

Glass-forming meta-toluidine: A thermal and structural analysis of its crystalline polymorphism and devitrification

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Abstract

The structural processes of transformation of the fragile glass former *m*-toluidine have been investigated by calorimetric (DSC) and X-ray experiments with some additional kinetic studies of the devitrification process. Recrystallisation is found to be controlled by the passage of the undercooled liquid at temperatures well below the glass transition. This atypical behaviour is basically due to the formation of cracks which cause heterogeneous nucleation. However, an additional non-classical decrease of the nucleation barrier is suspected. The investigation of the phase diagram of the crystalline state itself has revealed an interesting monotropic situation between two phases α and β with distinct X-ray diffraction patterns. This identification is useful in the investigation of the medium-range order which may develop in the liquid state. © 1997 Elsevier Science B.V.

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1. Introduction

Meta-toluidine is liquid at room temperature [1]. As for others disubstituted benzene ring compounds meta-isomerization favours greatly the tendency to supercool [2]. This ability is presently considerably magnified: *m*-toluidine can be deeply supercooled even at cooling rates as low as 10 K/day and gives rise to a calorimetric glass transition at $T_g \approx 186$ K (Fig. 1). It is an interesting glass-forming material for two main reasons:

- The heat capacity jump at T_g is very large ($\Delta C_p / C_{p \text{ glass}} \approx 1$ which, apparently, indicates

that this liquid is very fragile in accordance with Angell's definition [3].

- The metastable liquid can be continuously studied, without interfering recrystallisation effects during isothermal steps of several hours. This is a practical advantage to investigate the structural changes when approaching T_g . Such an investigation is of utmost fundamental interest, since important configurational rearrangement may be suspected in this fragile liquid, in connection with the rapid temperature changes of entropy. We have initiated an investigation of the structural changes of the liquid state by X-rays [4].

For the same reasons which make the non-equilibrium conditions easy to reach and study, the equilibrium phase diagram of this compound is difficult to

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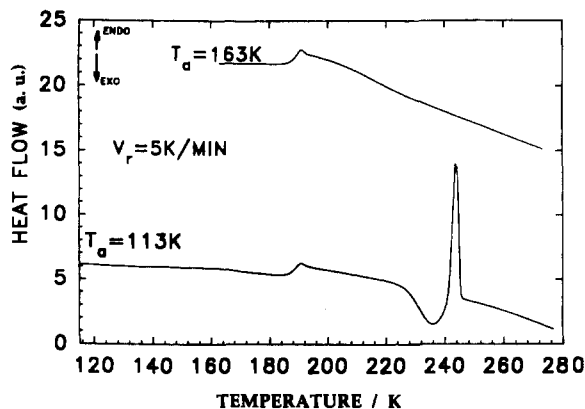


Fig. 1. DSC curves obtained during heating (heating rate 5 K/min) after a quench to two different temperatures $T_a = 163$ K and $T_a = 113$ K. The figure clearly shows the importance of quenching at low temperatures to enhance crystallization at higher temperatures.

determine. Of course, it is fundamental to accurately locate the equilibrium melting temperature T_m in order to know the degree of supercooling of the liquid phase at T_g . It is also of importance to determine the Kauzmann temperature T_K which is the virtual sub- T_g temperature, where the entropy of the undercooled liquid intersects the entropy of the stable crystal [5,6]. In studying the glass behaviour of the system, it is essential to clarify the connection between the structural local order which may develop in the liquid phase and the long-range order of the underlying crystalline phase. The determination of the crystalline-phase diagram is also necessary in order to investigate the possibility of connecting the competition between different crystalline phases to the glass properties. This is truly an open question which may affect both the vitrification (bypassing of crystallisation) and the dramatic freezing behaviour itself [6,7].

In this paper, we report the results of a first investigation by X-ray diffraction of the structural processes involved in the transformation of *m*-toluidine. This study involves some kinetic aspects that, because of their slow evolution, can be followed easily in a time resolved X-ray investigation. It is complemented by a differential scanning calorimetry (DSC) investigation.

This study allows to clarify the devitrification process of the compound. It highlights two crystalline

phases characterised by their X-ray patterns that can form after thermal annealing. The kinetic analysis of the interconversion of these phases is used to discuss their relative stability and to propose a phase diagram for *m*-toluidine.

2. Experimental details

Commercial *m*-toluidine was carefully purified by fractional distillation and checked for purity by gas chromatography. X-ray diffraction measurements were carried out using $\text{CuK}\alpha$ radiation and a curved position-sensitive detector. The whole $I(2\theta)$ pattern of the liquid phase and Debye–Scherrer spectrum of the recrystallised sample were thus recorded over a 120° range in 2θ with a 4096-channel analyser. Low temperatures were achieved by positioning the sample in a gaseous nitrogen flow at the required temperature. This system allows the sample to be quenched in a few seconds. For some experiments, requiring a better temperature control, a cryostat was also used which assures a temperature control of 0.5 K and allows cooling rate equal to 5 K/min.

Thermal measurements were performed in the range 100 K to room temperature (R.T.) on a DSC7 Perkin–Elmer calorimeter. The calibration in temperature was made using the transition points of cyclohexane and the calibration in energy by measuring the C_p of sapphire.

These measurements were complemented by direct optical observation of the compound at low temperature.

3. Crystallisation condition

We tried to specify the conditions in which the crystallisation process can be understood by a systematic DSC investigation. Preliminary measurements consisted in a series of cooling and heating cycles at various undercooling depths. The investigation was then made more quantitative by including several steps of isothermal observations at selected annealing temperatures. The cycles performed between R.T. and different temperatures down to T_g never revealed any sign of crystallisation exotherm in the range of metastability of the liquid. This behaviour was

not changed by slowing down the heating rate or by annealing the sample for several hours before reheating it.

Scans (Fig. 1), which were obtained from samples hold isothermally for several hours at temperatures as low as 160 K, only show the glass transition. Sub- T_g relaxation of the glass towards the metastable liquid state in internal equilibrium is revealed by the usual C_p overshoot with no sign of crystallisation exotherms at higher temperatures. In the course of this study, we have found an empirical way to induce crystallisation by first cooling the sample down to, at least, 40 K below T_g . Upon reheating, the crystallisation then occurs most rapidly near 230 K. Endothermic melting peak appears at $T_m \approx 241$ K (Fig. 1).

On the basis of nucleation and growth mechanisms [8] describing the recrystallisation process, these observations lead us to conclude that the crystallisation which occurs rapidly just below melting is the growth of crystalline nuclei which do not form throughout the transformation. It has been frequently observed that devitrification takes place on already existing nucleation cores formed during the quench of the melt [9]. The temperature at which the nucleation rate reaches a maximum can be very distinct of the temperature at which the growth rate reaches a maximum. The unexpected finding in our experiment of the present situation is that the maximum of the nucleation rate must occur at very low temperatures and is highly dependent on how much below T_g the system is quenched.

In order to estimate more quantitatively the temperature variation of the nucleation process, we have applied the following simple temperature–time programme: the system is first rapidly cooled for a given exposure at a low temperature T_a , where nucleation rate is expected to be high. This is followed by a rapid increase of temperature to a chosen constant temperature at which the crystallisation process is investigated by DSC used in the isothermal mode. The peak of the exotherm (inset of Fig. 2) which may, thus, be observed roughly corresponds to the maximum crystallisation rate. The time t_p , required to reach the peak of the exotherm, is inversely proportional to the number of nuclei sites formed at lower temperatures. The experimental observation of t_p vs. exposure temperature T_a produces consistently the curve illustrated in Fig. 3. It indicates a dramatic increase of the

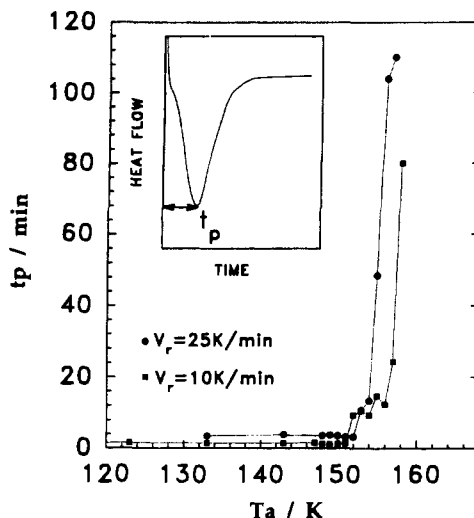


Fig. 2. The dependence of t_p (the maximum of growth rate at 223 K) vs T_a for two different heating rates. It shows that there exists a threshold temperature at ca. 152 K.

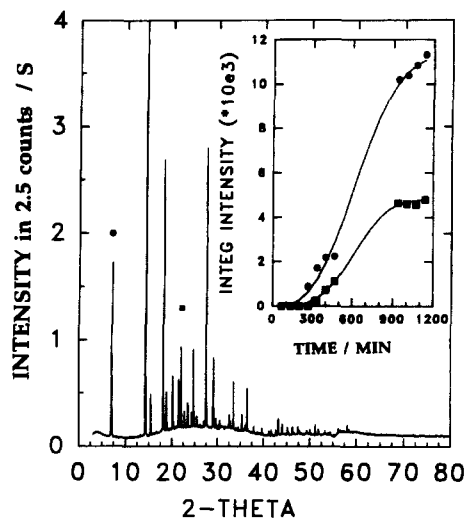


Fig. 3. X-ray pattern of the α -phase of *m*-toluidine recorded at the end of an annealing at 227 K. Such a pattern is obtained after quench to very low temperatures ($< T_g - 77$ K). The pattern is characterised by the presence of one Bragg peak isolated at low angles ($2\theta_1 = 7.06^\circ$). The inset shows the time evolution of the integrated intensities of two Bragg peaks of this X-ray pattern located at $2\theta_1 = 7.06^\circ$ and $2\theta_2 = 22.05^\circ$. The growth law describing the kinetics is an Avrami law, according to which the transformed fraction evolves as $X(t) = 1 - \exp(-kt^n)$ (with $n = 2.6$).

nucleation rate when the sample is quenched to $T = 152$ K.

A direct visual observation on a sample of the same size that has experienced the same temperature–time history reveals that cracks suddenly appear in the glassy sample at this temperature. We believe that the presence of these cracks supports the role of heterogeneous nucleation process upon reheating. Photographs taken during the high temperature recrystallisation effectively confirmed that grain growth occurs on a few nuclei which are localised in the zones of the cracks. The nucleation mechanism is certainly speeded up by these heterogeneities. However, the direct inspection of the evolution of these cracks upon reheating shows that they are cured at ca. 170 K (i.e. ca. 15 K below T_g) since the sample becomes transparent again. The efficient heterogeneous nucleation process is thus expected to be limited between 152 and 170 K, i.e. in a temperature range where the time scale of the molecular motions is considerably lowered. One may thus suspect that, in addition to the effect of heterogeneities, there should also be an unexpected decrease of the thermodynamic barrier of nucleation to account for the higher recrystallisation rates observed after quenching at ca. 152 K. All these rather qualitative observations, correlating quenching temperature to the recrystallisation process in *m*-toluidine, may be useful for a better control of the vitrification of other molecular liquids.

4. Crystalline polymorphism

In order to characterise further the crystalline transformation observed in the DSC study, the kinetics of crystallisation has been followed by time resolved X-ray measurements. The following experimental procedure which takes into account the thermal history of the sample which has already been shown to be able to promote the crystallisation process. The liquid is first cooled to 130 K; thereafter, the temperature is raised to 227 K, close to the maximum of crystallisation rate. At this temperature, the evolution of the X-ray pattern is followed as a function of time. Several experiments, carried out at the growth temperature, have shown that it is possible to obtain two clearly distinguishable X-ray patterns. This suggests the existence of crystalline polymorphism in the

system. In the following, we present a detailed investigation of this polymorphism and discuss the associated phase stability of each individual phase.

The most often observed X-ray pattern is shown in Fig. 3. A characteristic feature of this diagram is the presence of a strong isolated Bragg peak at $2\theta = 7.06^\circ$. The crystalline phase giving rise to this pattern will be designated by α . The corresponding isothermal kinetics of conversion is shown in the inset of Fig. 3, where the time evolutions of the integrated intensities $I(t)$ of two selected Bragg peaks at $2\theta_1 = 7.06^\circ$ and $2\theta_2 = 22.05^\circ$ are plotted. The growth curves are practically sigmoidal and can be well fitted to an Avrami law [10–12]: $I(t)/I(\infty) = 1 - \exp(-(t/\tau)^n)$. The exponent value has been found to be $n = 2.6$. Such a value is compatible with the suspected growth out of nuclei formed at lower temperature. The saturation is nearly reached after 16 h.

The stability of phase α has been tested by cooling gradually the crystallised sample down to the lowest accessible temperatures followed by heating. The evolution has been followed for the corresponding change of the X-ray pattern shown in Fig. 4. There is no change in the diffraction pattern which implies that no transformation is present in the temperature range

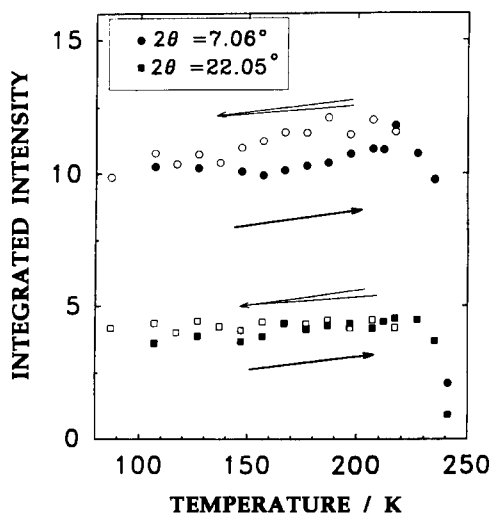


Fig. 4. Temperature evolution of the integrated intensities of the Bragg peaks in the X-ray pattern of the phase α located at $2\theta_1 = 7.06^\circ$ and $2\theta_2 = 22.05^\circ$ (the pattern is obtained after cooling down to 97 K and then reheating). It shows that phase α is stable in the entire covered temperature range. Melting is observed at $T_m = 241.5$ K.

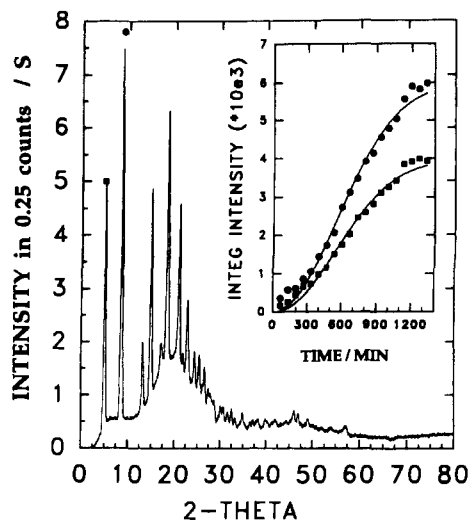


Fig. 5. X-ray pattern of the occasionally observed β phase. A specific feature of the pattern is the presence of two isolated Bragg peaks at lower angles $2\theta_3 = 4.87^\circ$ and $2\theta_4 = 8.52^\circ$. The inset shows the isothermal time evolution ($T = 227$ K) of the integrated intensities of two Bragg peaks marked by proper symbols.

covered. The melting of phase α is observed on heating at 242 K. This measurement clearly shows that this phase is identical to the crystalline phase detected by DSC; moreover, it is, ultimately, the stable phase.

Fig. 5 shows a different X-ray pattern which could be obtained in rare circumstances after identical thermal treatment. It reveals the possibility of crystallisation in another phase, denoted by β . The clear difference with the one of phase α , is the presence of two Bragg peaks isolated at low angles, namely $2\theta_3 = 4.87^\circ$ and $2\theta_4 = 8.52^\circ$. We may, moreover, notice that the peak intensities in the pattern of the β phase decrease faster with the Bragg angle, and that the peaks appear systematically broader. This could be a sign that the structure of the β phase is more disordered than the one of the α phase. The X-ray pattern shown on Fig. 5 has been recorded at the end of an isothermal kinetics at 227 K (Fig. 5 inset). Comparison with Fig. 3 reveals that the growth kinetics of α and β phases can be followed at the same temperature with roughly the same characteristic times. Direct conversion of the metastable liquid to β phase was rarely observed. It is thus impossible to specify the thermal treatment which could specifically favour its appearance.

5. Phase transformations and stability

After a particular low temperature thermal treatment (cf. Fig. 6), we could observe the X-ray pattern shown in Fig. 6 upon reheating. This diagram was obtained at 207 K after 10 h annealing. The presence of the three peaks at low Bragg angles clearly shows that the pattern is the superposition of the patterns characteristic of phases α and β . We use this information to learn more about possible transformations between the phases.

Fig. 6 shows the temperature evolution of the integrated intensities of the three first peaks (designated by α , β_1 , β_2) of the spectrum upon slow reheating:

- There is a small, apparently, anti-correlated variation of the α and β lines which occurs at 211 K. More pronounced evolution is observed above 217 K.
- At ca. 217 K, the intensity of the β peaks is slowly decreasing with increasing temperature, whereas the intensity of the α line is concomitantly increasing.

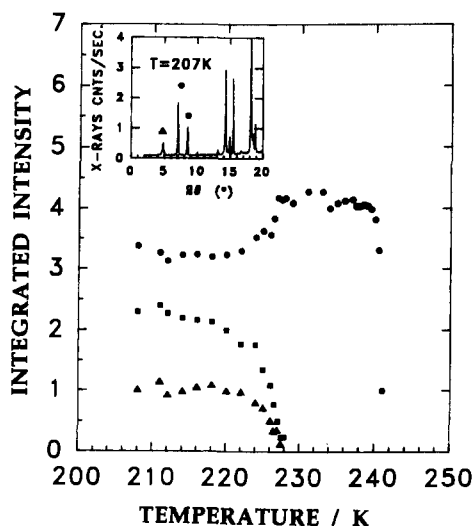


Fig. 6. The temperature evolution of the integrated intensities of the three lowest angle peaks of the X-ray pattern shown in the inset. The comparison of the evolution of the three peaks can be used to discuss the relative stability of α and β phases. The inset shows the X-ray pattern of a sample crystallised in a state with species of the two phases β and α coexisting.

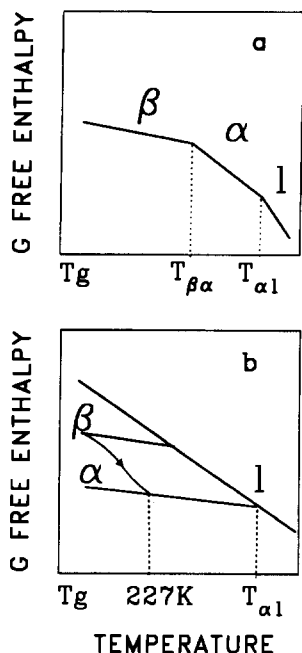


Fig. 7. Two possible free enthalpy diagrams. For crystalline *m*-toluidine, the discussion given in the text favours the monotropic coexistence of α and β phases corresponding to the diagram in Fig. 7(b). The kinetic transformation from β to α , as seen in Fig. 6 is represented by the curved line in the diagram in Fig. 7(b).

- At ca. 227 K, the β lines disappear while the intensity of the α line saturates and stays constant till it dramatically drops at 242 K.

The experiments show that the α phase is definitely the stable one just below the melting point at ca. 242 K and at least above 227 K. Since we have observed the transformation $\beta \rightarrow \alpha$ at ca. 227 K two different types of Gibbs enthalpy diagram can be a priori considered (Fig. 7(a and b)). They correspond, respectively, to the situations in which phases α and β form either (a) an enantiotropic or (b) a monotropic system.

The enantiotropic case (Fig. 7(a)) seems to be excluded since Fig. 4 proves the absence of reversibility of the $\beta \rightarrow \alpha$ transformation. From this result, the α phase appears to stay stable down to the lowest temperature studied. The β phase is thus metastable with regard to α in this temperature range. It remains to identify the origin of the $\beta \rightarrow \alpha$ conversion observed between 217 K and 227 K. In the eventuality of a monotropic case described by the Gibbs diagram

(Fig. 7(b)) one can consider that the conversion corresponds to the melting of β (at a temperature $T_{\beta l}$) immediately followed by the growth of α within the melted fraction of the sample. The process being completed at 227 K, this would lead to locating $T_{\beta l}$ at a somewhat lower temperature. However, Fig. 5 clearly shows that a transformation of the liquid into the β phase can be observed isothermally at 227 K. This contradicts the hypothesis that the melting of the β phase is responsible for the $\beta \rightarrow \alpha$ transformation. The most likely mechanism is the kinetic conversion of β in α which becomes more favourable in the 214 K–227 K range. The temperature of conversion does not correspond to the temperature of an equilibrium phase transition but to a temperature, where the kinetic growth rate of the formation of the more stable α phase is more rapid. The rather large range in temperature of this conversion by itself seems to confirm the kind of process sketched in Fig. 7(b). The melting of β is expected to occur at a temperature somewhat higher than 227 K.

6. Conclusion

In summary, we have found that *m*-toluidine is an extremely good glass former because of its large propensity for easy undercooling. The conditions to succeed in devitrifying the compound have been specified. The maximum of the crystallisation growth rate occurs somewhat below the melting point, $T \approx 242$ K. However, the nucleation is controlled by the passage of the undercooled liquid by ca. 152 K, i.e. well below the glass transition. The catastrophic formation of cracks which occurs at this sub T_g temperature is certainly one probable cause of heterogeneous nucleation. However, the heterogeneous nucleation can only operate within a finite temperature range, well below T_g , i.e. in the temperature range where cracks are observed. As a result, the nucleation rate is maximum while the dynamics is considerably slowed down. This can signal a non-classical decrease of the nucleation barrier and the close existence of a thermodynamic instability of the liquid. It would be an interesting point to investigate further, especially as the Kauzmann temperature T_K is expected to be in the temperature domain where nucleation is presently more rapid.

The investigation of the phase diagram of the crystalline state itself revealed an interesting monotropic situation between two phases α and β with distinct X-ray diffraction patterns. This identification is useful in the investigation of the medium range order which may develop in the stable, metastable, and glassy liquids. All these results are important in order to situate and discuss the glass properties of *m*-toluidine which seems to be a new promising model compound in the study of glass.

We have also found a monotropic situation of this type in an orientational glass-former [11]. The possibility of a correlation between such a monotropism and the development of a structural frustration in the glass-forming material is certainly an interesting point to investigate further.

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