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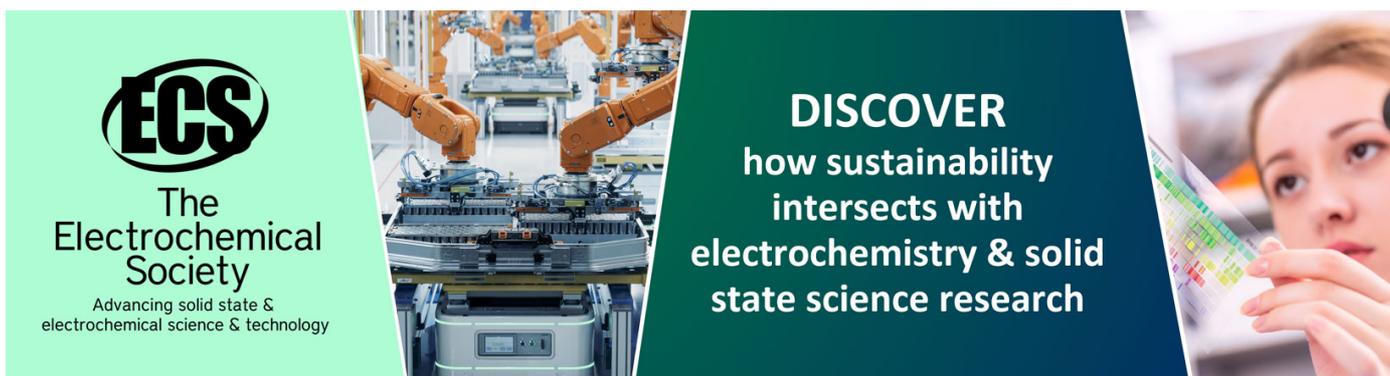
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## In-situ WAXS study of the crystal structure of R-BAPB oligoimide during heating

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**Abstract.** In the process of this work, an oligoimide FT-BAPB-R-BAPB-FT was synthesized, the particles of which consist of numerous lamellas having a semi-crystalline structure. On the DSC thermogram of oligoimide powder, two endo peaks were observed at 281.1°C and 306.4°C. A unique WAXS experiment was performed *in-situ* by heating the reactor oligoimid powder in a heat chamber. There was no significant difference in the X-ray profiles when the sample was heated. It should be noted that the transformation of the crystalline cell does not occur until the sample melts. It was revealed that the degree of crystallinity decreases during heating. We believe that the low-temperature endopeak is associated with the melting of small crystallites and amorphization of the sample. However, a significant increase in crystal size was found to be a result of recrystallization. Thus, the high-temperature endopic corresponds to the melting of larger crystallites.

### 1. Introduction

It is found that typical semirigid-chain polymers such as poly(ethylene terephthalate), PET, poly(butylene terephthalate), (PBT), poly(trimethylene terephthalate), PTT, and poly(ether ether ketone), PEEK, demonstrate a very complex thermal behavior [1–3]. To date, based on the data obtained by the differential scanning calorimetry (DSC) method [4, 5], it is known that a multiple melting peak can be observed upon heating and cooling of thermoplastic polymers. It is assumed that such double melting peaks appear on the basis of two different crystal growth mechanisms. Namely, these mechanisms correspond to the growth and melting of spherulite and epitaxial crystals. To study the growth of crystallites in partially crystalline polymers, it is very important to investigate the process of crystallite melting, which can affect the final polymer crystallinity. Nowadays, it is clear that conventional thermal analysis methods, such as DSC, cannot provide the full understanding of the nature of different thermal transitions.

In the present work, double endothermic behavior, i.e. the appearance of double melting peaks and the corresponding morphology of crystallites of model FT-BAPB-R-BAPB-FT oligoimide were investigated using scanning electron microscopy (SEM), DSC and *in-situ* wide-angle X-ray scattering



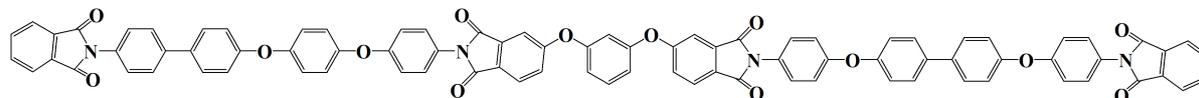
(WAXS) methods. Thus, a comprehensive fundamental study on the new polymer was carried out making an invaluable contribution to the modern physics of polymers.

## 2. Experimental part

### 2.1. Material

The following monomers were used to synthesize oligoimide: 1,3-bis(3', 4-dicarboxyphenoxy) benzene dianhydride (R dianhydride),  $T_m \sim 163-165^\circ\text{C}$ , (OOO TechHimProm, Yaroslavl, Russia), diamine 4,4-bis(aminophenoxy) diphenyl (BAPB),  $T_m \sim 198-199^\circ\text{C}$ , manufacturer VWR International. Phthalic anhydride was chosen as the chain growth limiter during polycondensation ( $T_m \sim 131-134^\circ\text{C}$ , Sigma-Aldrich Co. LLC). Triethylamine, benzene, acetic anhydride were obtained by Sigma-Aldrich Co. LLC.

The synthesis of oligoimide bis (phthalimide-4-N- phenoxybiphenyl[bis(4' - oxy, 4'' - N-phenylimide) 1,3-bis(3', 4-bicarboxyphenoxy)benzene] by chemical imidization was carried out. In the first step, an oligomeric diaminoamido acid was prepared by reacting a twofold excess of 4,4'-bis(4''-aminophenoxy) diphenyl with 1,3-bis(3', 4-dicarboxyphenoxy) benzene dianhydride in N-MP. Phthalic anhydride was added to the resulting amidoacid in an amount equivalent to the number of amino groups. The resulting oligomeric amic acid was imidized by adding a mixture of pyridine, acetic anhydride and benzene at room temperature. After imidization, an FT-BAPB-R-BAPB-FT oligoimide (see Figure 1) powder particles precipitated. The powder was filtered, washed with sulfuric ether and methyl alcohol, dried in vacuum at a temperature of  $80^\circ\text{C}$ . The process of the oligoimide synthesis is described in detail in [6, 7].



**Figure 1.** A chemical structure of the FT-BAPB-R-BAPB-FT oligoimide.

### 2.2. SEM

The morphology of the FT-BAPB-R-BAPB-FT oligoimide reactor powder was studied using a SUPRA 55VP scanning electron microscope (Carl Zeiss, Germany). The samples were coated with a thin layer of Pt.

### 2.3. DSC

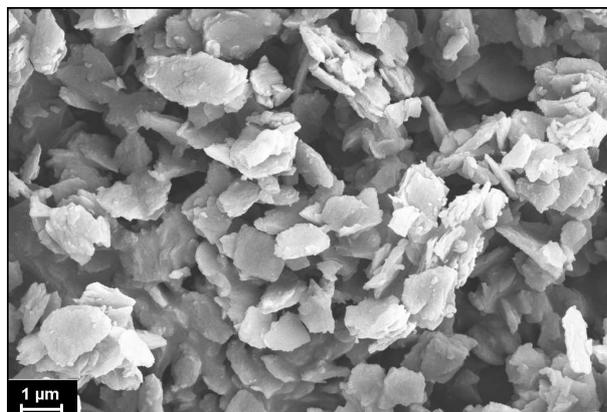
The thermophysical properties of the obtained FT-BAPB-R-BAPB-FT powders were investigated by differential scanning calorimetry using the DSC 204 F1 instrument (NETZSCH, Germany). The tests on the oligoimide powder were carried out in the temperature range from  $30$  to  $380^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in an inert atmosphere (argon). NETZSCH Proteus® software was used to determine the the melting temperature  $T_m$ .

### 2.4. In-situ WAXS

The fine crystalline structure of the FT-BAPB-R-BAPB-FT oligoimide powder was studied by the WAXS using a Rigaku Ultima IV ( $\text{CoK}_\alpha$ ) diffractometer equipped with a thermal camera. X-ray profiles were recorded online in the range from  $150$  to  $320^\circ\text{C}$  in increments of  $5^\circ\text{C}$ .

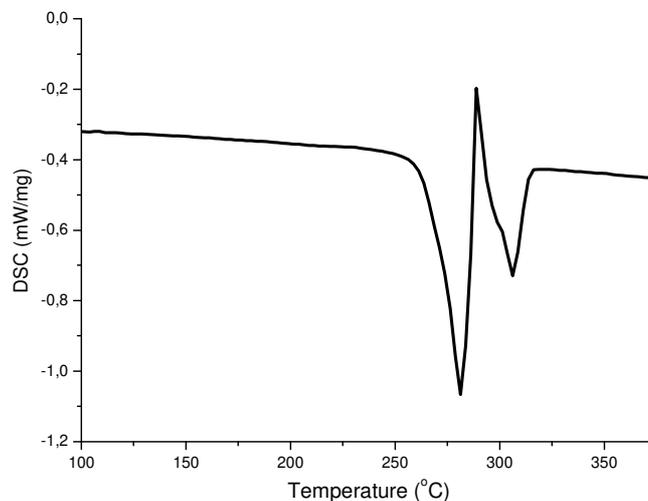
## 3. Results and Discussion

An SEM study of FT-BAPB-R-BAPB-FT oligoimide powder particles revealed that these particles have lamellae morphology (Figure 2). It is assumed that these lamellas have a partially crystalline structure and are most likely formed during synthesis. To confirm this assumption, a thermogram of FT-BAPB-R-BAPB-FT oligoimide powder was recorded by DSC.



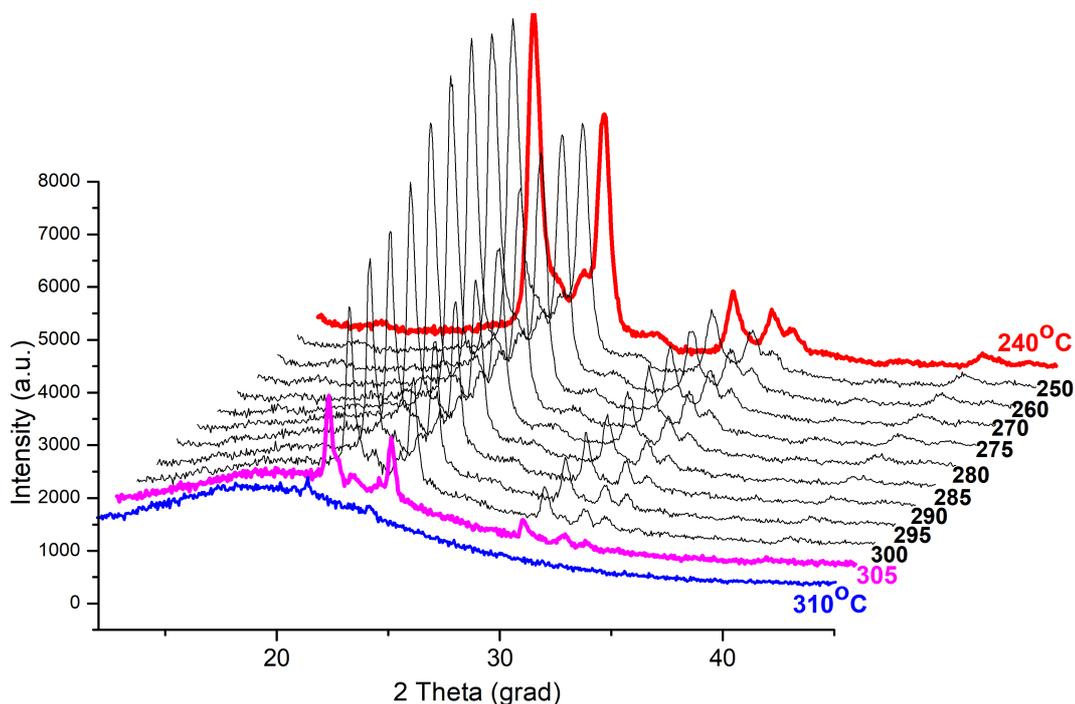
**Figure 2.** SEM image of the reactor oligoimid powder.

Figure 3 shows a thermogram of FT-BAPB-R-BAPB-FT oligoimide powder, the main feature of which is the presence of two endopeaks at 281.1°C and 306.4°C. Moreover, it is clearly seen that the areas under these two endopeaks are not the same. It can be concluded that oligoimide lamellas consist of crystallites that melt in a special way. Thus, it should be assumed that the initial reactor oligoimide powder has two phases that melt at different temperatures (this difference is more than 20°C). Based on this, the following two hypotheses can be proposed: 1) the lamellas of oligoimide FT-BAPB-R-BAPB-FT consist of two types of crystallites having different crystal cells; 2) or crystallites are identical in terms of crystallography, but their sizes are very different (according to [8]).



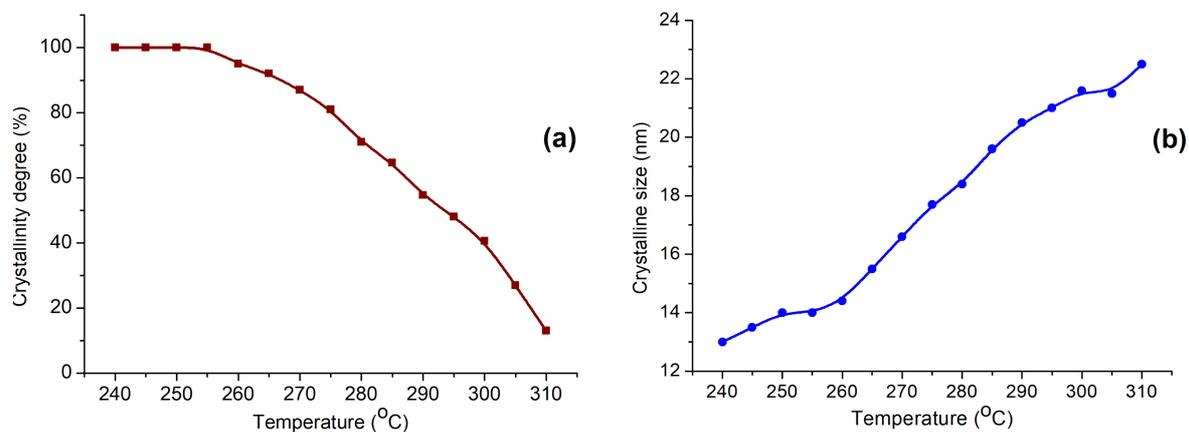
**Figure 3.** DSC thermograms of the oligoimid reactor powder.

Thus, a very interesting phenomenon was discovered in the test material. For a detailed study of the nature of the observed thermodynamic behavior, X-ray diffraction profiles were recorded online while heating the reactor powder. Figure 4 represents the results obtained in these *in-situ* WAXS experiments. No significant difference in the X-ray profiles is observed throughout the heating of the sample, except that the WAXS reflections become narrower and better resolved. It should be noted that until the oligoimide powder melts, no transformation of the crystalline cell occurs. Consequently, these results give us the opportunity to assert that our second hypothesis was true.



**Figure 4.** WAXS profiles obtained by *in-situ* heating of the oligoimid reactor powder.

The sizes of crystalline regions and the degree of crystallinity at each temperature were calculated (see Figure 5). It turned out that heating the sample leads to a double increase in crystallite sizes and a gradual decrease in the degree of crystallinity (i.e., amorphization) during heating.



**Figure 5.** Dependencies of crystallinity degree (a), the average crystalline size (b) of the oligoimid sample on the temperature.

This confirms the previously described idea regarding the attribution of a high-temperature endopic to the melting of larger crystallites. Thus, the following explanation of double melting peaks on DSC thermograms can be suggested: the oligoimide reactor powder consists of two crystallite fractions with different sizes. When heated, these fractions melt at different temperatures: small crystallites are stable up to 281.1°C, while larger crystallites melt further at 306.4°C. At an intermediate temperature point between two melting peaks of 289.1°C, the mobility of the molten chains is quite high, that leads to recrystallization of the material. Finally, this leads to the formation of large crystallites. This process is

similar to Oswald recrystallization, which has been well studied for low molecular weight solids. Recrystallized large crystallites exhibit a higher melting point, which is very logical.

#### 4. Conclusions

Summarizing all the results obtained, one can draw the following conclusions:

- FT-BAPB-R-BAPB-FT reactor powder particles are composed of numerous lamellas that have a semicrystalline structure;
- When heating the studied oligoimide, two endopes were detected at 281.1°C and 306.4°C using the DSC method;
- A unique WAXS experiment was conducted *in-situ* by heating the reactor powder in a heat chamber. It was found that when the sample was heated, there was no apparent difference in the WAXS profiles, i.e. to the end of the low-temperature endopeak. At the same time, WAXS peaks become narrower and better resolved. It should be noted that the transformation of the crystalline cell does not occur until the sample melts;
- It was found that the degree of crystallinity gradually decreases until the sample is completely melted. Thus, one can conclude that the low-temperature endopeak is associated with the melting of small crystallites and amorphization of the sample. On the other hand, a smooth increase in crystal size was found to be a result of recrystallization process attributed to the high-temperature endopeak to the melting of larger crystallites.

#### Acknowledgments

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