Influence of fragility and molecular symmetry on the formation of stable glasses

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M.Sc. Yeong Zen, Chua, geb. am 24.09.1985 in Kuala Lumpur

aus Kuala Lumpur, Malaysia.

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Gutachter:

1. Gutachter:

Prof. Dr. Christoph Schick

Institut für Physik, Universität Rostock

2. Gutachter:

Prof. Dr. Andreas Schönhals

Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin

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Abstract

Glasses of toluene, ethylbenzene, ethylcyclohexane and tetrachloromethane with high kinetic stability have been produced by physical vapor deposition and characterized by *in situ* AC chip nanocalorimetry. The highest kinetic stability of the as-deposited glasses is achieved with deposition at substrate temperatures around 0.85 T_g and with lower deposition rates. The isothermal transformation of the as-deposited glasses into the supercooled liquid state gave further evidence to the stable glass formation with high kinetic stability. The successful formation of vapor-deposited glasses with high kinetic stability of ethylcyclohexane, a strong glass former of $m \approx 60$, and tetrachloromethane, with a pseudo isotropic molecular structure, indicates that fragility and molecular asymmetry are not prerequisites for stable glass formation. In order to investigate these glass formers, AC chip nanocalorimetry was developed utilizing a closed-cycle helium cryostat to reach temperatures down to 10 K. On the other hand, the AC chip nanocalorimetry was improved with laser modulation, in order to reach frequency up to 1 MHz. This allows for the determination of the dynamic glass transition in a frequency range of up to 11 orders of magnitude with measurements from laser-modulated AC chip nanocalorimetry and four different temperature modulated differential scanning calorimeters (TMDSC).

Zusammenfassung

Ultrastabile Glaszustände von Toluol, Ethylbenzol, Ethylcyclohexan und Tetrachlormethan konnten durch physikalische Gasphasenabscheidung realisiert werden. Die hohe kinetische Stabilität der Gläser wurde durch *in situ* AC Chip-Nanokalorimetrie nachgewiesen. Die höchste kinetische Stabilität der abgeschiedenen Gläser konnte bei Substrattemperaturen um 0.85 T_g und niedrigen Abscheidungsraten erzielt werden. Die isotherme Transformation der abgeschiedenen Gläser in den Zustand der unterkühlten Flüssigkeit bestätigte die Bildung von ultrastabilen Gläsern mit hoher kinetischer Stabilität aus Ethylcyclohexan, einem Glasbildner mit einer Fragilität von $m \approx 60$, und Tetrachlormethan, einem pseudo isotropen Molekül. Diese Beispiele zeigen, dass Fragilität und molekulare Asymmetrie keine Voraussetzungen für die Bildung ultrastabiler Gläser sind. Im zweiten Teil der Arbeit wird die für die Untersuchungen notwendige Weiterentwicklung der AC Chip-Nanokalorimetrie beschrieben. Mit einem geschlossenen Helium-Kryostaten wurde der Temperaturbereich nach unten auf 10 K erweitert. Eine Erweiterung des Frequenzbereichs bis 1 MHz wurde durch den Aufbau eines AC Chip-Nanokalorimeters mit Laser-Modulation erreicht. Dies ermöglicht die Bestimmung des dynamischen Glasübergangs in einem Frequenzbereich von 11 Größenordnungen. Dazu werden Messungen mit dem lasermodulierten AC Chip-Nanokalorimeter mit denen von vier verschiedenen temperatur-modulierten Differential-Scanning-Calorimetern (TMDSC) kombiniert.

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Chapter 1: Summary

1.1 Introduction

In recent years, the number and variety of glass-forming materials have increased tremendously. By understanding the physics of a glass-forming material, its properties can be manipulated to fit various specific uses. Glasses have been produced and utilized in many current and developing technologies, e.g. amorphous organic electronics,[1, 2] amorphous pharmaceuticals,[3] though it was and still is a continuous challenge to understand the main principles behind glass formation and its structure. Glasses can be produced from variety of glass-forming materials, such as organic, inorganic, polymeric, colloidal and metallic components.[4, 5]

A glass is commonly formed by cooling a supercooled liquid from liquid below glass transition without crystallization, shown in Figure 1. In order to reach equilibrium state, the liquid (solid green line) tends to crystallize (solid red line) with a sharp first order phase transition below the melting temperature, T_m. However if crystallization is avoided upon cooling, the liquid transforms into a supercooled liquid (SCL) and on further cooling, the molecular motions in the SCL slow down until metastability is lost at the glass transition temperature, T_g.[6] At this point, the SCL "freezes-in" into a non-equilibrium glass, as the molecules do not have enough mobility to move and to rearrange freely in a given time, which is dependent on the experimental conditions such as the cooling rate. This process of cooling down yields increasing viscosity and slowing down of dynamics, but no obvious structural changes occur. The molecules do not have possibility to move and rearrange, which is necessary to reach the equilibrium volume.

A characteristic behavior of volume V, or enthalpy H, or entropy S is observed at the glass transition. At a constant cooling rate and constant pressure, the temperature coefficient of the enthalpy, denoted as heat capacity C_p, shows a smooth step-like change at the glass transition, with

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \tag{1}$$

The non-equilibrium glass represents a thermodynamically unstable state and seeks continuously to relax or rearrange via physical aging to reach equilibrium. Physical aging happens naturally under undesirable conditions, while crystallization occurs when the molecules have sufficient mobility to arrive at a thermodynamic equilibrium state. For glasses at constant T and P, the free energy is not at a local minimum. This continuous relaxation changes the properties of the glasses, and subsequently affects the lifetime of devices. When the cooling rate is decreased, the molecules of the liquid have more time to find an arrangement closer to equilibrium, hence lower glass transition temperature, T_g'. Unfortunately, there is a limit to decreasing the cooling rate, thus limiting the partly equilibrated state that the glasses can reach. The same equilibrated state can be achieved by annealing the glass. However even when annealing at a few Kelvin below T_g, this process is so slow that low energy states in the energy landscape will never be reached on the experimental time-scale.

These limitations lead to the question whether it is possible to produce glasses closer to equilibrium in deeper minima on the potential energy landscape. When the glasses relax closer to equilibrium, the relaxation slows down considerably until it is almost insignificant, thus can increase the lifetime of the device.

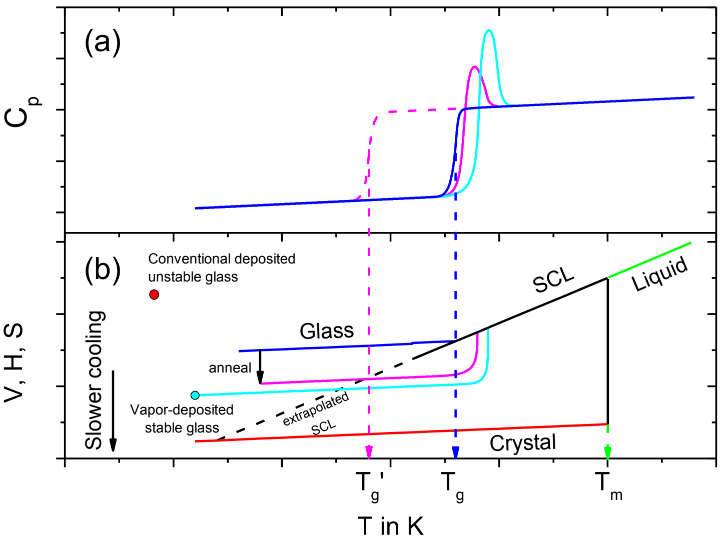


Figure 1: **Schematic of (a) heat capacity and (b) enthalpy versus temperature. Formation of liquid (solid green line) to supercooled liquid (solid black line) to amorphous glass (solid blue line). For the glass transition region, the enthalpy curve shows a smooth change in slope, while heat capacity shows a step. Annealing the amorphous glass yields a lower glass transition temperature, T_g' and an overshoot in heat capacity upon reheating. Physical vapor deposition at substrate temperature close to T_g produces glass with high kinetic stability (solid cyan line), while conventional deposition at very low substrate temperature produces unstable glass (red dot).**

It has recently been established that highly stable glasses can be prepared by physical vapor deposition. Enhanced mobility at the surface of these glasses allows molecules to efficiently explore configuration space and find a lower position on the energy landscape.

Even though there are several active researches on stable glasses from vapor deposition, the principle behind the formation of stable glasses is still not completely understood or well established. In this work, the characteristics of the stable glasses and correlation to the ability to stable glass formation are investigated. This is important in attempt to better understand glasses and to determine the prerequisite for the formation of stable glasses, as not all glass formers can form stable glasses or form partially stable glasses (e.g. butyronitrile,[7, 8] 1-pentene,[9] ethanol,[10] *n*-propanol[10]).

Therefore, the aim of the present thesis is to provide answers to the following two main questions:

(i) can strong liquids or least fragile liquids form stable glasses, and

(ii) is molecular anisotropy a prerequisite for stable glass formation?

In order to investigate the vapor deposited glasses, calorimetry is used as the main experimental measuring method, as it has proven its ability to provide useful information regarding stability of glasses from the determination of the heat capacity of materials.

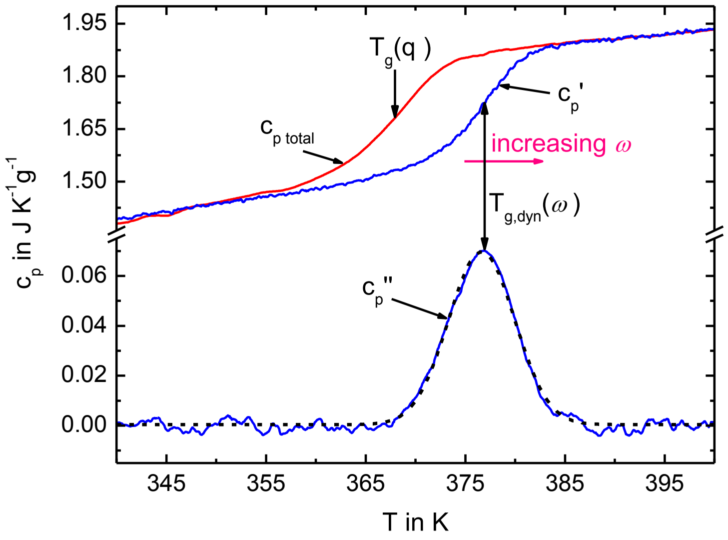


Figure 2: **Total specific heat capacity $c_{p,\mathrm{total}}$, read c_p' and imaginary part c_p" of the complex specific heat capacity of polystyrene determined from temperature modulated DSC (TMDSC). Figure taken from [11] and modified.**

The glass transition temperature T_g describes an equilibrium-to-non-equilibrium transition, while dynamic glass transition temperature $T_{g,dyn}$ occurs in the thermodynamic equilibrium. The molecules of a sample remain immobile on the timescale of the oscillation for temperatures around the glass transition temperature T_g, as determined by adiabatic calorimetry or DSC. At temperatures above T_g, the molecular rearrangement can follow the oscillation and is measured as a step in the real part of the susceptibility *c*' and a peak in the imaginary part *c*'', shown in Figure 2. The dynamic glass transition temperature $T_{g,dyn}$ is dependent on the frequency used for the dynamic experiment, where the $T_{g,dyn}$ is shifted to higher temperatures in comparison to T_g with increasing frequencies

The AC chip nanocalorimetry is a very useful technique to determine the complex heat capacity at the dynamic glass transition of thin films down to a few nm. With the possibility to measured very small samples, the frequency range of measurement is increased to kHz region. By using the AC chip nanocalorimetry in an ultra-high vacuum (UHV) and cooled with liquid nitrogen, the samples can be cooled to cryogenic temperatures under high vacuum condition. This system allows measurements of highly volatile small molecular glass formers, which will vaporize at room temperature. In order to measure to much lower temperatures, the cryostat is replaced with a closed cycle helium cryostat. For further development on the AC chip nanocalorimetry, laser light heating is implemented as the source for the modulated power instead of the resistive heating from the built-in heaters embedded in the sensor membrane, in order to reach even higher frequencies range up to 1 MHz. This means reaching relaxation times down to almost 100 ns.

This thesis is structured as follows: (i) investigation of vapor-deposited glasses with AC chip nanocalorimetry and (ii) development of AC chip nanocalorimetry. In the first part of the thesis, the kinetic stability of vapor-deposited glasses and correlation to form stable glasses are discussed (Paper 2.1, Paper 2.2 and Paper 2.5). The AC chip nanocalorimetry was developed with different cooling systems and modified with laser modulation, and subsequently the frequency range was extended up to MHz, which is presented in the second part of the thesis (Paper 2.3 and Paper 2.4). Through the development and improvement, the AC chip nanocalorimetry allows measurements in a wide temperature and frequency range with sufficient sensitivity for investigation of nm thin films. This will provide information regarding the two main questions of this thesis.

1.2 Part I: Investigation of vapor-deposited glasses

The glasses produced by physical vapor deposition with substrate temperatures near 0.85 T_g exhibit extraordinary properties, including higher kinetic stability,[12-15] lower enthalpy,[12, 13, 16-18] lower heat capacity[19, 20] and higher density.[15, 21] The ability to create stable vapor-deposited glasses is attributed to a surface layer with enhanced mobility, where the molecules can efficiently find a lower energy configuration before being buried by next layer of molecules.[13]

1.2.1 Influence of deposition conditions on stable glasses

Prior to 2007, the literature reported that vapor deposition prepared unstable materials with high enthalpy and low density.[7, 9, 22-24] This is due to vapor deposition of samples at very cold substrates, where the molecules stick to the substrate and are immobile for configurational sampling. At substrate temperatures not too far below the glass transition temperature, molecules arriving at the sample surface may have sufficient mobility to sample different configurations in the time for which they are part of a mobile surface layer. On the other hand, if the sample is deposited at substrate temperatures very near or above glass transition temperature, the molecules are deposited in the supercooled liquid and on cooling will form an ordinary liquid-cooled glass. Following this line of argument, the deposition conditions (e.g. substrate temperature and deposition rate) influence the kinetic stability of the as-deposited glasses.

Stability of as-deposited glasses is indicated by the characteristics of the heat capacity curves: the heat capacity of the as-deposited glass and the onset temperature for the transformation of the as-deposited glass into the supercooled liquid.[12]

The onset temperature, T_{onset} is defined as the intersection of the extrapolated glassy line and the tangent of the transformation from glassy state to supercooled liquid state. At T_{onset}, the molecules have sufficient energy to surmount the barriers imposed by stable glass packing. This allows transformation into supercooled liquid, and an increase in heat capacity is observed as a consequence of configurational sampling. On the contrary, the molecules remained immobile below T_{onset}. Therefore T_{onset} for the transformation into the supercooled liquid is an important measure of the kinetic stability of the as-deposited glasses. The higher the temperature is required to dislodge the molecules from the glass, the greater is the kinetic stability of the as-deposited material.

The fractional C_p decrease is utilized to characterize the difference in heat capacity between as-deposited (AD) and ordinary glasses (OG)[19, 20]

$$\text{Fractional } C_p \text{ decrease} = 1 - \frac{C_p(\text{AD})}{C_p(\text{OG})} \tag{2}$$

The lower heat capacity of the as-deposited glasses can be linked to the vibrational degrees of freedom which may be associated to the packing of the glasses.[25]

The increased stability of a glass due to the enhanced surface mobility was also observed directly by other experiments (not involving vapor deposition) that molecular glasses have highly mobile surfaces at temperatures just below T_g, and theoretical models support this idea.[26-30] For the glass formers that do form stable glasses, it has been established that deposition conditions affect the kinetic stability of the glass. Thus far, influence of the deposition conditions has been investigated in a wide substrate temperatures but limited deposition rates.[14, 18, 20, 25-34]

When a molecule is deposited onto the surface of a growing glass film, it becomes part of a mobile surface layer, only if the temperature of the substrate is not too low. The molecules near the surface have the mobility to rearrange to reach more efficient packing configuration, before being buried and becoming part of the bulk glass by further deposition. The substrate temperature yielding maximal stability, often around 0.85 T_g, can be viewed as a compromise between molecular mobility at the free surface (which decreases with decreasing temperature) and the driving force towards deep states within the energy landscape (which increase with decreasing temperature).[12] If a sample is deposited at temperature far below T_g, unstable glasses are formed, as investigated by Suga *et al.*, presumably because the surface is essentially immobile on the time scale of deposition. The molecules hit the substrate and have little opportunity to optimize packing before they are trapped.[22]

When the molecules are deposited at lower deposition rates, the molecules would have more time to equilibrate on the surface, resulting in packing arrangements with lower energies and higher barriers to rearrangement.[25, 32, 33] Furthermore, at a given temperature, lowering the deposition rate beyond some values should have no further impact on glass properties because the surface should reach a structure corresponding to a metastable state different from the crystal. Published data are consistent with these ideas but do not fully test them in a large enough range of substrate temperatures and deposition rates for a complete understanding.

Figure 3 shows the heat capacity curves of as-deposited ethylcyclohexane and tetrachloromethane, deposited at different substrate temperatures $T_{\text{substrate}}$. The film thickness is kept constant at 400 nm, while the deposition rate is 2 nm s^{-1} for ethylcyclohexane and 1 nm s^{-1} for tetrachloromethane. The onset temperature and fractional C_p decrease of ethylcyclohexane and tetrachloromethane are collected in Figure 4. The trends of the T_{onset} and fractional C_p decrease are consistent with other reports on stable glasses, where C_p reaches its maximum decrease and the T_{onset} reaches its maximum at substrate temperatures from 0.7 T_g to 0.85 T_g.

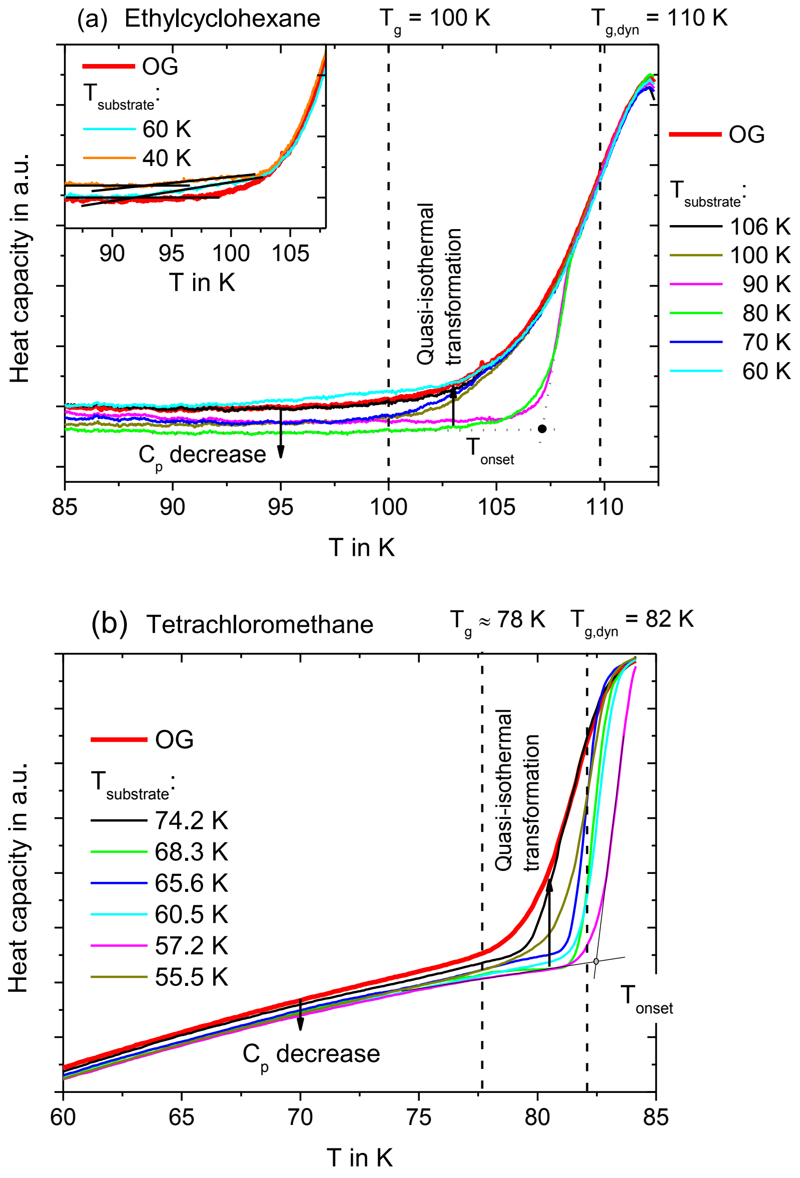


Figure 3: **Heat capacity for glasses of (a) ethylcyclohexane and (b) tetrachloromethane, deposited at different substrate temperatures. A heating curve corresponding to an ordinary liquid-cooled glass (OG, solid red line) is shown for comparison. The determination of the C_p decrease and T_{onset} are also shown. Quasi-isothermal transformation measurements are done at transformation temperatures between $T_g - 1$ K and $T_g - 5$ K. The results are measured with frequency of 20 Hz.**

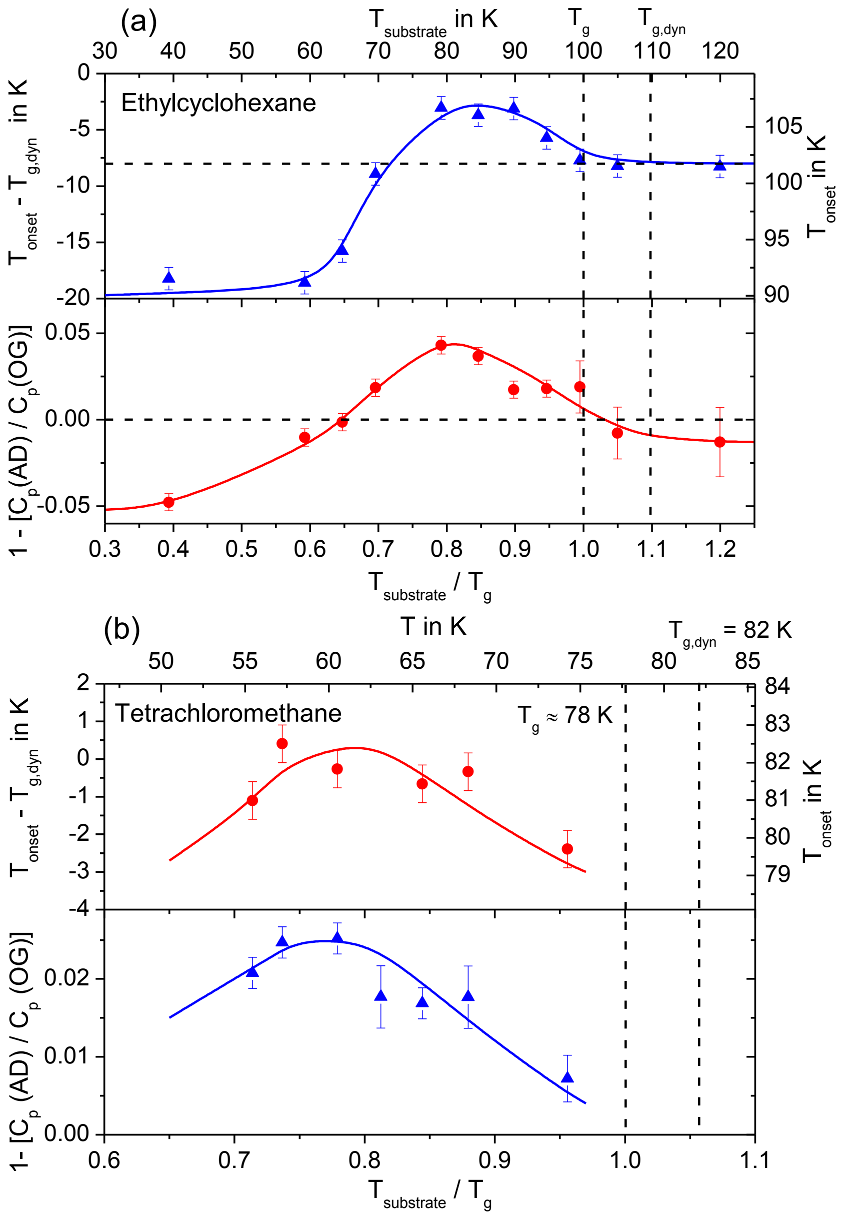


Figure 4: **Onset temperature and fractional C_p decrease of substrate temperature dependency measurement of (a) ethylcyclohexane and (b) tetrachloromethane.**

On the other hand, Figure 5 shows the influence of deposition rate on the kinetic stability of as-deposited glasses of ethylcyclohexane, across the deposition rate by more than four orders of magnitude from 0.002 nm s^{-1} to 60 nm s^{-1} and at seven substrate temperatures from 95 K to 60 K. For each deposition rate at different substrate temperatures, the transformation is collected and presented in Figure 6. At each substrate temperature, lower deposition rates result in higher kinetic stability, presumably because the time available for a molecule to sample different configuration increases. In Figure 6, the deposition rate (top x-axis) is recalculated to free surface residence (bottom axis) by dividing the thickness of one monolayer of ethylcyclohexane (~0.6 nm) with deposition rate in units of nm s^{-1}. The free surface residence time defines the time needed to deposit one monolayer, before being buried by further deposition.

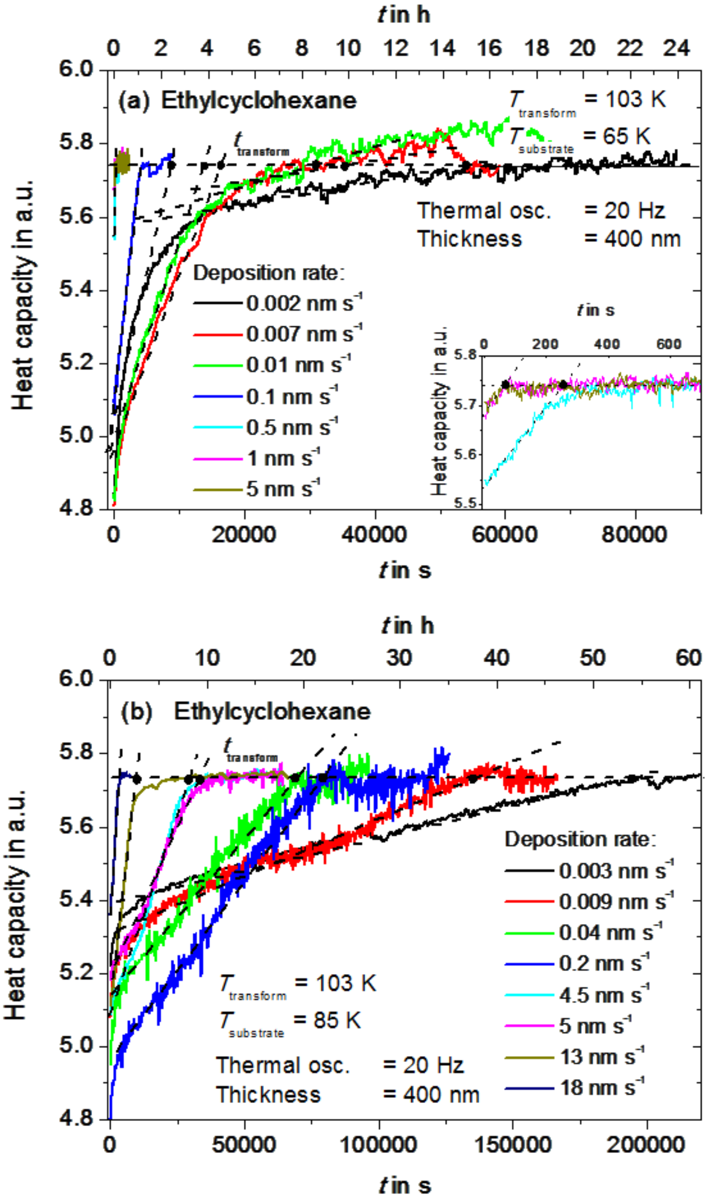


Figure 5: **Quasi-isothermal transformation kinetics at transformation temperature 103 K of as-deposited glasses of ethylcyclohexane into supercooled liquid, for different deposition rates. The samples were deposited at substrate temperatures (a) 65 K and (b) 85 K.**

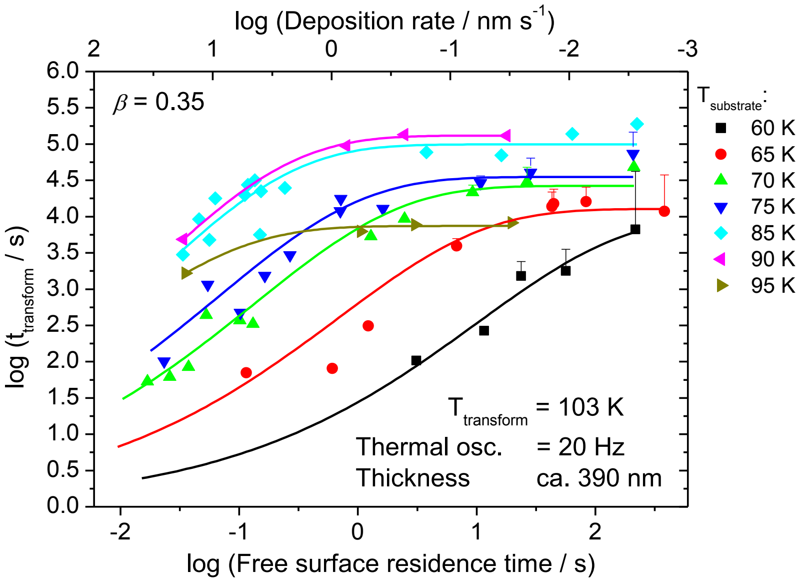


Figure 6: **Quasi-isothermal transformation time as a function of free surface residence time, which is the time needed to deposit one monolayer of ethylcyclohexane. The free surface residence time is calculated from the deposited rate which is given on the top axis.**

1.2.2 Quasi-isothermal transformation experiments

Quasi-isothermal transformation experiments with AC chip nanocalorimetry provide a precise analysis of the kinetic stability of the as-deposited glasses, in addition to temperature scanning measurements. The kinetic stability of the as-deposited glasses is quantified by the time needed for transformation from an as-deposited glass to the supercooled liquid.

Figure 7 shows isothermal transformation of as-deposited glasses of ethylcyclohexane and tetrachloromethane at different transformation temperatures $T_{\text{transform}}$. The as-deposited glasses transformed to supercooled liquid with the increase in heat capacity and the time needed to complete the transformation is denoted as $t_{\text{transform}}$.

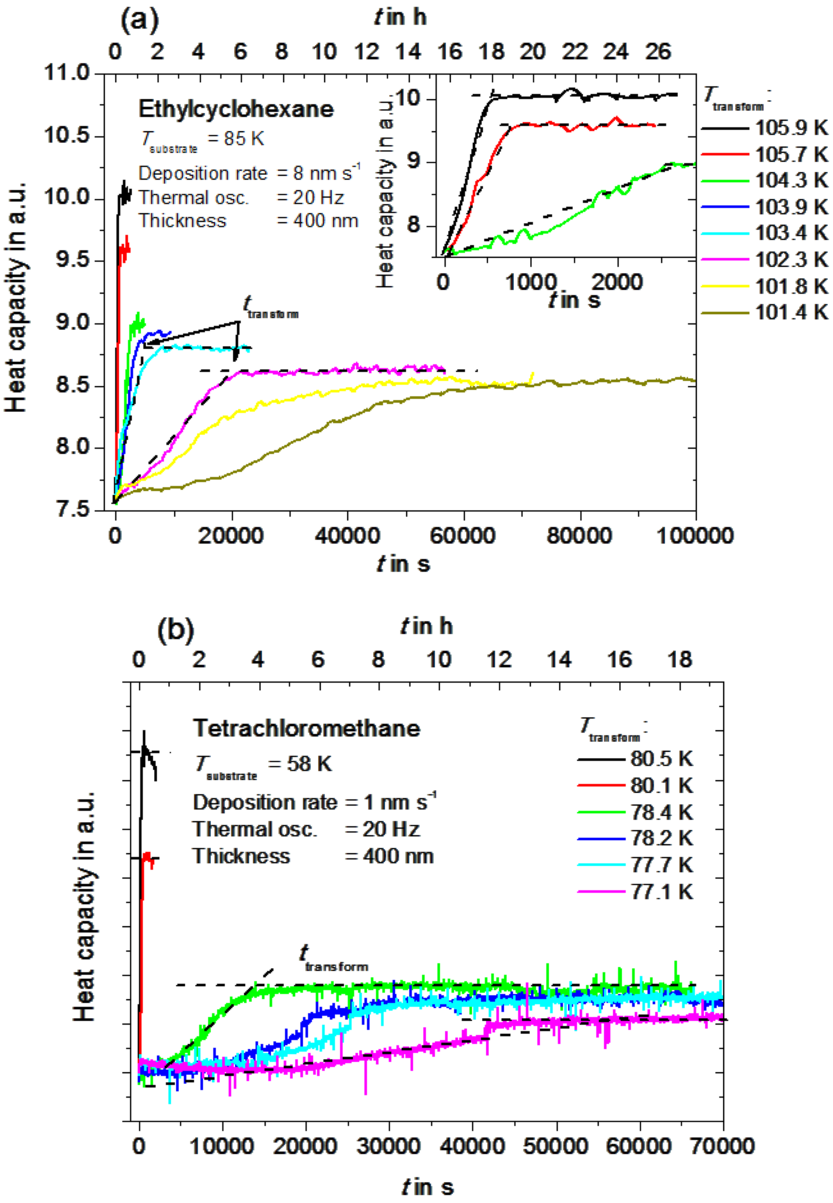


Figure 7: **The increase in heat capacity during isothermal transformation of (a) ethylcyclohexane and (b) tetrachloromethane, from the as-deposited glass to the supercooled liquid at the indicated transformation temperature, $T_{\text{transform}}$.**

1.2.3 Role of fragility in stable glass formation

There have been long discussions as to why some glass formers form stable glasses, while others do not. For most investigated stable glass formers, the common feature is that they have relatively large values of fragility.[35, 36] Some authors have concluded that glasses of high kinetic stability can only be formed from very fragile liquids via vapor deposition,[35, 36] instead of strong liquids.[8, 37]

Glass formers are distinguished with regards to their steepness index or fragility, *m*. The fragility, *m* is defined as the derivative of the logarithm of the structural relaxation time, $\log(\tau_\alpha)$ over T_g / T as the temperature approaches T_g

$$m = \left.\frac{d\log(\tau_\alpha)}{d(T_g / T)}\right|_{T=T_g} \tag{3}$$

where $\log(\tau_\alpha)$ is determined from the Vogel-Fulcher-Tammann (VFT) equation of glass forming materials. The fragility characterizes how rapidly the dynamics of a material slows down as it is cooled towards the glass transition, shown in Figure 8 as Angell plot and in Table 1 for a wide range of fragility.

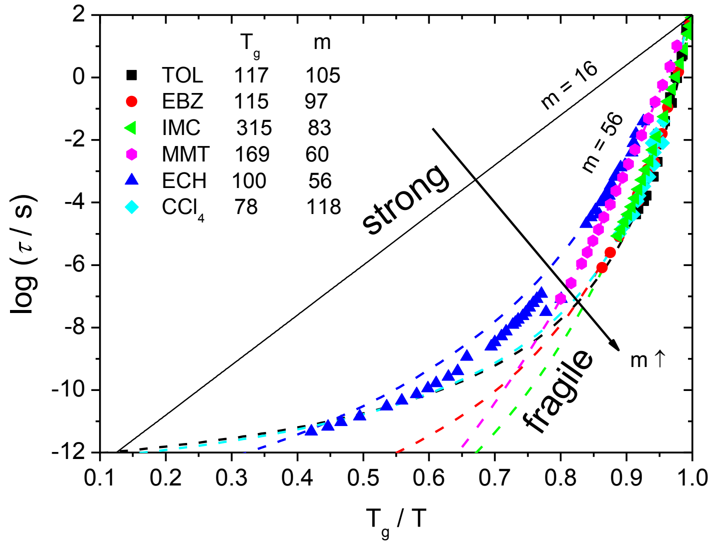
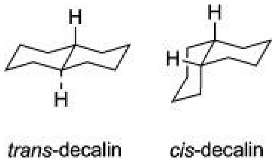
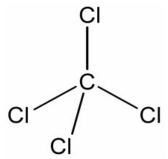
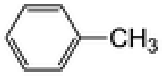
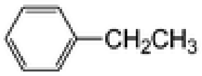
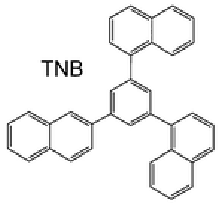
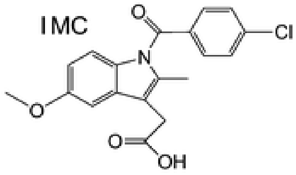
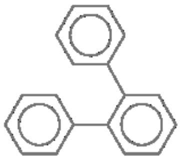
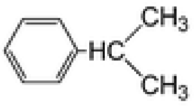
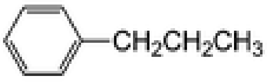
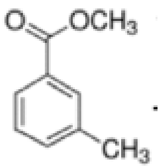
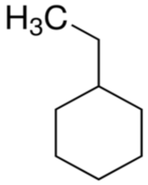


Figure 8: **Angell plot depicts the fragility of glass formation from strong to fragile glass formers. The solid black line indicates Arrhenius behavior of a very strong glass former.**

Table 1: **Stable glass formers produced by vapor deposition over a wide range of fragility and molecular structures.**

Glass formers		T_g in K	m	Molecular structure	References
cis/*trans*-decalin		135	145		38

Tetrachloromethane	CCl_4	78	118		
Toluene	TOL	117	105		20, 39, 40
Ethylbenzene	EBZ	115	97		18, 20, 21, 37
1,3-bis-(1-naphthyl)-5-(2-naphthyl)-benzene	TNB	348	86		13
Indomethacin	IMC	315	83		13, 41
o-terphenyl	OTP	242	81		42, 43
Isopropylbenzene	IPB	129.4	78		15
Propylbenzene	PB	125.7	75		15
Methyl-*m*-toluate	MMT	169	60		44, 45

Ethylcyclohexane	ECH	100	56		[37, 46]

Recent investigation of methyl-*m*-toluate and ethylcyclohexane, which are among the least fragile organic glass formers with $m \approx 60$, shows that these systems also exhibit stable glass formation.[44, 46]

1.2.4 Role of molecular structure in stable glass formation

Another common molecular characteristic among the stable glass formers is that they have anisotropic molecular structure. To date, only a few organic substances have been studied by vapor deposition to investigate the ability to form stable glasses, shown in Table 1. These stable glass formers have molecules with ring structure that allows anisotropic orientation on the surface during deposition. Stable glasses with anisotropic molecular orientation have been demonstrated by ellipsometry measurements of their optical properties.[47-49] and determination of their structure by x-ray scattering experiments.[50] This leads to the question whether an asymmetric structure is a prerequisite for the ability to form stable glasses. This hypothesis is put forward by the observation that some stable glasses show optical anisotropy.[47-49, 51, 52] In order to clarify this hypothesis, the nearly isotropic glass former, tetrachloromethane, is investigated.

1.3 Part II: Development of AC chip nanocalorimetry

The basic physical background of AC calorimetry is described in details by Kraftmakher,[53] where a small periodic heat flow is provided and the resulting complex temperature amplitude is measured. The AC calorimetry is a useful measuring technique, as it can be straight forwardly linked to the dynamics of the molecular processes under investigation (e.g. dynamic glass transition, structural relaxation). Temperature oscillation caused by a periodically applied power to the sample is linked to its heat capacity. The fundamental formula of AC calorimetry in the complex plane is

$$C(\omega) = \frac{p}{i\omega\theta_0} \tag{4}$$

where $C(\omega)$ is the apparent complex heat capacity, p the power amplitude, ω the corresponding angular modulation frequency and θ_0 the modulated temperature amplitude. The complex modulated temperature amplitude is inversely proportional to the total heat capacity, which is the sum of sample and addenda heat capacities.

By applying semiconductor chip sensors in calorimetry, a new level of sensitivity and an extended frequency range of up to a few kilohertz are achieved,[54-56] due to decrease in size of the measured sample (sub-microgram). The addenda heat capacity of the chip sensor is often smaller than the sample heat capacity, thus reducing the errors of the sample heat capacity determination.

In order to investigate the vapor-deposited glassy samples, an *in situ* differential AC chip nanocalorimetry was used in a vapor deposition chamber.[54, 55, 57] The differential setup of the AC chip nanocalorimetry further increases the sensitivity as the influence of the apparent addenda heat capacity is minimized, in order to allow measurement of very small differences in glassy heat capacity. In the first setup by Ahrenberg,[57] the vapor deposition chamber was cooled by liquid nitrogen in a vacuum system that can reach a base pressure of about 10^{-6} Pa. The cooling system allows measurements down to about 100 K.

The limitation is overcome by a closed cycle helium cryostat, Model CH-204SN, Cold Edge Technologies, USA, which allows measurements in a wider temperature range down to 10 K. The second setup, shown in Figure 9, also has two pairs of sensors located in the calorimeter cell, which allows simultaneous measurements for fast-scanning and AC calorimetry. Fast scanning calorimetry measurements are still in progress for future works. The sensors XI39390 (Figure 10) used for the vapor deposition measurements are chip nanocalorimeters fabricated by Xensor Integrations, NL.[58] The sensors are coated with SiO_2, which is the substrate material.

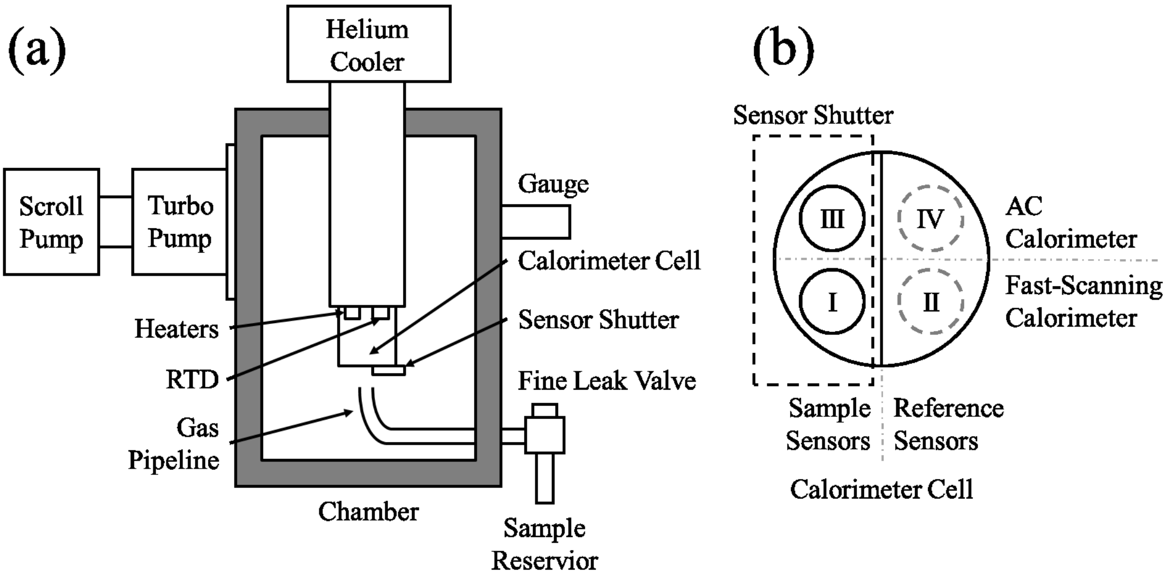


Figure 9: **Schematic of (a) vapor deposition chamber and (b) calorimeter cell. The sensor shutter is shown as the dashed rectangle, which can be slid over and fully cover the sample sensors.[46] This shows the second setup, which is slightly different from the first setup by Ahrenberg.[57]**

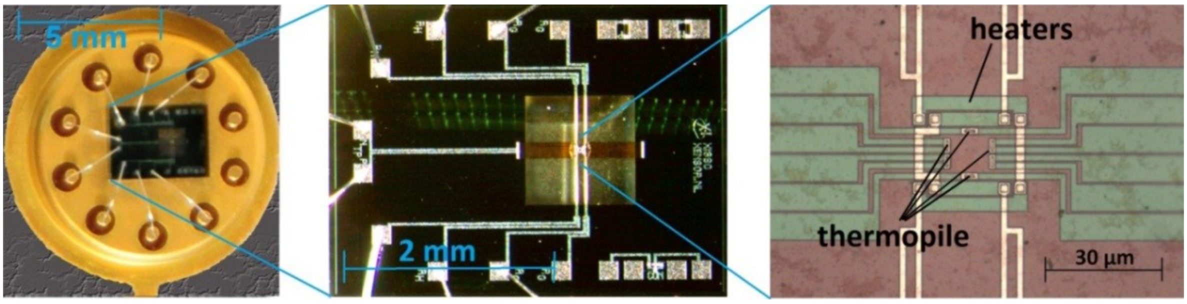


Figure 10: **Images of the chip-nanocalorimeters, XI39390, at three different magnifications. (Left) Chip mounted on TO-5 housing; (middle) the chip, (right) the central part, including the active area with the inner and outer heaters, the six hot junctions of the thermopile and the conducting stripes.[57]**

As AC chip nanocalorimetry can be used to measure very small sample and addenda heat capacity, as well as a small heated area,[59, 60] measurements to higher frequencies (higher cooling rates) can be achieved. But the frequency range of AC chip nanocalorimetry is limited to less than 10^4 Hz. This limitation is due to the small distance (µm) between the thermopile and the heaters on the sensor, which causes an electrical crosstalk at high frequencies. This limits the frequency range as the thermopile signal at the second harmonic of the voltage frequency is undetectable at higher frequencies because of the dominating base frequency signal. A solution to this would be a decoupling of temperature measurement and heating, by introducing a modulated laser as the external heating source.

For the laser heated AC chip nanocalorimeter shown in Figure 11, a heating power on the order of 10 µW is adequate. A light beam is generated by a laser diode, and was directed and shaped by a glass fiber onto the thermocouple hot junction, as shown in Figure 13. The fiber must be placed very close (≈ 10 µm) to the calorimeter chip to avoid the enlargement of the spot size. The modulation depth is adjustable and can reach close to 100 %. It is controlled by the oscillator output of the digital lock-in amplifier. The device can work as a single sensor AC calorimeter.[61]

The chip sensors with only one thermopile used are XI274 with XEN014 ceramic flat housing, shown in Figure 12, similar to the sensors in AC chip nanocalorimetry. The central heated region of dimension 10 × 8 µm^2 for XI274 sensor is much smaller than the membrane and can be considered as point source of heat into the surrounding gas. This smaller working area decreases the thermal lag, and increases accuracy and frequency range up to 10^6 rad s^{-1} at still detectable temperature amplitudes of about 1 mK as shown in reference [62].

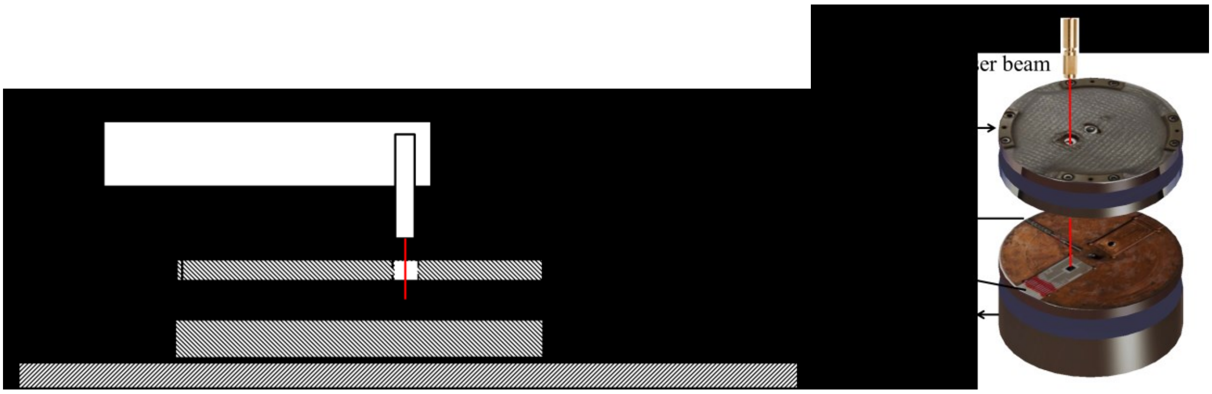


Figure 11: **Schematic of (a) the laser-modulated AC chip nanocalorimeter and (b) the calorimetric cell.**

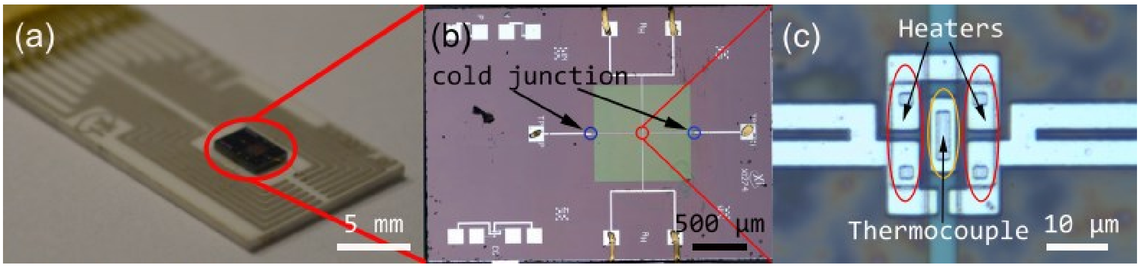


Figure 12: **(a) Calorimetric sensor XI274 on ceramic housing XEN-40014. (b) Enlarged view of the chip with the free-standing SiN_x membrane (green square) and the bond pads (small white squares). (c) The working area with the heater and the thermocouple hot junction.**

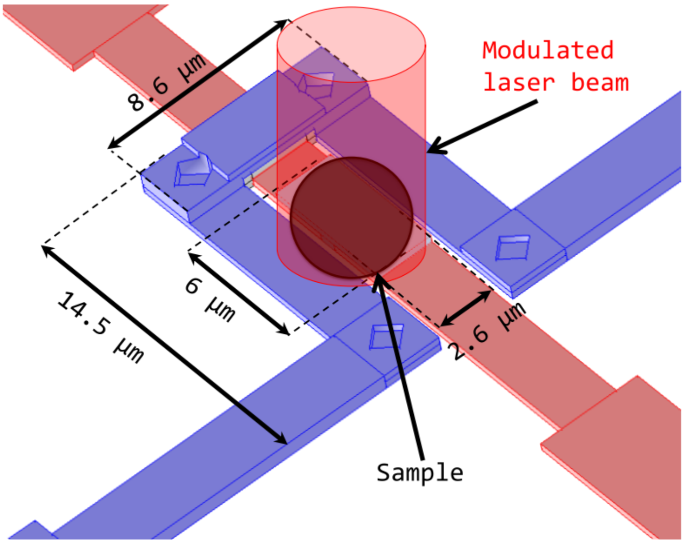


Figure 13: **The position of the modulated laser beam that shines directly only on the sample and on the hot junction of the thermocouple. The two heaters and the aluminum electric connections are shown in blue. The doped poly-Si stripes of the thermocouple are in red and the hot junction of the thermocouple, made by an aluminum connection, in gray.**

The dynamic glass transition is shown as a step in the real part and a peak in the imaginary part of the laser modulated AC chip nanocalorimetry. The empirical Vogel-Fulcher-Tammann (VFT) equation describes well the typical nonlinear behavior of the dynamic glass transition in a relaxation map, log (τ_α) with $\tau_\alpha = 1/\omega$ versus reciprocal temperature

$$\log(\tau_\alpha) = A + \left(\frac{B}{T - T_0} \right) \tag{5}$$

with τ_α the primary structural relaxation time, T temperature and T_0 the Vogel temperature. The laser modulated AC chip calorimetry measurements in a broad frequency range add valuable knowledge about the glass transition, as only segmental relaxation (dynamic glass transition) process appears which is linked to entropy fluctuation. The nonlinear behavior of log(τ_α) as function of the reciprocal temperature in the relaxation map describes a slowing down of the dynamics, angular frequency, ω of the molecular fluctuation, in a supercooled liquid at decreasing temperature.

Laser modulated AC chip nanocalorimetry is used to characterize the dynamic glass transition of polystyrene (PS) and poly(methyl methacrylate) (PMMA) over a wide range of frequencies, shown in Figure 14. PS and PMMA both do not crystallize and are chemically stable after being heated to high temperature of about 250 °C for a short times (<100 s).

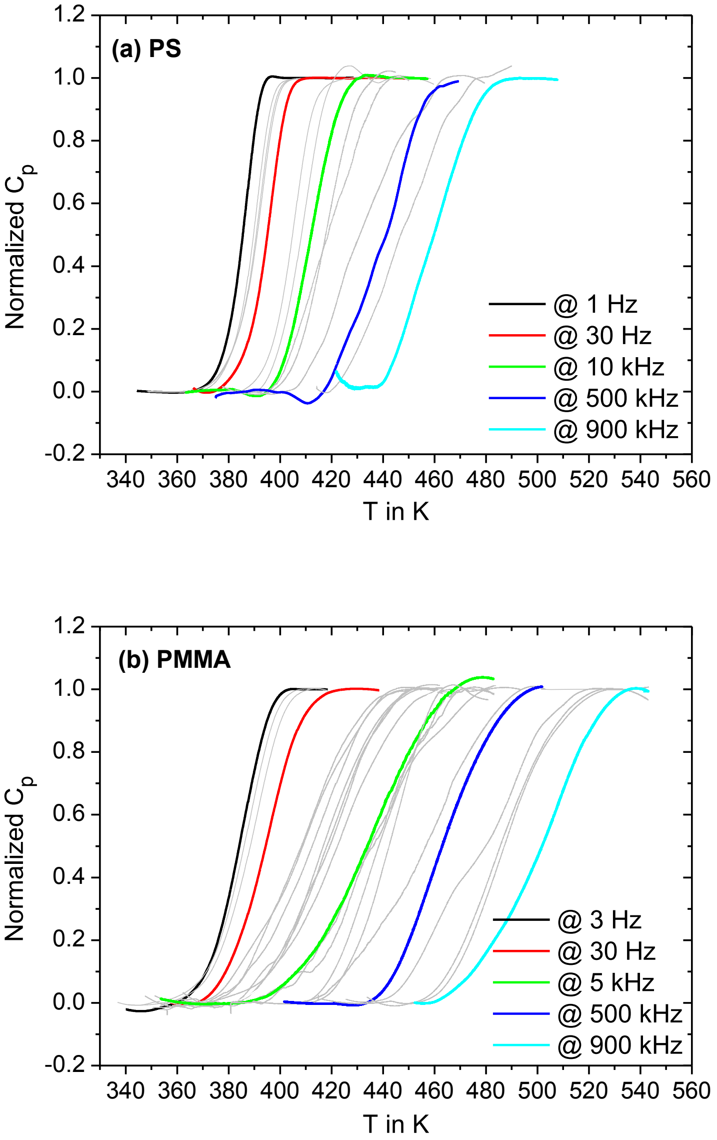


Figure 14: **The heat capacity of (a) PS and (b) PMMA was normalized at the dynamic glass transition for frequencies ranging from 1 Hz to 900 kHz.**[62, 63]

1.4 General Conclusions

In first part of this thesis, glasses produced by physical vapor deposition have been extensively investigated. In order to understand the stable glasses, vapor-deposited glasses of toluene, ethylbenzene, ethylcyclohexane and tetrachloromethane are characterized with an *in situ* differential AC chip nanocalorimetry. With the AC chip nanocalorimetry, the transition of the as-deposited glass into the supercooled liquid by temperature scanning measurements and isothermal transformation measurements can be followed and consequently the kinetic stability of the as-deposited glasses can be quantified. This will provide information regarding the properties of the stable glass formers and verify the possible correlations on the ability of stable glass formation.

The results have shown the dependency of the deposition conditions, such as deposition rate and substrate temperature, on the stability of the as-deposited glasses (Paper 2.1, Paper 2.2 and Paper 2.5).

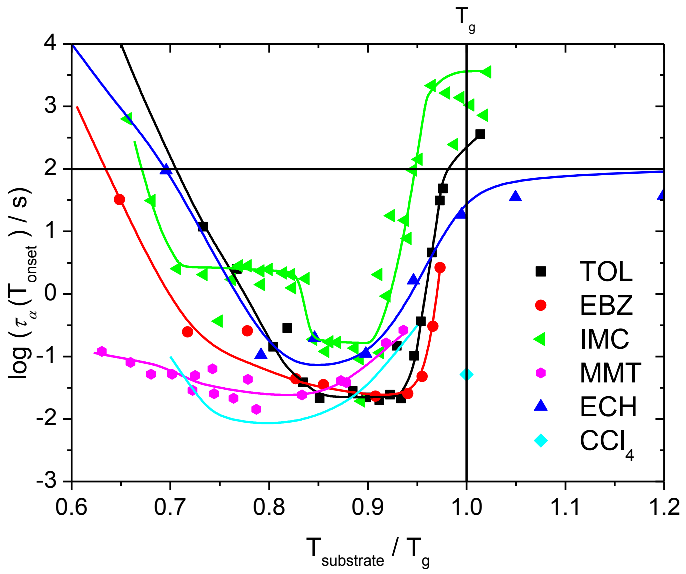


Figure 15: **Comparison of kinetic stability of vapor-deposited ethylcychlohexane (ECH; blue triangles),[46, 64] and tetrachloromethane (CCl_4, cyan diamonds), with other stable glass formers: toluene (TOL; black squares),[20, 40] ethylbenzene (EBZ; red circles),[20, 37] indomethacin (IMC; green left triangles)[41, 48] and methyl-*m*-toluate (MMT; magenta hexagonals),[44, 45, 65] by comparing the α-relaxation time at the beginning of the transformation, $\tau_\alpha(T_{onset})$. For the y-axis, the T_{onset} is converted to $\tau_\alpha(T_{onset})$ to develop a scale that is independent of the glass transition temperature and fragility. Lower values of $\tau_\alpha(T_{onset})$ indicate greater kinetic stability for the as-deposited glass.**

The most kinetically stable glasses with lower heat capacities and high onset temperatures of ethylcyclohexane and tetrachloromethane are formed with substrate temperature during deposition between 0.7 T_g to 0.85 T_g, which is consistent with results for other stable glass formers shown in Figure 15. In Figure 15, the T_{onset} of the as-deposited glasses was recalculated into the corresponding structural relaxation time at T_{onset}, $\tau_\alpha(T_{onset})$, to remove any dependence on the glass transition temperature and only the mobility of the supercooled liquids at the transformation temperature was compared. As shown in Figure 15, the similar curves for the different substances highlight the importance of mobility in the supercooled liquid for the transformation from the stable glass into the supercooled liquid. For all substances, the most stable glass transforms when $\tau_\alpha(T_{onset}) \approx 0.1$ s. That is about three orders of magnitude faster than $\tau_\alpha(T_g) \approx 100$ s at the glass transition temperature, T_g, where ordinary glasses transform into the supercooled liquid. This means that the as-deposited glasses require significantly higher mobility in the liquid to allow transformation into the supercooled liquid state, in comparison to liquid-cooled glasses.

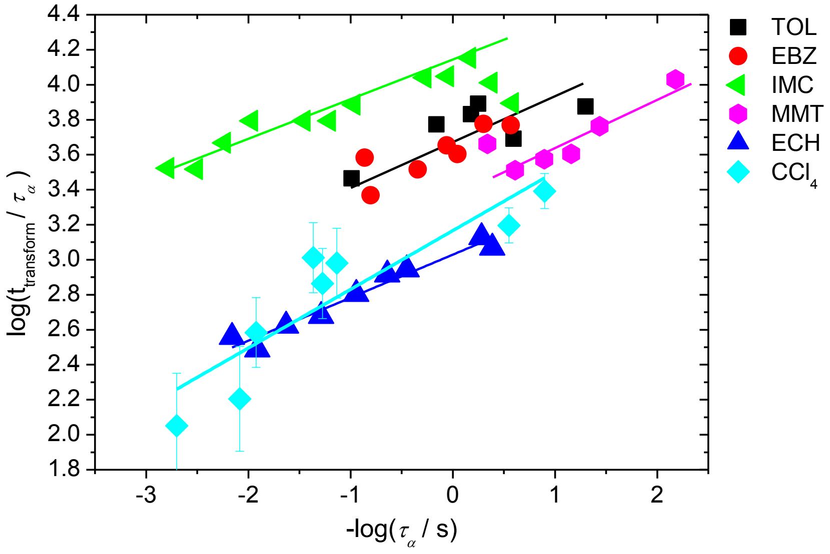


Figure 16: Normalized isothermal transformation time, $t_{transform}$ by structural relaxation time, τ_α as a function of τ_α at the transformation temperature, $T_{transform}$ for ethylcyclohexane (ECH, blue triangles) and tetrachloromethane (CCl_4, cyan diamonds). The substrate temperature and deposition rate of ethylcyclohexane (85 K, 8 nm s^{-1})[46, 64] and tetrachloromethane (58 K, 1 nm s^{-1}) glasses were kept constant. Also included are results for other stable glass formers deposited at comparable substrate temperatures ca. 0.85 T_g and at the given rates for comparison are: toluene at 2 nm s^{-1} (TOL; black squares),[20 40]ethylbenzene at 2 nm s^{-1} (EBZ; red circles),[20, 37] indomethacin at 0.2 nm s^{-1} (IMC, green left triangles),[41, 66] and methyl-*m*-toluate at 0.2 nm s^{-1} (MMT, magenta hexagonals).[44, 45, 65] The transformation times of these stable glass formers are recalculated for thickness of ca. 400 nm.

Figure 16 shows a comparison between the isothermal transformation times for stable glasses of ethylcyclohexane and tetrachloromethane with other stable glass formers.[20, 44, 46, 65, 66] The isothermal transformation time, $t_{\mathrm{transform}}$, was normalized by the structural relaxation time, τ_α, with logarithm of the ratio $t_{\mathrm{transform}}/\tau_\alpha$ at the respectively $T_{\mathrm{transform}}$, while the $T_{\mathrm{transform}}$ was replaced by its respective τ_α in x-axis, in order to allow comparison to other substances. From the normalization as shown in the y-axis of Figure 16, it is seen that the $t_{\mathrm{transform}}$ are much longer in comparison to τ_α. When annealing above T_g, the ratio of isothermal transformation time to structural relaxation time reaches nearly four orders of magnitude, which is similar to the ratio obtained from onset temperatures in Figure 15. The as-deposited glasses require almost four orders of magnitude longer time to transform into supercooled liquid, indicating much greater kinetic stability in comparison to traditional liquid-cooled glasses, which transform on a timescale roughly equal to τ_α. Similar trends for ethylcyclohexane, tetrachloromethane and other substances were observed, which again signified glasses with comparable kinetic stability. The strong connection of $t_{\mathrm{transform}}$ on τ_α indicates that the mobility of the supercooled liquid controls the rate at which a growth front can move into the stable glass.

In Paper 2.1, kinetic stability of as-deposited glasses of ethylcyclohexane at deposition rates by more than four orders of magnitude from 0.002 nm s^{-1} to 60 nm s^{-1} is also investigated. These measurements are performed at seven substrate temperatures from 95 K to 60 K, which covers the range from 0.95 T_g to 0.6 T_g. The experiments provide the first opportunity to investigate how the kinetic stability of the as-deposited glasses depends upon the deposition rate across a wide range for different substrate temperatures.

The investigations of several glass formers so far have shown that some glass formers form stable glasses by vapor deposition while others do not. There have been some suggestions as to the controlling factors (e.g. fragility, molecular structure) to the ability to form stable glasses. However no conclusive results have been presented, which leads to our work.

In Paper 2.1, ethylcyclohexane was chosen to study if a less fragile liquid can form stable glasses because ethylcyclohexane has kinetic fragility m of 56, which is near the strong limit of organic glass formers. The results in Paper 2.1 show that ethylcyclohexane can form highly kinetically stable glasses, which disproves that kinetically stable glasses can only be made from highly fragile liquid as suggested by some authors.[35, 36] This concludes that fragility is not a controlling factor in the ability to form kinetically stable glasses by vapor deposition and extends the range of m values currently between 56 and 147.[38]

On the other hand in Paper 2.5, tetrachloromethane was investigated as it has pseudo spherical structure with no polarity. Given its nearly spherical structure, it is not surprising that tetrachloromethane is not a good glass former. On the contrary, its structure and lack of polarity increase surface mobility that could improve the packing during vapor deposition. Therefore, it is of interest to determine whether near isotropic structure of tetrachloromethane will increase the possibility of stable glass formation.

The results in Paper 2.5 present not only the first stable glass formation of tetrachloromethane by vapor deposition, but also shows that highly stable glasses can be formed from nearly isotropic molecules, indicating that anisotropy is not an essential feature of stable glass formation. This also indicates that enhanced surface mobility plays a more important role for stable glass formation regardless of the molecular structure.

The results on stable glass formation presented were only possible due to further developments of the AC chip nanocalorimetry. In the second part of this thesis, these developments of the AC chip nanocalorimetry are presented, particularly the extension of the temperature range down to 10 K and the frequency range towards 1 MHz.

With the combination of chip technology and micro-electro mechanical systems (MEMS), it is possible to fabricate calorimeter sensors that are able to measure samples with nanogram masses and energies in pJ, hence increasing the sensitivity to characterize vapor-deposited glasses. In order to measure low temperatures, liquid nitrogen cryostat is incorporated with AC chip nanocalorimetry and later replaced with closed-cycle helium cryostat for even lower temperatures down to 10 K. However there is still limitation to the measurable frequency range due to the electrical crosstalk between heaters and thermocouple at high frequencies. Therefore in order to further extend the frequency range, the AC chip nanocalorimetry is improved with modulated laser heating. This allows for the measurement of the dynamic glass transition for 11 orders of magnitude in frequency, which was verified with polystyrene and poly(methylmethacrylate). (Paper 2.3 and Paper 2.4) These data provide an overlap in time scales with quasielastic neutron scattering (QENS), leading to a new interesting field of application of AC chip nanocalorimetry in glass transition investigations.

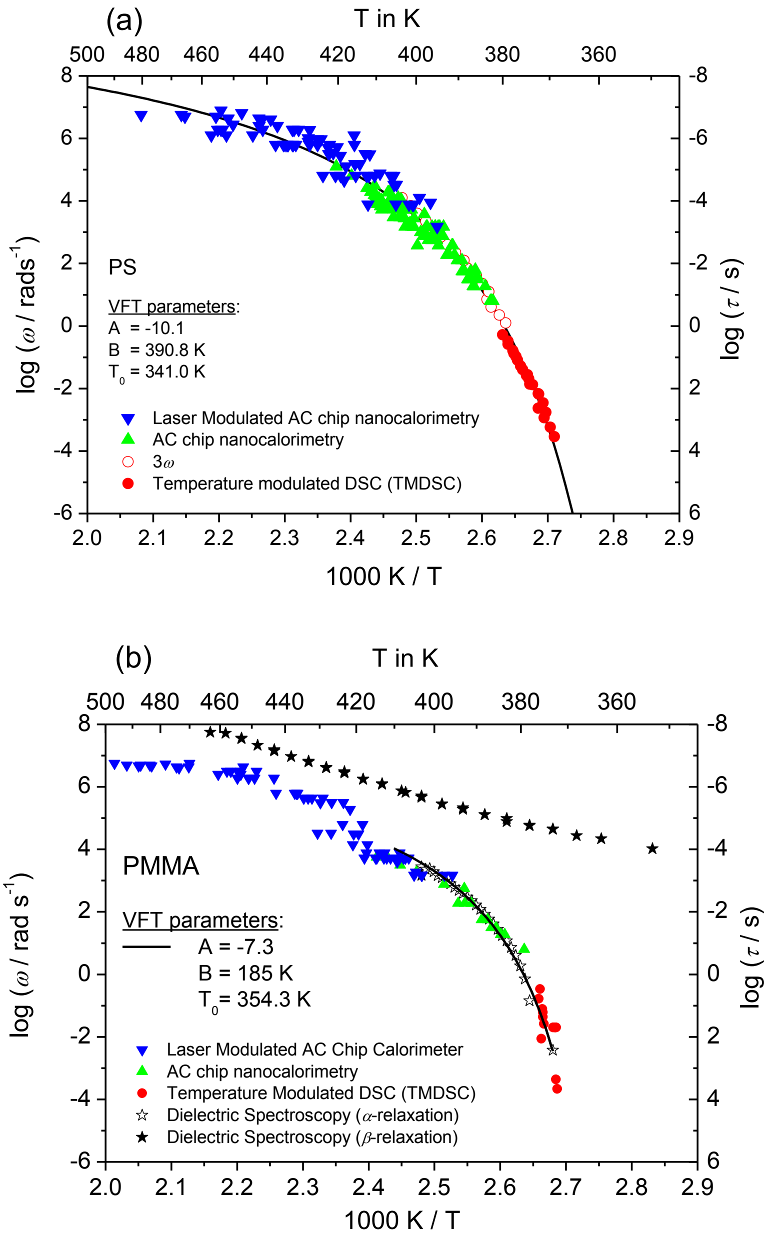


Figure 17: **Relaxation map of (a) polystyrene (PS) and (b) poly(methylmethacrylate) (PMMA) over 11 orders of magnitude in frequency range.**

In Paper 2.3 and Paper 2.4, dynamic glass transition of polystyrene (PS) and poly(methyl methacrylate) (PMMA) are presented in a wide frequency range up to almost 1 MHz. The results from laser modulated AC chip nanocalorimetry provide overlaps and in good agreement with data from other devices, e.g. TMDSC and dielectric spectroscopy.

1.5 General Summary

In summary, there are several achievements in this thesis listed as follows:

(i) The as-deposited glasses of toluene, ethylbenzene, ethylcyclohexane and tetrachloromethane show apparent lower heat capacity and higher onset temperature. These indicate that glasses with high kinetic stability can be produced by physical vapor deposition. (Paper 2.1, Paper 2.2 and Paper 2.5)

(ii) The kinetic stability of the as-deposited glass formers has dependency on the deposition conditions, where highest kinetic stability is achieved with deposition at substrate temperatures around 0.85 T_g and lower deposition rate increases the kinetic stability at lower deposition temperatures. (Paper 2.1)

(iii) Ethylcyclohexane, which is a strong glass former of $m \approx 60$, exhibits stable glass formation, disproven the correlation between fragility and the ability to form stable glasses. The fragility range is extended down to $m \approx 60$. (Paper 2.1)

(iv) Tetrachloromethane, which has a pseudo isotropic molecular structure, also exhibits stable glass formation, indicating that anisotropy is not an essential feature of stable glass formation, while enhanced surface mobility plays a more important role for stable glass formation regardless of the molecular structure. (Paper 2.5)

(v) Frequency range of up to 11 orders of magnitude is achieved by combining measurements from laser-modulated AC chip nanocalorimeter and four different temperatures modulated differential scanning calorimeters (TMDSC). (Paper 2.3 and Paper 2.4)

With these achievements, it is shown that fragility and molecular symmetry are not the controlling factors for the formation of stable glasses.

1.6 Outlook

The as-deposited tetrachloromethane at substrate temperatures close to glass transition temperature exhibits extraordinary properties as other stable glasses. However due to the pseudo isotropic structure of tetrachloromethane, there is a chance of forming nanocrystalline structures at deposition, similar to the phases described in references [67, 68]. Exact determination of the structure of the as-deposited tetrachloromethane might be possible with infrared spectroscopy and would be very interesting for better understanding of stable glasses.

Glass formers like ethanol, *n*-propanol, benzyl alcohol, 2-ethyl-1-hexanol, propylene glycol and ethylene glycol will be investigated next. These glass formers have hydroxyl group but with different chain length or with other functional groups. This will provide a more comprehensive study on the influence of molecular structures (e.g. phenyl, hydroxyl functional groups) on formation of stable glasses.

On the other hand, propylene glycol has been measured with laser-modulated AC chip nanocalorimetry and conventional calorimetry for relaxation times down to about 100 ns and its characteristic length is determined from the dynamic glass transition according to Donth.[67] Since quasielastic neutron scattering (QENS) can finally achieve time scales to about 1 μs, an overlap is achieved and the characteristic lengths from QENS and from calorimetry measurement are compared. Independent determinations of characteristic length from calorimetric measurements and QENS may provide some information on thermodynamics of considerably small systems, particularly whether temperature fluctuates and insight on whether there is a characteristic length associated to the glass transition.[68] With this, the developed AC chip nanocalorimetric methods may contribute to a better understanding of glass transition, in addition to studies on stable glass formation.

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Chapter 2: Publications

2.1 **How much time is needed to form a kinetically stable glass? AC calorimetric study of vapor-deposited glasses of ethylcyclohexane**

Contributions: Preparation of the manuscript, AC chip nanocalorimetry measurements and analysis of experimental data

2.2 **In situ investigation of vapor-deposited glasses of toluene and ethylbenzene via alternating current chip-nanocalorimetry**

Contributions: Preparation of the manuscript, AC chip nanocalorimetry measurements and analysis of experimental data

2.3 **High frequency alternating current nano calorimeter with laser heating**

Contributions: Preparation of the manuscript, TMDSC, AC calorimetry and laser-modulated AC chip nanocalorimetry measurements, analysis of experimental data

2.4 **Glass transition cooperativity from broad band heat capacity spectroscopy**

Contributions: Preparation of the manuscript, TMDSC, AC calorimetry and laser-modulated AC chip nanocalorimetry measurements, analysis of experimental data and theoretical calculations

2.5 **Glass transition and stable glass formation of tetrachloromethane**

Contributions: Preparation of the manuscript, AC chip nanocalorimetry measurements and analysis of experimental data

2.1 How much time is needed to form a kinetically stable glass? AC calorimetric study of vapor-deposited glasses of ethylcyclohexane

Journal of Chemistry Physics, 2015, 142: 054506

DOI: http://dx.doi.org/10.1063/1.4906806

Author contributions

Y.Z. Chua	Preparation of the manuscript, AC chip nanocalorimetry measurements and analysis of experimental data
M. Ahrenberg, M. Tylinski and M.D. Ediger	Discussion and improvement of the manuscript
C. Schick	Discussion and improvement of the manuscript, and supervision of the research

2.2 *In situ* investigation of vapor-deposited glasses of toluene and ethylbenzene via alternating current chip-nanocalorimetry

Journal of Chemistry Physics, 2013, 138: 024501

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Author contributions

M. Ahrenberg	Preparation of the manuscript, AC chip nanocalorimetry measurements and analysis of experimental data
Y.Z. Chua	Assistance in AC chip nanocalorimetry measurements
K.R. Whitaker, H. Huth and M.D. Ediger	Discussion and improvement of the manuscript
C. Schick	Discussion and improvement of the manuscript, and supervision of the research

2.3 High frequency alternating current nano calorimeter with laser heating

Review of Scientific Instruments, 2013, 84: 073903

DOI: http://dx.doi.org/10.1063/1.4812349

Author contributions

E. Shoifet	Preparation of the manuscript, improvement and development of the laser modulated AC chip nanocalorimetry
Y.Z. Chua[#]	Preparation of the manuscript, TMDSC, AC calorimetry and laser modulated AC chip nanocalorimetry measurements, analysis of experimental data
H. Huth	Discussion and improvement of the manuscript
C. Schick	Discussion and improvement of the manuscript, and supervision of the research

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[#] Contributed equally as first author with E. Shoifet

2.4 Glass transition cooperativity from broad band heat capacity spectroscopy

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Author contributions

Y.Z. Chua	Preparation of the manuscript, TMDSC, AC calorimetry and laser modulated AC chip nanocalorimetry measurements, analysis of experimental data and theoretical calculations
G. Schulz	Contribution on experimental data for cooling rate dependency
E. Shoifet, H. Huth, R. Zorn and J.W.P. Schmelzer	Discussion and improvement of the manuscript
C. Schick	Discussion and improvement of the manuscript, and supervision of the research

2.5 Glass transition and stable glass formation of tetrachloromethane

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Author contributions

Y.Z. Chua	Preparation of the manuscript, AC chip calorimetry measurements and analysis of experimental data
M. Tylinski, S. Tatsumi, M.D. Ediger	Discussion and improvement of the manuscript
C. Schick	Discussion and improvement of the manuscript, supervision of the research

List of Contributions

Publications

1. **Y.Z. Chua**, M. Tylinski, S. Tatsumi, M.D. Ediger, C. Schick. *Glass transition and stable glass formation of tetrachloromethane.* J. Chem. Phys. 144, 2016, 244503
2. M. Tylinski, A. Sepulveda, D. Walters, **Y.Z. Chua**, C. Schick, M.D. Ediger. *Vapor-deposited glasses of methyl-m-toluate: How uniform is stable glass transformation?* J. Chem. Phys. 143, 2015, 244509
3. **Y.Z. Chua**, M. Ahrenberg, M. Tylinski, M.D. Ediger, C. Schick. *How much time is needed to form a kinetically stable glass? AC calorimetric study of vapor-deposited glasses of ethylcyclohexane*. J. Chem. Phys., 2015, 142: 054506
4. **Y.Z. Chua**, G. Schulz, E. Shoifet, H. Huth, R. Zorn, J.W.P. Schmelzer, C. Schick. *Glass transition cooperativity from broad band heat capacity spectroscopy*. Col. Poly. Sci., 2014, 292: 1893-1904
5. M. Ahrenberg, **Y.Z. Chua**, K.R. Whitaker, H. Huth, M.D. Ediger, C. Schick. *In situ investigation of vapor-deposited glasses of toluene and ethylbenzene via alternating current chip-nanocalorimetry*. J. Chem. Phys., 2013, 138: 024501
6. E. Shoifet, **Y.Z. Chua**,[#] H. Huth, C. Schick. *High frequency alternating current nano calorimeter with laser heating*. Rev. Sci. Instr., 2013, 84: 073903

[#] Contributed equally as first author with E. Shoifet

Conferences

1. **Y.Z. Chua**, M. Tylinski, M.D. Ediger, C. Schick. *Glass transition and stable glass formation of carbon tetrachloride*. Lecture, 80. Jahrestagung der DPG und DPG-Frühjahrstagung, 06.03.2016 – 11.03.2016, Regensburg, Germany
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3. **Y.Z. Chua**, M. Ahrenberg, C. Schick, M. Tylinski, M.D. Ediger. *Stable glasses for organic electronics from physical vapor deposition*. Lecture, 3. Treffen des Graduiertennetzwerkes Life, Light and Matter 2016, 22.01.2016, Rostock, Germany
4. **Y.Z. Chua**, M. Ahrenberg, M. Tylinski, M.D. Ediger, C. Schick. *Stable glasses from strong liquids*. Lecture, 79. Jahrestagung der DPG und DPG-Frühjahrstagung, 15.03.2015 – 20.03.2015, Berlin, Germany
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8. **Y.Z. Chua**, G. Schulz, E. Shoifet, H. Huth, R. Zorn, J.W.P Schmelzer, C. Schick. *Glass transition cooperativity from broad band heat capacity spectroscopy*. Poster, APS March Meeting, 02.03.2015 – 06.03.2015, San Antonio, Texas, USA
9. **Y.Z. Chua**, M. Ahrenberg, C.Schick, K.R. Whitaker, M. Tylinski, M.D. Ediger. *Unusual behavior of vapor-deposited glasses of 1-pentene and ethylcyclohexane*

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Erklärung

Hiermit versichere ich, dass ich die beigefügte Dissertation selbstständig verfasst und keine anderen als die angegebenen Hilfsmittel genutzt habe. Alle wörtlich oder inhaltlich übernommenen Stellen habe ich als solche gekennzeichnet.

Yeong Zen Chua