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Physical aging of polystyrene investigated by dynamic viscoelasticity

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Abstract

Physical aging of polystyrene (PS) in the glassy state was investigated by dynamic viscoelasticity measurements. Two kinds of PS sample ($T_g = 110$°C), almost equal in weight-average molecular weight but different in molecular weight distribution, were used. Physical aging was observed for the samples aged at 60 and 80°C after having been quenched from 190°C. The physical aging was not affected by molecular weight distribution. The temperature dispersion curves of the dynamic viscoelastic functions of the samples changed with aging time from the lower temperatures below T_g during aging at 60°C. In a high-temperature range, however, the curves of the aged samples agreed with that of the sample right after quenching. On the other hand, the curves of the samples aged at 80°C changed within the whole temperature range. The experimental results were discussed in terms of the segmental motion. © 2001 Published by Elsevier Science Ltd.

Keywords: Physical aging; Polystyrene; Dynamic viscoelastic properties

1. Introduction

Mechanical properties of polymeric materials in the glassy state are generally affected by the thermal history [1–14]. When a glassy polymer sample is quenched from the molten state and annealed at a temperature (T_A) near but below the glass transition temperature (T_g), the mechanical properties change toward the equilibrium at T_A because of change and relaxation of the chain conformation. The process is called 'physical aging'. The internal structure of polymeric materials changes and relaxes owing to a change of chain conformation by the molecular motion.

The studies of physical aging by measuring the dynamic viscoelastic properties of glassy polymers have shown that the storage modulus (E') increases and the loss modulus (E'') decreases with the aging time [15–21]. The time dependence of the properties has been investigated under isothermal annealing at T_A in most works. Generally, the values of viscoelastic functions change linearly against the logarithm of the aging time at T_A. It is little known how temperature dispersion curves of viscoelastic functions change during isothermal annealing.

We have reported effects of thermal history on dynamic viscoelasticity of polymeric materials [22–25]. The samples were quenched from the molten state and then aged at temperatures below T_g in our studies. We have shown that the shape in the temperature dispersion curves of the dynamic viscoelastic functions changes with aging time. Moreover, we have shown that the aged sample has the memory of being quenched before aging.

In this work, we investigate the physical aging of polystyrene (PS) by dynamic viscoelasticity measurements, and discuss the phenomenon in terms of the segmental motion. We also discuss whether the physical aging on the viscoelasticity is a common phenomenon for polymeric materials in the glass state, comparing the results with those obtained using other polymeric materials [16,23–25].

2. Experimental

2.1. Materials

The samples used in this study are two kinds of PS having almost equal weight-average molecular weight, but different molecular weight distributions. The samples are L211 ($M_w = 243\,000$, $M_w/M_n = 1.1$, $T_g = 110$°C) and PS666 ($M_w = 227\,000$, $M_w/M_n = 3.1$, $T_g = 110$°C). M_w and M_w/M_n were measured by gel permeation chromatography and T_g by differential scanning calorimetry at a heating rate of 10°C min^{-1}. L211 was synthesized by an anionic polymerization. The polymerization was performed in benzene–tetrahydrofuran at 0°C, using *sec*-butyllithium as an initiator. PS666 is a commercial polystyrene Styron® 666 supplied by Dow Chemical Co. Ltd.

Films were prepared by casting from 20 wt% 2-butanone

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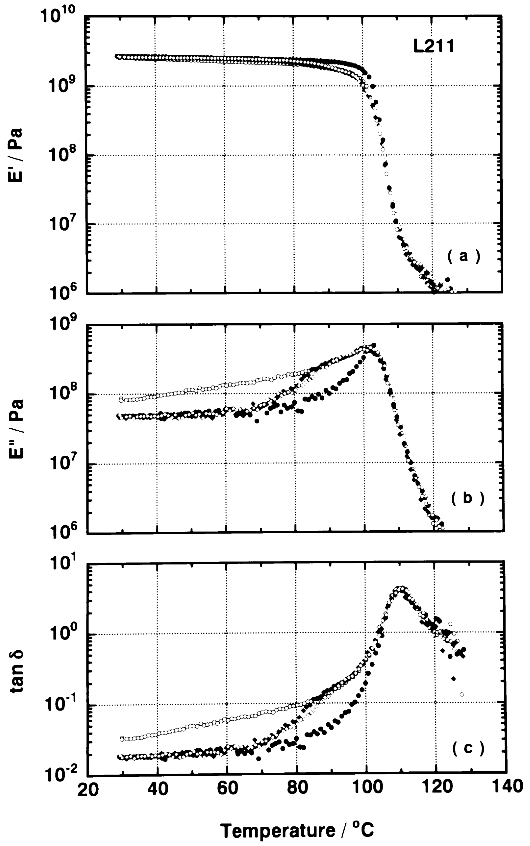

Fig. 1. The temperature dispersion curves of E', E'', and tan δ of L211-QA60C series with L211-SC (●) and L211-QU (○). The QA60C samples were annealed at 60°C for 24 (◆) and 150 h (◇) after having been quenched from 190 to 0°C.

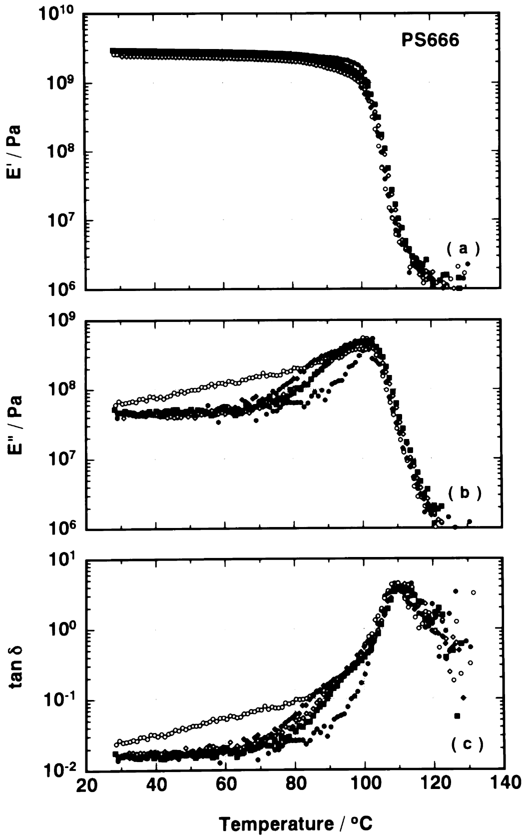

Fig. 2. The temperature dispersion curves of E', E'', and tan δ of PS666-QA60C series with PS666-SC (●) and PS666-QU (○). The QA60C samples were annealed at 60°C for 24 (◆), 150 (◇) and 320 h (■) after having been quenched from 190 to 0°C.

solution. The films were dried in air at room temperature for a few days, and then in a vacuum oven to remove 2-butanone further. During the drying process in the vacuum oven, the temperature was raised stepwise by 10°C a day up to 130°C $> T_g$, and then was kept at 130°C for 3 days. The films obtained were less than 0.1 mm in thickness.

The film samples were prepared on a compression-molding machine at 190°C for 5 min to eliminate the previous thermal histories at low temperatures and then were cooled in two ways. One was slow cooling from 190°C toward room temperature T_r (15–25°C), the sample thus obtained is called SC. The average rate of the cooling was 0.7°C min^{-1}, and the thermal history in the course of cooling has been shown in a previous paper [22]. Another was rapid quenching in an ice-water bath, the sample is called QU. Various thermal histories were applied to QU samples below T_g. QU samples were annealed at 60 or 80°C for various durations of time and then cooled slowly from the temperatures to T_r. The annealed samples thus obtained are called QA60C and QA80C, respectively.

2.2. Measurements

The temperature dispersion of dynamic viscoelastic functions, E', E'' and loss tangent (tan δ) of the samples was measured at an angular frequency of 1 s^{-1} and at a static strain of 0.05% with a Rheometrics RSA-II. All measurements were performed on heating at a heating rate of 2°C min^{-1}.

3. Results and discussion

The temperature dispersion curves of E', E'' and tan δ of L211-QU, L211-SC, and L211-QA60C samples are shown in Fig. 1. The temperature at onset of the steep decrement of the E' curve of L211-SC is higher than that of the others. The E'' and tan δ curves of L211-QU locate higher than the curves of L211-SC at the glass region. The E', E'' and tan δ curves of L211-QA60C samples agree with the curves of L211-SC below 65°C and agree with the curves of L211-QU above 90°C. As the aging time increases, the crossover portion of the E'' and tan δ curves of L211-QA60C samples appearing in the intermediate temperature range moves to high temperatures.

The agreement of the temperature dispersion curves of L211-QU and -QA60C samples at high temperatures suggests that both samples have the same structure at this

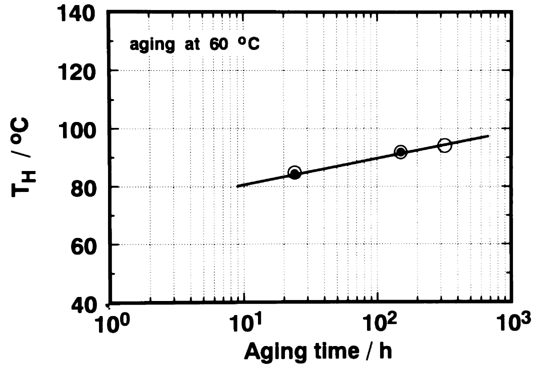

Fig. 3. Semi-logarithmic plot of T_H against aging time. The tan δ curve of QA60C samples merge into that of QU sample at T_H. (●) L211 (from Fig. 1); (○) PS666 (from Fig. 2).

temperature range and that L211-QA60C samples keep the memory of being quenched from 190 to 0°C. The movement of the crossover portion of the curves of L211-QA60C samples suggests that the samples approach the equilibrium state at 60°C, losing the memory by changing the segmental conformation in the glassy state.

The temperature dispersion curves of E', E'' and tan δ of PS666-QU, PS666-SC, and PS666-QA60C samples are shown in Fig. 2. The effect of aging at 60°C on the dynamic viscoelastic properties of PS666-QA60C samples is similar to that of L211-QA60C samples as shown in Fig. 1. The curves of PS66-QA60C samples agree with those of PS666-QU at high temperatures and agree with those of PS666-SC at low temperatures. The crossover portion of the E'' and tan δ curves of PS666-QA60C samples between 65 and 90°C moves to high temperatures with increasing isothermal aging time at 60°C.

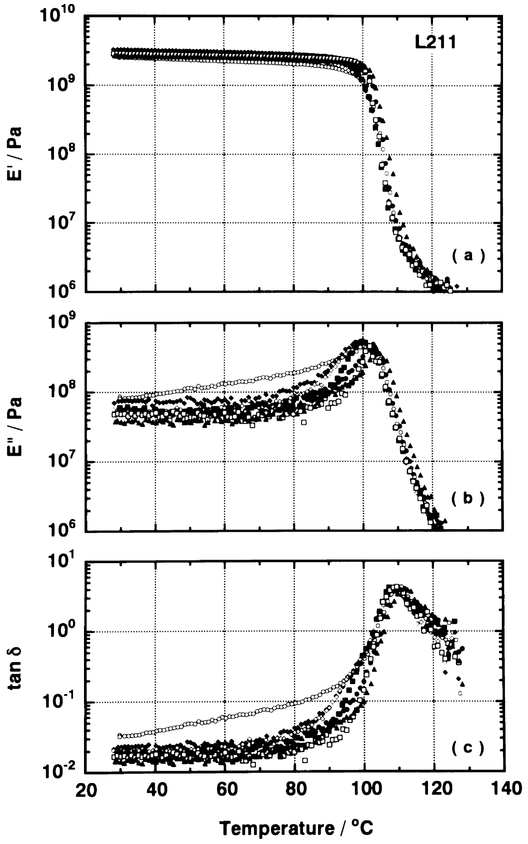

Fig. 4. The temperature dispersion curves of E', E'', and tan δ of L211-QA80C series with L211-SC (●) and L211-QU (○). The QA80C samples were annealed at 80°C for 3 (◆), 6 (◇), 24 (■), 72 (□), and 320 h (▲) after having been quenched from 190 to 0°C.

We focus on a temperature (T_H) at which the tan δ curves of QA60C samples merge into the curve of the QU sample at high temperatures. Fig. 3 is the plot of T_H versus aging time for L211-QA60C and PS666-QA60C samples. As can be seen from the figure, the data points of both the PS samples are represented by a single straight line. Thus the effect of molecular weight distribution on T_H is not observed.

The change in shape of the temperature dispersion curves of the dynamic viscoelastic functions of PS samples during isothermal aging at 60°C is similar to the change of other polymeric materials; poly(acrylonitrile-butadiene-styrene) [16], poly(methyl methacrylate) [23], poly(α-methylstyrene-*co*-acrylonitrile) [24], and polycarbonate [25] annealed at temperatures far below the T_g. Thus, segments in polymeric glasses relax by the same mechanism as that by which amorphous polymer materials do.

The shape of the temperature dispersion curves of the viscoelastic functions changes and T_H increases for the quenched sample during aging. This is due to a change of the chain conformation by a segmental motion at the aging temperature. The scale of segmental mobility corresponds to the temperature. The movable segment size increases with aging temperature. Thus, the change in shape of the curves on proceeding to higher temperatures must correspond to the development of segmental relaxation from the smaller to larger scale of segmental size at the aging temperatures. Moreover, the conformation of the large scale of segmental length above T_H has not relaxed, because T_H might be characterized as the temperature corresponding to the segmental scale.

The temperature dispersion curves of E', E'' and tan δ of L211-QA80C samples are shown in Fig. 4. The samples were aged at 80°C for various durations of time after having been quenched from 190 to 0°C. The curves of L211-QU and L211-SC are added in the figure. The effect of aging on the temperature dispersion of the viscoelastic functions is easily seen on E'' and tan δ. The temperature dispersion curves of E'' and tan δ locate lower with the aging time at a temperature range below 90°C. The E'' and tan δ curves of L211-QA80C samples turn up at a temperature near 90°C. The portion of the curves from 90°C to the peak temperature moves to the higher temperature, as aging time increases. Notice that the behavior is different from those shown in Fig. 1. The curves of L211-QA80C samples disagree with the curves of L211-QU. The disagreement suggests that the QA80C samples completely lose the memory of having

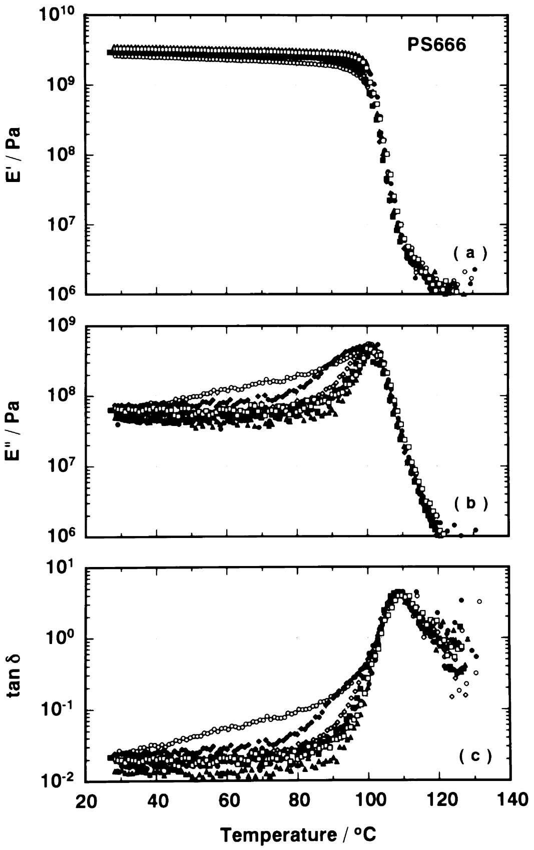

Fig. 5. The temperature dispersion curves of E', E'', and tan δ of PS666-QA80C series with PS666-SC (●) and PS666-QU (○). The QA80C samples were annealed at 80°C for 3 (◆), 6 (◇), 24 (■), 72 (□), and 320 h (▲) after having been quenched from 190 to 0°C.

been quenched by annealing at 80°C for 3 h. Since the curves of L211-QA80C samples change within the whole temperature range by aging, all the chain conformation changes to approach the equilibrium state at 80°C. In this case, the structural relaxation proceeds by thermal motion of the whole chain, but of the segment at 80°C that is below 30°C from T_g.

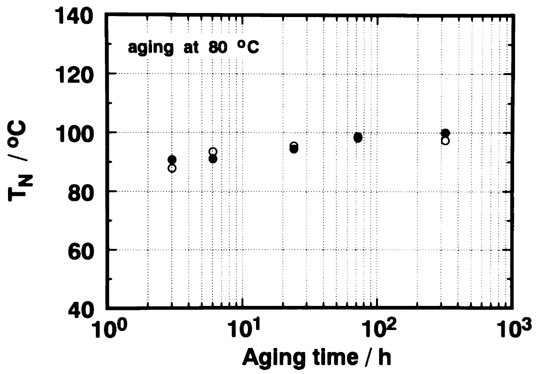

Fig. 6. Semi-logarithmic plot of T_N against aging time. These were obtained from the results of physical aging at 80°C for L211 and PS666. T_N is the temperature at which the value of tan δ of QA80C samples is 10^{-1}. (●) L211 (from Fig. 4); (○) PS666 (from Fig. 5).

Fig. 5 shows the temperature dispersion curves of E', E'' and tan δ of PS666-QA80C samples with PS666-QU and PS666-SC. The results are similar to that of L211-QA80C samples in Fig. 4. We focus on a temperature (T_N) at which the value of tan δ of QA80C samples is 10^{-1} to investigate the molecular weight distribution dependence of the change. Fig. 6 is the plot of T_N of L211-QA80C and PS666-QA80C samples. As can be seen from the figure, the data points of both the PS samples are the same within the experimental errors. Thus the effect of molecular weight distribution on T_N is not observed.

Struik [26] has investigated the effect of cooling rate from 110°C on the temperature dispersion of tan δ of PS. It has been shown that tan δ decreases at the glassy region and that the temperature at which the curve of tan δ turns steeply up moves to higher temperatures on decreasing the cooling rate. The results show that the relaxation proceeds with decreasing cooling rate. The shape of the temperature dispersion curve of tan δ of PS obtained by Struik [26] is similar to those shown in Figs. 4 and 5, although the thermal histories are different (i.e. cooling or aging process). Moreover the changes show similar behavior on proceeding with the structural relaxation. The similarity might be caused by changing the conformation of the full chain toward the equilibrium state during the aging or the cooling processes. The details of the structural relaxation of polymeric glasses would be clarified by studying carefully the cause of the similarity.

4. Conclusions

Physical aging of PS in the glassy state was investigated by measuring dynamic viscoelasticity. The temperature dispersion curves of dynamic viscoelastic functions of the samples changed with aging time within a temperature range below T_g during aging at 60°C. In the high-temperature range, the temperature dispersion curves of tan δ of the aged samples merged into the curve of the quenched one at T_H. T_H increased with aging time. The experimental results suggest that the aged sample has the memory of having been quenched and that the sample approaches the equilibrium state, losing the memory. The increase of T_H indicates that the structure of the chain in the glassy polymer relaxes with time of aging from the small scale of segments, because the scale of the movable segments is related to temperature. The experimental results are similar to the results obtained for other polymeric materials. Thus, segments in polymeric glasses relax by the same mechanism as that by which amorphous polymer materials do far below T_g.

In the case of aging at 80°C, the temperature dispersion curves of dynamic viscoelastic functions of the samples changed with aging time within the whole temperature range at the glass region. The experimental results suggest that the aged sample loses the memory of having been quenched completely during annealing at 80°C and approaches the equilibrium at this temperature. The change is due to thermal motion of the whole chain.

Acknowledgements

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