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A contribution to the understanding of the polyamorphism situation in triphenyl phosphite

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Triphenyl phosphite (TPP) is now well known to exhibit an intriguing transformation of the supercooled liquid. The transformation was firstly interpreted as a first-order polyamorphic transition between the supercooled liquid and an apparently amorphous state different from the glass and the ordinary liquid, the so-called glacial state. In this paper, we describe and analyze, from experimental investigations (Raman spectroscopy, calorimetric measurements, X-ray and neutron diffraction), the transformation into the glacial state and the structural organization of this state. The latter is interpreted as a heavily nucleated state composed of nanocrystals of the stable crystalline phase embedded in the matrix of non-transformed supercooled liquid. The origin of the intriguing relative stability of this state could result in the combination of two phenomena: the time lag required to attain steady-state values of the nucleation rate (connected to the high viscosity of TPP), and a high nucleation rate in the temperature range where the growth rate is low. These results converge into a description of the glacial state as a mixed supercooled liquid/crystallites state, and then contradict recent claims that the glacial state of TPP is a homogeneous amorphous phase.

Introduction

First-order liquid–liquid phase transitions are excessively rare in pure compounds. The existence of liquid polymorphs is beginning to be recognized and a growing interest is devoted to the first-order polyamorphic transitions. These phase transitions are principally observed by applying high pressure,[1,2] and are generally associated with a change of density. The evidence of an apparently rigid amorphous phase in the molecular glass-forming liquid triphenyl phosphite (TPP, $P(OC_6H_5)_3$) at atmospheric pressure,[3,4] distinct from the glass, the supercooled liquid and the normal liquid (and so named glacial phase) was considered as an original manifestation of polyamorphism, and a real opportunity to analyze such a situation.

The glacial state was first described, in the general frame of the recent thermodynamic theory of supercooled liquids (frustration limited domain, FLD[5,6]), as a "defect-ordered phase". From the FLD theory, the liquid is described as small groups of neighboring molecules grouped in locally preferred structures (LPS) which are compact, dense and not space-filling. At a temperature low enough these structures are favored but their extension is accompanied by strain which limits the growth of LPS, because of geometric frustration. Consequently, the supercooled liquids could change into solid metastable phases called "defect-ordered phases". The evidence of such solid amorphous states is considered as an important contribution to the understanding of the supercooled liquid state and the subsequent formation of the glass.

The polyamorphism is analyzed in the general context of the liquid–liquid phase transition. The glacial phase in TPP and the large-scale fluctuations in o-terphenyl ("Fischer clusters"[7]) are considered in this context as the direct signatures of a second liquid.[8] From these considerations, the glacial phase was recently described as composed of crystallites embedded in a second amorphous phase (glass II) of the second liquid.[9]

The opportunity to form the intriguing glacial state of TPP by a mere variation of temperature has given rise to numerous experimental investigations leading to controversial descriptions of this state (defect-ordered crystal,[3,4,10–12] crystal liquid phase,[13] plastic phase,[12,13] and liquid phase[14–18]). In this paper, we report experimental investigations leading to a description of the glacial state as composed of nanocrystallites of the stable crystal within a matrix of non-transformed metastable liquid. An interpretation of the origin of the glacial state, consistent with this description, is proposed.

Preparation of the glacial state; identification of the glaciation process

The glacial state of TPP, can be formed, either by slow heating from the glass (protocol 1) or by maintaining the temperature constant above the calorimetric glass transition ($T_g = 201.8$ K (ref. 19) in the range 210–235 K (protocol 2). In both cases, liquid TPP is previously quenched from room temperature down to 190 K.

In protocol 1, differential scanning calorimetric (DSC) experiments[20] reveal two exothermic features (Fig. 1) in agreement with Wiedersich et al.,[14] above the step-like anomaly associated to the glass transition. These features appear clearly connected and strongly dependent on the heating rate. The first exotherm observed on heating above T_g for the low T-values (Fig. 1a) is assigned to the transformation between the supercooled liquid and the glacial state (glaciation), and the second one should correspond to the conversion of the glacial state into the crystal. The temperature of transformation into the glacial state drastically increases with the scanning rate, while the crystallization temperature is only slightly shifted in the same way. For a scanning rate above 1 K min^{-1} (Fig. 1b), the exotherm associated with the glaciation is not observed.
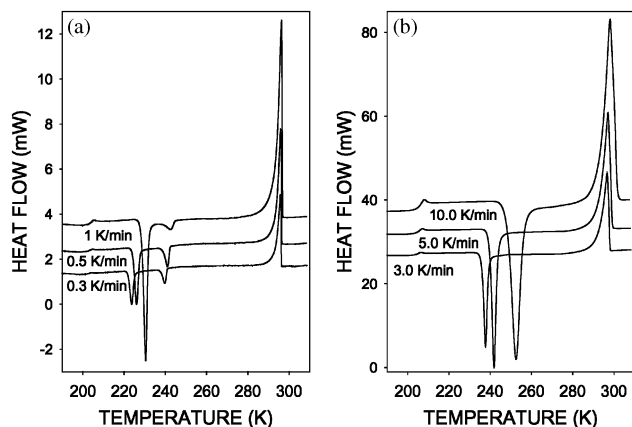
Fig. 1 DSC curves obtained by heating with different scanning rates (protocol 1).

A detailed analysis of the thermodynamic data[20] indicates that the enthalpy of exothermic (glaciation and crystallization) peaks roughly corresponds to the enthalpy of the endothermic (melting) peak, after corrections corresponding to ΔCp between liquid and solid TPP. This set of DSC curves reveals a strong influence of the heating rate on the temperature of glaciation and the fraction of transformed matter into the glacial state.

The glacial state can also be prepared by isothermal aging at $T_a \in$ 210–235 K, after the sample was first quenched from room temperature down to 190 K (*i.e.*, below T_g) and heated to T_a at 10 K min^{-1} (protocol 2). Some of these isotherms are plotted in Fig. 2. This figure points out:

(i) the observation of an exotherm indicative of a complete first-order transformation;

(ii) a drastic influence of the aging temperature upon transformation of the supercooled liquid into the glacial state. It is clearly observed that the time of transformation drastically decreases while the area of the exothermic peak increases with increasing T_a, in good agreement with Dvinskikh *et al.*[15]

The study of protocols 1 and 2 reveals that the glaciation is a first-order transformation, and the glacial state depends drastically on the thermal conditions in which it is prepared (heating rate, T_a).
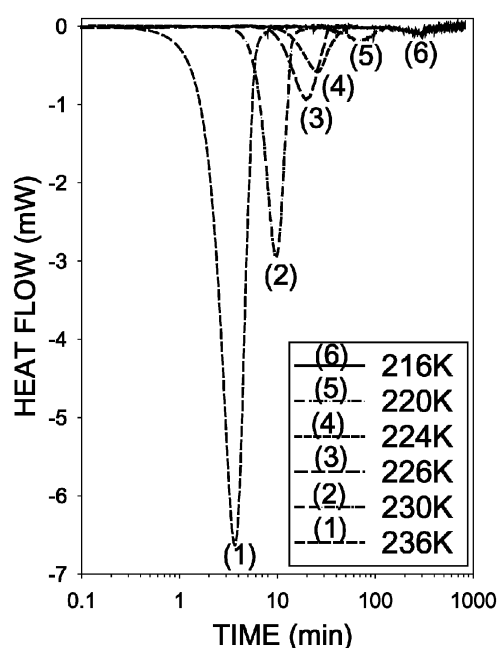
The formation of the glacial state using protocol 2 (for $T_a \in$ 210–235 K) was studied by Raman spectroscopy.[21–23] The high sensitivity of the cooled charge-coupled device multichannel detector of the XY DILOR spectrometer allows us to record spectra in the 5–600 cm^{-1} domain in 100 s with a resolution of about 2 cm^{-1}. The time dependence of the Raman intensity in the 5–200 cm^{-1} range during the isothermal ageing at 216 K is plotted in Fig. 3a. The first stage ($t = 0$) of this aging process provides the Raman spectrum of the undercooled liquid. The glaciation process is observed *via* a turbiding effect, starting after about 15 min, and a transformation of the Raman spectrum in the 5–200 cm^{-1} region. The three arrows localize the main changes in the Raman spectrum, *i.e.*: (i) the progressive transformation of the quasi-elastic component, characteristic of a liquid, into a broad low-frequency band; (ii) a structuring of the Raman line shape in the 80–100 cm^{-1} region; (iii) and the emergence of a Raman band around 150 cm^{-1}. After about 50 min, the sample gets clear again and the Raman spectra remain stable until the end of the analysis (*ca.* 24 h). The stability of the glacial state was further studied during one week, and no evolution of the Raman spectrum was detected during this period.

Description of the glacial state

The low-frequency Raman intensity in the different amorphous states (liquid and glass) and the glacial state of TPP is converted into Raman susceptibility (Fig. 3b). The Raman susceptibility in the glacial state formed at $T_a = 216$ K exhibits a clear amorphous line shape. The observation of a double hump around 100 cm^{-1} and a band around 150 cm^{-1} in the low-frequency spectrum of the glacial state indicates that this state is indubitably different from the glass and the liquid. The Raman spectrum of the glacial state can further be compared to that of the stable crystalline phase. The crystal was obtained by heating the glacial state above 235 K. The temperature of the sample was then decreased down to 216 K to give a rigorous comparison between the Raman spectra recorded in the glacial state formed at 216 K and in the crystal at the same temperature (216 K). This comparison is reported in Fig. 4. From the latter, one can infer that the main changes observed in the Raman spectrum of TPP during the glaciation correspond to crystal features. First, the quasi-elastic component was transformed in a broad vibrational band corresponding to the envelope of the low-frequency phonons of the crystal (< 50 cm^{-1}). Second, the broad Raman band around 80 cm^{-1} in the spectrum of the liquid splits during the glaciation in two

Fig. 2 DSC curves obtained by isothermal ageing at different temperatures (protocol 2).
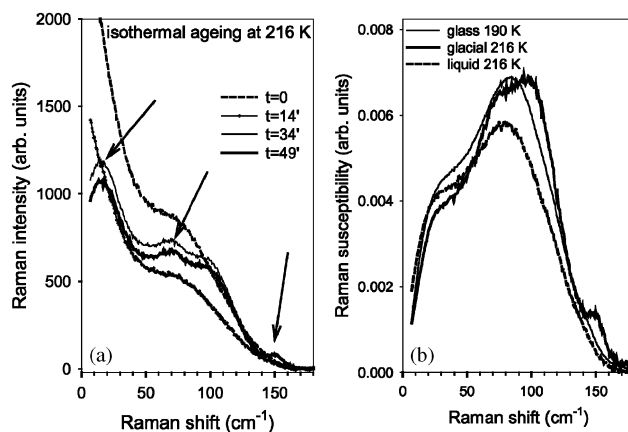
Fig. 3 Low-frequency Raman spectra of amorphous states and the glacial state of TPP. (a) Time dependence of the Raman intensity during a glaciation at 216 K. (b) Comparison of the low-frequency susceptibility of TPP in the supercooled liquid, the glass and the glacial states.
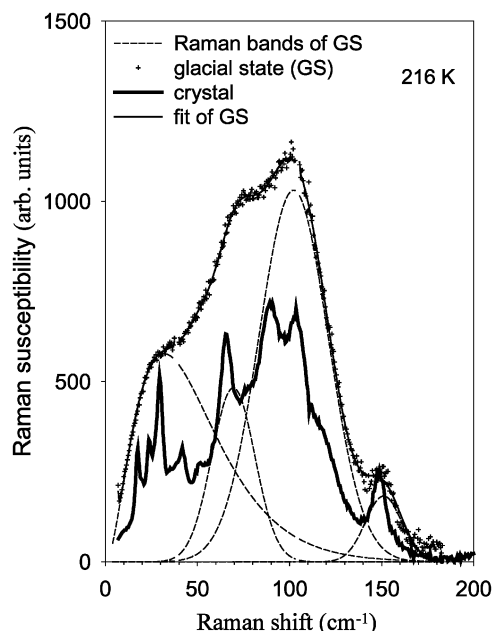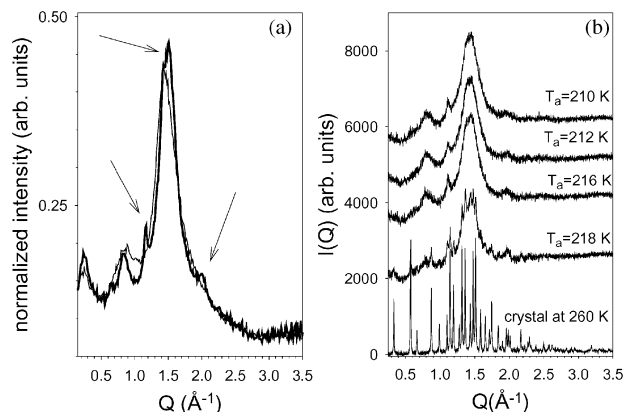
Fig. 4 Comparison between the Raman spectra of the glacial state (+) and the crystal (thick black line) at 216 K. The best fit of the spectrum of the glacial state (thin black line) is performed using 4 components (dashed line). Each component corresponds to a group of phonons of the crystal.

Fig. 5 Structure factor (X-ray diffraction) of the different states of TPP: (a) Supercooled liquid and the glacial state, respectively, at the beginning (thin line) and at the end (thick line) of the isothermal transformation at 216 K. The arrows point out the most significant changes of $S(Q)$ during the isothermal ageing. Experiments were performed on BM16 (ESRF). (b) The glacial state formed by isothermal ageing (protocol 2) at different temperatures T_a compared with the diffraction pattern of the crystal, from powder laboratory X-ray diffraction data.

components corresponding to two groups of phonons in the spectrum of the crystal. Third, the Raman band emerging around 150 cm^{-1} in the Raman spectrum taken during the glaciation is also observable in the Raman spectrum of the crystal but not in the spectra of the amorphous states (liquid, supercooled liquid and glass). To summarize this analysis, the low-frequency Raman spectrum of the glacial state appears as the precise envelope of the broadened phonons of the crystals. In this context, the low-frequency Raman spectrum of the glacial state was interpreted as reflecting the presence of sub-microscopic domains of the crystal.

X-ray diffraction experiments were also performed in order to determine the nature of the glacial state, using both conventional laboratory X-ray source,[24] and synchrotron radiation.[25,27] The use of the synchrotron radiation (BM16, ESRF, Grenoble, France) and, in particular, its high X-ray intensity is crucial for determining the changes in the structure factor of TPP during the isothermal transformation of the undercooled liquid into the glacial state. The structure factor of TPP in the undercooled liquid state (at the beginning of the isothermal transformation at 216 K using protocol 2) and in the glacial state (at the end of the transformation) measured on BM16 are plotted in Fig. 5a. This figure shows the amorphous-like line shape of $S(Q)$ in this glacial state and points out structural features occurring during the glaciation. These features (localized by arrows in Fig. 5a) can be summarized as an increase of intensity on the high Q-side of the main peak and the structure organization of the whole structure factor. From the structure organization of $S(Q)$, on the low-Q side of the main peak, an unusually sharp peak ($\Delta Q = 0.035$ Å^{-1}) for an amorphous material emerges around $Q = 1.1$ Å^{-1}.

Laboratory X-ray diffraction patterns of the crystal and glacial states formed at different temperatures (protocol 2)[24] are plotted in Fig. 5b. One can recognize the emerging structure organization in the glacial state on the low- and high-Q sides of the main peak as signatures of submicro particles of the crystalline state. The determination of the width of this sharp peak detected in the $S(Q)$ of the glacial state formed at different temperatures[24] leads to the coherence length which provides an estimation of the crystallite size. This estimation is reported in

Table 1 for different temperatures T_a at which the glacial state is formed using protocol 2. In the low-temperature range [210 K, 216 K] the size of nanocrystallites is *ca.* 30 Å and increases drastically for $T_a > 216$ K. This is in agreement with the fact that the crystalline signatures appear more and more marked as the temperature of formation of the glacial state (T_a) is increased (Fig. 5b). The enhanced scattered intensity detected in the very low-Q regime of the structure factor of glacial states (Fig. 5b) appears as a broadened peak, using synchrotron radiation (Fig. 5a), which is also observed in the liquid with a weaker intensity. This shoulder seems to correspond to the first Bragg peak observed in the diffraction pattern of the crystal. Accurate diffraction investigation in the crystalline phase,[25] carried out on BM16 at ESRF (Grenoble) has allowed to state that the symmetry of crystal TPP is trigonal (space group $R\bar{3}$), with unusual large dimensions of the associated hexagonal unit-cell [$V = 7075.7\ (4)$ Å^3, $Z = 18$, $a = 37.766\ (1)$ Å and $c = 5.7286\ (2)$ Å]. The determination of the crystalline lattice was confirmed by a single-crystal laboratory X-ray diffraction analysis.[26] The first Bragg peak observed in the diffraction pattern of the crystalline phase at $Q = 0.32$ Å^{-1} (at 110 K) and indexed as (1 1 0), corresponds to the enhanced scattered intensity detected in the very low-Q regime of $S(Q)$ measured in the liquid and glacial states. This correspondence could be indicative of a structural organization on a mesoscopic scale in both the glacial and the supercooled liquid states reminiscent of the long-range order developing in the hexagonal plane of the crystal. The relative sharp peak detected around 1.1 Å^{-1} in the glacial state, which was previously considered as unusually sharp for an amorphous state,[24] corresponds to the (1 0 1) Bragg peak of the crystal, which coincides roughly with the (0 0 1) plane taking into account the platelet-like shape of the unit-cell.

From two different structural analyses of the crystal,[25,26] the long-range order can be described as a hexagonal packing of one-dimensional infinite rods formed by TPP molecules aligned parallel to the c-axis of the hexagonal unit-cell. Two neighboring rods are anti-parallel. However, from the combination of Raman and diffraction data,[25] it was determined that the stability of TPP molecules, *i.e.* the cohesion in one infinite rod is assumed *via* two different C–H···O hydrogen bonds, not in agreement with Senker *et al.*[26]

From these structural considerations and the correspondence observed between the diffraction patterns of the glacial

Table 1 The coherence length deduced from a Lorentzian fit of the sharp peak around 1.1 Å^{-1} in $S(Q)$ of the glacial state (laboratory X-ray diffraction[24])

T_a/K	210	212	216	218	224
Coherence length/Å	33	24	28	57	284

state and the crystal, the scattered intensity detected near 1.1 Å^{-1} and in the very low-Q regime, can, respectively, be assigned to the formation of the rods along the [001]-direction and their hexagonal packing in the (001)-plane.

Recent micro-structural refinements of powder synchrotron X-ray diffraction data[27] recorded in a glacial state formed at 222 K (where microcrystals are expected, see Table 1), has firstly revealed that crystallites in the glacial state are also composed of rods aligned along the c-direction. Secondly one type of C–H···O inter-molecular associations was preserved in the glacial state. This analysis shows that the long-range order in crystallites of the glacial state is very close to the long range order in the stable crystal. However, the slight modification in the hydrogen-bond network in crystallites of the glacial state is associated with a subtle modification of the molecular conformation with respect to that determined in the stable phase. This modification could be assigned (taking into account uncertainties on refined atomic positions) to a slight enhancement of the discrepancy between the rigorous molecular conformation in the crystal and the C_s molecular symmetry.[27]

A detailed inspection of the Raman spectra of the liquid, crystal and glacial state of TPP in a wider spectral range,[23] provides additional informations to give a more accurate description of the glacial state. The analysis of the high-frequency spectrum of glacial states formed at different temperatures T_a[23] have revealed a significant influence of T_a on the Raman line-shape in the 600–1650 cm^{-1} connected with the size of crystallites which increases with increasing T_a. This is consistent with results obtained in the low-frequency range[22] and with X-ray diffraction data.[24] The 1100–1200 cm^{-1} range appears as very informative about the nature of the glacial state since in this latter range the spectral signatures of the crystal (I_c component) are especially distinguishable from that of the undercooled liquid (I_a component). From this assignment represented in Fig. 6, one can recognize the spectrum of the glacial state as a combination of the liquid and the crystal ones. Consequently, the whole Raman spectrum of the glacial state was interpreted as reflecting the coexistence of nanocrystals of the stable phase and the undercooled liquid. The volume fraction of crystalline matter in the glacial state was determined from the analysis of the low- and high-frequency regions.[23] In the low-frequency range, the volume fraction crystallinity (ρ_c) is determined from the area of the crystalline features, while at higher frequencies it is determined from the area of the Raman band (I_c component) interpreted as the signature of nanocrystals. In this latter method, the size of crystallized domains is requested for the calculation of ρ_c. Consequently, the estimation of ρ_c from the analysis of the high-frequency range was performed only for glacial states where the size of crystallites has been determined from the X-ray diffraction analysis. The values of ρ_c determined from the low- and high-frequency analyzes are reported in Table 2.

The analysis of the Raman[21–23] and X-ray diffraction[24,25,27] data leads to the same description of the glacial state in terms of a two-phase (undercooled liquid/nanocrystalline) system. Both X-ray diffraction and Raman data suggest that nanocrystals have the long-range order of the stable crystal. Neutron diffraction experiments performed in a wide Q-range,[28] confirm that no structural features can be detected to distinguish the long-range order in nano-crystallized domains of the glacial state from that of the stable crystal.
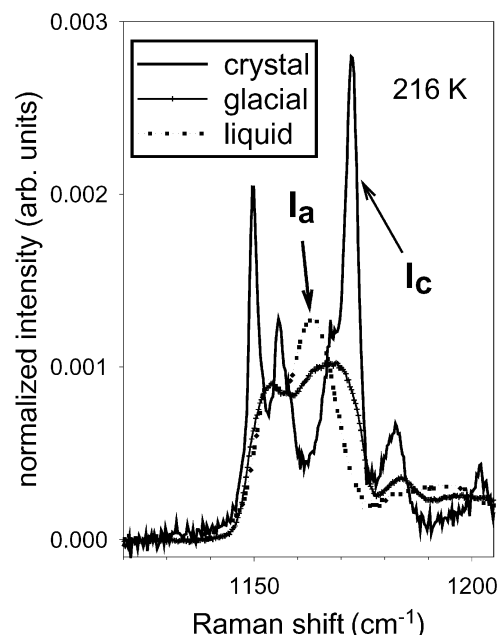
Fig. 6 Raman spectra taken in the undercooled liquid, glacial and crystalline states of TPP in the 1100–1200 cm^{-1} range. The confrontation of these spectra gives the clear evidence for a mixing of nano domains of the stable crystal and undercooled liquid in the glacial state from the observation of a Raman band around 165 cm^{-1} composed of distinguishing features of the liquid and the crystal.

Nature and origin of the glaciation

From the description of the glacial state as composed of nano-domains of the stable crystalline state in the matrix of the undercooled liquid it is reasonable to consider the glaciation as an abortive crystallization. In this context, the first exotherm observed (by heating from the glassy state) in Fig. 1a should correspond to the abortive crystallization (the glaciation) and the second one to the overall crystallization. This interpretation can indeed be confirmed by the energy balance between the exothermic and endothermic peaks. It was noticed that the area of the first exotherm increases as the heating rate is increased at the expense of the area of the second exotherm. For heating rates above 1 K min^{-1} (Fig. 1b) the overall crystallization is obtained in only one process, as usually observed. This observation suggests that the increase of the heating rate promotes the crystallization. The area of exotherms, reported in Fig. 2, obtained by isothermal ageing at different temperatures T_a (protocol 2), were systematically determined. The isothermal transformation at 236 K was interpreted as the true crystallization from the comparison of the area of the exotherm at 236 K to that of the melting

Table 2 Volume fraction of crystallinity (ρ_c) in the glacial state prepared at T_a using protocol 2 from different experiments: DSC (2nd column[20]), low-frequency Raman experiments (3rd column[23]), and high-frequency Raman experiments in the range [1120,1200 cm^{-1}] (4th column[24]). The values of ρ_c determined from Raman investigations are systematically higher than those determined from DSC data. This can be explained by the use of different low-temperature devices

T_a/K	DSC	L-f Raman	H-f Raman
214		0.44	0.43
216	0.25	—	—
218	0.35	0.50	0.51
220	0.44	0.54	0.58
222	0.53	0.64	—
224	0.53	0.74	—
226	0.68	0.97	—

endotherm.[20] Consequently, the ratio of area of exotherms at $T_a < 236$ K to the area of the exotherm obtained at $T_a = 236$ K is interpreted as the volume fraction crystallinity (ρ_c) of the glacial state prepared at T_a. This quantity is reported in Table 2. Each DSC trace recorded during isotherms is converted into a volume fraction of crystallinity (ρ_c) using a procedure described in ref. 20. The corresponding curves $\rho_c(t)$ plotted in Fig. 7a have a clear sigmoidal shape. This time behavior is consistent with the time dependence of the frequency shift of vibrational excitations,[21,23] and with the enhancement of the density of vibrational state obtained during the glaciation.[29] Such a behavior is generally suggestive of a nucleation and growth process or merely a growth of incipient nuclei. Both phenomena are governed by the Avrami law. However, the poor quality of the fit of $\rho_c(t)$ with an Avrami law (Fig. 7b) and the very small size of crystallized domains in the 30 Å-range[24] are not consistent with the interpretation of the time dependence of the transformation rate as an Avrami behavior, for the low T_a values. The description of the glacial state as composed of nuclei of the crystalline state in the remaining liquid-rich matrix, leads us to consider that the sigmoidal shape of the transformation rate should merely correspond to a nucleation process, and not to the growth of nuclei according to the Avrami law. It is well known[30–32] in the case of glasses or deeply supercooled liquids or for systems where there is a little overlap between the nucleation- and growth-rate curves, that a time lag is required to attain steady-state values of nucleation rate. This induction time characterizes the reorganization of the system until a steady flow of nuclei is produced, and then is responsible for transient kinetics of nucleation which is also described by a sigmoidal shape.[33–35] In this context, the time-dependence of the transformation rate into the glacial state (Fig. 7a) has been tentatively fitted by sigmoid curves corresponding to the expression of the normalized transient nucleation rate.[33] The good agreement between the experimental data taken during the glaciation at 216 K and the fitting procedure with a double-exponential time-dependent nucleation rate[33,34] suggests that the crystallization process in TPP is driven by a transient kinetics of nucleation. It is worth pointing out that experimental data reported in Fig. 7b should correspond to the number of nuclei, not to a nucleation rate. The time evolution of the number of critical clusters for transient nucleation exhibits the shape plotted in Fig. 7c.[36]

Consequently, it can be assumed that the saturation of the number of nucleated clusters is observed just after the steady state of nucleation has been attained, i.e. just after the nucleation rate has reached maximum. In this context, the DSC traces obtained using protocol 1 and reported in Fig. 1 are interpreted as follows. It can easily be understood that rapid heating from the glassy state favors low nucleation density because of the induction time, and then promotes crystallization, whereas slow heating favors high nucleation density and then frustrates crystallization.

The conversion of the glacial state into the crystal

The overall crystallisation of TPP from the glacial state is obtained only by heating the glacial state. This procedure was analyzed from DSC,[9,18–20] NMR,[12] Raman spectroscopy and dielectric[37] experiments. All these experimental features are observed just below the conversion glacial to crystal (<236 K). These features are interpreted either as a glass transition[9,18,19] or as a partial melting.[12,20] It can be outlined that no systematic analysis of the conversion of the glacial state into the crystal was performed for different glacial states formed at different temperatures T_a, except in ref. 20. DSC experiments carried out during heating glacial states prepared at different temperatures T_a are reported in Fig. 8a. It is worth noticing the complexity of the DSC trace above the pre-melting and the extreme sharpness of the exothermic peak corresponding to the overall crystallization. It was demonstrated[20] that the overlap of the pre-melting and the crystallization is responsible for these features. On this figure, one can recognize the pre-melting, through a weakly intense endothermic peak, leading up the crystallization. Fig. 8a provides two crucial observations on the origin of this pre-melting. Firstly, the enthalpy of the endotherm decreases when T_a is increased, i.e. when the volume fraction of crystallinity in the glacial state increases. Secondly, the pre-melting shifts towards the high temperatures with T_a increasing. These two observations lead us to interpret this pre-melting as the melting of the smallest crystallized particles which become unstable after heating because of the temperature dependence of the critical radius of nuclei. From the description of the glacial state in terms of heavily nucleated state, the volume fraction of crystallinity and the size of nuclei increase with T_a increasing. In this context, the shift of the
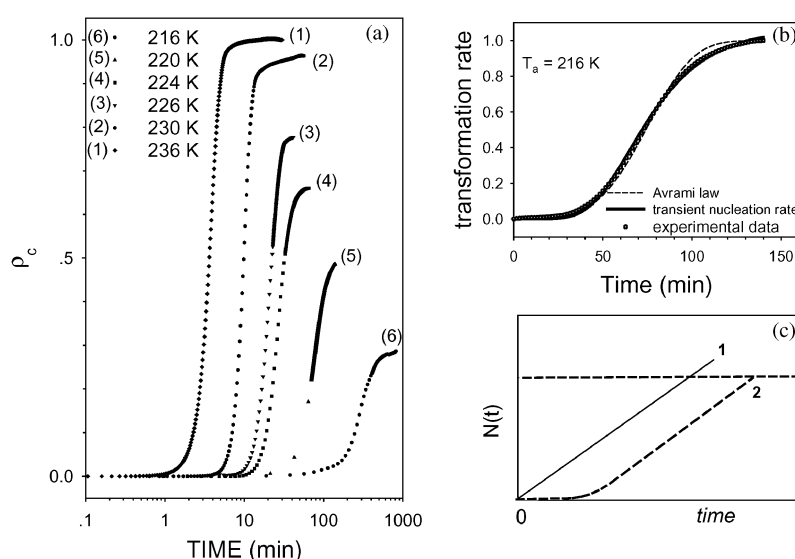
Fig. 7 Transformed matter fraction into the glacial state during isothermal ageing at T_a. (a) T_a-dependence of the volume fraction of crystallinity determined from isotherms plotted in Fig. 2. (b) Experimental data obtained during glaciation at 216 K are fitted using an Avrami-like function, and the function representative of a transient nucleation rate. (c) Theoretical shape[32] of the time dependence of the number of clusters $N(t)$ for steady state nucleation (1) and transient nucleation (2). Time-lag effects result in a parallel shift of the $N(t)$-curves. The horizontal dashed line indicates the saturation phenomenon.
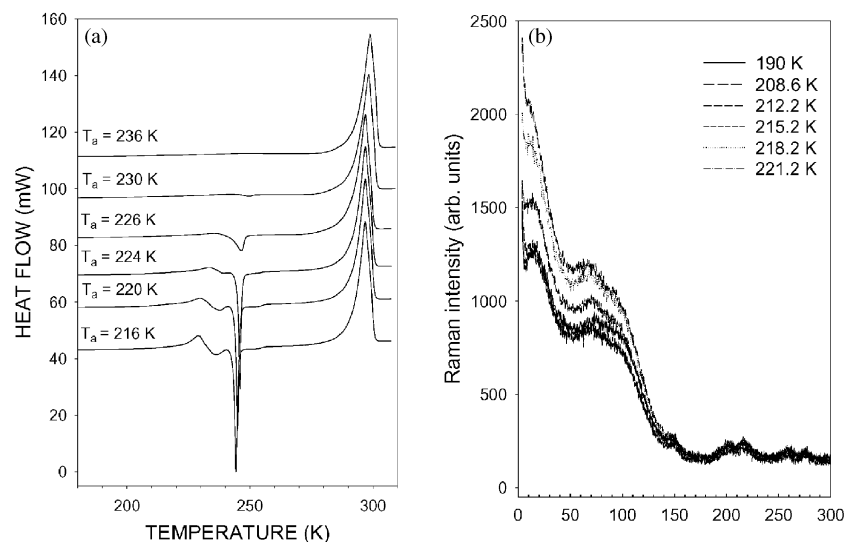
Fig. 8 Experiments performed during the heating of the glacial state. The glacial state was formed at T_a using protocol 2, cooled at 190 K and then heated for analysis. (a) DSC traces recorded on heating (10 K min^{-1}) the glacial state prepared at different temperatures T_a. (b) Raman spectra were recorded during a heating ramp at 5 K min^{-1} from a glacial state prepared at $T_a = 220$ K.

endothermic peak can be interpreted in the frame of the Gibbs–Thomson theory predicting a decrease of the melting temperature as the cluster size decreases.

The Raman spectra taken during the heating of a glacial state formed at $T_a = 220$ K[37] are reported in Fig. 8b. This latter reveals the emergence of a quasi-elastic component characteristic of the presence of liquid. The Raman line-shape remains coarsely the same between 50 and 150 cm^{-1} and Raman spectra are superimposed above 150 cm^{-1}. These experiments show that a partial melting occurs by heating the glacial state. No change in the molecular conformation was detected on heating (as assumed in refs. 11 and 12) since the high-frequency spectra are rigorously superimposed. The changes observed in the low-frequency region are assigned to the emergence of a liquid contribution resulting in the melting of the smallest nanocrystals.

Discussion

The discovery of the intriguing glacial state[3] has given rise to numerous experimental investigations and numerous descriptions of this state. The origin and the description of this state have been considered as a clue to the understanding of the supercooled liquid state and the subsequent formation of the glass.[10,11] This paper reports a contribution to the description of the polyamorphism situation in TPP from the combination of DSC analysis and structural investigations that gives complementary and consistent results converging into the description of the glacial state as a mixed crystalline/undercooled liquid state. A scenario to understand the frustration responsible for the origin and the relative stability of the glacial state is proposed on the basis of experimental features.

The equivalence of the enthalpy of exothermic peaks (glaciation + crystallization) and the melting enthalpy points out that glaciation and crystallization are two complementary transformations. This point associated with the observation of crystal-like features in the glacial state by X-ray diffraction and Raman spectroscopy investigations, give a very clear evidence that the glaciation corresponds to an incomplete crystallization. The consistence between values of the volume fraction of crystallinity determined from different kinds of experiments supports this interpretation.

The origin of the relative stability of this state was associated to a time lag of nucleation caused by the high viscosity of the deeply undercooled liquid at low-temperature. The high nucleation rate in a temperature range where the growth rate

is low can be considered as a feature which favors the formation of a heavily nucleated state just above T_g in the 210–220 K low-temperature range. The consideration of both the time lag of nucleation and a little overlap between the nucleation- and growth-rate curves, indicates that the temperature at which the glacial state is formed and the heating rate are two crucial parameters to form the glacial state. A rapid heating from the glass in the temperature range where the nucleation rate is maximum (around 210 K) prevents the nucleation because of the induction time and favors the crystallization in the temperature range where the growth rate is high (around 235 K). On the opposite, slow heating or an isothermal aging around 210 K favors a high nucleation rate. In such a case, a high density of very small crystallites subdivides the residual undercooled matrix and impedes further crystallization where the matrix dimensions of the remaining undercooled liquid are less than the critical value for nucleation. The number of clusters isothermally nucleated in the 216–224 K range can be considered as rapidly saturated, just after the steady state of the nucleation rate has been attained and no growth occurs. This process is consistent with the particle dimensions in the 30 Å-range, determined from X-ray diffraction measurements.[24] From Table 2, it can be noticed that the volume fraction of the nuclei does not exceed 60% in the 210–220 K temperature range. Taking into account the large hexagonal unit-cell of the crystal ($a = 37.766$ Å, $c = 5.7286$ Å, $Z = 18$, refs. 25 and 26) long-range order may not be fully achieved in the smallest crystallites, and it may be difficult to distinguish structurally between crystallites and local structures in the non-transformed supercooled liquid with similar short-range order. In this context, for a glacial state formed in the 210–220 K range it can be considered that nanocrystals have no "crystalline identity". Such a picture of the glacial state is very close to the description of a defect-ordered crystal given by Kivelson et al.,[3,4,10,12] and consistent with the consideration of a polyamorphism situation in TPP. The description of the glacial state as apparently heterogeneous is not far from the description of the glassy state as a non-continuous glass structure.[41,42] In this case, the glass would consist of cohesive domains separated by less cohesive zones. This model supports the description of the Boson peak as being representative of a size distribution of the cohesive domains centred at about 40 Å in polymeric glasses.[43] In this context, the frequency of the Boson peak should decrease with increasing the domain size. Inelastic neutron scattering experiments[29] have revealed that the frequency of the Boson peak in the glacial state decreases with

increasing the T_a, *i.e.* as the size of nanocrystals increases. From these considerations the glacial state formed at low-temperature (in the range [210 K, 216 K]) exhibits some dynamical features observed in glassy states in relation to their structural description.

However, its origin would be fundamentally different from that emerging from the FLD theory.[5,6] From the latter, the development at low-enough temperature of a LPS aborts in a defect-ordered crystal (a solid phase), because of a topological frustration. This LPS should be highly compact as determined for a liquid of hard spheres,[38] and then in this context, the glacial state should be denser than the stable crystal. This consideration is contradicted by different kinds of experimental features[27,39] reported by different groups. This description of the glacial state in terms of defect-ordered crystal is mainly supported by neutron diffraction and small-angle neutron scattering (SANS) experiments.[11] However, in this work neutron diffraction data in the glacial and crystalline states were compared at different temperatures. In these conditions no relationship between the two diffraction patterns can be properly detected. SANS experiments[11] have revealed a structural organization on a mesoscopic scale (80 Å). This result is not in contradiction with our description of the glacial state, since no information on the structural organization can be obtained from this analysis. A more thorough SANS investigation[39] has given a detailed description of the glaciation, interpreted in a four-step model; cluster formation, rapid nucleation, agglomeration and saturation. This description is consistent with our interpretation of the glacial state as a heavily nucleated state and the observation of a turbiding effect at the beginning of the glaciation.

Other experimental investigations carried out on the glacial state of TPP converge into the description of the glacial state as a homogeneous liquid phase. This consideration is based on dielectric and NMR experiments.[14–18] The transformation of the undercooled liquid into the glacial state was tentatively interpreted as a change of fragility.[14] This interpretation is firstly based on the Arrhenius-like temperature dependence of relaxation times in the glacial state, determined by dielectric experiments,[14] while the data was satisfactorily fitted with the Vogel–Fulcher–Tammann function in the undercooled liquid. However, the unphysically small exponential pre-factor is indicative of a non-Arrhenius behavior. Moreover, it is worth pointing out that the relaxation spectrum of the glacial state is characterized by an unusually broad distribution of relaxation times.[14,37] If the description of the glacial state as composed of nanocrystals in the undercooled matrix is adopted, dielectric data in the glacial state can be interpreted either as slow motions of nanocrystals or as slow molecular motions developing in the undercooled liquid confined in the interstitial volumes between nanocrystals. In the latter case, the dynamics of the confined undercooled liquid appears totally different from that of the normal liquid. If the glacial state is considered as homogeneous (liquid or solid), there is no realistic interpretation of dielectric data. The consideration of the glacial state as liquid is secondly based on NMR experiments.[14–18] The reorientational correlation function determined in the glacial state[14–18] corresponds to characteristic reorientational behavior observed in liquids and was considered as atypical of a crystal environment. This statement was not fundamentally in contradiction with the description of the glacial as a liquid–nanocrystalline mixed phase, since it is reported in Table 2 that the principal contribution of the glacial state prepared in the 210–220 K temperature range is liquid. Moreover, recent ^{2}H-NMR investigations[40] in the different states of TPP have revealed the difficulty to state about the nature of the glacial state, only from the consideration of NMR data. The two different descriptions of the glacial state—liquid or biphasic—are consistent with experimental NMR data. The evidence for monoexponential relaxation function in a glacial state formed at 217 K[15] is not in contradiction with our description of the glacial state, since at this temperature the glacial state is composed of a low contribution of nanocrystals which has no crystalline identity.

It emerges from our investigations that several experimental conditions have to be required to understand the origin and the nature of the glacial state.

(i) Systematic analyzes of glacial states formed at different temperatures T_a in the 210–235 K range are necessary to give a clear description of the glacial state.

(ii) All parameters which define the thermal history of the sample have to be drastically controlled, *i.e.* in protocol 1: the temperature of quench (T_q), the temperature of aging (T_a), and the heating rate from T_q up to T_a, which is not carefully controlled in several experimental investigations.[11]

(iii) Structural investigations appear as crucial probes for describing the glacial state. Using such techniques, sharp crystalline signatures emerge from broad contributions of amorphous states, even for small volume fraction of crystallinity. Pure dynamical probes only are not able to lead to a structural description of an unusual and intriguing state. Indeed, the glaciation has been the focus of numerous investigations because it is an unusual transformation, and the dynamics of the glacial state (*i.e.* the broad low-frequency band observed in dielectric experiments[14,37] is also very intriguing and not yet explained.

Experimental results reported in this paper, obtained from Raman spectroscopy, X-ray and neutron diffraction and inelastic neutron scattering, converge into the same description of the glacial state as a mixed phase composed of a high density of nuclei of the stable crystal in the matrix of undercooled liquid. The origin of the glacial state was determined as resulting from the high viscosity of the deeply undercooled liquid in the temperature range where the nucleation rate is high. The ability to control drastically the volume fraction of crystallinity in the glacial state, *i.e.* the stage of the aborted crystallization, from the determination of T_a can be considered as a very original feature in molecular glass-forming liquids. This feature gives the opportunity to investigate the behavior of deeply undercooled liquid close to T_g, especially the earliest stages of crystallization, and could be the source of further analyzes on the time-dependent nucleation phenomenon.

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