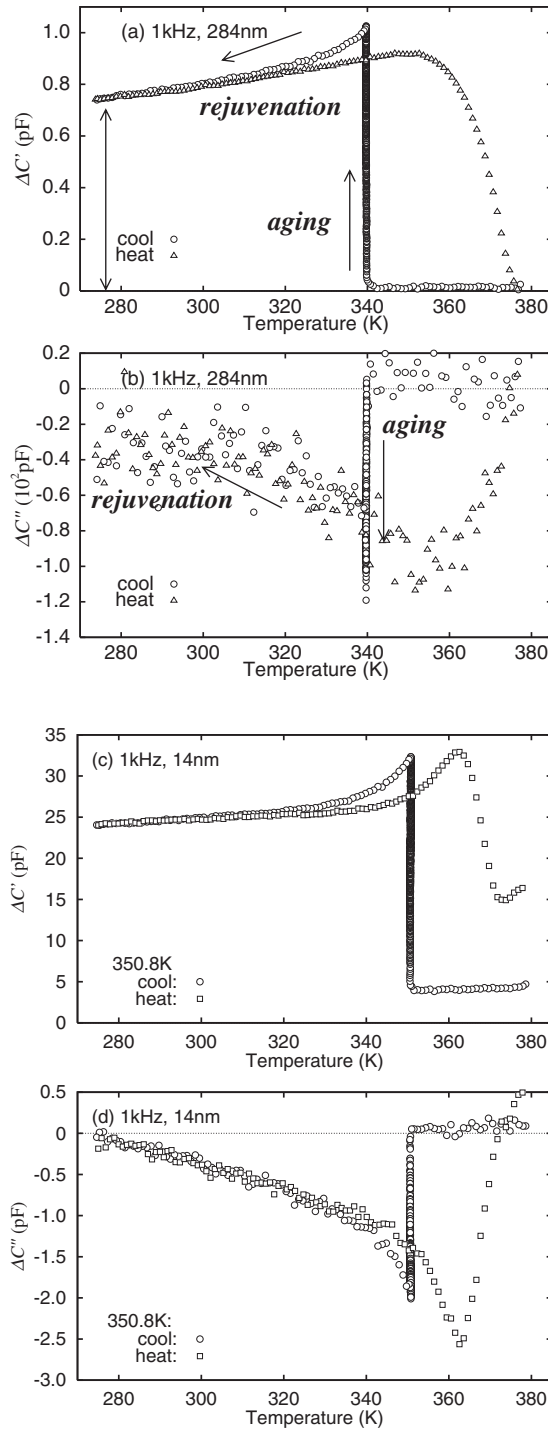


FIG. 7. Temperature dependence of the deviation $\Delta C'$ ($\Delta C''$) of the component of the complex electric capacitance C' (C'') from the reference values observed for the cooling process including an isothermal aging at 339.7 and 350.8 K and the subsequent heating process for thin films of a-PS with $d=284$ nm and $f=1$ kHz [(a) and (b)] and $d=14$ nm and $f=1$ kHz [(c) and (d)].

D. Memory and rejuvenation in thin films

Figure 7 shows the temperature dependence of $\Delta C'$ and $\Delta C''$ observed during the cooling process with isothermal aging at T_a and the subsequent heating process for f

$=1$ kHz in a-PS films with $d=284$ nm [(a) and (b)] and 14 nm [(c) and (d)]. In this case, $\Delta C'(T)$ [$\Delta C''(T)$] is evaluated as the deviation of $C'(T)$ [$C''(T)$] from the reference values $C'_{\text{ref}}(T)$ [$C''_{\text{ref}}(T)$] at the same temperature T . For the reference value C'_{ref} (C''_{ref}) to the cooling process including isothermal aging, we used the data measured for the preceding cooling process without any isothermal aging, and for the reference value for the heating process after the isothermal aging, we used the data measured for the preceding heating process.

Figure 7(a) shows that as the temperature decreases from 380 K to 340 K, $\Delta C'$ remains almost zero, and the deviation $\Delta C'$ increases as the aging time increases during isothermal aging at 340 K (see open circles). During the cooling process, after the isothermal aging, the deviation decreases and then approaches a constant value, but not zero. As a result, most of the deviation $\Delta C'$ induced during the isothermal aging remains even at 273 K. This result is thought to be associated with the fact that the isothermal aging increases the density. For the subsequent heating process, $\Delta C'$ changes along the path traced by $\Delta C'$ for the preceding cooling process after isothermal aging, and then $\Delta C'$ reaches a maximum just above T_a (see open triangles). The value of $\Delta C'$ subsequently decreases approaching zero. This behavior can be interpreted as follows: the fact that the sample experiences aging at T_a by the way of the preceding cooling process is memorized within the sample, and the memory is recalled during the subsequent heating process.

The temperature dependence of $\Delta C''$ is different from that of $\Delta C'$, as shown in Fig. 7(b). For the cooling process from 380 K, $\Delta C''$ remains almost zero, and then $\Delta C''$ decreases with increasing aging time for the isothermal aging. $\Delta C''$ subsequently increases with decreasing temperature and reaches zero at 273 K. In this case, there is a large scatter in the values of C' , because the thickness is 284 nm and the geometrical capacitance C_0 is not large enough. Figure 7(d) shows the temperature dependence of $\Delta C''$ during the constant rate mode for $d=14$ nm. For $d=14$ nm, the scatter of C'' is suppressed, therefore; it is clear that the value of $\Delta C''$ reaches zero at 273 K after cooling from T_a . This result suggests that the system is rejuvenated as far as the dielectric response is concerned. For the subsequent heating process, $\Delta C''$ decreases along the curve observed during the preceding cooling process, and reaches zero after showing a minimum just above T_a . Because the temperature dependence of $\Delta C''$ is primarily attributed to that of ϵ'' , it follows that ϵ'' exhibits a memory and rejuvenation effect. A similar effect has been observed for ϵ' and ϵ'' in the case of PMMA [4,6].

Combining the results observed for $\Delta C'$ and $\Delta C''$, it is concluded that the volume of a-PS films decreases during isothermal aging, and the deviation from the reference value is maintained below the aging temperature. On the other hand, dielectric permittivity also decreases during isothermal aging, and the deviation of the dielectric permittivity from the reference value is totally rejuvenated at lower temperatures. The existence of the volume change observed in the present measurement is consistent with the fact that there are several reports relating to the change in volume or density due to physical aging [1]. Based on the volume, the system does not appear to be rejuvenated, however, the dielectric

response to the ac-electric field is fully rejuvenated.

In disordered systems, similar memory and rejuvenation effects are often observed during the aging process. In spin glasses, magnetic ac susceptibility shows a memory and rejuvenation effect during the constant rate mode and the temperature cycling mode. A possible mechanism for this effect has been extensively discussed by a number of research groups [19–25].

In spin glasses, memory and rejuvenation effects have been investigated through the measurements of magnetic ac susceptibility. A number of experiments clearly show the existence of a strong rejuvenation effect in aging phenomena through the so-called temperature-cycling mode, where the aging temperature is maintained at T_1 for the first and third stage and at T_2 (smaller than T_1) for the second stage. At the beginning of the second stage of the temperature-cycling mode, the imaginary part of the magnetic ac susceptibility χ''_{ac} returns to the initial value for χ''_{ac} at the beginning of the first stage, although χ''_{ac} decreases during the first stage. However, it should be noted here that the magnetic ac susceptibility is associated with a time scale, defined by $t_\omega = 2\pi/\omega$ (where ω is the angular frequency of the ac-magnetic field). There is a relationship between the time scale and the length scale [24], therefore, the magnetic ac susceptibility is associated with the length scale $\xi(t_\omega)$. The experimental results suggest that the dielectric ac susceptibility shows a rejuvenation effect, whereas the volume of the system changes with increasing aging time and shows no rejuvenation. Although these findings appear to be inconsistent, this can be explained as follows. Similar to magnetic ac susceptibility, the dielectric ac susceptibility is associated with a length scale $\xi(t_\omega)$ defined by the angular frequency ω of the applied electric field. The volume or density is a macroscopic physical quantity and has a characteristic length scale significantly larger than $\xi(t_\omega)$ for the present frequency range. This suggests that, even if the volume changes during the isothermal aging process and the change is maintained at lower temperatures, the dielectric response to the applied electric field is not influenced by the change in volume. Therefore, the

dielectric ac susceptibility can be rejuvenated during the cooling process after the isothermal aging process.

If both magnetic ac susceptibility and a macroscopic physical quantity such as the remaining magnetization are measured simultaneously during the isothermal aging process, it can be expected that for spin glasses the magnetic ac susceptibility will show a rejuvenation, whereas the magnetization is not rejuvenated.

IV. SUMMARY

Herein, we investigated the aging dynamics for thin films of atactic polystyrene through measurements of complex electric capacitance using dielectric relaxation spectroscopy. The results obtained in this study are summarized as follows:

(1) During the isothermal aging process at a given aging temperature the real part of the electric capacitance increases with aging time, while the imaginary part decreases with aging time.

(2) The aging time dependences of the real and imaginary parts of the electric capacitance are mainly associated with the change in volume or film thickness and dielectric permittivity, respectively.

(3) Memory effect can be observed for both ac-dielectric permittivity and volume. On the other hand, a strong rejuvenation effect can be observed for the ac-dielectric permittivity, but not for the volume.

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