

Analysis of Nucleation and Glass Formation by Chip Calorimetry

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Featured Application: Authors are encouraged to provide a concise description of the specific application or a potential application of the work. This section is not mandatory.

Abstract: The advent of chip calorimetry has enabled an unprecedented extension of the capability of differential scanning calorimetry to explore new domains of materials behavior. In this paper, we highlight some of our recent work: the application of heating and cooling rates above 10^4 K/s allows for the clear determination of the glass transition temperature, T_g in systems where T_g and the onset temperature for crystallization, T_x overlap, the evaluation of the delay time for crystal nucleation, the discovery of new polyamorphous materials and the in-situ formation of glass in liquid crystals. From these application examples it is evident that chip calorimetry offers a promising potential to explore new reaction and transformation behavior and to develop new understanding.

Keywords: Chip calorimetry; Glass transition; Nucleation kinetics; Delay time; Polyamorphism; Amorphous materials, Liquid crystal

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1. Introduction

In many materials processing technologies, the thermal history involves various heating and cooling cycles as well as isothermal treatment. With the treatment of bulk components, the rate of heating and cooling is limited and is not constant throughout the volume. While the thermal history can be calculated by a heat flow analysis, the non-uniform thermal history can yield microstructural gradients and varying properties that confound accurate measurements. By a careful design of the thermal protocol and reduced sample volumes a uniform thermal history can be attained to enable the use of standard calorimetry techniques to measure material properties accurately. However, the standard techniques only allow for a limited heating and cooling rate of less than a few K/s. The recent advances in chip calorimetry have circumvented this limitation and allow for unprecedented rates of $2\text{--}5 \times 10^4$ K/s which has vastly expanded the capability of calorimetry to examine thermally activated reactions and phase transformations.

In this paper the application of chip calorimetry is demonstrated for the examination of glass transition temperature T_g and crystallization of metallic glass (MG) and amorphous polymers, and the development of polyamorphism as well as glass formation in liquid crystals. In each case the unique capability of chip calorimetry has enabled the exploration of new and novel transformation behavior that has permitted the development of new understanding.

2. Materials and Methods

Metallic glass samples. The ingots of the compositions of $\text{Al}_{92}\text{Sm}_8$ and $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ were prepared by arc melting the elemental components for several times in a Ti-gettered

argon atmosphere to ensure the homogeneity. For the $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ alloy, the ingot was prepared by an induction melting method in an argon atmosphere. Then, the ribbon-like samples were prepared by single-rolling melt spinning on a copper wheel with a tangential speed of 55 m/s. The thickness and the width of the ribbon-like samples were about $20 \times 2 \mu\text{m} \times \text{mm}$. The melt spinning process was performed in inert argon gas. The structure of these as-cast samples and the annealed samples was characterized by X-ray diffraction. Meanwhile, the thermal properties of the above samples were measured by conventional diamond DSC (Perkin Elmer). The TEM tests were conducted on a Tecnai T12 instrument at 120 kV. The in-situ continuous heating, annealing treatment and the following thermal analyses were performed on a high-rate Flash DSC platform (Flash DSC2, Mettler Toledo) with chip sensor (UFS1). TEM samples from the annealed Flash DSC samples were prepared by Zeiss Auriga Focused Ion Beam (FIB) with a 10 nA FIB current and a 2 kV voltage to avoid sample damage.

Polybutylene terephthalate (PBT) sample. The commercial PBT film-like specimen was purchased from Sigma-Aldrich Co. (Product number is GF14031447). The thickness is 0.55 mm, and the melting temperature is about 250 °C. For PBT, the critical cooling rate for glass formation is about 1000 K/s [1]. To prepare the totally amorphous sample, one tiny piece was cut from the film-like commercial specimen and then was placed on the sample area of the chip sensor. The small piece firstly was heated into 270 °C and then was cooled down with the cooling rate of 10^4 K/s. The obtained amorphous sample was subjected to a series of annealing treatments with different annealing times under the same annealing temperature.

D-mannitol sample. D-mannitol (Aldrich, > 99%) was used as received. If cooled rapidly enough (> 30 K/s), the supercooled liquid (SCL) avoids crystallization, entering the glassy state below the T_g of 284 K (the glass transition temperature T_g) [2, 3]. Before measurement, the sample was heated to 15 K above the melting point (440 K) for 10 s to allow the development of good contact with the detector chip. The schedule for a typical Flash DSC measurement, involves melting (100 K/s heating to 455 K), quenching (10^3 K/s cooling to 223 K), annealing at temperatures ranging from 288 K to 333 K with annealing times ranging from 0 s to 10^4 s, and quenching and reheating (100 K/s) to temperature above the melting point [4]. The calibration of each chip was performed by the manufacturer and further validated against the melting point of D-mannitol.

Itraconazole (ITZ) sample. The sample material – itraconazole (ITZ) was supplied by Alfa Aesar with purity greater than 99% and used without further purification. The starting material was completely crystalline with a melting point of 440 K. For ITZ it was recently reported that at slow cooling (generally slower than 10 K/min), the isotropic liquid transforms to a nematic phase and then to a smectic phase, and finally produces a smectic ordered glassy solid [5]. However, at fast cooling (from 0.5 K/s to 20 K/s), smectic ordering can be avoided altogether or avoided partially [5]. To further obtain different structural ordered glassy solids in situ, before measurement, the sample was heated to about 33 K above the melting point for 2 s to allow the development of good contact with the detector chip, then the molten sample was quenched at a series of cooling rate from 10 to 10^4 K/s. The subsequent reheating curve at 10^3 K/s was used to conduct the thermal analyses.

3. Results and discussions

3.1. Nucleation and primary crystallization

3.1.1. Separation of glass transition temperature and crystallization temperature by increasing heating rate in marginal Al-based MG

For most MG systems with good glass formation ability, the glass transition signal is strong enough to be detected in the heating DSC traces, which makes it possible to

measure the glass transition temperature and the supercooled liquid region by the conventional DSC method. However, for marginal MGs such as the Al-based MGs, the glass transition signal is prone to be overlapped by a primary crystallization for Al nanocrystals precipitation [6, 7]. Thus, the traditional DSC is not a good thermal analysis tool to observe the glass transition of Al-based MGs. On the other hand, considering that the glass transition and crystallization are significantly different kinetic processes, they should follow different evolution paths with different heating rates, so that the two kinetic signals should be separated under higher heating rates. Here, we take the typical $\text{Al}_{92}\text{Sm}_8$ MG as an example. The conventional DSC with heating rate of 0.33 K/s was applied to measure the heat flow curve shown in Figure 1a. It is clear that the conventional DSC heat flow curve only displays the primary and secondary crystallization peaks as shown in Figure 1b and there is no clearly defined glass transition signal. In contrast, the maximum heating and cooling rates for high-rate Flash DSC instrument with chip sensors (Flash DSC1, Mettler Toledo) are 4×10^4 and 4×10^3 K/s and the temperature range is between -90 °C and 450 °C [8, 9]. The optical picture of tiny MG sample being loaded onto the Flash DSC chip is shown in Figure 1b and the inserted optical picture gives the ribbon-like Al-based MG sample. A series of Flash DSC heat flow curves corresponding to different heating rates from 50 K/s to 1000 K/s were measured as shown in Figure 1c. For all heating rates by Flash DSC, the Flash DSC heat flow curve exhibits both the obvious glass transition and crystallization signals marked by T_g and T_{x1} .

To further study the dynamic properties of glass transition and primary crystallization for the $\text{Al}_{92}\text{Sm}_8$ MG, the evolutions of T_g and T_{x1} with heating rate are analyzed based on

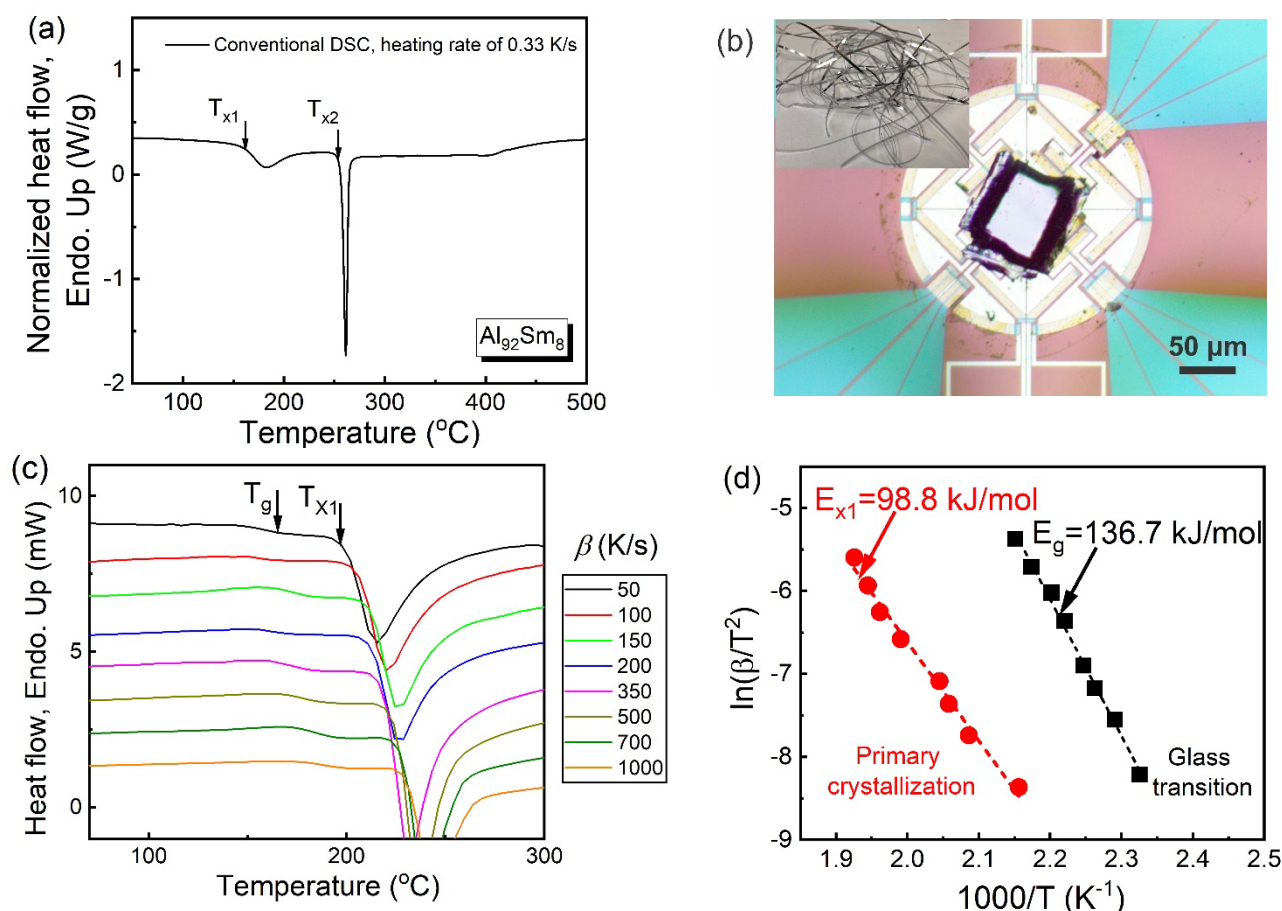


Figure 1. (a) Heat flow curve by conventional DSC with the heating rate of 0.33 K/s for $\text{Al}_{92}\text{Sm}_8$ MG; (b) Optical picture of tiny MG sample on Flash DSC chip (the left inserted picture gives the optical photo of ribbon-like MG sample); (c) A series of Flash DSC heat flow curves by Flash DSC with the heating rates ranging from 50 to 1000 K/s; (d) Activation energies of glass transition and primary crystallization by fitting the experimental T_g and T_{x1} based on the Kissinger equation.

the Kissinger equation. For MGs, the glass transition temperature and the primary crystallization temperature usually follow the Kissinger equation [7]:

$$\ln(\beta/T^2) = (-E/(RT)) + \text{constant} \quad (1),$$

where β is the heating rate, T is the value of the onset temperature of primary crystallization or the glass transition, E_g and E_{x1} are the activation energies for the glass transition and primary crystallization respectively and R is the gas constant. Thus, the activation energy for the glass transition and primary crystallization for $\text{Al}_{92}\text{Sm}_8$ MG can be calculated by fitting the experimental results with Kissinger equation and the detailed results are shown in Figure 1d. The activation energy for primary crystallization is 98.8 kJ/mol and 136.7 kJ/mol for the glass transition. These activation energy values are comparable with those of previous researches in other Al-based MG systems [10–12]. Thus, for marginal Al-based MG, the glass transition requires a larger activation energy than that for the primary crystallization process. At a low heating rate in a conventional DSC, the T_g signal is superposed by the primary crystallization peak and the weak T_g signal is swallowed by the strong crystallization signal. With the increase of heating rates, both T_g and T_{x1} move to higher temperatures. However, T_g requires more activation energy to shift, and T_g will be left behind by T_x . Therefore, it is possible to discriminate the two signals and then determine the glass transition temperature for Al-based MGs. This result is consistent with the above observed glass transition signal in the Flash DSC heat flow curves with a series of fast heating rates in Figure 1c.

3.1.2. Delay time determination in various amorphous materials

An important application of amorphous materials is to serve as a precursor for the nucleation of crystalline phases that often develop with nanocrystalline sizes. The typical crystallization reaction is illustrated in figure 2a. Upon isothermal annealing, initially no crystals are present. During this delay time, τ period crystalline embryos evolve with increasing size towards a critical size range where they can then proceed to grow as crystals. Within this delay time there is a transient nucleation as the equilibrium cluster size distribution is established to develop into a steady state nucleation rate. The steady state rate continues until a saturation of nucleation sites is reached and is then followed by a size coarsening regime. The transient nucleation rate, $J(t)$, is represented by [13,14]

$$J(t) = J_{ss} \exp[-\tau/t] \quad (2),$$

where t is the time and J_{ss} is the homogeneous nucleation that is given by

$$J_{ss} = \Sigma Z C_0 \exp[-\Delta G^*/kT] \quad (3),$$

where Σ is the atom attachment frequency to the evolving nucleation clusters, Z is the Zeldovich factor that has a typical value of 0.1, C_0 is the nucleation site density, ΔG^* is the work for nucleus formation, k is the Boltzmann constant and T is the temperature. Often Σ is taken as D/a^2 where D is the bulk diffusivity and a is the atom spacing. Further since D is not always available it is estimated from the Stokes-Einstein relation

$$D = kT/[6\pi r\eta] \quad (4),$$

where η is the viscosity and r is the atom size. However, this approach has problems since the bulk diffusivity does not necessarily represent the interface attachment process governing cluster growth and it has been demonstrated that the Stokes-Einstein relation breaks down near T_g [15]. However, from nucleation theory there is a direct relation between Σ and τ given by [14]

$$\Sigma = 1/2\tau Z^2 \quad (5).$$

Thus, a measurement of τ offers an accurate approach to evaluating β and the nucleation rate. Moreover, the magnitude of τ also provides an effective evaluation of the glass formation ability as large τ values are necessary for bulk glass formation. For example, a longer delay time at one temperature endows the higher thermal stability and the better glass formation ability, which is critical for developing bulk MGs [15]. Thus, it is of great importance to experimentally and precisely determine the delay time corresponding to different temperatures.

There are two common methods to experimentally measure the delay time for primary crystallization in amorphous materials: I. TEM method by plotting the measured crystal number density and the annealing time at one temperature and then extrapolating the steady state nucleation slope line to the time axis, the delay time can be established (see Figure 2a) [16, 17]; II. Isothermal test method by holding the amorphous sample at one temperature and then observing the onset time for the crystallization reaction (see Figure 2b) [18, 19]. For the method I, a great deal of TEM sample preparation and testing is required and thus it is very time-consuming, which is not a preferential method. For method II, the crystallization signal should be strong enough to show up in the isothermal annealing DSC trace, which makes it possible to directly measure the delay time for crystallization by isothermal tests. Thus, the amorphous system should have a good glass formation ability and thermal stability, such as the Zr-, Pd- and Ce-based bulk MG systems [18, 19]. However, for some marginal amorphous materials, such as the typical marginal Al-based MGs with poor glass formation ability, there usually appears a primary nucleation peak for Al nanocrystals followed by secondary or tertiary crystallization reactions involving intermetallic phases [20]. The signal from the primary nucleation of the precipitation of FCC Al nanocrystals is so weak that the crystallization peak is difficult to detect in the isothermal DSC tests [21]. Therefore, one precise and convenient method would be valuable for the determination of delay time for crystal nucleation in various amorphous materials.

Based on the Flash DSC with ultrafast heating and cooling rates, a new method is demonstrated to decide the delay time for primary crystallization. Under isothermal treatment, the evolution of glass transition temperature with annealing time for amorphous materials should follow two different paths: structural relaxation before the onset of crystal nucleation and the composition or ordering change after the onset of crystallization. Thus, the break time point in the slope of the plot of the glass transition temperature change with annealing time should correspond to the delay time for the primary crystallization [22, 23]. Three different kinds of amorphous systems were selected to verify the effectiveness and universality of the method, including one typical marginal Al-based MG with poor glass formation ability ($\text{Al}_{92}\text{Sm}_8$), two stable MG systems with good glass formation ability ($\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ and $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$) and one amorphous polymer (Polybutylene terephthalate, PBT).

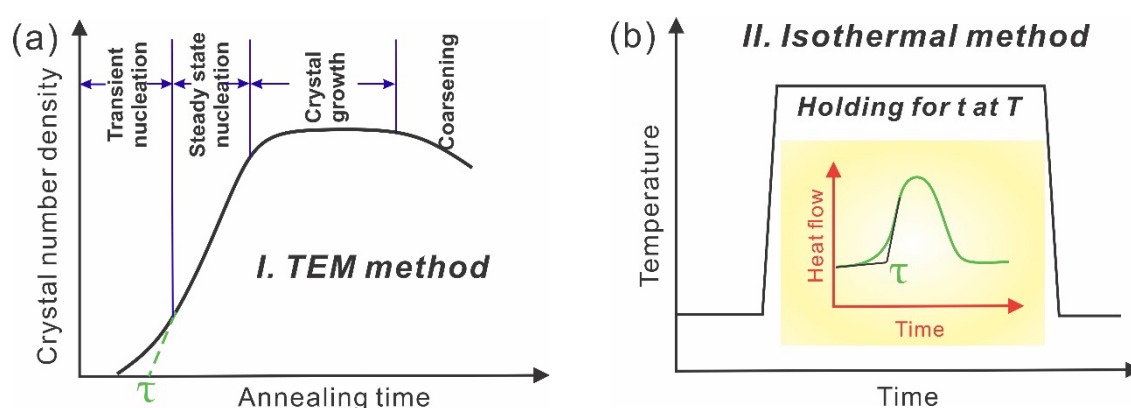


Figure 2. Schemes of traditional experimental methods to determine the delay time τ for primary crystallization in MGs: (a) TEM method (I); (b) Isothermal method based on the thermal tests (II). The inserted graph in (b) gives the confirmation details of delay time by method II.

3.1.2.1. Marginal Al-based MG

For the conventional DSC with heating rate of several K/s, the thermal signal of the glass transition for marginal Al-based MGs cannot be detected due to the close overlap of

the strong crystallization exotherm. In contrast, the Flash DSC with the large heating rate range from several K/s to 10^4 K/s allows for the separation of the T_g and T_x signals, as described in part 3.1.1. Thus, the ultrafast chip calorimetry instrument provides a good opportunity to study the delay time for marginal Al-based MGs. For an $\text{Al}_{92}\text{Sm}_8$ MG, a series of Flash DSC heat flow curves with the same heating rate of 1000 K/s was measured after annealing at 150°C for different times ranging from 20 s to 10000 s, as shown in Figure 3a. It is obvious that all of Flash DSC heat flow curves display the obvious endothermic reaction signals corresponding to glass transition and the T_g shifts to the higher temperature with the increase of annealing time t_a . These results are very close to the previous research on the structural relaxation effect on MGs [24, 25]. To study the evolution of the glass transition temperature T_g with annealing time t_a , T_g is plotted against t_a at 150°C , as is shown in the Figure 3b. From Figure 3b, it is evident that with the increase of t_a , there appears one break point at 930 s. Before and after 930 s, the evolution paths of T_g with t_a can be roughly fitted by two lines with different slopes. These two different evolution paths correspond to the structural relaxation effect and the composition effect and the samples before and after the break points should be amorphous and contain nanocrystals, respectively [22, 23].

To further test if the delay time for primary crystallization corresponds to the experimental breaking time of glass transition temperature with annealing time, two annealing time points were selected before and after the breaking time, t_1 (550 s) and t_2 (1200 s). Then, for these two annealed samples by Flash DSC, TEM samples were prepared by FIB methods in order to observe the corresponding crystallization morphology. The corresponding TEM images corresponding to t_1 and t_2 are shown in Figure 3c and Figure 3d, respectively. It is evident that at 150°C , the sample with the annealing time of 550 s before the break

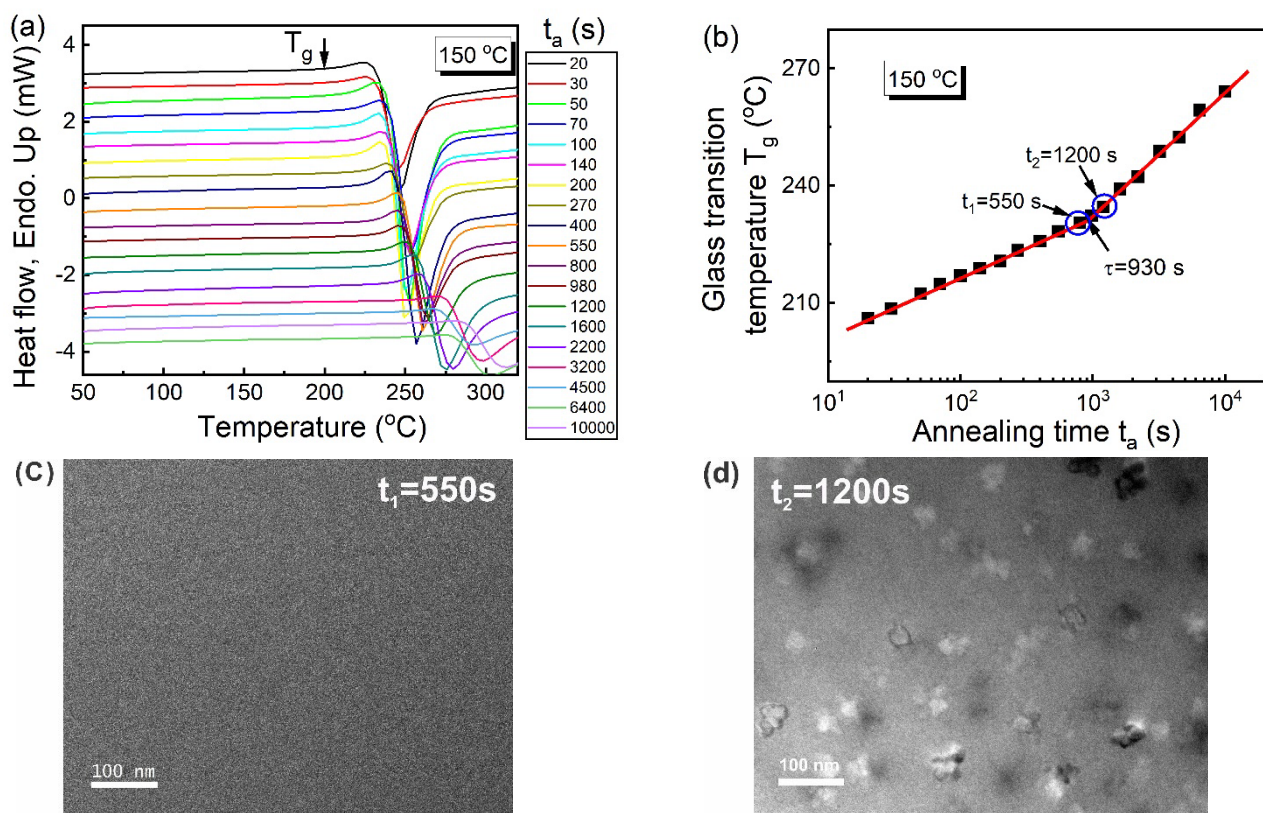


Figure 3. (a) A series of Flash DSC heat flow curves corresponding to different annealing times ranging t_a from 20 to 10000 s at 150°C for $\text{Al}_{92}\text{Sm}_8$ MG; (b) Plot of T_g and t_a at 150°C (t_1 and t_2 are two selected annealing times before and after the break point of 930 s); (c) TEM image for annealed sample corresponding to the annealing time of t_1 ; (d) TEM image for annealed sample corresponding to the annealing time of t_2 .

point is still amorphous without any crystals; in contrast, for the samples with the annealing time of 1200 s after the break point, a great number of nanoscale crystals are observed. Thus, the above results and analyses verify that the break point of 930 s is actually the delay time at 150 °C for the $\text{Al}_{92}\text{Sm}_8$ MG, which is consistent with previous research [22, 23].

3.1.2.2. Stable La-based MG

For the stable La-based MG system, the thermal signals for the glass transition and primary crystallization are strong [26]. To verify if the above new method to confirm the delay time for primary crystallization is effective for the La-based MG, one typical composition of $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ was selected and the target temperature was set of 270 °C. Then, a series of Flash DSC heat flow curves corresponding to different annealing times ranging from 1 s to 50 s with the heating rate of 500 K/s were measured, as shown in Figure 4a. From Figure 4a, the heat flow curves with different annealing times for $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ MG exhibit the obvious signals of the glass transition and primary crystallization. The onset values of the glass transition obviously shift to the higher temperature range with the increase of the annealing times, which is consistent with the structural relaxation effects in MGs [24, 25]. Similar to the analyses process for the delay time confirmation method in part 3.1.2.1 for Al-based MG, the onset value of the glass transition T_g with the annealing time t_a can be plotted as shown in Figure 4b. From Figure 4b, it is apparent that with the increase of t_a at 270 °C, there appears a break point time at 22.5 s. Before and after 22.5

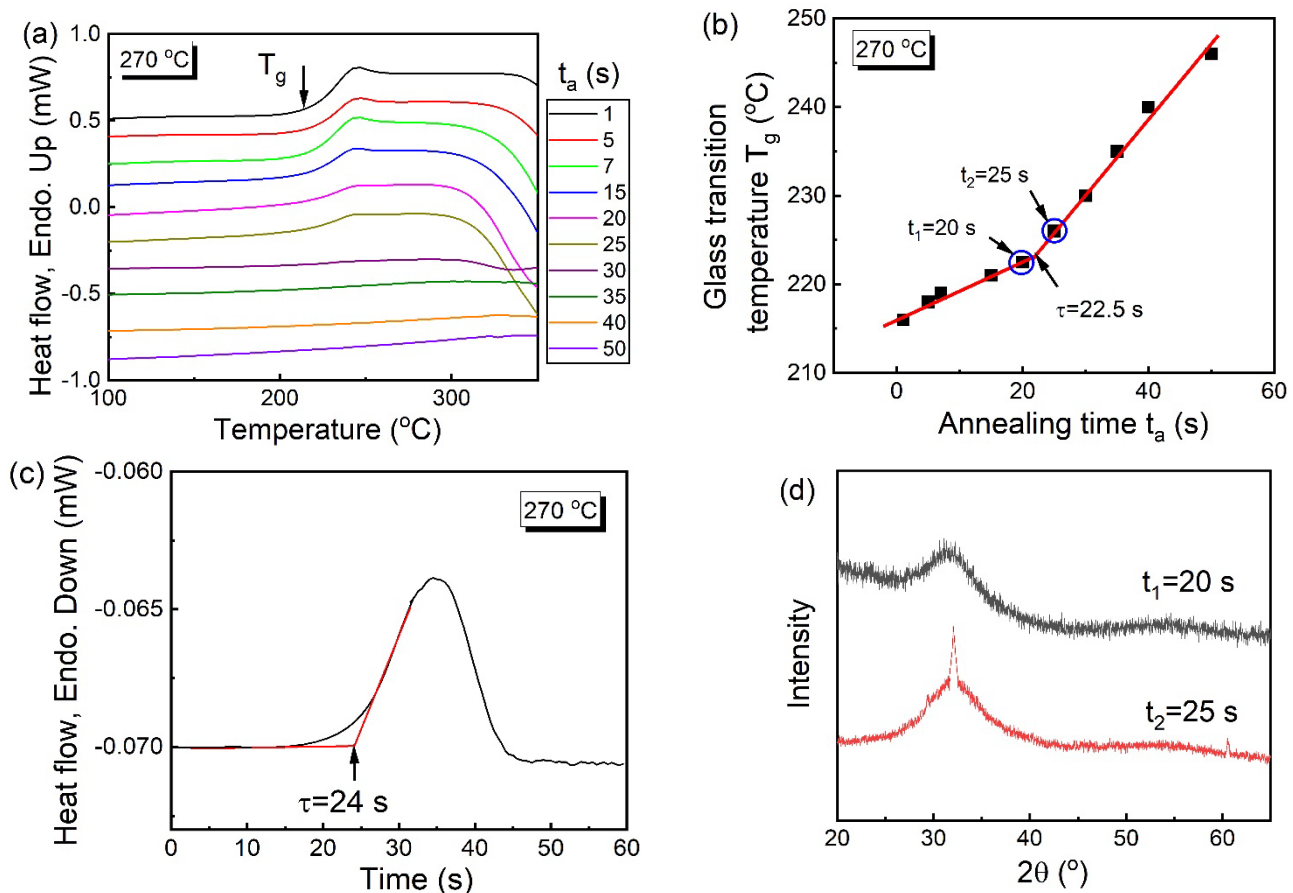


Figure 4. (a) A series of Flash DSC heat flow curves corresponding to different annealing times ranging t_a from 1 to 50 s at 270 °C for $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ MG; (b) Plot of T_g and t_a at 270 °C (t_1 and t_2 are two selected annealing times before and after the break point of 22.5 s); (c) The isothermal test for $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ MG at 270 °C; (d) XRD patterns for annealed samples corresponding to the annealing times of t_1 and t_2 .

s, the evolution paths of T_g with t_a can be roughly fitted by two lines with different slopes corresponding to two different governing mechanism of the structural relaxation and the composition change induced by the crystallization. In comparison, the isothermal method (method II in Figure 2b) was also applied to measure the delay time for $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ MG sample at 270 °C. The detailed temperature program can be seen in Figure 2b. As shown in Figure 4c, at 270 °C, when the annealing time increases into about 24 s, the exothermic peak corresponding to the primary crystallization appears. The time of 24 s is the delay time at 270 °C, which is very close to the experimental data of 22.5 s by the Flash DSC method.

To confirm if the delay time of the experimental breaking time of glass transition temperature with annealing time in Figure 4b corresponds to the onset time for primary crystallization, two annealing time points were selected before and after the break time, t_1 (20 s) and t_2 (25 s). Then, for these two annealed samples obtained by Flash DSC, XRD tests were conducted to characterize the sample state. The corresponding XRD patterns corresponding to the annealing times of t_1 and t_2 are shown in Figure 4d. It is apparent that at 270 °C, the sample with the annealing time of 20 s before the break point is still amorphous without any crystals; in contrast, for the samples with the annealing time of 25 s after the break point time, one sharp crystallization peak was observed, which indicates that the annealed sample is crystallized. Thus, the above results show that the break point time of 22.5 s is actually the delay time at 270 °C for the stable $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ MG.

3.1.2.3. Stable Mg-based MG

Similar to the stable La-based MG, the Mg-based MG with a composition of $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ is also one of the typical stable MG systems [27]. As shown in Figure 5a, a series of Flash DSC heat flow curves were obtained corresponding to different annealing times ranging

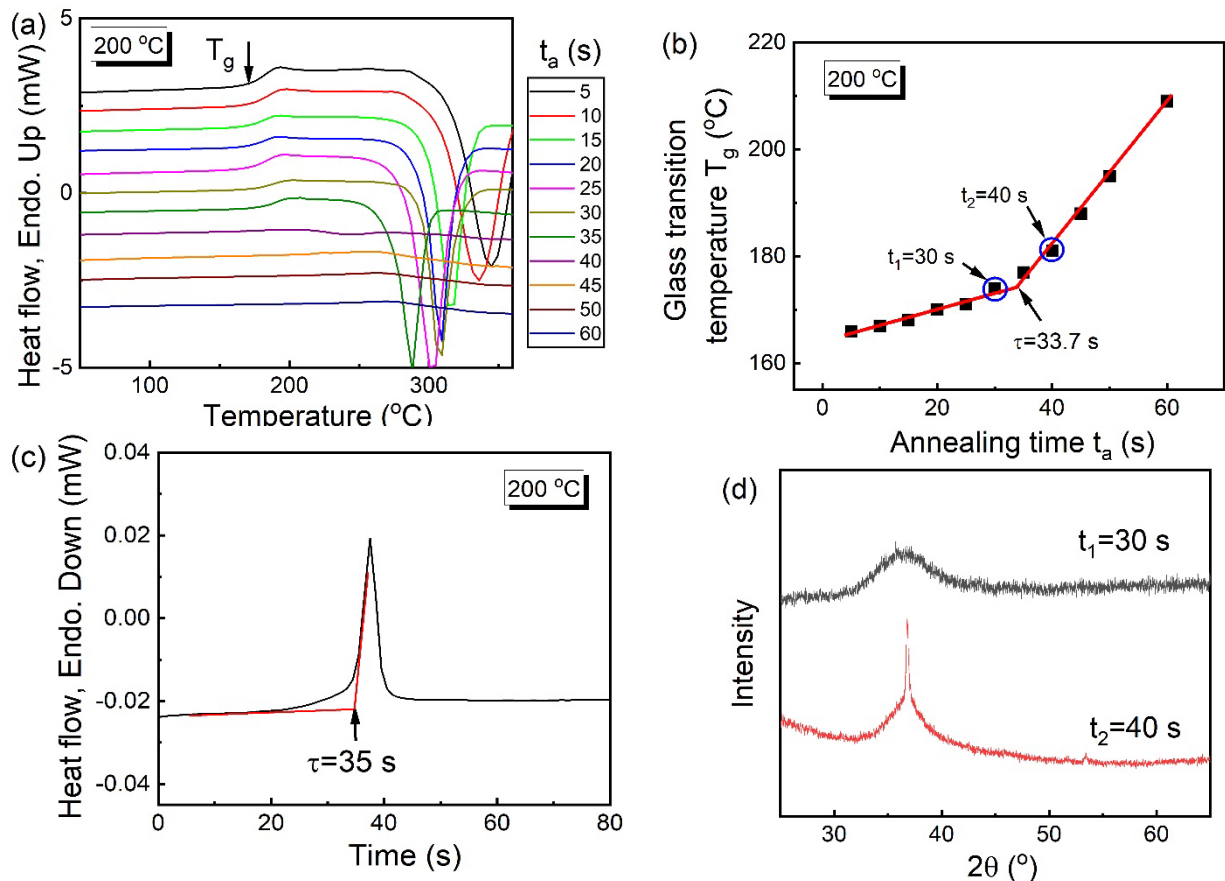


Figure 5. (a) A series of Flash DSC heat flow curves corresponding to different annealing times ranging t_a from 5 to 60 s at 200 °C for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ MG; (b) Plot of T_g and t_a at 200 °C (t_1 and t_2 are two selected annealing times before and after break point of 33.7 s); (c) The isothermal test for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ MG at 200 °C; (d) XRD patterns for annealed samples corresponding to the annealing times of t_1 and t_2 .

from 5 s to 60 s at 200 °C with the heating rate of 500 K/s. The heat flow curves with different annealing times for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ MG exhibit the clear signals of the glass transition and primary crystallization, which are consistent with the thermal behaviors for La-based MG in part 3.1.2.2. What is more, the T_g shifts to the higher temperature with the increase of the annealing time t_a . Similar to the analyses process for the delay time confirmation method in part 3.1.2.1 for Al-based MG and in part 3.1.2.2 for La-based MG, the onset value of the T_g with the annealing time t_a can be plotted as shown in Figure 5b. From Figure 5b, with the increase of t_a at 200 °C, there appears one break point time at 33.7 s. Before and after 33.7 s, the evolution paths of T_g with t_a follows two different paths corresponding to the structural relaxation and the composition effect. Meanwhile, the isothermal method was also applied to measure the delay time for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ MG sample at 200 °C. As shown in Figure 5c, at 200 °C, when the annealing time increases into about 35 s, the exothermic peak corresponding to the primary crystallization appears. The time of 35 s is the delay time at 270 °C, which is very close to the experimental data of 33.7 s based on the evolution of the glass transition T_g with the annealing time t_a .

To confirm if the delay time of the experimental breakpoint time by Flash DSC corresponds to the onset time for primary crystallization, two annealing time points were selected before and after the break point time, t_1 (30 s) and t_2 (40 s). XRD tests for these two annealed samples were conducted. The corresponding XRD patterns corresponding to the annealing times of t_1 and t_2 were shown in Figure 5d. One can see that at 200 °C, the sample with the annealing time of 30 s before the breakpoint time are still amorphous without any crystals; in contrast, for the samples with the annealing time of 40 s after the breakpoint time, one sharp crystallization peak was observed. Thus, the above results show that the break point time of 33.7 s is actually the delay time at 200 °C for the stable $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ MG.

3.1.2.4. Amorphous polymer material

To verify if the delay time confirmation method by Flash DSC can be applied for the amorphous polymer materials, one typical amorphous polymer-polybutylene terephthalate (PBT) was chosen for examination [1, 29]. At an annealing temperature of 50 °C, a series of heat flow curves with different annealing times ranging from 2 s to 12 s were measured and are shown in Figure 6a. Similar to the MG systems, the glass transition temperature T_g for PBT sample also shifts to the higher temperature with the increase of the annealing time t_a , which indicates the structural relaxation effect. Moreover, the corresponding T_g - t_a dependence can be plotted in Figure 6b. When t_a increases into about 6.6 s, a break point appears between the two evolution paths. Meanwhile, the isothermal method was also applied to measure the delay time for PBT sample at 50 °C. As shown in Figure 6c, at 50 °C, when the annealing time increases into about 6.3 s, the exothermic peak corresponding to the primary crystallization appears. The time of 6.3 s is the delay time at 50 °C, which is very close to the experimental data of 6.6 s based on the evolution of the glass transition T_g with the annealing time t_a . By selecting three annealing time points before (t_1 , 6 s) and after the break point (t_2 , 8 s), the XRD tests for these two annealed samples were conducted. The annealed samples before and after break point are respectively amorphous and crystalline in Figure 6d, which confirms the delay time at 50 °C for the PBT sample. Based on the previous research [28], for amorphous polymer materials, with the increase of the annealing time, the crystalline phase gradually grows and the ordering degree within polymer increases. Considering that the polymer is one single composition, the break point for T_g - t_a plot in amorphous PBT in Figure 6b corresponds to the transition from the relaxation effect to the ordering effect.

Based on the above results and discussions in parts 3.1.2.1-3.1.2.4, the experimental method to determine the delay time for primary crystallization based on the chip calorimetry is an effective method for various amorphous materials, which provides a good opportunity to investigate the nucleation and crystallization behaviors in glassy materials.

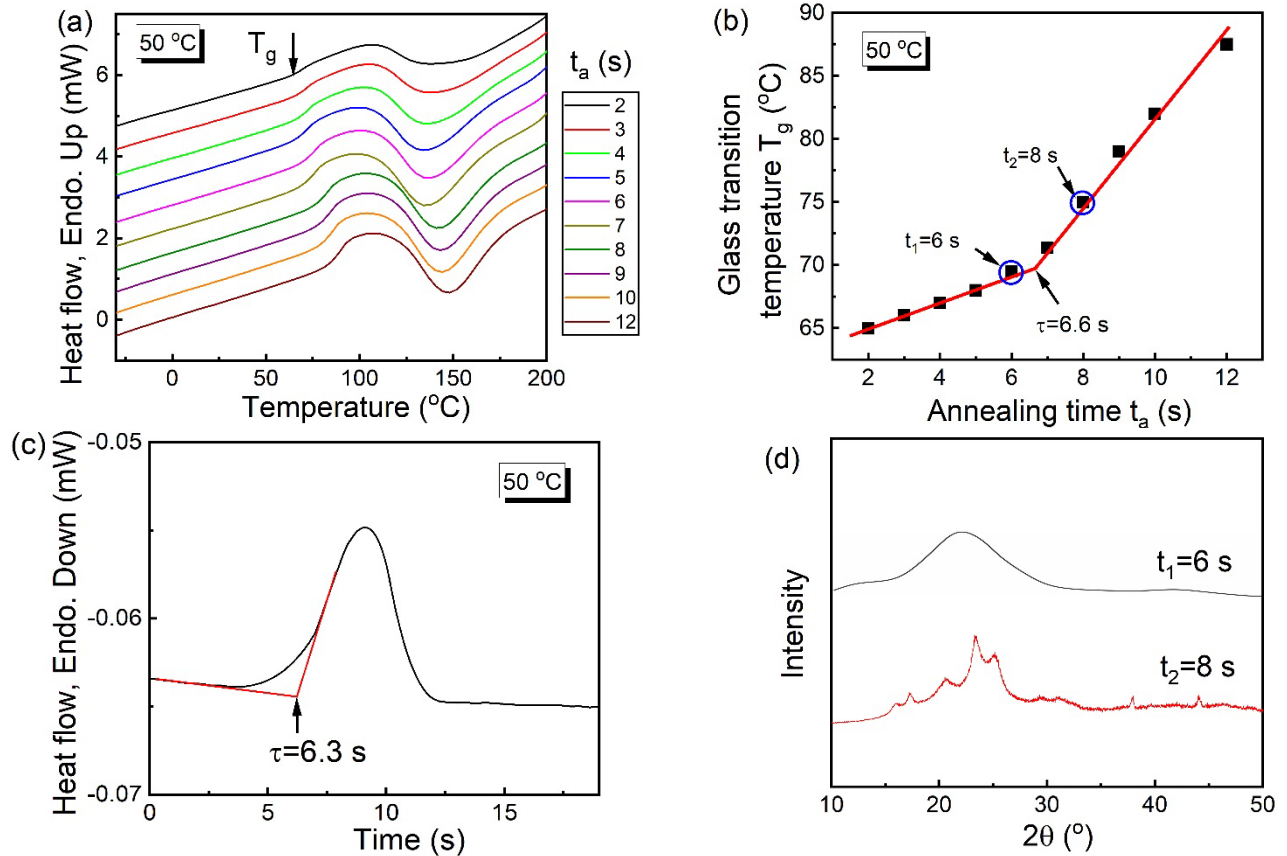


Figure 6. (a) A series of Flash DSC heat flow curves corresponding to different annealing times ranging t_a from 2 to 12 s at 50 °C for amorphous PBT sample; (b) Plot of T_g and t_a at 50 °C (t_1 and t_2 are two selected annealing times before and after the break point of 6.6 s); (c) The isothermal test for PBT sample at 50 °C; (d) XRD patterns for annealed samples corresponding to the annealing times of t_1 and t_2 .

3.2. Glass formation

3.2.1. New polyamorphous material-D-mannitol

Polyamorphism refers to the existence of two amorphous phases of the same composition separated by a first-order transition. This phenomenon is analogous to crystal polymorphism exemplified by diamond and graphite but is less well understood and even controversial [30]. Zhu *et al.* reported that the melt-quenched glass of D-mannitol can transit into another apparently amorphous state by continuous heating or isothermal annealing, with a first-order characteristic [2]. In agreement with this report, the first-order transition can be completed by annealing the melt-quenched sample at 310 K for 180 s in the conventional DSC. Figure 7a shows when heating the melt-quenched glass (GN) sample with a 20 K/min heating rate, the sample begins the glass transition to a supercooled liquid (SCL-1) at 287 K, but further heating results in an exothermic transition from SCL-1 to amorphous phase X (GX) beginning at 298 K. When heating a sample that has been aged at 310 K for 180 s, the sample shows neither a glass transition at 287 K nor a sharp exothermic peak at 298 K [3]. This is identical to the DSC heating trace of the GX sample which is obtained by first being heated to 313 K (above the first exothermic transition) and then quenched [2].

The X-ray diffraction patterns of GN, GX, and the α crystal polymorph are shown in Figure 7b. It is evident that GX does not have crystal-like diffraction features, which strongly indicates that the GX is an amorphous state. Also, the diffraction pattern of GX is distinct from that of GN. The GX has a featured broad maximum that appears at lower 2θ than that for the GN, with an additional small peak around 15° , which likely results from a different local structure with long range correlation. This is consistent with the report that the GN has a smaller specific volume than GX at 273 K, which is the measuring temperature of the X-ray diffraction experiments [3, 4].

Due to the slow heating rates of the conventional DSC, GX can form from SCL-1 of GN to produce an exothermic peak. In the Flash-DSC, however, the 100 K/s or even a 10 K/s heating rate is too fast to allow for this transition so that no exothermic peak can be observed on the heating trace of a melt-quenched GN sample. On the other hand, if the GN sample is annealed with a combination of annealing temperature that can trigger the GN/SCL-1 to GX transition and annealing time that is longer than the delay time of the transition, GX can be formed in the annealed sample and the glass transition of GX can appear in the following heating trace.

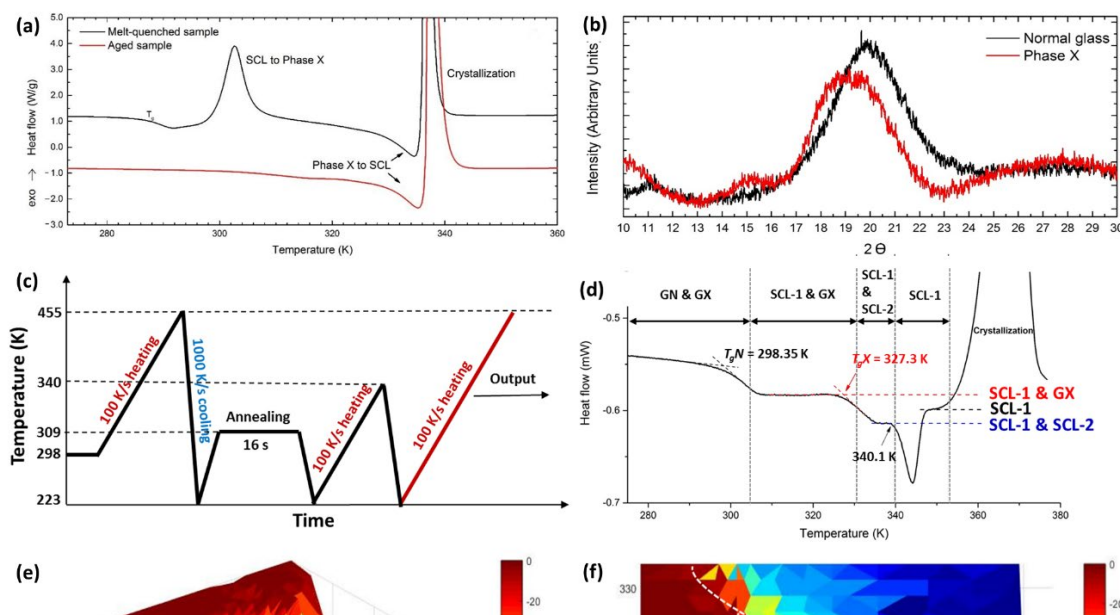


Figure 7. (a) Conventional DSC measurements on a normal glass (GN) and a phase X (GX) D-mannitol sample[31, 33]. (b) X-ray diffraction patterns of GN and GX[31, 33]. (c) The experimental protocol for the sample preparation in (d). (d) Transition path during heating. Sample was annealed at 309 K for 16 s, preheated to 340 K and quenched down before this heating. Sample starts as a mixture of normal (melt-quenched) glass and phase X, and shows 3 endothermic transitions: (1) glass transition of GN (298 K); (2) glass transition of GX (328 K); (3) liquid-liquid from SCL-2 to SCL-1 (340 K)[33]. (e) and (f) Enthalpy change with different annealing conditions, (e) is 3-D plot of the enthalpy change with T_a and $\ln(t_a)$, (f) is the result of projecting the profile onto T-t plane, the boundaries between adjacent plateaus are the Time-Temperature-Transition curves of the corresponding transition[33].

An example of that protocol is shown in Figure 7c. After an anneal at $T_a = 309$ K and annealing time $t_a = 16$ s, the sample is then reheated to 340 K to obtain the supercooled liquid state and immediately quenched. The following heating trace in Figure 7d clearly shows three endothermic transitions before crystallization as T_g of GN at 298.3 K, T_g of GX at 327.3 K and the transition from SCL-2 to SCL-1 at 340.1 K. It is also worth noting that the mixture of SCL-1 and SCL-2 has a larger specific heat capacity than that for pure SCL-1, which means that pure SCL-2 has a larger specific heat value compared to pure SCL-1 [4].

By choosing the Flash-DSC heating trace of the unannealed GN sample as a baseline that is subtracted from each of the annealing traces, the enthalpy changes under each annealing condition can then be calculated by integrating the remaining curve from T_a to 458 K. By normalizing the enthalpy change with the corresponding sample weight, a three-dimensional plot of the enthalpy change with T_a and $\ln(t_a)$ can be constructed as shown in Figure 7e. There are three plateaus in the 3-D profile, which correspond to unannealed GN/SCL-1 ($\Delta H = 0$ J/g red), GX/SCL-2 ($\Delta H = -50$ to -65 J/g, yellow and orange), and α crystalline ($\Delta H = -160$ J/g, blue), respectively. Figure 7f is obtained by projecting the three-dimensional surface onto the T - $\ln(t)$ plane. In this projection, the boundaries between adjacent plateaus are actually the Time-Temperature-Transition (TTT) curve. The transition boundary between the two amorphous states has a C shape, which is a main feature of thermally activated phase transitions. As a consequence, the time length to reach the boundary at a certain temperature is the delay time τ for the reaction. It can also be seen that, although the difference is not very large, the height of the plateau corresponding to GX formed at lower annealing temperature (below 305 K) is greater than that formed at higher annealing temperature [4].

3.2.2. In-situ formation of glass in liquid crystals

Liquid crystals (LCs) usually are known to undergo rapid ordering transitions with virtually no hysteresis. These transitions are so fast that nearly no supercooling can be observed under ordinary conditions. This allows LCs to serve as standards for temperature calibration at fast cooling rates (up to 2×10^4 K/s) [31, 32]. Recently, ITZ was reported as an exceptional case. At slow cooling, the isotropic liquid transforms to a nematic phase and then to a smectic phase, but at fast cooling, smectic ordering can be avoided altogether

or avoided partially to produce glassy solids with variable smectic order [5]. To exhibit the smectic ordering in an equilibrium liquid of ITZ, Figure 8a shows that the isotropic liquid of ITZ transforms to a nematic phase ($T_{NI} = 363$ K) and then to a smectic phase ($T_{Sm/N} = 347$ K) [33–35]. In the nematic phase, the molecules are aligned with their long axes approximately parallel to each other, while in the smectic phase, the molecules are further organized into layers [5]. Further cooling transforms the smectic liquid to a glassy solid ($T_g = 328$ K). Upon reheating, the transitions noted above are reversible.

At different cooling rates (R_c) ITZ glasses can be prepared with and without smectic order. When the cooling rate faster than the relaxation of nematic to smectic transition so that at $R_c > 20$ K/s ITZ can be free of smectic order [5]. The rates of molecular rotations in a liquid crystal can be obtained by dielectric spectroscopy as shown in Figure 8b [36]. Similar to other LCs [37–39], ITZ shows two relaxation processes [40, 41]. The fast process has been associated with the glass transition detected by DSC [38, 40] and is termed the α process, where the R_c value for glass formation is given by the right axis in Figure 8b. This process is attributed to molecular rotation about the long axis and precession of the long axis about the nematic director, whereas the slow process (called the δ mode) is attributed to molecular rotation about the short axis (end over end). The rates of the two processes can be significantly different in a liquid crystal; this is a result of a nematic potential that favors the alignment of the long axis along the director and reduces the average rate of end-over-end rotation [5].

From Figure 8b it is evident that if $R_c > 10^3$ K/s which is even faster than the rate of the isotropic to nematic transition, the two LC transitions will be avoided, and the liquid can be directly quenched into glassy state. Therefore, to obtain the isotropic glass, the molten sample was quenched at a series of cooling rate from 10 to 10^4 K/s and then reheated at 10^3 K/s to determine the different quenched glassy state structures. Different from the heating curve measured by conventional DSC as shown in Figure 8a, at a high heating rate under Flash DSC the peak of glass transition overlaps with the peak of the smectic to nematic transition. The evolution of the profile of heating curve is guided by the dash line shown in Figure 8c. Even at the low heating rates from 10 to 100 K/min under

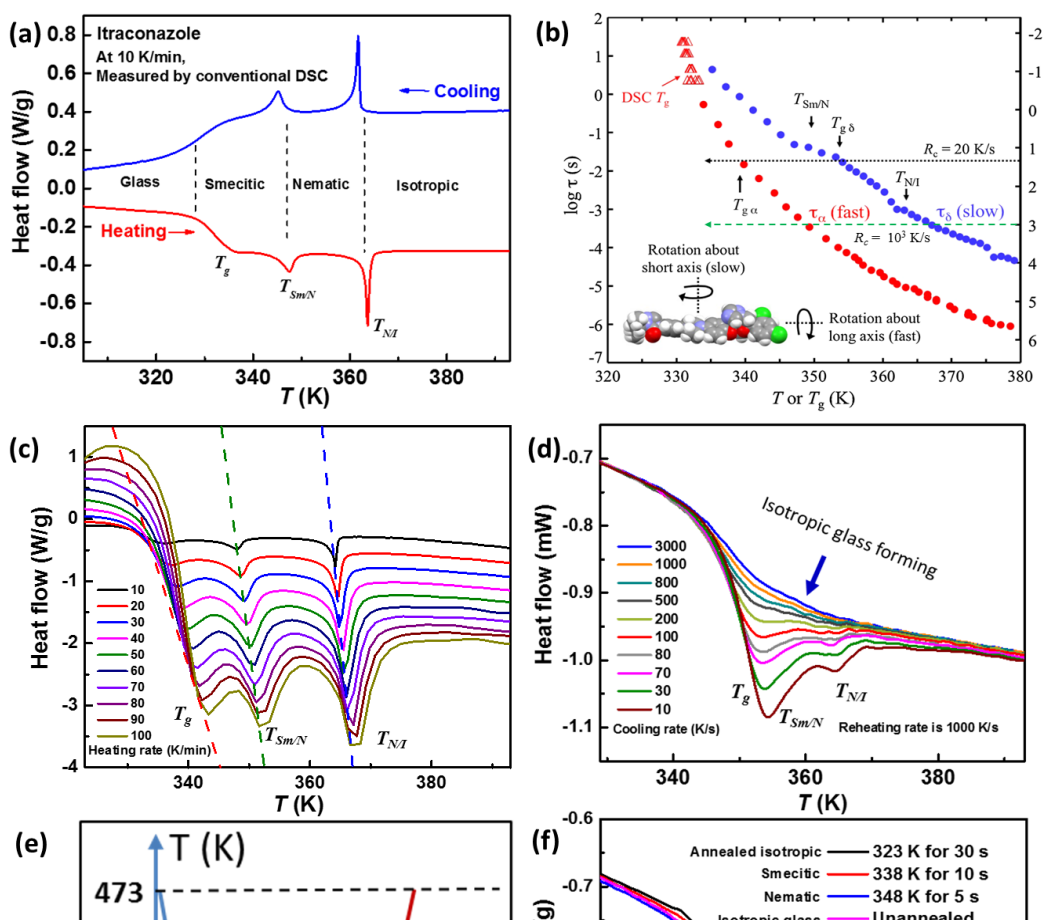


Figure 8. (a) Conventional DSC traces of ITZ during cooling and reheating at 10 K/min. (b) Fast (red circles) and slow (blue circles) relaxation processes in ITZ from dielectric spectroscopy [from Ref. 45], conventional DSC T_g onset (triangle) is shown as a function of cooling rate R_c (right axis) [34]. (c) A series of conventional DSC reheating traces with different heating rates, started from the melt quenched ITZ glass at 10 K/min cooling rate. (d) Flash DSC reheating curves with 10^3 K/s heating rate, the measured ITZ glass formed upon a series of cooling rates from 10 to 3×10^3 K/s. (e) The experimental protocol for the different ITZ glass formation in (f). (f) Flash DSC reheating curves at 10^3 K/s heating rate, to examine the ITZ glassy state after the different annealing conditions.

conventional DSC, the endothermic hump signal of T_g shows the obvious tendency to merge with the peak of $T_{Sm/N}$ while the distance between the peaks of $T_{Sm/N}$ and $T_{N/I}$ stays almost the same. Meanwhile the profile of the peaks smooths with increasing heating rate gradually. Therefore, for Flash DSC measurements see in Figure 8d, the reheating curves upon slow cooling ($R_c < 100$ K/s) show two apparent peaks about the overlapped T_g with $T_{Sm/N}$ and then the small one about $T_{N/I}$. Consistent with the relaxation process in Figure 8b [5, 40], upon cooling at $R_c > 500$ K/s in Figure 8d, there is only the glass transition without the signal of the LC transitions, which indicates that the isotropic to nematic transition was avoided during this fast cooling process to form the isotropic ITZ glass.

Since the highly disordered isotropic glass can be formed upon 10^3 K/s quenching, to obtain more kinds of ITZ glass, we conducted annealing treatments on the as-quenched sample according to the protocol shown in Figure 8e. The sample was annealed at 323 K ($T_a > T_g$), 338 K ($T_g < T_a < T_{Sm/N}$) and 348 K ($T_{Sm/N} < T_a < T_{N/I}$) for sufficient time according to the relaxation process [5, 40], respectively. As a result, in Figure 8f the reheating curve of the sample annealed below T_g only shows one deep endothermic peak due to the aging effect of the glass which indicates that there was no apparent smectic or nematic order formed during annealing and sample remained in the isotropic glassy state. While for the higher T_a annealed samples, the red curve shows both endothermic peaks of the overlapped T_g with $T_{Sm/N}$ and then $T_{N/I}$, indicating the formation of smectic layers during annealing. Then the blue curve only shows the obvious $T_{N/I}$ and the weaker signal of T_g with $T_{Sm/N}$ as a shoulder, indicating that the nematic to isotropic transition dominates in this heating process. Therefore, upon annealing in-situ the various LC orders can be effectively trapped in a glass at a 10^3 K/s cooling rate.

4. Conclusions

In this work, recent work is highlighted on nucleation and glass formation by chip calorimetry with ultrafast heating and cooling rate. First, for marginal Al-based MG system, based on the separated evolution of glass transition and primary crystallization with heating rates, the glass transition signal is successfully separated from primary crystallization within huge heating rate range. Second, one effective and universal method to experimentally determine the nucleation delay time of primary crystallization based on the

chip calorimetry platform. This method has been verified to be applied for various amorphous materials including the marginal MG system, the stable MG systems and the amorphous polymer system. Third, results from flash DSC experiments provided insights into the characteristics of the amorphous-amorphous transition, in particular the precise annealing conditions that could be reached by flash DSC enabled the construction of the Temperature-Time-Transformation (TTT) plot of D-mannitol for the transition between GN/SCL-1 and GX/SCL-2, as well as the transition between amorphous and crystalline phases revealing thermally activated behavior. Fourth, for LC material ITZ, upon annealing in-situ the various of LC orders can be effectively trapped in a glass at a high cooling rate.

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