

Enthalpy Relaxation and Nucleation Density for Isotactic Polystyrene: Annealing Effect

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Abstract: The enthalpy relaxation of isotactic polystyrene (iPS) under annealing conditions was studied by optical microscopy (OM) and differential scanning calorimetry (DSC). The magnitude of the relaxation and the maxima of the relaxation endotherm were found to increase with annealing time and temperature, near the glass transition temperature region. The progress of enthalpic relaxation may be attributed, to changes in molecular conformation as well as molecular mobility during annealing toward the equilibrium state. A higher relaxation was observed for an amorphous system, where partial crystallinity hinder the relaxation since the induced crystallinity alters the quantity and the quality of the remaining amorphous phase. The crystal nucleation density, which is found to be related with the relaxation, increases with annealing time. The molecular conformations as well as the mobility in the remaining amorphous phase is found the factor for relaxation and the nucleation density.

Keywords: Enthalpy relaxation; annealing effect; glass transition temperature; isotactic polystyrene.

I. INTRODUCTION

Enthalpy relaxation is one of several physical changes that depend on the thermal processing and temperatures, and the time given for the polymers to adjust to changes in temperature. The relaxation can provide information of time dependent changes in glassy structures. Amorphous glassy states of polymers are thermodynamically unstable and their structures tend to relax toward the equilibrium state [1]. It has been observed that annealing below the glass transition temperature (T_g), increase the magnitude of the relaxation endotherm [2, 3]. Many studies have been reported on enthalpy relaxation for glassy polymers [2-5]. The factors that found to be affect on the relaxation by annealing are; the heat of enthalpy (ΔH_{relax}) and the temperature that shows maxima for relaxation, as well as maximum glass transition temperature (T_{gmax}). These parameters vary with the experimental conditions, for example, the annealing time (t_a) and temperatures (T_a). Another factor that affects the relaxation parameters is the degree of crystallinity, which clearly changes the state of the remaining amorphous phase. As such, a detailed experimental analysis is required to study the annealing effect on relaxation.

The saturated nucleus density (N_s), defined as a density of the number of nucleus sites or as a density of the crystal nuclei in the polymer melt, might be influenced by the relaxation of polymer. Since the crystal nuclei are difficult to observe directly by standard methods because of their very small size. Therefore, small spherulites are assumed to have started on an active individual site and observed after a certain induction time. Beyond that time, an embryo with a size greater than the critical size becomes stable and the number of nuclei increases linearly with time. For heterogeneous nucleation process, after sufficient time, the number of nuclei reach to a saturated value [6]. These saturated nucleation density might be associated with the relaxation where the entanglement and chain mobility of amorphous phase varies with annealing conditions. In previous study the saturated nucleation density is found quite high during crystallization from glassy state compare to molten state due to enthalpy relaxation.

In this paper, the enthalpy relaxation and the maxima of its temperature are studied for amorphous isotactic polystyrene with annealing conditions. The influence annealing on crystallinity and their effect on relaxation are also explained. A relationship between the enthalpy relaxations and saturated nucleus densities are drawn.

II. EXPERIMENTAL

Isotactic polystyrene ($M_w=400,000$, tacticity: 96%) was supplied by Scientific Polymer Products. Before doing the actual experiments the samples were melted and crystallized several times to erase any thermal history. A schematic representation of the entire temperature program is shown in Fig. 1. Program A is used to study the influence of the partial crystallinity on relaxation parameters. Under this program, the samples were melted at 300°C for 5 min to ensure complete melting before being cooled at 130°C/min to the crystallization temperature of 160°C. Following the crystallization treatment for eight hours the samples were rapidly transferred to another hot stage for annealing at $T_a=80^\circ\text{C}$, for a time t_a from few minutes to several months, and refer for thermal and optical analysis. Program B and C are used to study in situ measurement of complete amorphous samples, from just below the glassy state and far below glassy state, respectively. The samples were first melted at 300°C for 5 min and cooled at 130°C/min to temperature at 80 and -90°C, respectively, annealed for a time t_a , and refers for analysis. The samples used with temperature program A, B and C will be treated as sample A, sample B and sample C, respectively.

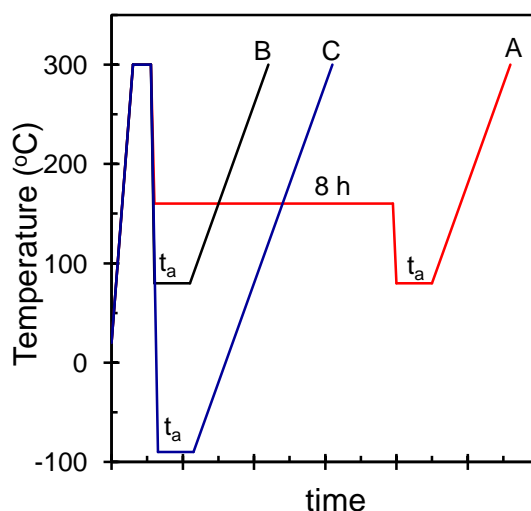


Fig. 1. Schematic diagram of the temperature programs.

The DSC scan was performed using a TA instrument Q2000 differential scanning calorimeter where an empty aluminum pan employed as a reference. The DSC was calibrated for temperature using indium with melting point of 156.6°C. For all DSC experiments, the scan was made with a heating rate of 10°C/min with a typical samples weight of 3 ± 0.1 mg. To prevent thermal degradation, nitrogen gas was circulated around the sample pan. The enthalpy relaxation was calculated from the endothermic peak area observed around T_g . Since the sample A is isothermally crystallized at 160°C for eight hours so the corresponding heat of melting of the crystallites (ΔH_m), can reflect the degree of crystallization. The crystallinity was measured by comparing the heat of melting of the crystallites of the sample with the specific heat of fusion (ΔH_f) as reported as 80.5 J/g for iPS [7]. Only 40 % crystallinity is calculated for sample A, and no crystal melting peaks are observed for sample B and C, since the molten polymer is rapidly quenched to glassy state and are confirmed by the absence of any melting endotherm.

A Zeiss Axioscop polarizing optical microscope was used to capture images of the melt press films placed in a Linkam hot stage, including a temperature controller and a cooling unit. Photomicrographs were recorded with a Toshiba HV-D27 3CCD camera and analyzed with the Image-Pro Plus 4.0 software. The saturated nucleation density is calculated by counting the number of small spherulites per unit volume of the sample observed by OM.

III. RESULTS AND DISCUSSION

Figure 2 shows the DSC thermograms of samples A as a function of annealing time as indicated in the figure. For simplicity, the DSC scan is focused only glass temperature region. An endothermic peak known as the recovery of enthalpy relaxation is present in the temperature range between 90 to 120 °C in each of the thermograms of annealed samples, while the untreated shows just an endothermic transition. From figure it can be seen that the endothermic area increase with annealing time. For a comparison of the enthalpy relaxation with different thermal treatment, the heat of relaxation of sample A, B and C are plotted with annealing time (Fig. 3a). No significant change in enthalpy was observed for sample C, since the samples annealed at (-90°C) much lower of the glass temperature. In this case the sample becomes rigid, and there is no possibility of polymer chain to move for relaxation. For samples A and B, the endothermic peak is increase with annealing time. Initially, the endothermic peak increases very rapidly and then seems to be saturation. For sample B, the increase is very rapid upto 5 hours where sample A shows 200 hours before reach to be saturation. The increases of relaxation for sample B is found higher and more rapid than sample A. This might be due to the complete amorphous structure of sample B that goes under a thermal relaxation. On the other hand, for sample A, containing 40% crystalline phase has reduced relaxation due to less available amorphous phase which undergoes into relaxation. The immobilization of the segments bound in the crystallites is the reason for the reduction of the relaxation for sample A. From this it can be concluded that crystallinity inhabit the relaxation process.

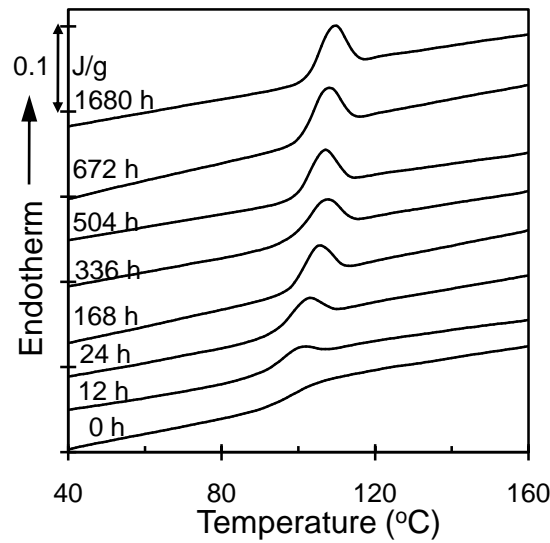


Fig. 2. Typical DSC thermograms of samples A, showing enthalpy relaxation endotherm around the glass transition temperature as a function of annealing time.

The maximum of the transition peak in glass transition region, T_{gmax} is plotted against annealing time shown in Fig. 3b. It can be seen that with the annealing time, T_{gmax} shifts to higher temperatures, and are also influenced by the crystallinity. For example, for sample C, no significant shift was observed, where for sample B shifted only few degree and sample A shifted almost 10°C. This type of temperature shifting with annealing time is well established for glassy polymer when the thermodynamic state of the annealed glass is not too close to equilibrium [8].

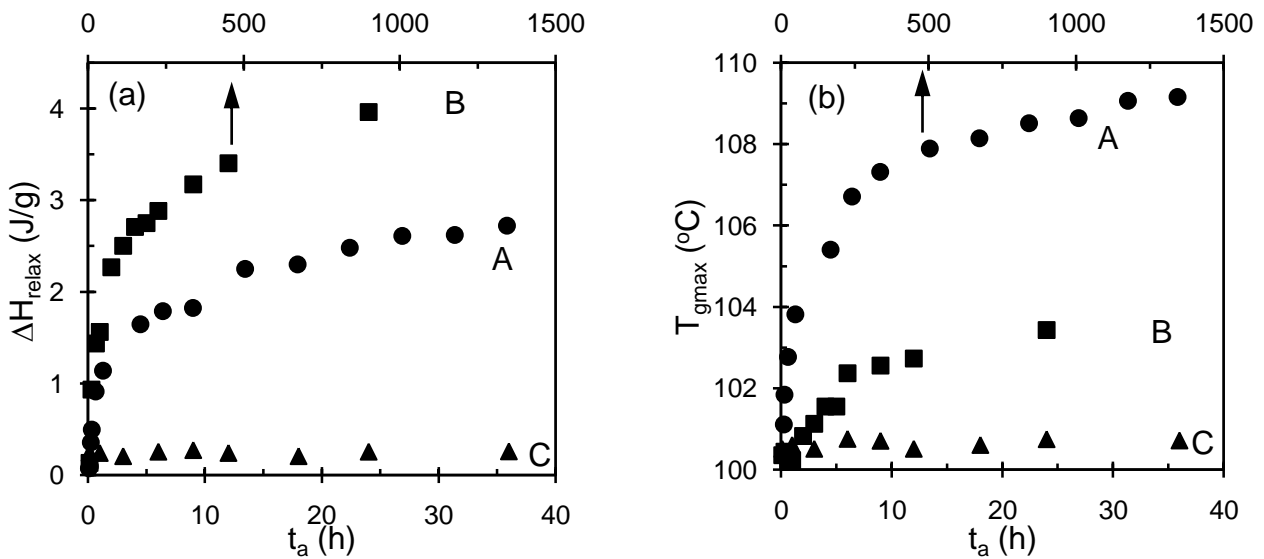


Fig. 3. Annealing time, t_a dependent; (a) heat of relaxation, ΔH_{relax} , and (b) maximum of relaxation endotherm, T_{gmax} as a function of annealing conditions for different samples.

The observed differences in ΔH_{relax} and T_{gmax} of partially and completely amorphous samples could be interpreted considering the Struik model, [9] which state that, in the vicinity of the crystalline regions, there exist some regions of reduced segmental mobility, the so called disturbed regions, which provoke a shift of the T_g area. The extension and the state of these disturbed regions depends on the state of the crystalline phase, e.g. the extension and the quality of the crystallites [10]. Therefore, annealing near the glass temperature affect the T_g of the material and consequently the relaxation process of the glassy state towards equilibrium.

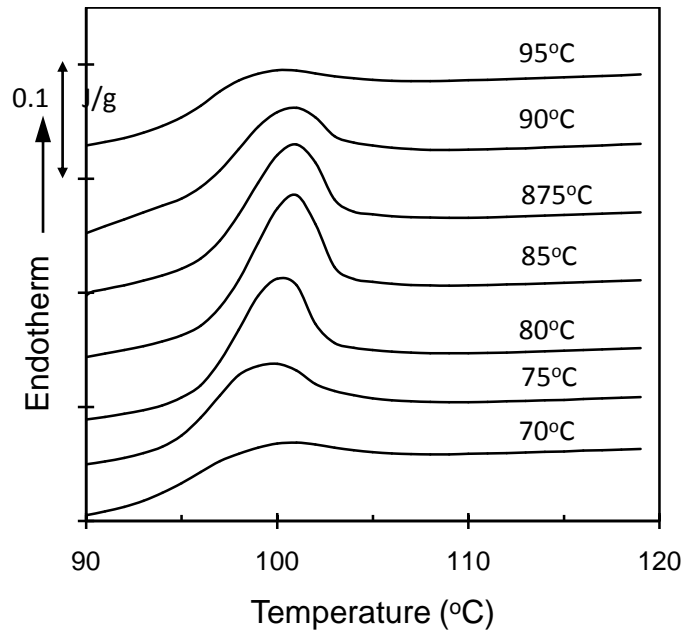


Fig. 4. DSC thermograms annealed for one hour as a function of annealing temperature.

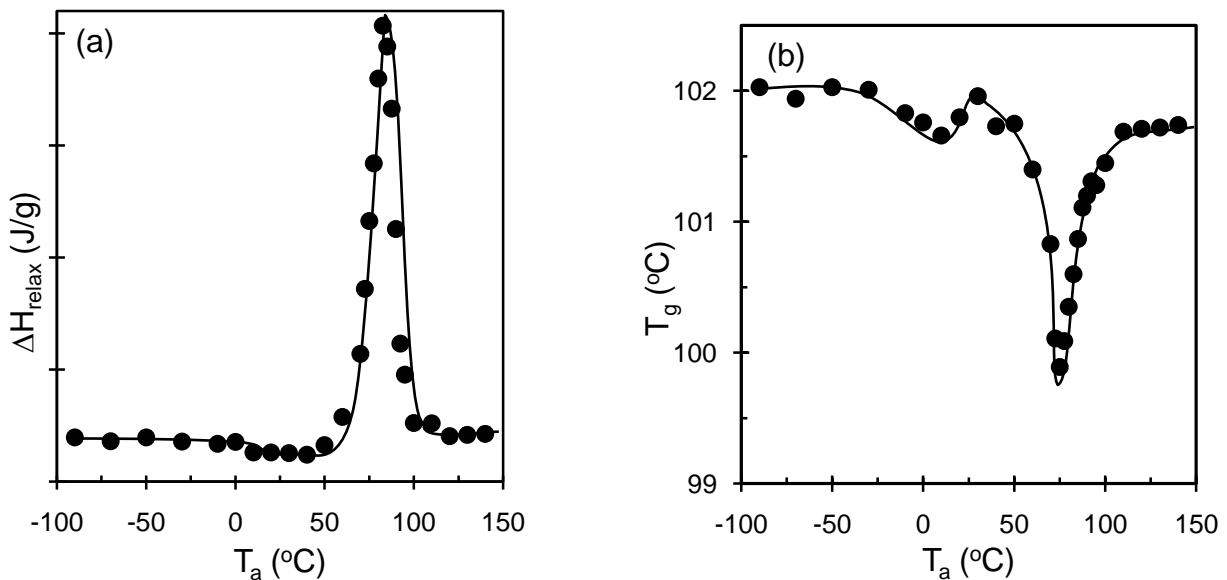


Fig. 5. Annealing temperature, T_a dependent; (a) heat of relaxation, ΔH_{relax} , and (b) glass transition temperature, T_g annealed for one hour.

To observe the effect on relaxation parameters for a complete amorphous sample over a wide range of annealing temperature from -90 to 130 °C. Here it is important to note that after annealing at higher temperature, the DSC heating scan was started by jumping temperature below T_g . Figure 4 shows the DSC endotherm of sample C annealed at different temperature for one hour. For simplicity, in Fig. 4 only few DSC runs of selected temperatures are shown in selected temperature region. The relaxation endotherm is found shifted to higher temperatures first and then back to lower temperature. For details, the relaxation enthalpies ΔH_{relax} with annealed temperatures are plotted in Fig. 5a. No significant increase of relaxation was observed during annealing between -90 to 50°C, then increases with further increases, showing a highest value at 82.5°C (very close to the glass transition temperature of 85°C for iPS), and decreases for further higher annealing temperatures. This observation suggests that molecular movement is higher, when annealed near glass temperature. Our results agree with other studies, where the enthalpy relaxation increased with time for various amorphous polymers [11-13]. Similarly, the glass transition temperature also influences with annealing temperature is plotted in Fig. 5b. The glass transition temperature decreases few degrees during annealed above 50°C and, further increase at above 80°C. A minimum value was observed few degrees below the glass transition temperature. This might be due to the molecular conformation, changed during annealing in the direction toward the equilibrium state, as a result of a decrease of the free volume and molecular mobility in the glassy state. The result suggests that during annealing, the molecules might have come close together to form a rigid glass with low molecular movement, resulting in an increase of the glass transition temperature.

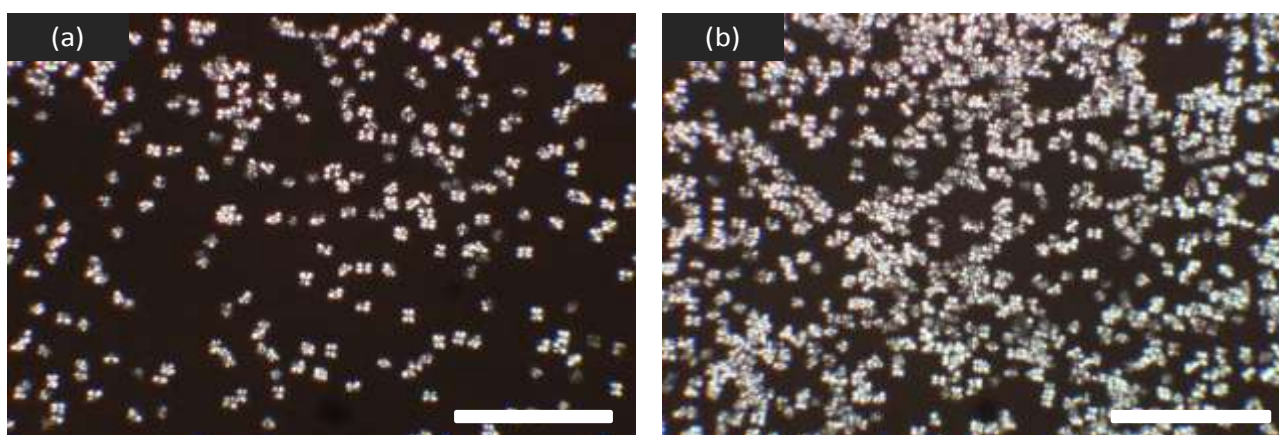


Fig. 6. OM images for sample B annealed at 80°C for; a) 5 min, and b) 24 h before crystallization at 160°C. The scale bar represent 10 μ m.

The saturation nucleus density (N_s) is defined as the density of the number of effective sites or as a density of the crystal nuclei in the polymer melt might be influenced by annealing conditions. Since the crystal nuclei are difficult to observe directly by standard methods because of their very small size. Therefore, small spherulites are assumed to have started on an active individual site and they are observed after a certain induction time whereas the aggregation of polymer molecules is reversible up to the critical nucleus size. Beyond that time, an embryo with a size greater than the critical size becomes stable and the number of nuclei increases linearly with time. Therefore, the saturated nucleation density is determined by assuming the total number of spherulites per unit volume. To calculate the nucleation density by OM, program B is selected. After melt the samples at 300°C, cooled to temperature to 80°C, annealed for a time t_a , and then reheat to crystallization temperature of 160°C to count the number of spherulites. It was found that the saturated

nucleation density increase with annealing time. Figure 6 shows the OM images annealed at 80°C for 5 min and 24 h, respectively. The nucleation density, annealed for 24 h (Fig. 6b) is found 3 times higher than that of annealing for 5 min (Fig. 6a).

Annealed at glass transition region has significant influence on saturated nucleation density. Annealing far below the glass transition temperature does not show any significant changes in nucleation density (Fig. 7), increases drastically showing maximum number around glass transition and then goes down with annealing at higher temperatures. This result is related with relaxation of the amorphous molecules; annealing far below the glass transition temperature restrict the molecules to be relax, where around glass transition temperature yeilds the relaxation and the nucleation density increases. Annealing above the glass temperatures the system goes similar to the crystallization from molten state without any relaxation and the nucleation density is always very low compare to glassy state those have molecular relaxation [14].

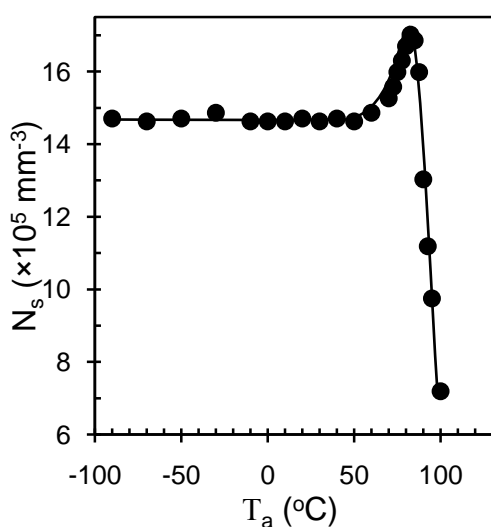


Fig. 7. Annealing temperature, T_a dependence saturated nucleation densities, N_s as counted from OM images.

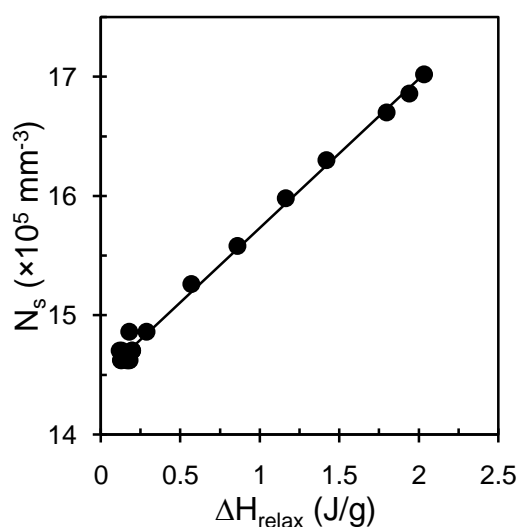


Fig. 8. Heat of relaxation, ΔH_{relax} versus saturated nucleus density, N_s at different annealing temperatures.

The saturated nucleus density against endothermic area observe in DSC is plotted (Fig. 8). A linear dependence indicates the saturation nucleus density is directly proportional to the relaxation of the iPS. This linear increase of nucleation density might be related with the entanglement of amorphous iPS that goes to relax of polymer molecules during annealing at glassy state.

IV. CONCLUSION

The enthalpy relaxation in the complete and partially amorphous iPS and the influence by annealing conditions has been studied. The relaxation was found to increase with annealing time and temperature. The annealing parameters were found strong dependence with the crystallinity as the induced crystallinity alters the quantity and the quality of the remaining amorphous phase. A maximum relaxation was observed for amorphous phase, annealing near the glass transition temperature, and decrease with further higher or lower temperatures, and with induced crystallinity. The resulting relaxation in amorphous phase due to annealing significantly increases the nucleation density during crystallization of isotactic polystyrene. The mechanical properties that enhanced by annealing process will be published elsewhere.

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