Response to the Comment

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The purpose of this publication was to find an analytical way to describe the enthalpy relaxation phenomenon[1]. We ordinarily started with the simplest case, a single relaxation time model. I think that the mathematical treatment of this model in our paper is correct. Unfortunately, this simple model does not fully represent the amorphous polymer's glass relaxation process. As discussed in the paper, the parameters obtained did not follow the theoretical prediction. To correctly describe the relaxation process as indicated in the Comment, a distribution of the relaxation time is necessary. An example is equation (1) in the Comment although it is not completely accurate over the entire annealing time. In this case, our mathematical treatment can also be applied to find β and τ_0 if the relaxation time shift factor μ can be independently determined through experiments. The non-linear Williams–Watts function can be written as

$$\phi(t) = \exp\left[-\frac{t^{\beta(1-\mu)}}{(1-\mu)^{\beta}\tau_0^{\beta}} \right] \tag{1}$$

Because μ is a constant, taking the double logarithm of $\Delta H = \Delta H_\infty[1 - \phi(t)]$ leads to

$$\log\left[-\ln\left(1 - \frac{\Delta H}{\Delta H_\infty}\right)\right] = (1-\mu)\beta \log t - \beta \log[(1-\mu)\tau_0] \tag{2}$$

Other functions may be tested by this method to obtain analytical expressions for enthalpy relaxations.

I fully agree with the Comment on an instantaneous temperature step during quench from the melt in order to relate $\phi(t)$ to ΔH_∞. Our experiments were carried out by quenching the samples to liquid nitrogen from their isotropic melts before the isothermal ageing experiments, as described in the Experimental section. Therefore, no errors should be introduced here. The numerical calculation reported in the Comment was under the condition of a finite cooling rate ($100\ \mathrm{K\ min^{-1}}$), which did not mimic the experimental procedure. It would be interesting to find out how much difference in the parameters may be introduced if the calculation was carried out in an instantaneous quenching.

The criticism on ΔH_∞ in the Comment is correct. Recently, we have found that, indeed, ΔH_∞ is temperature dependent, and is approximately proportional to $\Delta C_p \Delta T$, where ΔC_p is the heat capacity increase at T_g and ΔT is undercooling which is defined as $(T_g - T_a)$.

In summary, I believe that our treatment on enthalpy relaxation may be a starting point to achieve analytical expressions for the glass relaxation phenomenon through experimental observations. When additional parameters have to be introduced to describe a distribution of relaxation time, independent experiments must be necessary to determine these parameters.

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REFERENCE

1 Cheng, S. Z. D., Heberer, D. P., Janimak, J. J., Lien, S. H.-S. and Harris, F. W. *Polymer* 1991, **32**, 2053

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