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Structural Relaxation Investigations of Glassy Polystyrene by Radial Distribution Functions

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ABSTRACT

The structural relaxation of an atactic polystyrene under sub- T_g annealing at 50°C and at 70°C was investigated by the radial distribution function (RDF) derived from its wide-angle x-ray scattering (WAXS). By recording the changes in RDF (i.e., $\Delta H(r)$, where r is the radial distance from an arbitrary reference atom) after it had been annealed for a certain period of days, and taking the integration of $\int_0^r \Delta H(r)^2 dr$, we found that the atom density within structural domains in a size below 15 Å was changed dramatically, but that the tendency leveled off as annealing proceeded. However, the atom density outside the domains is barely changed by sub- T_g annealing. The size of the domain is similar to the statistical segment length reported in the literature. The behavior of the domains—that the segmental relaxation inside the domains in the initial sub- T_g annealing is unconstrained by their neighbors outside the domains—is also similar to the behavior of the statistical segments. The domains are believed to be composed of a statistical segment across the center, which has about 6 styrene repeat units, and 6 equal-distanced parallel segments tangent to the edge of the domain. On the other hand, as the annealing temperature is closer to the glass transition temperature,

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the frozen unstable chain segments reach equilibrium sooner and with less disturbance in their conformation.

Key Words. Polystyrene; Physical aging; RDF; Relaxation; Sub- T_g annealing.

INTRODUCTION

When an amorphous polymer is quenched through its glass transition temperature to a temperature below its T_g , three important structural elements—i.e., the conformation of molecular segments, free volume distribution, and content of free volume—are more or less frozen in the glassy structure. Then, as it is annealed at that temperature, the polymer will relax toward its equilibrium state by rearrangement of its segmental conformations, redistribution of free volume, and decreasing the content of free volume. Although the change of each structural element during sub- T_g annealing has potential to influence the physical and mechanical properties of final products, many researchers have preferred to attribute their changes, such as enthalpy relaxation, creep, etc., to the loss of free volume [1–4]. Nevertheless, there have been reports of discrepancies in predicting the change in creep during sub- T_g annealing in parallel with the changes in free volume and enthalpy relaxation [5, 6]. Very recently, Lee and McGarry [7] questioned Kovacs' model [2] which predicts the nonequilibrium behavior of a glass based on the total free volume of the structure at any time and temperature.

Furthermore, Wendorff [8] has reported that the thermal density fluctuations for polycarbonate measured by small-angle x-ray scattering do not relax toward their equilibrium value during sub- T_g annealing as does the enthalpy relaxation. He suggested that the motions which cause the relaxation are different from the cooperative motions characteristic of the fluid state. Similar results were also reported by Roe and Curro [9] for polystyrene. Thus, the only way to decrease the free volume during sub- T_g annealing is by van der Waal's contraction between adjacent chain segments. In that case, if the frozen chain segments rearrange their conformations substantially during sub- T_g annealing, they would cause a redistribution of free volume so that their influence on the structure should not be ignored if one tries to predict the physical and mechanical properties as functions of annealing time and temperature.

In this regard, to provide direct experimental evidence to show that rearrangements of frozen segmental conformations do occur and that their cooperative motions are retarded during sub- T_g annealing, we monitored the changes in radial distribution function (RDF) for the atactic polystyrene derived from wide-angle x-ray scattering (WAXS) [10]. The change in RDF represents the change in density of atoms $\rho(r)$ in a spherical shell of thickness dr at a radial distance r from

a reference atom. Thus, the change in local atom density associated with the redistribution of frozen segmental conformations could be detected.

EXPERIMENTAL SECTION

Material Characterization

An atactic polystyrene sample was obtained from the G/M Company in Taiwan. The atactic structure was verified by infrared spectroscopy (Hitachi 270-30 model; IR) according to Ref. 11. The molecular weight distribution was measured by gel permeation chromatography (Shodex KF-806 model; GPC). The number average molecular weight was 1.235×10^5 g/mol and the weight average molecular weight 2.639×10^5 g/mol. The glass transition temperature was 88 °C, measured by differential scanning calorimetry (Du Pont 9900-910 model; DSC) at a scanning rate of 10 °C/min from 60 °C to 150 °C.

Sample Preparation

The specimens, in pellet form, were compression molded into circular disks 15 mm in diameter and 2.5 mm thick. They were kept in the mold at 150 °C for at least 30 min and then quenched by air cooling to room temperature. X-ray diffractions were taken and then they were immediately placed in a desiccator preheated in an oven at 50 °C (or 70 °C). After a chosen time interval of annealing (in days), the specimens were removed for x-ray measurements and then placed back in the desiccator. The time spent for each x-ray measurement was less than 30 min.

X-Ray Measurements and Data Corrections

X-ray measurements were made on a Philips PW1710 model diffractometer with CuK_α radiation, using a graphite monochromator in the incident beam. The slit system consisted of a divergent slit $1/12^\circ$ and receiving slit 0.3° . Scattering data were collected by scanning at 0.05° intervals from 7° (2θ) to 115° . The measured intensity was corrected for background air scattering, absorption, polarization, and multiple scattering. The air scattering was measured by removing the sample from the sample holder and measuring the intensity. The correction for the absorption is based on the method given by Milberg [12]. The correction for multiple scattering was according to the method derived by Warren and Mozzi [13]. The polarization correction was calculated from the standard formula [14]

$$\text{Polarization} = \frac{1 + \cos^2 2\theta_M \cos^2 2\theta}{1 + \cos^2 2\theta_M} \quad (1)$$

where $2\theta_M = 26.65^\circ$ for the graphite monochromator. The intensities were then corrected as

$$I_{\text{exp}} = (I_{\text{measured}} - I_{\text{air scattering}})/[(\text{absorption}) (\text{polarization}) (\text{multiple scattering})] \quad (2)$$

The RDF

The RDF of polystyrene has been studied and described in detail by Wecker et al. [10]. A brief review of the RDF method is given here. The RDF, represented by $H(r)$, can be derived from the x-ray data by Fourier transformation:

$$rH(r) = 4\pi r^2[\rho(r) - \rho_0] = (2r/\pi) \int_0^\infty i(S) (\sin Sr) S dS \quad (3)$$

where r is the radial distance from an arbitrary reference atom, $\rho(r)$ the atomic density at r , ρ_0 the average atomic density, $S = 4\pi \sin \theta/\lambda$, and $i(S)$ for a monoatomic material is given by

$$i(S) = [(\alpha I_{\text{exp}} - I_{\text{inc}})/f^2] - 1$$

where f is the scattering factor, I_{inc} is the incoherent scattering, and α is the normalization constant calculated from the limit method [15] by using the equation

$$-2\pi\rho_0 Z^2 = \alpha \int_0^{S_{\text{max}}} I_{\text{exp}} S^2 dS - \int_0^{S_{\text{max}}} S^2 (f^2 + I_{\text{inc}}) dS \quad (4)$$

where Z is the atomic number of the atom. For a multiatomic system, $i(S)$ is given by

$$i(S) = \left[(\alpha I_{\text{exp}} - I_{\text{inc}}) - \sum_{i=1}^n x_i (f_i)^2 \right] / \left[\sum_{i=1}^n x_i f_i \right]^2 \quad (5)$$

where n is the number of species in the system, x_i is the atomic fraction of the species i , and f_i is the scattering factor of the species i .

When Eq. (3) is integrated, the loss of data between s_{max} and ∞ will cause a termination error, which can be seen from the presence of spurious ripples superimposed on the RDF data. To reduce the termination error, the sampled transform method given by Lovell et al. [16] was used with termination at a minimum point, $s_{\text{max}} = 6.9 \text{ \AA}^{-1}$.

RESULTS AND DISCUSSION

The Change of RDF During Sub- T_g Annealing

The corrected intensity (I_{exp}) of a quenched polystyrene sample as a function of scattering angle (2θ) is shown in Fig. 1. Its transformed RDF has four

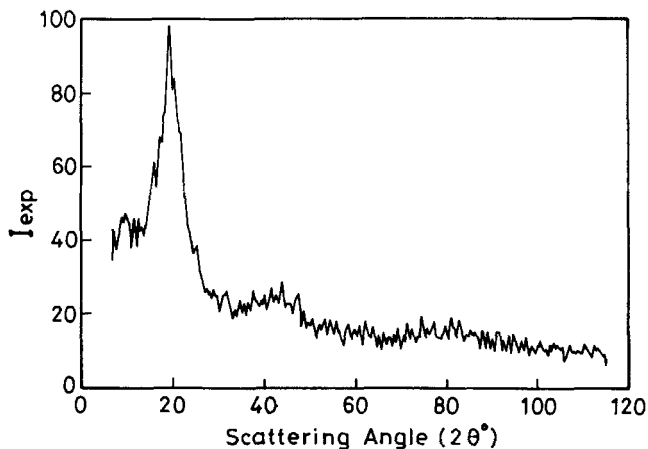


FIG. 1. Corrected intensity of a quenched polystyrene sample as a function of scattering angle.

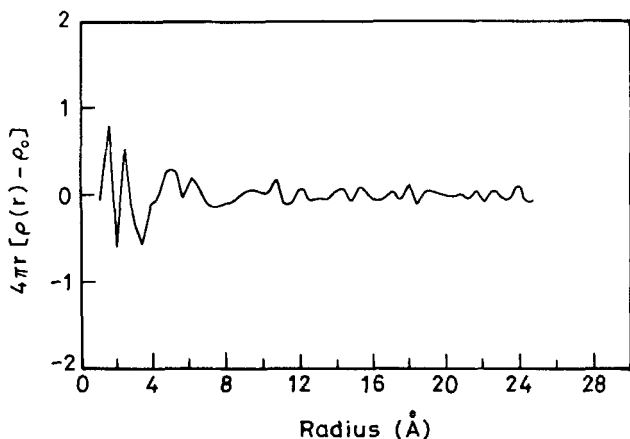


FIG. 2. RDF of a quenched polystyrene sample.

prominent peaks, at 1.5, 2.5, 5, and 6.2 Å; and several weak peaks at 4, 9.3, 10.6, 12.1 Å, and so on, as shown in Fig. 2. Similar RDF data have also been reported by Wecker et al. [10] for quenched atactic polystyrene. The peak at 1.5 Å corresponds to the bonded nearest-neighbor C-C distance, whereas that at 2.5 Å corresponds to the second nearest-neighbor bonded distances. The peaks located at r greater than 2.5 Å are broad and their origins are more complicated, because they involve many intramolecular and intermolecular spacings.

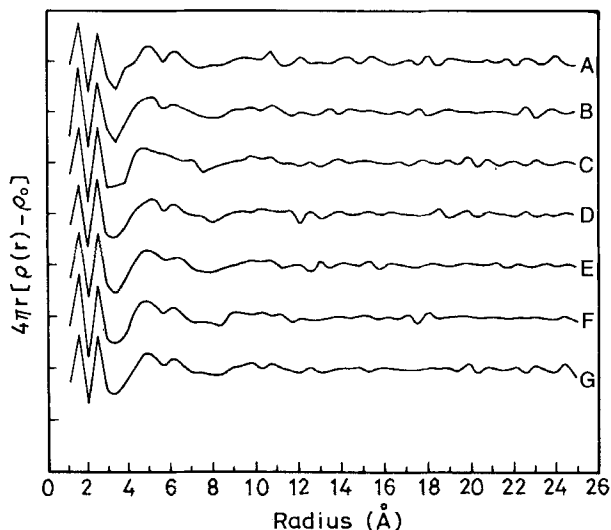


FIG. 3. RDF of the polystyrene sample after being quenched and annealed at 50°C for various times: A, 0; B, 7; C, 15; D, 22; E, 29; F, 36; and G, 50 days.

Since about three-fourths of the mass of the polystyrene repeat unit are phenyl rings, their positions related to the reference atom are an important factor in determining the peak positions at r greater than 2.5 Å. Wecker et al. [10] calculated the RDF of isotactic polystyrene based on its crystal structure determined by Natta and Corradini [17] and found that the peaks covering the range of 3.4 to 5.2 Å involve 164 spacings, of which 86 spacings are interchain; all but 10 of the interchain spacings are between phenyl atoms and all but 20 of the intrachain spacings are between phenyl and main chain atoms. The peaks covering the range of 5.2 to 8 Å involve nearly 700 spacings, two-thirds of which are interchain. The peaks beyond 8 Å are mostly contributed by the intermolecular spacings.

The RDF for the quenched sample after annealing at 50°C for 7, 15, 22, 29, 36, and 50 days is shown in Fig. 3. The peak at 1.5 Å did not change its shape and position as the specimen was annealed, indicating that the length of C-C bonds was not changed. As to the peak at 2.5 Å, it became narrower during annealing although the position did not change. This peak is mostly contributed by the C-C-C bonds. When the sample was quenched to below T_g , some unstable segmental conformations would be frozen into the glassy structure. As a result, the bond angle of certain C-C-C bonds would be under strain. During sub- T_g annealing, the strained bond angles gradually relaxed toward their stable position, resulting in the sharper peak at 2.5 Å. Moreover, the sharp valley at

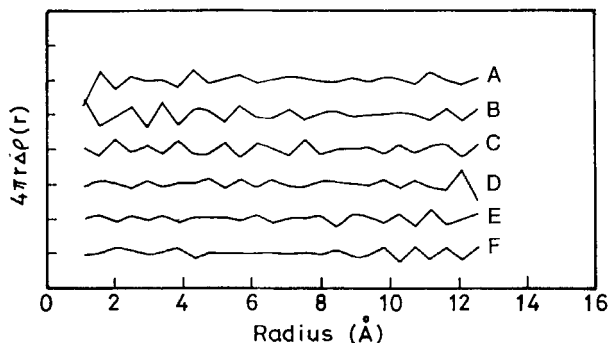


FIG. 4. $\Delta H(r)$ of the polystyrene sample between two sequential annealing periods at 50°C: A, 7 days—quenched; B, 15–7 days; C, 22–15 days; D, 29–22 days; E, 36–22 days; and F, 50–36 days.

3.3 Å right after the peak at 2.5 Å became shallower and the shoulder at 3.9 Å disappeared. According to the previous analysis on the RDF of polystyrene [10], these changes are contributed more by the change of intramolecular spacings (i.e., the change of polymer segmental conformations) than the intermolecular spacings.

On the other hand, the change of the broad peaks in the range from 4.5 to 7.5 Å during sub- T_g annealing is contributed more by changes in the intermolecular spacings. However, since their spacings are still small, the change of intermolecular spacings in this range should be affected by the conformations' rearrangement of neighboring segments.

So far, we have discussed the changes of the major peaks in RDF during sub- T_g annealing. To see the change of the entire RDF patterns, the difference in RDF, $\Delta H(r) = 4\pi r \Delta\rho(r)$, where $\Delta\rho(r)$ is the difference in atom density at r , of the specimen between two sequential annealing stages was calculated; they are shown in Fig. 4. From the figure, it can be seen that the change in RDF from 0 to 8 Å was pronounced in the initial 15 days of sub- T_g annealing at 50°C. However, the amount of change decreased greatly after the specimen had been annealed for 22 days. To estimate the number of atoms affected by sub- T_g annealing in a distance r from a reference atom, we calculated the $\Delta H(r)$ between two alternate annealing stages and integrated the $\int_0^r \Delta H(r)^2 dr = \int_0^r [4\pi r \Delta\rho(r)]^2 dr$. The integration of $\int_0^r \Delta H(r)^2 dr$ provides information about the accumulated change in atom density as a function of distance r regardless of whether the change is increased or decreased. Figure 5 shows the plot of $\int_0^r \Delta H(r)^2 dr$ versus r for every other annealing stage. As seen in the figure, the atom density changed dramatically inside the domains of 7.5 Å radius during sub- T_g annealing but the

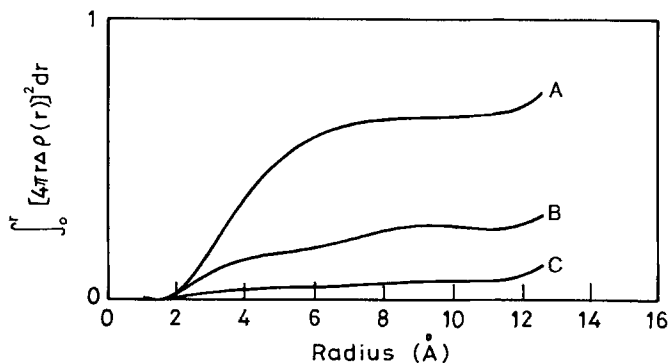


FIG. 5. $\int_0^r \Delta H(r)^2 dr$ versus r for the polystyrene sample between two alternate annealing periods at 50°C: A, 15 days—quenched; B, 29–15 days; and C, 50–29 days.

tendency leveled off as annealing proceeded. However, the density outside the domains barely changed during sub- T_g annealing. This could result from the intermolecular spacings wider than 7.5 Å being so wide that the rearrangements of segmental conformations do not affect their spacings. According to the definition of RDF, the affected domains in the structure are spheres with an average diameter 15 Å, whose centers are “average” reference atoms.

It has been reported that the statistical segment length of atactic polystyrene is in a range from 5 to 20 Å, measured by the neutron scattering technique [18]. The statistical segments in a polymer chain can be thought of as the average length of freely rotating straight segments of a randomly coiled chain [5]. By definition, the motion of statistical segments is not constrained by their neighbors. Since the size of domains affected by sub- T_g annealing is in a range similar to the statistical segment length and since their behavior—that the atom density outside the domains is not affected by the change inside—is also similar to that of the statistical segments, we suggested the domains are composed of the statistical segments. By taking the C–C bond length as 1.54 Å and the C–C–C bond angle as 109° [19], the length of a styrene repeat unit in a polystyrene molecular chain can be calculated as 2.52 Å. Thus, the statistical segments in the domains should have about six repeat units if a planar zigzag conformation is assumed. Moreover, it has been suggested that the chain segments in the glassy polystyrene tend to pack parallel to each other [10, 20]. The interchain spacing was also reported as 7.3 Å according to the crystal structure of isotactic polystyrene [10, 17]. Therefore, it is believed that the domains are composed of a statistical segment across their center and six parallel segments tangent to their edges. The distances between any two adjacent segments are the same and equal to the radius of the domain. On the other hand, the apparently unchanged atom density outside the

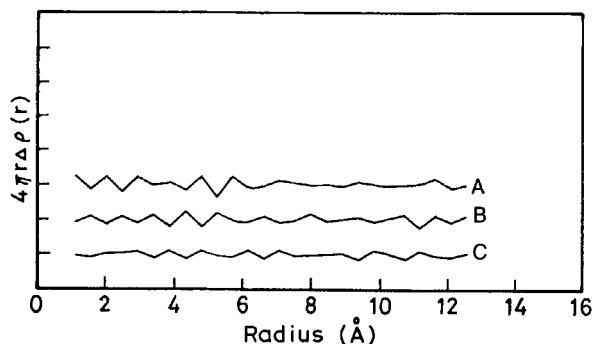


FIG. 6. $\Delta H(r)$ of the polystyrene sample between two sequential annealing periods at 70°C: A, 7 days—quenched; B, 14–7 days; and C, 21–14 days.

domains is consistent with the reported small-angle x-ray scattering results for the amorphous polymer indicating that the large-scale density fluctuations are not affected by sub- T_g annealing [8, 9]. This implies that the cooperative motions of statistical segments during sub- T_g annealing are prohibited or retarded. A possible way to decrease the specific volume is by van der Waals contraction between adjacent chain segments. It was also reported for epoxy resins that the local small-scale contraction in an epoxy network is easier and faster than that of the entire network during sub- T_g annealing [21], for the contraction of the latter should be by way of the van der Waals interactions between the adjacent chain segments.

Effects of Annealing Temperature

To investigate the effects of annealing temperature on the RDF of polystyrene, a quenched sample was annealed at 70°C and the RDF determined at 7, 14, and 21 days. Figure 6 shows their difference in RDF [i.e., $\Delta H(r)$] between two sequential annealing periods. As seen in the figure, the change in RDF is significant in the first 7 days of sub- T_g annealing. However, with further annealing the change in RDF from 7 days to 14 days was not only less significant but almost in the opposite direction compared to the first stage of annealing up to $r=6$ Å. The reason behind this was not clear. However, according to the previous study on sub- T_g annealing of epoxy resins [21], the local small-scale shrinkage is faster than that of the entire network, but the slow shrinkage of the latter in the latter stage of annealing decreases the density difference between the local and entire epoxy networks produced in the first stage of annealing. Accordingly, the opposite direction of change in the RDF of polystyrene after 7 days of annealing at 70°C might be

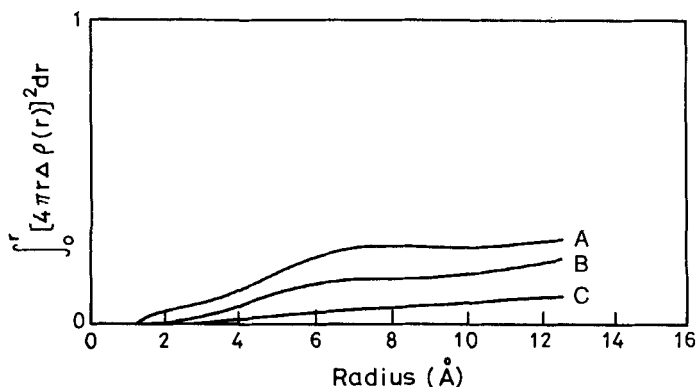


FIG. 7. $\int_0^r \Delta H(r)^2 dr$ versus r for the polystyrene sample between two sequential annealing periods at 70°C: A, 7 days—quenched; B, 14-7 days; and C, 21-14 days.

due to the fact that the annealing is dominated by the van der Waals contraction between adjacent chain segments, relieving some of the previous rapid contraction of chain segments themselves. Nevertheless, the change in RDF by sub- T_g annealing leveled off after 14 days, sooner than that at 50°C. In order to estimate the accumulated change in atom density as a function of distance r regardless of whether the change is increased or decreased, we calculated $\int_0^r \Delta H(r)^2 dr$ from the data shown in Fig. 6. The results given in Fig. 7 show that the change in atom density is less significant and reaches equilibrium sooner than at 50°C, although the size of the domain in which the atom density changes is not noticeably changed. The T_g of our polystyrene sample measured by DSC is 88°C, as shown in Fig. 8. The smaller change in atom density during annealing at 70°C than at 50°C suggested that, as the annealing temperature is closer to the glass transition region of the sample, the frozen unstable chain segments reach equilibrium with less change or disturbance in their conformation.

On the other hand, according to Flory [22], the temperature coefficient of the mean square unperturbed end-to-end distance—i.e., $d \ln \langle \bar{r}^2 \rangle_0 / dT$ —for atactic polystyrene is $4 \times 10^{-4} \text{ deg}^{-1}$. Thus, if the temperature coefficient of statistical chain lengths is similar to that of the mean square unperturbed end-to-end distance, the difference in statistical chain length between 50°C and 70°C would be less than 1%. This might explain why the size of the domain in which the atom density changed during sub- T_g annealing is not noticeably affected by the change of annealing temperature from 50° to 70°C.

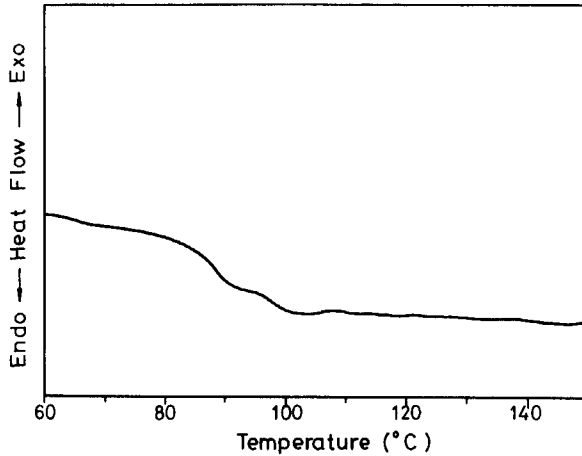


FIG. 8. DSC spectrum of a polystyrene sample.

CONCLUSIONS

By using the RDF method we were able to detect the changes of atom density associated with the segmental relaxation of an atactic polystyrene during sub- T_g annealing. The domain size in which those changes took place is similar to the statistical segment length and barely affected by the change of annealing temperature from 50° to 70°C. Furthermore, the intensity of change in atom density inside the domains in the initial sub- T_g annealing is increased by increasing the temperature difference between the glass transition and the annealing temperature. However, the change of atom density outside the domains was almost nil during sub- T_g annealing. Thus, the relaxations of frozen unstable chain conformations are considered to be the primary factor on the molecular scale in the initial sub- T_g annealing.

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