

Conformational relaxation in glassy state of poly(methyl methacrylate) in the course of cooling through the glass transition temperature

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Received: 4 December 1998/Accepted: 13 January 1999

Summary

Conformational relaxation of poly(methyl methacrylate) has been investigated by measuring the temperature dispersion of dynamic viscoelastic functions and the density under systematic thermal histories. Samples were quenched from various temperatures (T_Q) in the course of slow cooling through the glass transition temperature (T_g). The $\tan \delta$ curves of samples quenched from $T_Q < T_g$ agreed with that of the slow-cooled sample in a temperature range above T_Q . Densities of the samples at 30 °C were consistent to thermal histories. Segmental conformation is successively frozen from large to small scale of segmental motion during slow cooling.

Introduction

Physical properties of amorphous polymers in the glassy state are generally affected by the segmental conformation which depends strongly on the thermal history. The effects of thermal history on the viscoelastic properties of glassy polymers such as poly(methyl methacrylate) (PMMA)(1-9) and other polymers(1,10-15) have been reported in terms of physical aging and/or annealing. An important thermal history is the cooling through the glass transition temperature (T_g). The effect of cooling rate from a temperature above T_g on viscoelastic properties of polymeric materials has been reported(4). The temperature dispersion curve of the dynamic loss tangent ($\tan \delta$) of polymeric materials in the glassy state declines in a temperature range below T_g by lowering the rate of cooling. However, it has still not known that the quenching at various temperatures in the course of cooling through T_g affects viscoelastic properties of polymer materials. The study will clarify a process in which the polymer chains successively form their optimum conformation and are packed spontaneously.

To clarify the effects on amorphous polymers, it is necessary to measure the viscoelastic properties under various thermal histories which are systematically applied. In this study we have taken a new thermal history; the thermal history is quenching from various temperatures in the course of slow cooling from a temperature above T_g . The purposes of this paper are to try clarifying the quenching effect on the dynamic storage modulus (E'), the dynamic loss modulus (E'') and $\tan \delta (=E''/E')$ of PMMA. We also describe the process of conformational change in the glassy polymer, considering the

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change of both the viscoelastic properties and the density with various thermal histories given systematically.

Experimental Section

Material.

A homo-PMMA produced by Mitsubishi Rayon Co. was used in this study. Weight average molecular weight (M_w) is 72000 by light scattering; molecular weight distribution (M_w/M_n) is 1.7 by gel permeation chromatography (GPC); T_g is 115 °C by differential scanning calorimetry (DSC) under a heating rate of 10 °Cmin⁻¹. Sample code, PMMA72, was given according to weight average molecular weight in 10³. PMMA72 was dissolved in 2-butanone, filtrated, and then precipitated into methanol. Film samples were prepared by casting the 20 wt% 2-butanone solution. The films thus prepared were dried in air at room temperature, and in a vacuum oven to make 2-butanone removed further. During drying process in the vacuum oven, temperature was raised stepwise every 10 °C a day up to 130 °C > T_g , and then was kept at 130 °C for three days. The films obtained were about 0.1 mm in thickness.

Thermal histories applied to the samples.

The samples with various thermal histories were prepared as summarized in Table 1. First, the films were heated in a compression molding machine at 190 °C for 5 min to eliminate thermal history at low temperatures before measurements. Secondly, the heated samples were cooled in two ways; some samples were slowly cooled from 190 °C toward room temperature, T_r (15-25 °C), (SC) and others were rapidly quenched from 190 to 0 °C (QU). The quenching temperatures (T_Q) from which samples were quenched to 0 °C in the course of SC are shown in Table 1. T_Q were taken as 70, 100, 115, 130, and 160 °C. The samples quenched from T_Q are called SQ ones. The thermal histories are illustrated in Figure 1.

Table 1. Various Thermal Histories Applied to the PMMA Samples ^a and Density (ρ) at 30 °C for Them.

Sample	1st Step	2nd Step	ρ at 30 °C (g/cm ³)
	Cooling Process	Quenched from T_Q (°C)	
PMMA72-SC	slow-cool	–	1.1985
PMMA72-QU	quench	(190)	1.1968
PMMA72-SQ1	slow-cool	160	1.1968
PMMA72-SQ2	slow-cool	130	1.1970
PMMA72-SQ3	slow-cool	115	1.1984
PMMA72-SQ4	slow-cool	100	1.1984
PMMA72-SQ5	slow-cool	70	1.1985

^a Thermal histories were applied to the samples by two steps as indicated by 1st step and 2nd step in this table.

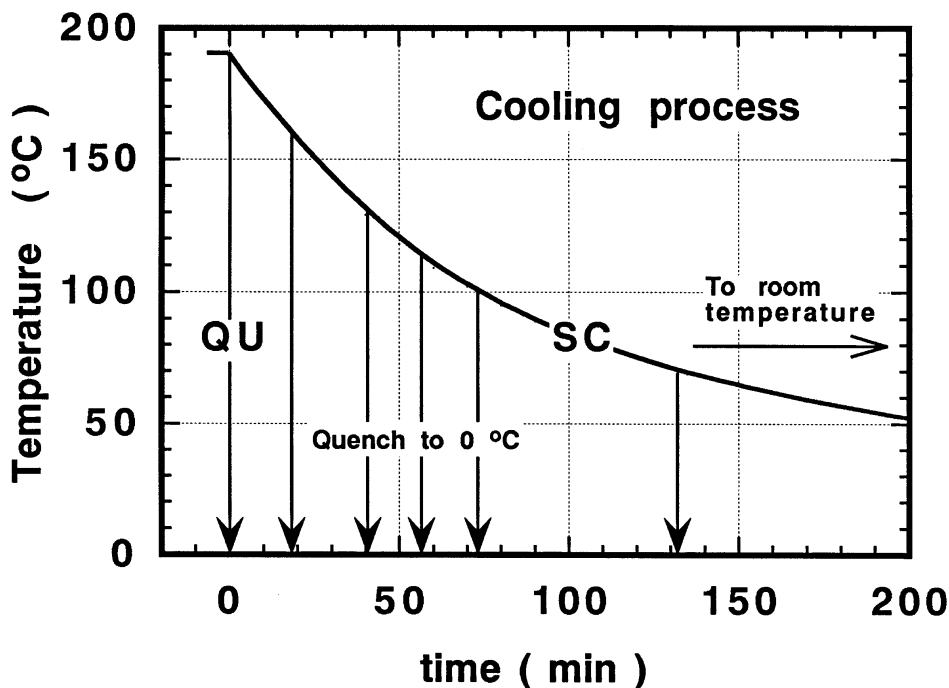


Figure 1: Cooling processes from 190 °C after annealing 5 minutes. QU: quenching from 190 to 0 °C, SC: slow cooling from 190 °C to room temperature, and quenching from various temperatures in the course of SC to 0 °C.

Measurements.

The temperature dispersion curves of dynamic viscoelastic functions, E' , E'' and $\tan \delta$ of the samples were measured at an angular frequency of 1 s^{-1} and under a static strain of 0.05% using a Rheometrics RSA-II. All the measurements were performed on heating at a heating rate of 2 °Cmin^{-1} . Densities of samples were measured by a density gradient tube of aqueous sucrose solution at 30 °C. The average density gradient was $2.0 \times 10^{-4} \text{ gcm}^{-3}/\text{cm}$ -distance. Accuracy of the value of density can be estimated within ± 0.0001 . The results are also tabulated in Table 1.

Results

Figure 2 shows the temperature dispersion curves of E' and E'' of PMMA72 samples with various thermal histories. Figure 3 shows the curves of $\tan \delta$ of the samples. The curves of PMMA72-SQ1 which were quenched from 160 °C in the course of SC are eliminated from the figures to avoid overlapping, because they are coincided with the curves of PMMA72-QU. All dispersion curves of the samples quenched from various temperatures are located between those of the slow cooled sample (PMMA72-SC) and the quenched sample (PMMA72-QU) in the temperature range near the mechanical transition. The effect of T_q on viscoelasticities appears for the samples quenched from T_q

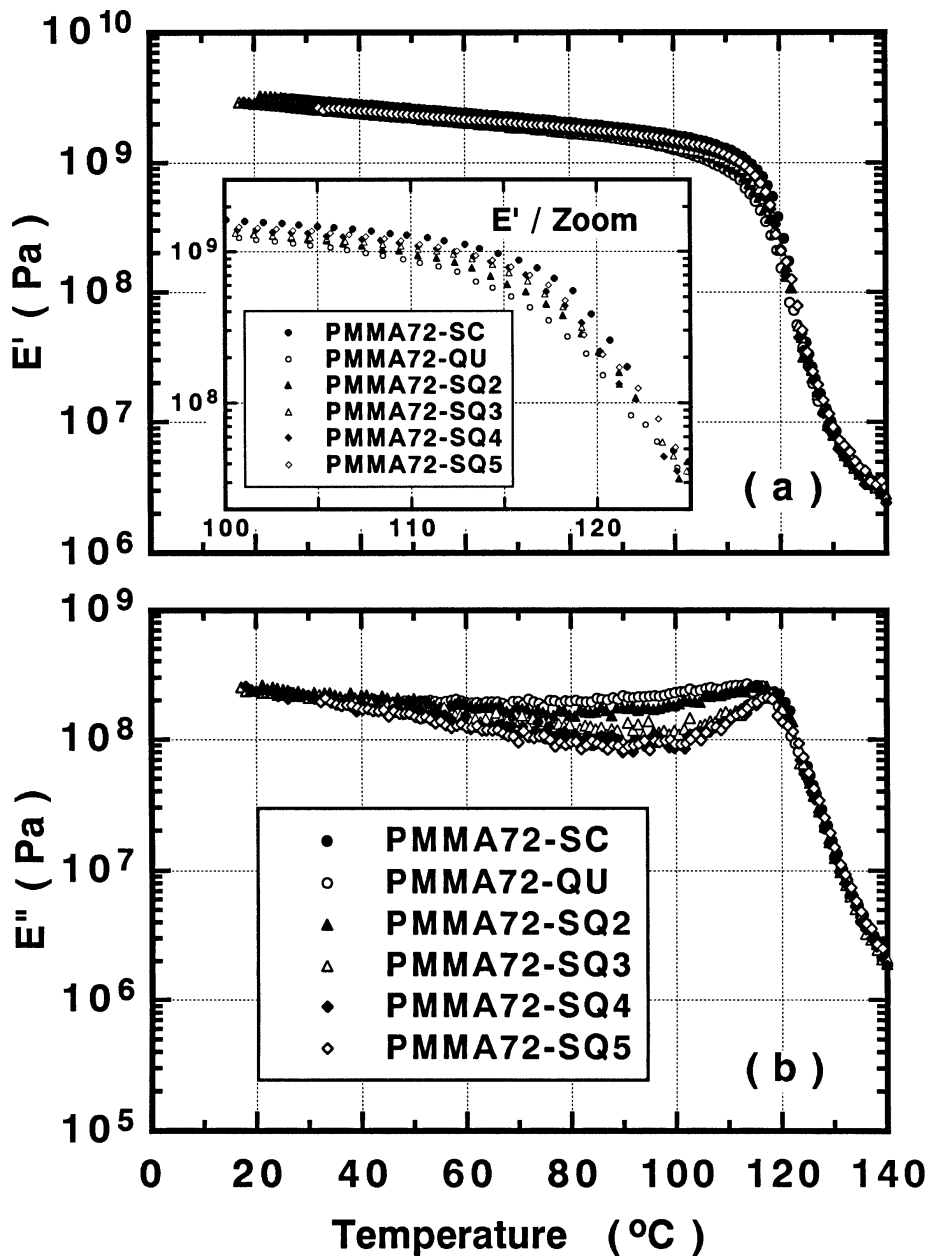


Figure 2: The temperature dispersion curves of E' (a) and E'' (b) for SC, QU and SQ samples. Inset in (a): the E' curves of the samples in a temperature range between 95 and 125 $^{\circ}\text{C}$.

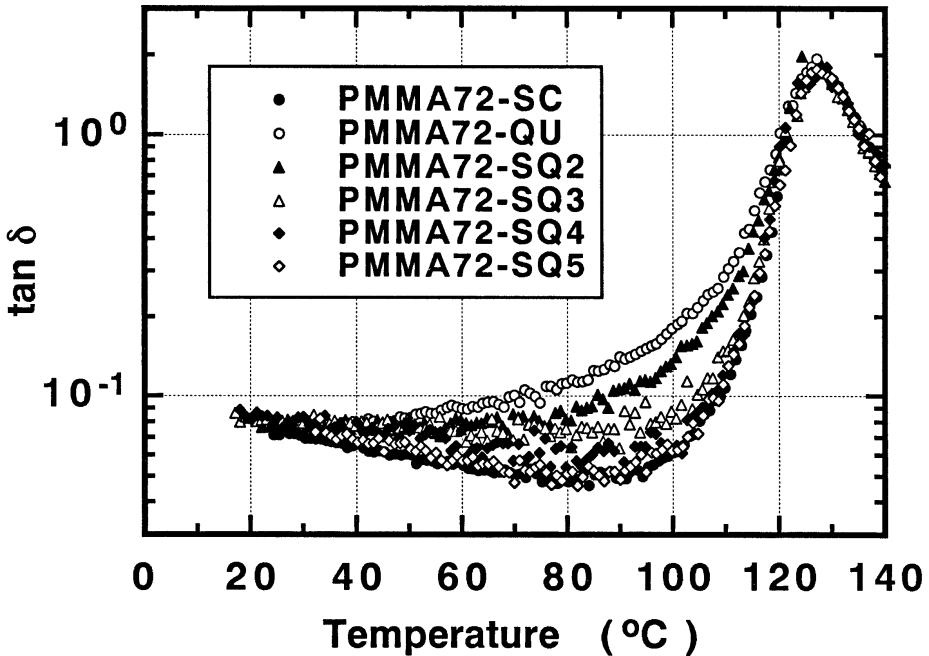


Figure 3: The temperature dispersion curves of $\tan \delta$ for SC, QU and SQ samples.

≤ 130 °C. At temperatures just below the transition the E' value of PMMA72-SC is the highest and that of PMMA72-QU is the lowest, and those of SQ samples quenched from $T_0 \leq 130$ °C are orderly located between them. The E' value decreases as the quenching temperature rises (Figure 2a). For the E'' and $\tan \delta$ values, the order is completely reversed. It is clear that the effect of T_0 on $\tan \delta$ curve is restricted within a range of measuring temperatures from 30 °C to the temperature at $\tan \delta$ peak, which can be called the α -transition temperature (T_α). The value of T_α is 127 °C for PMMA72 as shown in Figure 3. The E'' and $\tan \delta$ values of the samples quenched from $T_0 < T_\alpha$, namely PMMA72-SQ3, -SQ4, and -SQ5 agree well with those of PMMA72-SC in the temperature range above each T_0 . All the viscoelastic functions of the sample quenched at 130 °C (PMMA72-SQ2) are not exactly the same as, but are very close to those of PMMA72-QU. As mentioned before, the curves of PMMA72-SQ1 were coincided with those of PMMA72-QU. Then samples are classified into two groups; samples quenched from $T_0 \geq 130$ °C and those from $T_0 \leq 115$ °C in this study. Here, we should note that T_g of PMMA72 is 115 °C obtained by DSC. It is well known that T_α is corresponding to T_g . Thus T_α is a characteristic temperature to know the effect of T_0 in the course of cooling from temperatures $> T_\alpha$. The similar story can be told for the density of the samples. Densities of samples at 30 °C are shown in Table 1 and Figure 4. As more generally seen from the table and the figure, the values of density of samples are classified into two groups depending on the quenching temperatures; $\rho = 1.1969$ for $T_0 > T_\alpha$ and 1.1985 for $T_0 < T_\alpha$. The results clearly suggest that the α -transition temperature is important for the

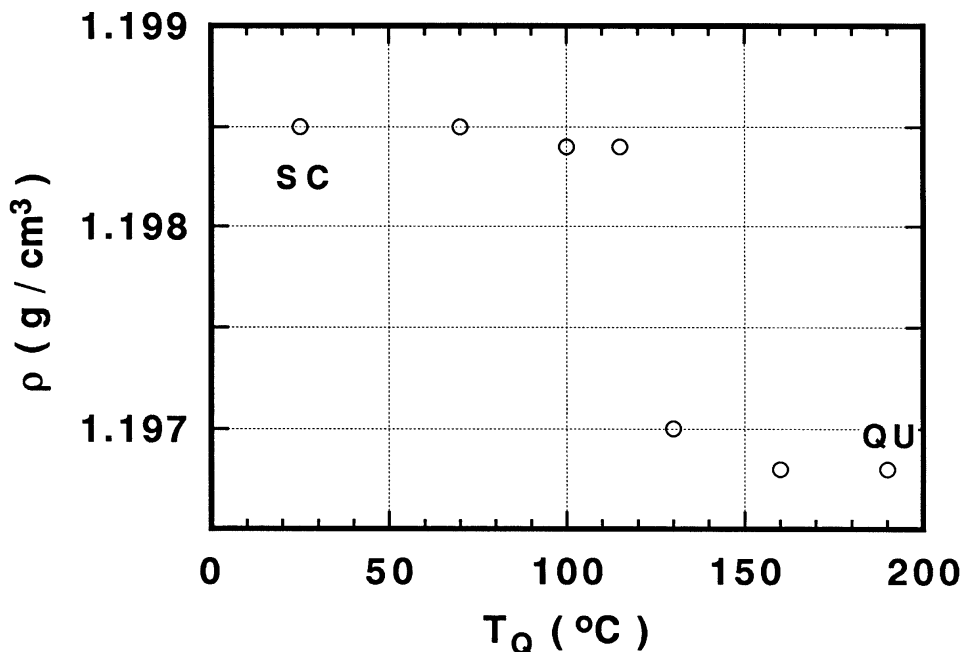


Figure 4: Density of samples at 30 °C against quenching temperature.

classification and that a structural relaxation makes PMMA samples dense.

Discussion

The effect of cooling rate from a temperature $> T_g$ on viscoelastic properties of polymeric materials has been shown by Struik(4). The temperature dispersion curves of $\tan \delta$ of polystyrene samples in the glassy state decline in a temperature range from - 40 to 90 °C by lowering the rate of cooling from 110 °C(4). The effect of T_Q in the course of cooling, however, still has not known. The study will clarify a process in which the polymer chains successively form their optimum conformation. The effect of T_Q on the dynamic viscoelastic properties of PMMA appeared in this study when T_Q is below T_α as stated before. Simultaneously, the volume of material decreases and a densification occurs as seen in Table 1. In other words, two types of relaxation, that is, the conformational relaxation and the volumetric relaxation proceed. Both types of relaxation essentially depend on a rate of cooling. If the rate is low enough, the conformational equilibrium structure is achieved and the material shows the maximum density. The conformational and volumetric relaxation must be related with each other, but the former reflects local segmental motion in a material and the latter does the overall material state. Thus, simultaneous measurements of the viscoelastic properties and the density are useful to investigate structural changes of glassy polymers.

Now we consider two states S_{T_1} and S_{T_2} of samples quenched from T_1 and T_2 ($T_1 < T_2 < T_\alpha$) in the course of slow cooling. Mobility of segment with a constant length in main chain is higher at T_2 than at T_1 . Movable segmental length would be larger than at T_2

than at T_1 . The polymer chain in S_{T_1} is more, in a sense, relaxed than that in S_{T_2} . Since the larger size segmental motion is frozen in the early stage of slow cooling, conformation in large scale frozen in both S_{T_2} and S_{T_1} is similar. On the other hand, small size segmental conformation in S_{T_1} and S_{T_2} is different; segments in S_{T_1} are in relaxed state and those in S_{T_2} are not. The effect was experimentally shown in Figures 2 and 3. The $\tan \delta$ curves of PMMA samples quenched from $T_Q < T_\alpha$, namely for PMMA72-SQ3, -SQ4 and -SQ5, coincide well with those of PMMA72-SC in the temperature range above each T_Q . Hence, the experimental results suggest that the polymer chains successively form their optimum conformation and that conformational relaxation occurs from large scale segment motion in the course of cooling.

The effect of T_Q on density at 30 °C has not been observed clearly in this case. The values of density of PMMA72-SQ3, -SQ4 and -SQ5, are almost the same as that of PMMA72-SC as listed in Table 1. The rate of slow cooling in the test is still too fast to achieve volumetric relaxation of materials, suggesting that the volumetric relaxation is very slow. Thus, the volume of a sample solidified at T_α is maintained for long time, and the densities of the samples are close to that of PMMA72-SC.

Materials at a temperature above T_α are in molten state; they have no fixed conformation of chain segments. Therefore, segmental conformations of samples quenched from $T_Q > T_\alpha$ would be similar and not be distinguished. The temperature dispersion curves of viscoelastic functions of PMMA72-SQ1 quenched from 160 °C coincided with those of PMMA72-QU quenched from 190 °C. The curves of PMMA72 quenched from 210 °C also coincided with those of PMMA72-QU as not shown in figures. The curves of PMMA72-SQ2 are slightly different from those of PMMA72-QU, although T_Q of 130 °C is a little higher than T_α . The small difference occurred experimentally at handling the sample; when the sample was taken out from a molding machine for quenching, it was cooled slightly below T_α . PMMA samples quenched from $T_Q > T_\alpha$ give the same density as listed in Table 1. The experimental results of the dynamic viscoelastic properties and density of PMMA suggest that the chain conformation in these samples quenched from $T_Q > T_\alpha$ is similar and that thermal history above T_α does not play any rule for physical properties of polymer glasses.

Conclusions

The conformational relaxation and the volumetric one of PMMA in the course of cooling through T_g were investigated by measuring the temperature dispersion of dynamic viscoelastic functions and density at 30 °C. The samples were quenched from various temperatures in the course of cooling from 190 °C which is much higher than T_g and/or T_α . The $\tan \delta$ values of the samples quenched from $T_Q < T_\alpha$ agreed well with that of SC sample in the temperature range above T_Q . Segmental conformation is successively frozen from large to small scales of segmental motion in the course of slow cooling. The $\tan \delta$ values of the samples quenched from $T_Q > T_\alpha$ agreed with each other in the whole temperature range. The densities of samples were classified into two groups depending on T_Q ; $T_Q < T_\alpha$ and $T_Q > T_\alpha$.

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