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Experimental evidence of formation of a new phase in supercooled liquid 2-biphenylmethanol

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Abstract

We report for the first time the formation of a new phase in a supercooled liquid molecular compound 2-biphenylmethanol by differential scanning calorimetry and x-ray diffraction measurements. It is found that at a crossover temperature $T_c \sim 1.2 T_g$ within a supercooled liquid metastable clusters (nuclei) start to appear where molecules are arranged in a different way than the stable phase. The development of the metastable nuclei into clusters of macroscopic size occurs at room temperature. Full crystallization into the new metastable phase happens after annealing for 10 min at the temperature of crystallization, 308 K. The structure of the new phase, as deduced from x-ray experiments, consists of hydrogen-bonded chains of molecules, contrary to the structure of the stable phase in which the molecules are joined into cyclic tetramers.

1. Introduction

The molecular structure of supercooled liquids, as well as the extraordinary viscous slow-down that accompanies supercooling and glass formation, remains an outstanding unresolved problem. For details on this problem, see reviews [1–3]. Experimental and theoretical evidence indicates that this slow-down is related to the growth of distinct relaxing molecular structures (cluster-like heterogeneities, structural organizations, large-scale density fluctuations, droplets, frustration-limited clusters, locally favoured structures etc) [4–15]. However, the structure of molecular organizations has not been established even at a basic level. It is quite likely that the key to understanding why slow dynamics start to appear when a liquid enters into the supercooled state upon cooling is understanding the nature and structure of the molecular organizations.

This is the purpose of this paper—to reveal the structure of molecular organization in supercooled liquid 2-biphenylmethanol (2BPM) using calorimetry, x-ray diffraction and IR spectroscopy.

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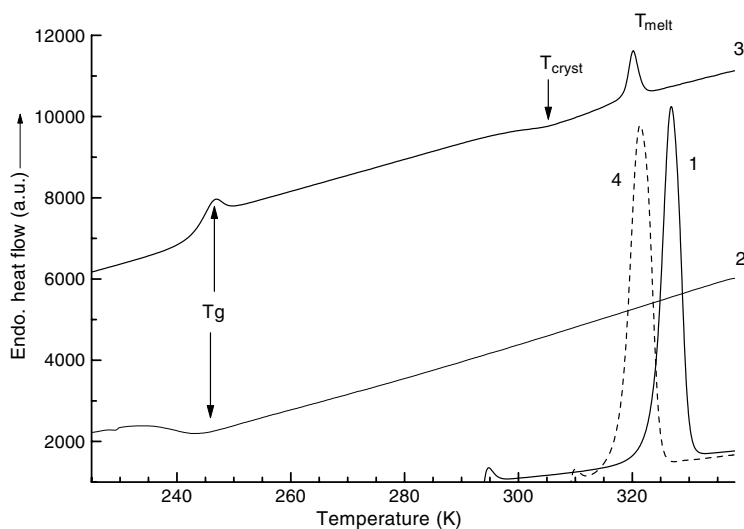


Figure 1. DSC curves for 2BPM: (1) heating of the crystalline phase from 300 to 343 K; (2) cooling of the liquid state from 343 to 104 K; (3) heating of the glassy state from 104 to 343 K; (4) heating of the glassy state from 308 to 343 K. In the cooling–heating cycle the scanning rate is 20 K min^{-1} . The sample mass is 10.93 mg.

2. Experimental procedure

The host material chosen for this study is 2BPM ($\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{OH}$), belonging to a class of molecular materials. 2BPM is a good glass former, meaning that its tendency to crystallization is effectively suppressed.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC-7 equipped with the CCA-7 low temperature accessory, using sealed Al pans. Liquid nitrogen was used as a coolant and the measurements were carried out in the temperature range 104–343 K.

The x-ray study was performed at room temperature on a KM-4 single crystal diffractometer with a CCD detector. The structure was solved and refined using the SHELX-97 program.

IR absorption spectra were recorded at room temperature in transmission on a Bruker model IFS-88 Fourier transform infrared spectrometer, with resolution 2 cm^{-1} and 32 scans being typically co-added. Data processing was performed with OPUS software.

3. Results and discussion

Figure 1 shows four DSC curves for 2BPM with a mass of 10.93 mg at heating/cooling rates of 20 K min^{-1} . Curve 1 shows the heating of the crystalline sample from room temperature to 343 K. Only one sharp endothermic peak is found at 326.8 K, which corresponds to the melting of the crystalline 2BPM. The onset of melting occurred at 323.7 K, and the melting enthalpy was determined to be 100.53 J g^{-1} . During cooling (curve 2) of the liquid sample from 343 to 104 K only a distinct glass transition at $T_g = 233.2 \text{ K}$ is clearly seen, indicating freezing of the supercooled liquid. Upon heating glassy 2BPM from 104 to 343 K (curve 3) the compound goes through the glass transition at 242.2 K (onset), crystallization at 297.7 K (onset) and then melts at 320.0 K. The onset of melting occurred at 318.4 K, and the melting enthalpy was determined to be 2.38 J g^{-1} .

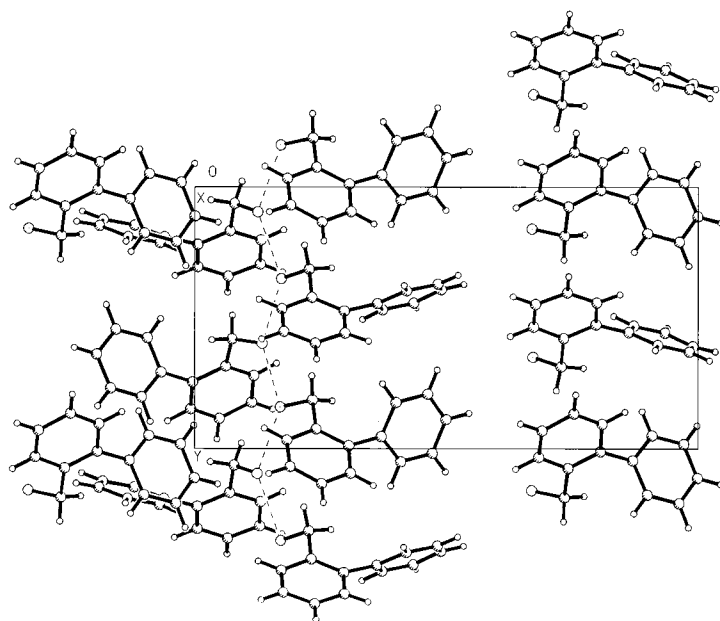


Figure 2. X-ray diffraction—the crystal structure of the metastable phase of 2BPM.

It is a surprising fact that the melting temperature of the phase formed in the supercooled liquid is different from that of the initial stable phase. Enthalpy of the melting of the new phase is very small in comparison with that of the stable phase. In other words the average fraction of the new phase in liquid is very small ($\sim 2\%$). It could be enlarged by annealing the sample at the crystallization temperature (308 K), which was previously quenched. The result of the annealing for 10 min at the temperature of crystallization, 308 K, is shown in figure 1 (curve 4). A large endothermic peak at 321.3 K, with a melting enthalpy of 82.2 J g^{-1} in curve 4 indicates that the crystallization process was completed during 10 min.

The question arises of whether the observed small endothermic peak at 320 K (figure 1, curve 3) corresponds to a new phase or whether it could come from the crystallization based on homogeneous nucleation due to the development of structural clusters. Such crystallization was found in *o*-terphenyl [16], salol [17] and triphenylethylene [18] and was interpreted to proceed through the coalescence of crystal embryos into the crystalline phase on the liquid–crystal interface. To answer this question we need to clarify the structure of the new phase, which we subsequently refer to as the metastable phase. Figure 2 shows the obtained metastable structure. The crystal of the metastable phase belongs to the monoclinic system with space group *Pc*. The four independent molecules are linked by hydrogen bonds into a chain. The lattice parameters are $a = 10.712 \text{ \AA}$, $b = 19.902 \text{ \AA}$, $c = 19.562 \text{ \AA}$, $\alpha = 101.25^\circ$. The density is 1.20 g cm^{-3} . The structure of the stable phase of 2BPM has been defined in our previous work [19]. It was established that the crystalline structure belongs to the triclinic system, space group *P1*. The lattice parameters are $a = 9.644 \text{ \AA}$, $b = 10.568 \text{ \AA}$, $c = 11.065 \text{ \AA}$, $\alpha = 75.74^\circ$, $\beta = 84.36^\circ$, $\gamma = 68.50^\circ$. The density is 1.21 g cm^{-3} . It is seen that the crystal lattice of the stable phase, as opposed to the metastable phase, is built up of hydrogen-bonded tetramers of 2BPM molecules.

The obtained results clearly indicate that the endothermic peak at 320 K really corresponds to a new phase and does not come from surface effects or strain on small crystallites in liquid. Surprisingly, the structure of the metastable phase detected in our work turns out to be just as reported in [20] for biphenyl-2-methanol.

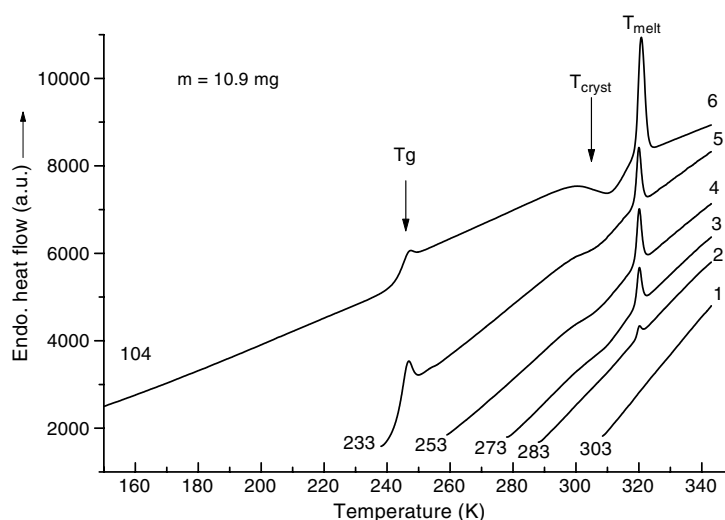


Figure 3. DSC heating curves for 2BPM obtained at a heating rate of 20 K min^{-1} . Each sample was previously cooled at 200 K min^{-1} from 343 K to the temperature indicated in the figure, and after that immediately reheated. The sample mass is 10.93 mg .

An important point is that 2BPM can stay in a liquid state at room temperature for as long as one likes (for example, a year). The only possibility to initiate crystallization is to quench the liquid 2BPM down to a low temperature and then reheat it. It is a well-known fact that for crystallization we need nuclei. No crystallization will proceed without nuclei. The fact that a liquid sample does not crystallize indicates that it does not contain nuclei, while nuclei emerge in the liquid sample after the quenching procedure. How can we elucidate the temperature at which nuclei start to appear? Using the DSC method, we could observe only macroscopic processes, such as crystallization or melting, while the process of nucleation, being a relatively microscopic process, is not directly observable by the DSC method. However, the appearance of the melting peak on the DSC curve means we could use this as a detector to examine at what temperature the process of nucleation starts. This method has been applied earlier and described in detail in [21].

Figure 3 shows six DSC curves all obtained at a heating rate of 20 K min^{-1} for a sample with a mass of 10.45 mg . Each sample for DSC measurement was previously cooled at 20 K min^{-1} from 343 K to the temperature indicated in the figure 4, and then subsequently heated. Curve 1 was obtained for the sample precooled to 303 K . We have not seen any endothermic peak due to melting. The next curve 2, for the sample precooled to 283 K , shows a melting peak with a very small enthalpy (0.16 J g^{-1}). In curve 3, for the sample precooled to 273 K , the melting peak area becomes larger (0.84 J g^{-1}). The sample precooled to 252 K (curve 4) shows an enthalpy of 1.14 J g^{-1} . In the cases of precooling to temperatures of 233 and 104 K , below the glass transition temperature (curves 5 and 6), the enthalpy continues to increase, reaching values of 1.75 and 2.38 J g^{-1} , respectively. Consider that the melting peak presupposes the presence of crystal nuclei; we can conclude that the nucleation process starts at about 283 K and proceeds to the glassy state. At 283 K there are only a few nuclei of the metastable phase; however, their number drastically increases with decrease in temperature. The obtained data are shown in figure 4, where the melting enthalpy (the average fraction) of the metastable phase is plotted as a function of temperature. The solid curve through the data in

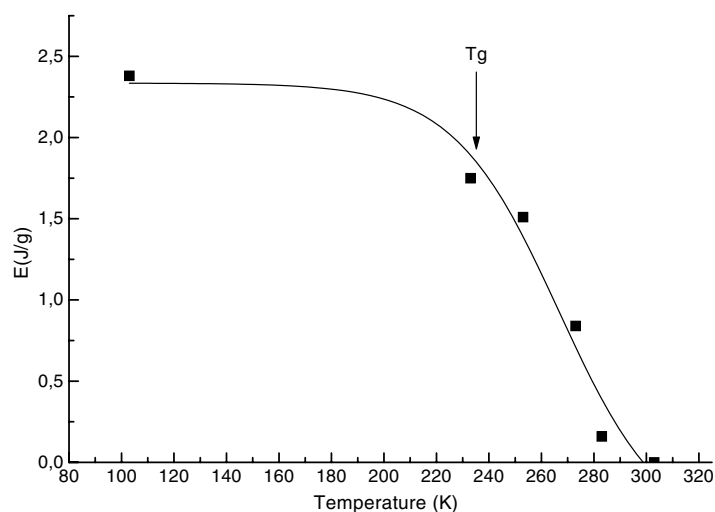


Figure 4. The melting enthalpy (the average fraction) of the metastable phase is plotted as a function of temperature. The solid line is the Boltzmann fit to the data.

figure 4 represents a Boltzmann (Sigmoidal) fit. For this purpose, the program package Origin 5.0 was used where Fit Sigmoidal menu command uses the Boltzmann equation for fitting:

$$Y = (A_1 - A_2) / \{1 + \exp[(T - T_0)/dT]\},$$

where T_0 is the centre, dT the width, A_1 the initial Y value and A_2 the final Y value.

Below 283 K nuclei are temporarily created and annihilated in a supercooled state that necessarily produces dynamic heterogeneity. In this temperature region nuclei could not increase their size due to high viscosity, and the liquid vitrifies without crystallization on cooling. However, nanometric scale nuclei turn out to be incorporated in the glass structure. If we go from low to higher temperatures, $T > 283$ K, nuclei then gain the possibility of moving around to undergo growth in their size. When the sizes of the nuclei become critical the process of crystallization begins.

These results are closely similar to the situation in benzophenone (BP). We have studied the process of nucleation in BP previously [22]. It has been established that the temperature at which nucleation starts is 243 K. Interestingly, the temperature of 283 K for 2BPM and 243 K for BP turn out to be close to the crossover temperature, $T_c = 1.2 T_g$, of mode-coupling theory (MCT) [23], at which the ergodic to non-ergodic transition takes place. In this connection, it is interesting to point out that the MCT critical temperature T_c in the supercooled liquid state of 2BPM and BP has been determined using optical Kerr effect experiments [24, 25]. It has been found that T_c is equal to 290 ± 4 and 250 ± 4 K for 2BPM and BP, respectively. These values of T_c are remarkably close to the temperature intervals where nuclei appeared in supercooled liquid 2BPM (303–283 K) and BP (253–243 K). Therefore, we can conclude that the origin of the crossover at T_c where the relaxation and slow dynamics start to proceed is related to the microscopic structure, namely, to the appearance of fluctuating metastable nuclei in the supercooled liquid.

It should be noted that the metastable phase is not stable and slowly transforms into a stable crystalline phase at room temperature. We have investigated the transformation of the metastable phase by means of IR spectroscopy. According to x-ray results, the hydroxyl groups ($-\text{OH}$) of methanol in the 2BPM molecule form intermolecular hydrogen bonds both

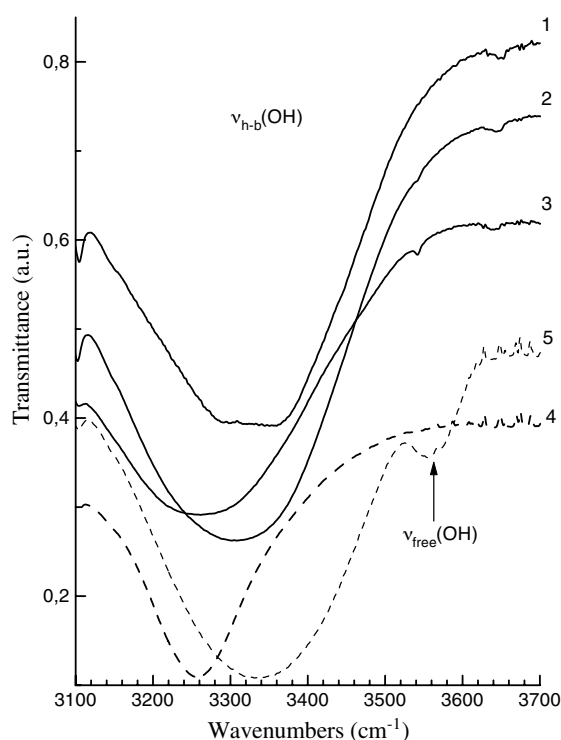


Figure 5. Transmittance spectra of 2BPM at $T = 293$ K: (1) the metastable phase recorded immediately after preparation; (2) the metastable phase recorded 15 min after recording 1; (3) the metastable phase recorded 30 min after recording 1; (4) the stable phase; (5) the liquid phase.

in the stable and metastable phases. In the IR spectrum the intermolecular interaction between hydroxyl groups results in the reduction of the stretching vibration frequency $\nu(\text{O-H})$ if compared to a free molecule. The value of a low-frequency shift depends on the energy of the hydrogen bonding. In our previous publications, we reported on the IR measurements of the stable crystal, glassy, and supercooled liquid phases of 2BPM and their temperature dependences [26, 27]. Figure 5 (curve 1) shows the IR spectrum of the metastable phase at room temperature in the OH stretching vibration region. For comparison, the spectra of the stable and liquid phases are also shown (figure 5, dotted curves 4 and 5). It is seen that only in the liquid phase is there a high-frequency band at 3550 cm^{-1} , which corresponds to the OH vibration of the non-associated free molecules (figure 5, curve 5). In the crystalline state of the stable phase (curve 4) only the wide intense OH band centred at 3250 cm^{-1} , which corresponds to the associated OH groups, is seen in the spectrum. In the metastable phase (figure 5, curve 1) the OH stretching band consists of two overlapping broad OH bands at 3290 and 3350 cm^{-1} , with the peaks positions somewhere in the interval between the positions of the OH bands in the stable and liquid phases. This indicates the presence of more close packing molecules in the metastable phase compared to the liquid phase and less close packing compared to the stable phase. The low-frequency component band in the metastable phase might be caused by a hydrogen-bonded interaction between the adjacent molecules in a chain, while the high-frequency component band might be caused by a hydrogen-bonded interaction between the molecules in the adjacent chains.

Next we study the evolution of the IR spectrum of the metastable phase (see figure 5, curves 1–3). Curve 1 shows the spectrum of the metastable phase recorded immediately after preparation; curves 2 and 3 were recorded 15 and 30 min, respectively, after recording 1. From figure 5 one sees that the OH band of the metastable phase show a gradual low-frequency shift, which means that the metastable phase grades into a stable one due to reconstruction of the network of hydrogen bonds. The observed transformation can be related to the presence of a small number of stable phase nuclei within the metastable phase.

The formation of nuclei within a supercooled state should not be unique to BP and 2BPM, but in our opinion could also be observed in other systems. The large-scale density fluctuations known as ‘Fischer clusters’ [12], which are observed in various molecular liquids and interpreted in terms of cluster-like heterogeneities [11], the ice-like water clusters in water [28, 29], and the mesoscopic array of domains (the glacial state) in the undercooled molecular liquid triphenyl phosphite [30] can reasonably be explained by the existence of the nanometric scale crystalline nuclei.

Recently Kurita and Tanaka [5] reported the nucleation-growth-type (at $T > T_g$) and continuous type (at $T < T_g$) transformations for another molecular liquid, *n*-butanol. Both transformations were directly observed with optical microscopy. The nucleation-growth-type transformation at $T > T_g$ is that in a supercooled liquid droplets emerge randomly in space and grow with time. It was suggested that such a transformation is governed by the cooperative ordering of the bond order parameter that is the number density of locally favoured structures. The types of locally favoured structures should depend on the details of molecular structures [4, 8]. The behaviour of the supercooled state of 2BPM resembles that in *n*-butanol. Really, in the case of 2BPM molecules have a strong ability to form hydrogen bonds that leads to the formation within a supercooled liquid of hydrogen-bonded associations of molecules. The molecules in such associations are linked by hydrogen bonds into chains. We can say that bond order parameter favours formation of chain-like structures (locally favoured structures) of 2BPM molecules. Such locally favoured structures, being a kind of crystal nucleus, have a fluctuating nature and their number increases on cooling. Crystallization occurs just after the glassy state becomes a liquid state.

Shintani and Tanaka have developed a simulation model [6]. Here the authors focus on the relationship between the dynamics and the medium-range crystalline structure and propose a possibility that this structure is a key structure for a supercooled state. It has also been shown that clusters of high crystalline order emerge below T_m . They are temporarily created and annihilated, and their average size remains constant with time. The authors concluded that dynamic heterogeneity and the slow dynamics are intrinsically related to medium-range crystalline ordering in supercooled liquids. In our opinion such behaviour of the supercooled liquid state is consistent with our experimental findings for 2BPM.

4. Conclusion

In conclusion, direct evidence has been found that at the crossover temperature T_c in supercooled liquid 2BPM the formation of a new phase starts with the creation within a liquid of a fluctuating hydrogen-bonded associations of molecules (nuclei), whose size is less than the critical size. This means that below T_c the supercooled liquid is dynamically heterogeneous. Hydrogen-bonded associations of molecules expand into clusters of macroscopic size upon heating. The full crystallization into the metastable phase happens at 308 K after annealing for 10 min. We have determined the structure, density and melting temperature of the metastable phase, which are found to be quite different from those of the stable phase.

Our experimental findings may be relevant to other molecular systems and give new insights into what happens in a supercooled liquid near glass transition.

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