OPTICS, ATOMS AND MOLECULES

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SPECTROSCOPIC AND THERMAL ANALYSES OF ORTHO-BENZYLPHENOL CRYSTALLINE POLYMORPHISM

In situ, we present the experimental spectroscopic proof of the existence of polymorphism in ortho-benzylphenol. Infrared spectroscopy was used for the first time to investigate the structural changes during the crystallization of a metastable phase, which is transformed, in the course of time, into a stable one. The results show that, in the stable and metastable phases, different conformers of ortho-benzylphenol molecule predominate, which differ in the orientation of the aromatic rings relative to the connecting methylene bridge. Namely, it is shown that the transformation of the metastable phase into a stable one is accompanied by the rotation of the OH-substituted aromatic ring relative to the connecting methylene bridge from 59.9° to 180.0° in the molecule of ortho-benzylphenol. The DSC experiment has shown that the process of nucleation of a metastable phase preferentially develops below ∼1.1 Tg (243 K), the crystallization occurs at ∼272 K, and the melting happens at 290.2 K. The difference in the temperature regions of nucleation and crystallization explains a good glass-forming status of ortho-benzylphenol.

K e y w o r d s: infrared spectroscopy, conformers, ortho-benzylphenol.

1. Introduction

Ortho-benzylphenol (o-benzylphenol) is an organic material with the formula ($C_{13}H_{12}O$, $C_6H_5CH_2C_6H_4OH$) that undergoes a glass transition and different polymorphic transitions. For this reason, it has been the subject of a number of experimental studies and theoretical considerations [1–5]. The molecule of o-benzylphenol consists of two phenol rings that are connected by methylene bridge (-CH_2-) and a hydroxyl group (-OH) attached to an ortho position of the ring. As well as the other OH-substituted benzene ring compounds (2-biphenylmethanol, 2-bromobenzophenone and salol) studied by us earlier [6–8], o-benzylphenol exhibits a strong tendency to supercooling. At present, there is a long list of evidences that some qualitative changes occur in the dynamics of supercooled liquid phases of glass forming systems in a particular temperature range 1.1–1.2 *Tg* [9]. The main question asked was about possible reasons for such universality. For 2-biphenylmethanol [6], salol [8], and benzophenone [8], we have shown that, at ∼1.2 *Tg*, the generation of fluctuating crystal nuclei of the metastable phase begins. Thus, it is the fluctuating nuclei that are responsible for dynamical heterogeneities in these

compounds. In our opinion, the formation of crystalline nuclei in a supercooled liquid state near *Tg* should not be unique only for 2-biphenylmethanol, benzophenone, and salol. To test this suggestion, we chose o-benzylphenol.

O-benzylphenol is an interesting material not only in connection with its glass-former status and the existence of polymorphism, but also in connection with the available information about the geometric structure of stable conformations of the molecule. It was established that the o-benzylphenol molecule can exist in four stable conformations, as shown in Fig. 1 of Ref. [1]. These conformers are defined by the two dihedral angles, which differ in the orientation of the aromatic rings respective to the connecting methylene bridge [1]. Calculations indicate that νCH_2 stretching vibrations are not especially liable to intermolecular interactions; however, they are conformationally sensitive and, therefore, could be used as a probe for conformational changes. This allows the changes in the IR spectra in the $\nu\ CH_2$ stretching vibration region to be associated with changes in the geometry of an o-benzylphenol molecule in different phases. However, to our knowledge, such studies of o-benzylphenol have not been performed. This provides a stimulus to the detailed spectroscopic study, which can give interesting information about the different crystal polymorphs of o-benzylphenol, as well as their conformational compositions.

As for the study of the different crystalline polymorphs of o-benzylphenol within the method of differential scanning calorimetry (DSC), only three works are known [3–5]. The old paper by McMaster and Bruner [3] reported the existence of two crystalline forms of o-benzylphenol: the metastable and stable phases that melt at $T = 294$ K and $T = 345$ K, respectively. In work [4] several metastable polymorphs were observed, with melting temperatures near 288, 290, and 294 K. It was shown that the most stable form is not easily recovered after the melting. The unusual crystallization of the metastable polymorph in o-benzylphenol with a melting temperature of 290 K was reported in Ref. [5]. In this context, we performed DSC measurements to determine, which of the metastable polymorphs crystallizes in supercooled liquid o-benzylphenol.

It is worth mentioning that o-benzylphenol is an efficient selective extractant for cesium [2], so the transformation of its structure under different conditions

can be of interest for chemists studying the processing of radioactive wastes. Considering the importance of o-benzylphenol for industrial applications, such investigation is of a certain interest.

2. Experimental

O-benzylphenol was purchased from Aldrich and used after the purification by the sublimation at room temperature.

Infrared measurements were done on a Fourier-transform infrared (FT-IR) spectrometer (Bruker model IFS-88) with a resolution of 2 cm^{-1}, and 32 scans were typically co-added for an individual spectrum in the frequency range of 400–4000 cm^{-1}. The data processing was performed with software OPUS. For the FT-IR transmittance measurements, a sample of a powder of o-benzylphenol was inserted in a cell with two KBr pellets at room temperature and then melted into a thin film. The thickness of such a cell was approximately a few micrometers. Such a sample was then fixed in an Oxford Duplex closed-cycle cryostat that can operate in the temperature range of 330–12 K with an accuracy of roughly 1 K.

Raman measurements were done at room temperature on a Fourier-transform infrared spectrometer equipped with a FRA-106 over a range of 100–3600 cm^{-1}, with a spectral resolution of 4 cm^{-1}, using a backscattering configuration. The wavelength of the excitation laser Nd:YAG was 1064 nm. The data processing was performed with software OPUS.

Calorimetric measurements were made by a differential scanning calorimeter (Perkin-Elmer DSC8000) equipped with a CCA low-temperature accessory. A small amount of the sample was enclosed in aluminum pans hermetically sealed with the use of a sample encapsulating press. Liquid nitrogen was used as a coolant, and the measurements were carried out in the temperature interval 104–348 K. Before the measurements, the calorimeter was calibrated, by using Indium.

3. Results and Discussion

3.1. Differential scanning calorimetry

Figure 1 shows calorimetric curves of o-benzylphenol measured at a scanning rate of 10 K/min. At first, the crystalline sample with a mass of 7.44 mg was

melted (curve *1*). It melts at $T_{\text{onset}} = 323.14$ K (maximum intensity is at $T_{\text{max}} = 324.7$ K), which gives rise to an endothermic peak (Fig. 1, dashed curve *1*). The melting enthalpy of this crystalline form, which is the most stable polymorph of o-benzylphenol, is $\Delta H = 115.66$ J/g. When this melted sample is cooled down to 213 K (at 10 K/min) the crystallization is avoided (absence of an exothermal peak on the DSC cooling curve *2*), only a distinct glass transition at $Tg_{\text{onset}} = 224.2$ K can be clearly seen (a step-like peak). Under the subsequent heating at 10 K/min from 213 K to 333 K (curve *3*), the compound goes through the glass transition at 223.8 K (onset), crystallizes (exothermic peak around 272 K), and then melts (endothermic peak) at $T_{\text{max}} = 290.2$ K (onset is at 287.4 K). The melting enthalpy of this crystalline form is $\Delta H = 74.8$ J/g. It should be noted that we have obtained only one metastable crystalline phase with the melting temperature at 290.2 K. This result is in accord with the DSC results reported by Paladi *et al.* [5]. The authors of Ref. [5] reported that o-benzylphenol samples were purified by the sublimation and repurified in the same way every half a month. We also purified our samples by the sublimation. Ramos *et al.* [4] indicated that they used the samples without preliminary purification. We think that this is the cause for that the authors of Ref. [4] observed three metastable polymorphs with melting temperatures at 288, 290, and 294 K.

Our interest is in the determination of the temperature, at which the process of nucleation starts. It should be noted that, by the DSC method, we could observe directly the macroscopic processes of crystallization and melting, while the nucleation, being a relatively microscopic process, is unobservable directly by any of the methods. However, the crystallization or melting peaks on DSC heating curves can be used as a detector to examine whether or not the nucleation process occurs, because the crystal growth presupposes the presence of crystal nuclei.

Figure 1 shows the DSC curves *3–7* obtained at a heating rate of 10 K min^{-1}. Each liquid sample for DSC measurements was previously quenched (precooled) at a cooling rate of 200 K min^{-1} from 333 K to the temperature Tn (precooling temperature) indicated in the figure and then measured on heating to examine if the crystallization (exothermic peak) or the melting (endothermic peak) appears on the DSC scans. Due to the fact that the crystallization begins
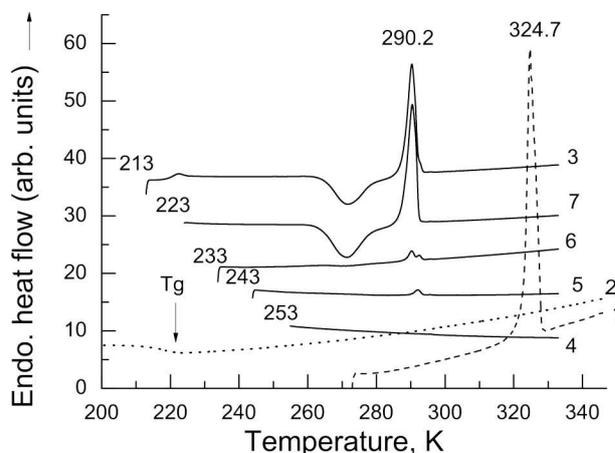

Fig. 1. DSC curves for o-benzylphenol obtained at a heating/cooling rate of 10 K min^{-1}. Curve *1*, melting of a crystalline sample. Curve *2*, cooling of a liquid sample from 345 to 200 K. Heating curves *3–7*. Each sample was previously cooled at 200 K min^{-1} from 345 K to the temperature indicated in the figure and, after that, immediately reheated. Temperature is given in K. The DSC curves are vertically shifted for the sake of clarity

with the formation of crystal nuclei, their formation can be judged from the appearance of corresponding peaks on a DSC curve. Upon the heating from the precooled temperature 253 K, no anomaly was observed on the DSC curve (Fig. 1, curve *4*). The next curves, *5* and *6*, for the samples precooled to temperatures 243 K and 233 K show tiny endothermal peaks at ~ 290 K with a very small enthalpy 1.1 Jg^{-1} and 2.9 Jg^{-1}, correspondingly. Curve *7* for the sample precooled to $Tn = 225$ K close to Tg shows a large endothermal peak at 290.2 K with an enthalpy of 50.19 Jg^{-1}.

In view of the fact that the crystal growth proceeds only in the presence of crystal nuclei, it follows from the above results that the nucleation temperature of the metastable phase lies in the interval 243–253 K, which corresponds to ~ 1.1 Tg. Below this temperature, a dynamic heterogeneity should appear in o-benzylphenol. It should be noted that the metastable phase tends to nucleate in preference to the stable phase in a supercooled liquid.

It can be seen in Fig. 1 that the intensity of the melting peak of the metastable phase at 290.2 K strongly depends on the precooling temperatures Tn. Namely, a partial quantity of the metastable phase in the supercooled liquid increases sharply
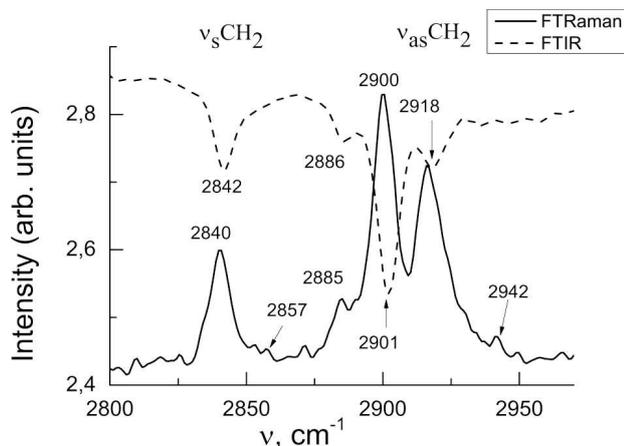
Fig. 2. Fragments of the FT-IR (top) and FT-Raman spectra of the stable crystalline phase of o-benzylphenol in the -CH$_2$-vibration region recorded at room temperature

as Tn approaches the glass transition temperature Tg. Another point, to which we pay attention, is that the crystal growth occurs at the temperature ~270 K, while the crystal nucleation occurs below 243 K. Therefore, when we cool a liquid sample through the temperature range at the maximum crystallization rate (270 K), the crystal nuclei are absent, so the crystallization is impossible (Fig. 1, curve *2*). When we approach the temperatures below 243 K, where the nucleation process starts, the viscosity is too high to allow nuclei to grow, so there is no crystallization. Only when the supercooled liquid sample is heated from 243 K through the crystallization temperature, these nuclei have the possibility to grow via molecular collisions. This explains the fact that the supercooled liquid sample is more stable in respect to the crystallization, when we cool the liquid phase, than when we reheated the glassy or deeply supercooled phase.

3.2. Infrared spectra

We have studied the FT-IR transmission spectra of o-benzylphenol in the wide spectral range (400–4000 cm^{-1}). However, in this study, we will analyze only the methylene bridge vibrations of CH$_2$ in the spectral interval 2800–3000 cm^{-1}, which depend on the dihedral angles between the plane of the aromatic rings and the plane of the connecting methylene bridge. Such a study will give an answer to the question of which conformers are realized in different condensed states.

The presence of several conformers in o-benzylphenol [1] should lead to the observation of a corresponding number of bands in the vibrational spectra related to symmetric ν_sCH$_2$ and antisymmetric ν_{as}CH$_2$ vibrations, whose wavenumbers are determined by dihedral angles. Figure 2 shows fragments of the FT-IR and FT-Raman spectra in the νCH$_2$ spectral region of crystalline o-benzylphenol recorded at room temperature. It can be seen that the spectroscopically detected bands are quite distinct from one another, which facilitates the assignment of the bands to conformers I, II and, III, by using the results of work [1].

In the FT-IR spectrum in the spectral interval 2888–2950 cm^{-1}, where antisymmetric ν_{as}CH$_2$ vibrations manifest themselves (Fig. 2, top), two distinct bands at 2901 and 2918 cm^{-1} are seen. In the FT-Raman spectrum in this region (Fig. 2, bottom), three bands at 2900, 2917, and 2942 cm^{-1} are seen. In the spectral interval 2800–2888 cm^{-1}, where symmetric ν_sCH$_2$ vibrations manifest themselves in the IR spectrum (Fig. 2, top), two bands at 2842 and 2886 cm^{-1} are observed. In the Raman spectrum (Fig. 2, bottom), two bands at 2840 and 2885 cm^{-1} are present. According to the assignment of Ref. [1], the bands around 2840 and 2900 cm^{-1} correspond to conformer I; the bands around 2857 and 2918 cm^{-1} correspond to conformer II, and the bands at 2885 and 2942 cm^{-1} to conformer III. The dihedral angles between the plane of the substituted aromatic ring and the plane of the methylene bridge for conformers I, II, and III are equal to 180.0°, 59.9°, and 94.5°, and the dihedral angles between the plane of the unsubstituted aromatic ring and the plane of the methylene bridge for conformers I, II, and III are equal to 89.9°, –132.1°, and –73.6°, correspondingly [1]. Using this information, it is possible to relate the changes in the CH$_2$ stretching vibration region in the FT-IR spectra to changes in the geometry of an o-benzylphenol molecule during phase transitions. At first, we study the temperature dependence of the FT-IR spectra of a crystalline sample from 12 K to 295 K (Fig. 3). No major evolution of the FT-IR spectra is observed in this temperature range. Only a small temperature shift of the frequency of the most intense band ν_{as}CH$_2$, which does not exceed 2 cm^{-1}, is seen. This band corresponds to antisymmetric stretching vibrations of the methylene bridge in conformer I.

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The melting temperature of the crystal is 324.7 K. So, as the temperature increases up to 330 K, the sample must melt. The dashed curve in Fig. 3 corresponds to the spectrum of the liquid phase recorded at 330 K. In the liquid phase, the most intense wide band at 2924 cm^{-1} is associated with antisymmetric stretching vibrations $\nu_{as}CH_2$ in conformer II. Analyzing the spectra of the liquid and stable crystal phases, we can say that, in the stable crystal, conformers I predominate, whereas conformers II do in the liquid phase.

According to the DSC data, the metastable phase of o-benzylphenol could be obtained by heating a supercooled liquid sample, which was precooled to a temperature close to Tg. So, we first cooled the liquid sample to 225 K. Curve 1 in Fig. 4 shows the spectrum of the supercooled liquid recorded at 225 K. Thereafter, the temperature was raised to 285 K, which is close to the temperature range of the crystallization. At this temperature, we followed the evolution of the FT-IR spectra as a function of the time. The dashed curve 2 in Fig. 4 shows the spectrum of the supercooled liquid phase recorded immediately after reaching 285 K. No major changes between these two spectra can be seen. In both spectra, the strongest is the wide band at 2919 cm^{-1}, which is associated with antisymmetric vibrations of the methylene bridge in conformer II. Curve 3 shows the spectrum recorded in 20 min after the recording of spectrum 2. It is seen that the FT-IR spectrum drastically changes with the time. In 20 min, the most intense wide band $\nu_{as}CH_2$ at 2919 cm^{-1} is transformed into a narrow band at 2917 cm^{-1}. The band ν_sCH_2 at 2850 cm^{-1} is split into two bands at 2839 and 2855 cm^{-1} corresponding to symmetric vibrations of the bridge in conformers I and II. Such transformation of the spectra is the evidence of the crystallization of the metastable phase, in which conformers II predominate.

The changes in the spectrum do not stop in the course of the time. In 35 min after the recording of spectrum 2, the new band at 2902 cm^{-1} associated with bridge vibrations $\nu_{as}CH_2$ in conformer I appears in the spectrum (Fig. 4, curve 4). Such a change in the spectrum is the evidence of that the metastable phase at 285 K is partially transformed into the stable phase. As a result, the spectrum represents a mixture of two phases: stable and metastable ones (curve 4). To verify that curve 3 in Fig. 4 repre-
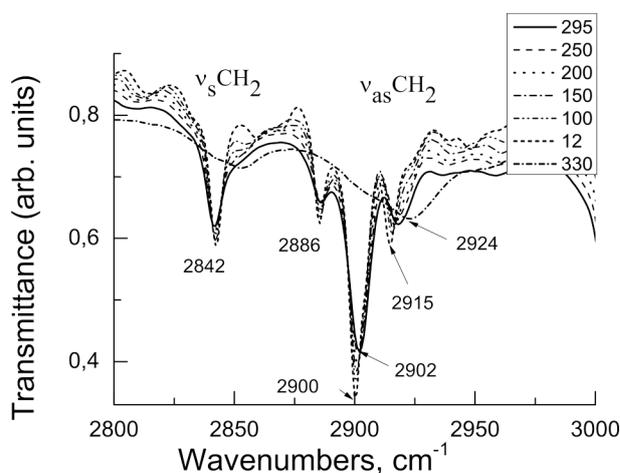

Fig. 3. Temperature dependence of the FT-IR spectra of the stable crystal in the -CH$_2$- spectral range. Temperatures are (top to bottom): 295, 250, 200, 150, 100, 12 K. The dashed curve is the spectrum of the liquid phase at 330 K
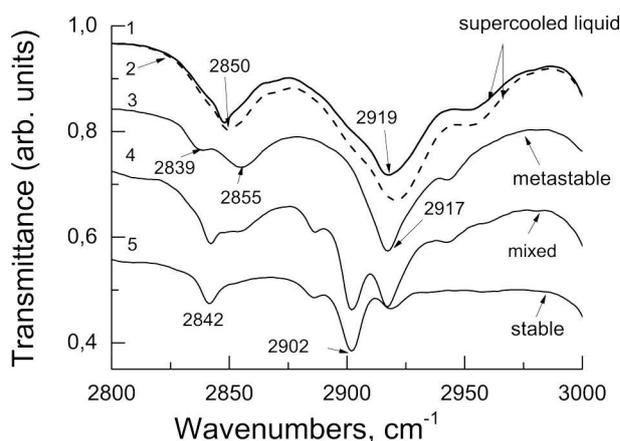

Fig. 4. Evolution of the FT-IR spectra of o-benzylphenol from the supercooled liquid through a metastable polymorph to the stable phase in the -CH$_2$- spectral range. Curve 1 is the spectrum of the supercooled liquid recorded at 225 K. Curve 2 is the spectrum of the supercooled liquid recorded at 285 K. Curves 3, 4 were recorded in 20 and 35 min after recording the spectrum (2). Curve 5 is the spectrum recorded at 300 K

sents the spectrum of the metastable phase, we heat the sample to 300 K, which is above the melting point of the metastable phase ($T_{\text{melt}} = 290.2$ K), but below the melting point of the stable phase ($T_{\text{melt}} = 324.7$ K). The metastable phase at 300 K should be absent in the spectrum. Indeed, in the spectrum recorded at 300 K, the intensity of the band at 2917 cm^{-1} corresponding to the antisymmetric bridge
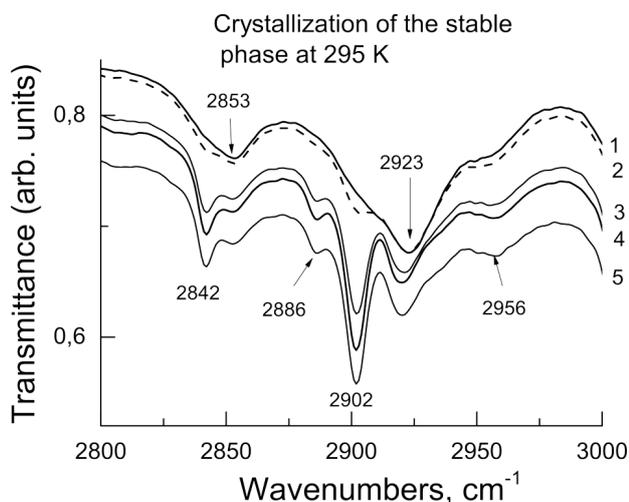
Fig. 5. Evolution of the FT-IR spectra at room temperature from the supercooled liquid to the stable phase in the -CH$_2$- spectral range. Curve *1* is the spectrum of the liquid phase recorded at 325 K. Curve *2* is the spectrum recorded at 295 K. Curves *3–5* were recorded in 12, 40, and 60 min after the recording of spectrum (2)

vibrations in conformer II decreases sharply, and the spectrum becomes similar to that of the stable phase (Fig. 4, curve *5*). The most distinguishing characteristic of the stable phase spectrum as opposed to the spectrum of the metastable phase in the spectral region of bridge vibrations T_{melt} is the existence of the strong band at 2902 cm^{-1}, which is absent in the spectrum of the metastable phase. This information allows us to identify each polymorph of o-benzylphenol by studying their IR spectra.

While the crystallization of the metastable phase occurs at 285 K when it is heated from 225 K, the crystallization of the stable phase occurs at room temperature. In Fig. 5, the crystallization of the stable phase is presented. The liquid sample was firstly cooled from 325 K to a temperature of 295 K, at which we followed the time evolution of the FT-IR spectra. Curve *1* in Fig. 5 represents the spectrum of the liquid phase at 325 K. The dashed curve *2* shows the spectrum of the supercooled liquid phase recorded immediately after reaching 295 K. Curves *3–5* were recorded in 12, 40, and 60 min, respectively, after the recording of spectrum 2. From Fig. 5, it can be seen that, in 12 min, the bands corresponding to the bridge vibrations ν_{as}CH$_2$ in conformer I begin to dominate in the spectrum. Changes in the spectrum

cease in 60 min (Fig. 5, curve *5*). This means that the crystallization of the stable phase is completed within 60 min.

As was mentioned above, the conformers are defined by the orientation of the aromatic rings relative to the connecting methylene bridge. From the results obtained, it follows that, in the stable phase, conformers I predominate, whereas, in the metastable phase, conformers II do. The dihedral angle between the plane of the OH-substituted aromatic ring and the plane of the connecting methylene bridge is equal to 180.0° and 59.9° for conformers I and II, respectively [1]. Thus, we can conclude that the transformation of the metastable phase into the stable one is accompanied by the rotation of the OH-substituted aromatic ring relative to the connecting methylene bridge from 59.9° to 180.0°.

4. Conclusion

The FT-IR spectroscopy gives the possibility to obtain information about changes in the molecular structure of o-benzylphenol during the transformation of the metastable phase into the stable one. It is shown that, in the stable and metastable phases, different conformers predominate. In molecules being in the stable phase, the dihedral angle between the plane of the OH-substituted aromatic ring and the plane of the connecting methylene bridge is equal to 180.0°. In molecules in the metastable phase, this angle is equal to 59.9°. Thus, the transformation of the metastable phase into a stable one is accompanied by a rotation of the OH-substituted aromatic ring relative to the connecting methylene bridge from 59.9° to 180°.

The DSC experiments have shown that the nucleation process of the metastable phase in o-benzylphenol preferentially develops below 1.1 *Tg*. The temperature region of the nucleation is significantly lower than that of the growth. The melting temperature of the metastable phase is found to be 290.2 K. The intensity of the melting peak of the metastable phase strongly depends on the temperature, to which the sample was cooled before DSC measurements.

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СПЕКТРОСКОПІЧНИЙ ТА ТЕРМІЧНИЙ
АНАЛІЗ КРИСТАЛІЧНОГО ПОЛІМОРФІЗМУ
ОРТО-БЕНЗИЛФЕНОЛУ

Р е з ю м е

На основі експериментальних спектроскопічних досліджень доведено існування поліморфізму у орто-бензилфенолі. Вперше для дослідження структурних змін у процесі кристалізації метастабільної фази, яка з часом трансформується в стабільну фазу, використана інфрачервона спектроскопія. Результати свідчать про те, що в стабільній і метастабільній фазах переважають різні конформери молекули орто-бензилфенола, які відрізняються орієнтацією ароматичних кілець по відношенню до з'єднувального метиленового містка. Зокрема, було показано, що трансформація метастабільної фази в стабільну супроводжується обертанням OH-заміщеного ароматичного кільця в молекулі орто-бензилфенола по відношенню до метиленового містка від кута 59,9° до 180,0°. Експеримент ДСК показав, що процес нуклеації метастабільної фази переважно розвивається нижче ∼1,1 *Tg* (243 K), кристалізація – при ∼270 K, а плавлення – при 290,2 K. Різниця в температурних інтервалах нуклеації і кристалізації пояснює хорошу здатність орто-бензилфенолу до склування.