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# Notes

## Effects of Sub-$T_g$ Annealings on the Anelastic Relaxation in Poly(methyl methacrylate)

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In a number of our earlier studies on the anelastic relaxations in polymers, the as-received and the room-temperature aged samples of a polymer were found to show a maximum or a peak at temperatures between the polymer's $\alpha$- and $\beta$-relaxation peaks.[1-3] Diaz Calleja et al.[4] have observed a similar feature on annealing PMMA at 319 K. This extra peak vanished when the sample was remeasured after heating to a temperature near or above its $T_g$. The effect was noted, but our immediate concern with the nature of $\beta$ and $\alpha$ relaxations kept us from its detailed investigation.[1-3] Elaborate studies of physical aging effects now reveal that the anelastic behavior of PMMA spontaneously changes on annealing at room temperature (about 90 K below its $T_g$) and enhances the weak effects we had earlier noted. Here we report new results on these observations and briefly consider their implications for both our thermodynamic concepts and structural relaxation.

Two different samples of atactic poly(methyl methacrylate) or PMMA were studied. The first of $M_n = 40\,000$ was obtained from Rohm and Haas Co., and the second of $M_n = 67\,000$ was provided by Norsolor, France. Their $M_w$ values are not known. The calorimetric glass transition temperatures (at the metastable equilibrium state) were measured for a heating rate of 10 K/min. These were 396 and 404 K, respectively. For our dynamic-mechanical measurements, the samples were cut into bars of about 2 × 6 × 45 mm dimensions. Data on both the Norsolor and Rohm and Haas PMMA are discussed here. Figures 1 and 2 correspond to the Rohm and Haas PMMA and Figure 3 to the Norsolor PMMA.

The real and imaginary parts of the shear modulus $G'$ and $G''$, respectively, and $\tan \Phi = G''/G'$ were measured as described before,[5] by means of an inverted forced torsional oscillation pendulum. Precautions were taken to avoid contamination of the samples by moisture, and all cooling and heating of the samples were done in hermetically sealed conditions.

To ensure that the thermodynamic and structural states of the samples when cooled from above $T_g$ to 125 K were identical in all cases, cooling and heating for the thermal treatment of the sample were done at a constant rate of 6.5 K/min. For the same reason, samples during all our measurements were heated at a constant rate of 0.6 K/min.

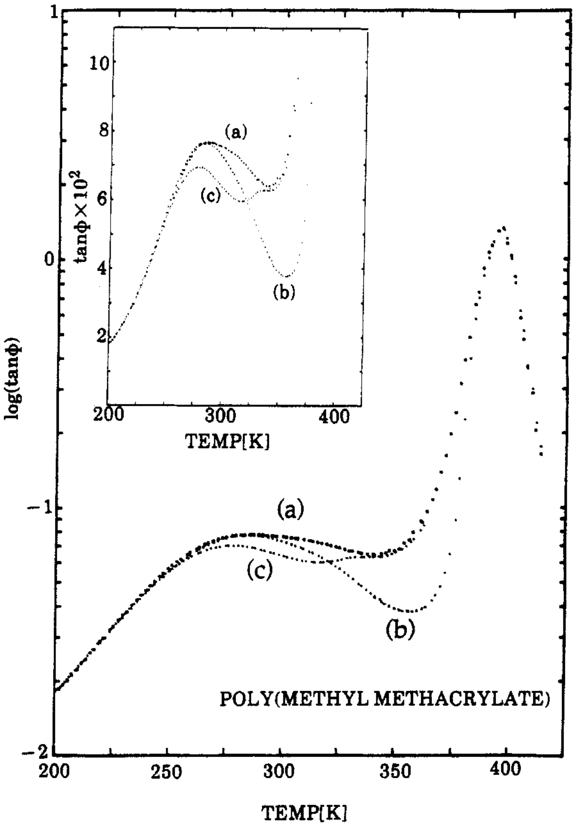

**Figure 1.** Mechanical loss tangent of the Rohm and Haas PMMA measured for a fixed frequency of 0.1 Hz plotted against the temperature. Plot a was obtained after rapidly cooling the sample from 406 to 125 K at a rate of 6.5 K/min. Plot b was obtained after similar cooling, heating to 363 K at 6.5 K/min, aging for 91.7 h at 363 K, and cooling to 125 K at a rate of 6.5 K/min. Plot c, shown by dots, refers to the state of PMMA obtained after similar cooling, heating to 296 K at 6.5 K/min, aging for 722 h at 296 K, and cooling to 125 K at a rate of 6.5 K/min. The inset shows the corresponding plots on a linear scale.

The mechanical loss tangent, $\tan \Phi$, of the Rohm and Haas sample of PMMA measured for a fixed frequency of 0.1 Hz is plotted against the temperature in Figure 1 where both the $\alpha$- and $\beta$-relaxation peaks are conveniently seen on a logarithmic scale. The linear scale plot, which is shown as an inset in Figure 1, enlarges the features observed in the vicinity of the $\beta$-relaxation peak and makes them more discernible. Here, plot a refers to the sample that was cooled from 406 to 125 K at a rate of 6.5 K/min and thereafter measured during heating; plot b refers to the sample similarly cooled, heated to 363 K at 6.5 K/min, aged at 363 K for 92 h, and thereafter cooled to 125 K and measured. Plot c refers to the sample similarly cooled, heated to 296 K at 6.5 K/min, kept at this temperature for 722 h, and thereafter cooled to 125 K and measured. This set of plots shows that at temperatures below 250 K and above about 382 K, the anelastic behavior of PMMA measured for a frequency of 0.1 Hz remains unaffected by its thermal history. It is noteworthy that at temperatures near or above 382 K the value of $\tan \Phi$ for the three samples is identical, and this has a certain physical meaning, i.e., that here the time required for the molecular dynamics of

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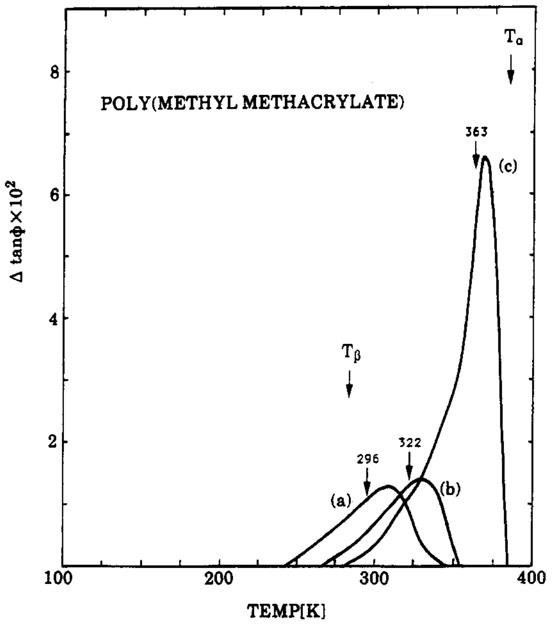

**Figure 2.** Decrease in tan Φ, Δ tan Φ, of the Rohm and Haas PMMA measured at 0.1-Hz frequency plotted against the temperature for different thermal histories. The reference in all cases was the tan Φ values of a sample cooled from 406 to 125 K at a rate of 6.5 K/min and thereafter measured. Curve a refers to a sample aged for 722 h at 296 K, curve b refers to that aged for 778 h at 322 K, and curve c refers to that aged for 92 h at 363 K. $T_\alpha$ and $T_\beta$ indicate the temperatures of $\alpha$- and $\beta$-relaxation peaks when measured at 0.1-Hz frequency. Other arrows indicate the aging temperature.

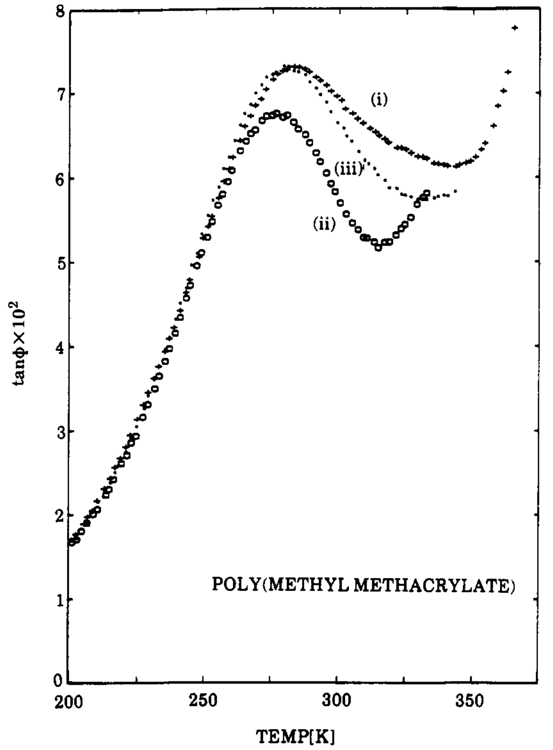

**Figure 3.** Mechanical loss tangent of the Norsolor PMMA measured for a fixed frequency of 0.1 Hz plotted against the temperature. Plot i was obtained after cooling the sample from 406 to 125 K at a rate of 6.5 K/min. Plot ii was obtained after similar cooling, heating to 296 K at 6.5 K/min, aging for 1222 h at 296 K, and cooling to 125 K at a rate of 6.5 K/min. The data shown by curve iii were obtained after the measurements as for curve ii up to 336 K, and thereafter immediately cooling to 125 K at 6.5 K/min.

the polymer chain becomes identical for the three cases, or that a thermodynamic metastable equilibrium corresponding to a $T_g$ at a heating rate of 0.58 K/min, as discussed by Perez et al.,[6] has been reached. As is expected, this temperature is less than the $T_g$ of 396 K measured for a heating rate of 10 K/min.

Figure 1 also shows that there is a wide temperature range below $T_g$ over which structural relaxation occurs. The difference between the tan Φ of rapidly cooled and aged samples or Δ tan Φ is plotted against temperature in Figure 2, where the temperatures of the $\alpha$- and $\beta$-relaxation peaks measured for 0.1-Hz frequency are indicated by arrows. It is clear that although a peak in Δ tan Φ appears in all cases, this Δ tan Φ peak shifts to a lower temperature when aging is done at a lower temperature, but its position remains between the $\alpha$- and $\beta$-relaxation peaks.

The thermodynamic state of the PMMA sample in our three experiments was initially the same before aging, as it was achieved by identical cooling procedures. During the measurements the state achieved after the different thermal histories changed gradually and spontaneously, to the extent allowed by the heating at a rate of 0.6 K/min, but this extent remained the same for all samples. Thus, the features of curves a–c in Figures 1 and 2 can be directly compared, and this comparison reveals that structural relaxation during the annealing of PMMA at 296 K (about 90 K below its $T_g$) causes changes in its anelastic behavior, which have not been observed before. These are (i) an apparent decrease in the height of the $\beta$-relaxation peak, (ii) a decrease in the temperature of this peak, and (iii) the recovery at about 340 K of the tan Φ value of a rapidly cooled sample between the $\beta$- and the $\alpha$-relaxation peaks. This recovery occurs such as to produce a peaklike feature, named here the aging-induced peak, at about 330 K, a temperature which our measurements at 0.01 and 1 Hz have shown to be independent of the fixed frequency used for the study. Briefly stated, the effects of structural relaxation at temperatures much lower than $T_g$ (90 K below $T_g$) are apparently different from the effects of structural relaxation at high temperatures just below $T_g$.

In order to examine whether or not the new, aging-induced peak that shows up at temperatures between the $\beta$- and $\alpha$-relaxation peaks is affected by thermal cycling below $T_g$, a separate experiment was carried out on a sample of the Norsolor PMMA. It was first cooled at the rate 6.5 K/min from 406 to 125 K, and thereafter its tan Φ was measured up to 406 K. These values are plotted against temperature as curve i in Figure 3. The sample was thereafter cooled to 125 K at a rate of 6.5 K/min, and then heated to 296 K at a rate of 6.5 K/min. After the sample was aged for 1222 h (51 days) at 296 K, it was cooled to 125 K at 6.5 K/min, and thereafter its tan Φ was measured up to 336 K, a temperature where the annealing-induced maximum appears (as in Figure 1). The data are shown as curve ii in Figure 3. The sample was then immediately cooled from 336 to 125 K at a rate of 6.5 K/min, and thereafter its tan Φ was again measured up to 346 K. These data are shown as curve iii in Figure 3. These experiments clearly show that heating the PMMA sample, whose aging at 296 K had caused its tan Φ to show the extra peak, to a temperature far below $T_g$ causes this extra peak to vanish. It also raises the height of tan Φ in the $\beta$-relaxation region and apparently shifts the $\beta$ peak to a higher temperature. This shows that the aging-induced peak is caused by the effect of the increase in temperature during the measurements after aging at 296 K. This increase in temperature partly erases the previous aging effect as the shape of curve iii approaches that of curve i. The aging-induced peak is not an intrinsic property of the polymer in the same sense as the

$\beta$-relaxation peak is.

The development of the aging-induced tan $\Phi$ peak at a temperature below $T_g$ may be analogous with the development of the heat capacity peak observed also below $T_g$ when DSC measurements are made on polymers. A variety of empirical equations have been shown to agree with the results of DSC experiments.[7–9] In all cases, the peak, also known as a shoulder in the heat capacity data at $T < T_g$, is formally related to a distribution of structural relaxation times; the broader the distribution, the more prominent is the peak in the heat capacity of a polymer.

A reviewer pointed out to us Roche's somewhat similar study of poly(vinyl chloride). Roche[10] reported that a sample quenched from 393 K ($T_g \approx 347$ K), when annealed for 332 h at 313 K, showed, after annealing, a peak in the loss modulus, but not in tan $\Phi$, at about 353 K which is 6 K above, not below, the calorimetric $T_g$ of 347 K. As the annealing temperature was only ~34 K below the $T_g$ of PVC, Roche[10] concluded that the observations are phenomenologically analogous with the sub-$T_g$ endothermic effects in PVC observed by Hodge and Berens[11] in their DSC studies. However, in Roche's experiments,[10] the cyclic frequency decreased from 20 Hz at 193 K to 5 Hz near $T_g$ and, since the new peak at ~354 K is above the $T_g$ of PVC, it is questionable that the effects he observed are similar to the ones observed on aging of PMMA at 90 K below $T_g$, which are reported here.

In addition to the thermodynamic implications of the aging-induced effect for our concepts of structural relaxation, the observations reported here are further significant as they show both the aging effect at a low temperature and more importantly the unusual recovery of the dynamic mechanical properties during rate heating. A detailed theoretical analysis of these observations and their thermodynamic implications along with further measurements of the anelastic behavior of other polymers are currently being carried out in our laboratory.

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