Experimental investigation on the thermal resistance of thermotropic aromatic oligoesters

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Abstract. Synthesis and characterization of liquid crystalline polymers based on 4-hydroxybenzoic acid, aromatic dibasic acids, and aromatic diols via a high-temperature polycondensation are described. FT-IR spectroscopy was employed to evaluate a molecular weight of the samples that can be considered as oligoesters. The mesophase existence ranges of the samples were estimated by means of DSC and optical polarizing microscopy. Liquid crystalline oligoesters offer excellent thermal ($T_0=250-373$ °C) properties. The macromolecules obtained contain reactive terminal groups and retain the ability to grow at elevated temperatures.

1. Introduction
High-molecular compounds that maintain their physical and operational properties under temperatures exceeding 250-300 °C are regarded as heat-resistant polymers. The presence of chemical moieties with high bond-dissociation energy in the macromolecules, such as multiple bonds and carbon-heteroatom bonds, contributes to the resistance of polymeric materials to high temperatures. One such group of polymers incorporates mesogenic fragments in the main chain and is called liquid-crystalline (LC) polymers, which are highly used due to the unique combination of rheological, mechanical, and thermal properties [1]. Depending on the structure of the main chain, these macromolecules may be divided into polyesters, polyamides, polyesteramides, polyimides, etc.

LC polyesters are currently acknowledged as the promising class of thermoplastics for developing multifunctional advanced materials. Such interest predominantly stems from their valuable properties: by low melt viscosity, high thermal stability, low flammability and smoke emission, excellent mechanical properties (self-reinforcement), resistance to UV and ionizing radiation, stress-crack resistance (impact strength), chemical resistance to aggressive media and solvents, low water absorption, anisotropic optical and dielectric properties. The optimal selection of comonomers enables the processing of LC polyesters at elevated temperatures (about 250-300 °C), which makes it possible to manufacture self-reinforced heat-resistant products [2, 3]. The low viscosity of LC melts diminishes processing costs and allows molding of thin-walled products.

In this work, we will report on a series of LC polymers based on 4-hydroxybenzoic acid via a high-temperature polycondensation route. Figure 1 depicts the molecular structures of the synthesized compounds.
2. Experimental
IR spectra were obtained, after averaging 16 scans in the interval from 4000 to 600 cm$^{-1}$ (4 cm$^{-1}$ of resolution), in an InfraLUM FT 08 FTIR spectrometer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests were performed using thermal analyzer TGA/DSC 3+0 (Mettler Toledo). The samples (0.1 g) were loaded in alumina pans and ramped to 773 K at a heating rate of 5 K/min in a nitrogen atmosphere. A Polam P-312 optical microscope equipped with a hot stage was used to investigate the melting behavior as a function of temperature. The samples were placed between glass slides upon heating using a heating rate of 20 °C·min$^{-1}$.

![Chemical formulas of LC oligoesters](image)

Figure 1. Chemical formulas of LC oligoesters.

3. Discussion
Structural features of the LC oligoesters have been investigated by FTIR analysis (Figure 2). The absorption band at 1732 cm$^{-1}$ is assigned to the stretching vibrations of carbonyl in polymers. This observation differs substantially from spectra of 4-HBA, for which it appears at 1670 cm$^{-1}$. The spectra of samples also contain bands associated with stretching vibrations of the aromatic ring at 1569-1627 cm$^{-1}$ and 1478-1530 cm$^{-1}$. The absorption bands at 1160 cm$^{-1}$ and 1050-1065 cm$^{-1}$ can be attributed to the stretching vibrations of the C-O bond, whereas absorbance at 1300-1250 cm$^{-1}$ is due to the presence of Ar-O-C linkage.

The FTIR spectroscopy was used to estimate the molecular weight of the obtained oligoesters. The content of the carboxyl end group was evaluated by calculating the absorbance ratio of the carbonyl group of carboxylic acid and that of the ester linkage. It was previously established that the stretching vibrations of the terminal carbonyl groups at 1695 cm$^{-1}$ have not coincided with those for carbonyl from the polymer backbone being observed at 1740 cm$^{-1}$. The molecular weight of the samples was found by the following Equation 1:

$$M = \frac{1}{\frac{D_1}{K_1} \cdot \frac{D_2}{K_2}} \cdot M_0,$$

where $M_0$ – the molecular weight of repeating unit;
$D_1$ и $D_2$ – the absorbance of bands at 1695 cm$^{-1}$ and 1740 cm$^{-1}$, respectively;
$K_1$ и $K_2$ – the absorbance coefficients for wavenumbers at 1965 cm$^{-1}$ and 1740 cm$^{-1}$, respectively.
The ratio $K_2/K_1$ was found from calibration curves for binary mixtures composed of phenyl ester of 4-HBA and the corresponding polyester. An average value of $K_2/K_1$ was equal to 0.444. The molecular weights of LC polyesters calculated from spectroscopic data were listed in Table 1.

Since the melting behaviour and processability of LC polymers are closely related to their chemical structure, differential scanning calorimetry was employed to study the thermal properties of samples (Figure 3). Poly(p-oxybenzoate) (C-1) show a peak at 330-350 °C corresponding to the transition of the orthorhombic crystalline modification to pseudohexagonal packing of macromolecules[4]. It was found that, regardless of polymerization degree, the sample C-1 cannot form the LC phase and isotropic melt due to strong intermolecular interactions between macromolecules up to a decomposition temperature.

Interestingly, the incorporation of flexible spacer fragments contained in bisphenol A results in a decrease in the melting point. The DSC curve of C-2 shows the presence of three endotherms at 140.4 °C, 159.0 °C, and 169.5 °C, corresponding to melting of crystalline phase, a transition between mesophases and an isotropization temperature. Experimental results obtained by polarized optical microscopy confirm the optical activity of C-2 in the range of 140-170 °C (Figure 4).

The introduction of kinked units into linear aromatic macromolecule also noticeably reduces temperatures of phase transitions. The DSC trace of polyester C-3, which was synthesized using kinked monomer (isophthalic acid), has been characterized by two endotherms - a wide peak in the range of
130-250 °C and a peak at 277.1 °C. Upon heating, the C-3 undergoes both melting of the crystalline phase and the formation of a mesophase in a fairly wide temperature range, which indicates a significant inhomogeneity of molecular weight distribution. According to the study of optical properties, the isotropization of sample C-3 occurs at 250 °C, while the temperature range for the existence of the mesophase fits 140 - 250 °C.

**Figure 4.** Optical micrographs of the samples: a) C-2 at 140 °C under normal light; b) C-2 at 140 °C under polarized light; c) C-3 at 170 °C under normal light; d) C-3 at 170 °C under polarized light.

A TGA analysis was performed to determine the thermal stability of these polymers (Figure 5). Decomposition kinetic parameters such as the 10% mass loss temperature ($T_{10}$), the temperature of maximal rate of the weight loss ($T_{dm}$), and the activation energy of thermal decomposition are commonly used to determine the thermal stability of polymers. The initial decomposition temperatures ($T_0$) are estimated to be 323, 250 and 272 °C for C-1, C-2 and C-3, respectively.

**Figure 5.** TGA traces of LC oligoesters.

The activation energy of thermal destruction can be calculated from TGA curves by using Horowiths-Metzger integral kinetic method (Equation 2) [5]:

$$E_a = -\frac{R}{\ln(2)} \frac{d\ln(T_{10})}{dT}$$
\[
\ln \left( \ln \frac{w_0}{w} \right) = \frac{E_t \theta}{R T_{dm}},
\]

where \(w_0\) – the initial weight of the sample, mg; \(w\) – the current weight of the sample, mg; \(E_t\) – the activation energy of thermal decomposition, kJ/mol; \(T_{dm}\) - the temperature of maximal rate of the weight loss, K; \(\theta\) - the variable auxiliary temperature defined as \(\theta = T - T_{dm}\); \(R\) - the universal gas constant J/(mol K). The \(E_t\) value may be estimated from the slope of the plot \(\ln \left( \ln \frac{w_0}{w} \right)\) versus \(\theta\).

**Table 1.** Results of TGA analysis of LC oligoesters.

| Samples | Molecular weight (g/mol) | \(E_t\) (kJ/mol) | \(T_0\) (°C) | \(T_{dm}\) (°C) |
|---------|--------------------------|-----------------|--------------|----------------|
| C-1     | 1100                     | 341             | 323          | 528            |
| C-2     | 9100                     | 253             | 250          | 485            |
| C-3     | 3400                     | 289             | 272          | 496            |

As shown in Table 1, the activation energy of thermal decomposition, the initial decomposition temperature, and the temperature of maximal rate of the weight loss decrease in the order C-1 > C-3 > C-2, which correlates with the chemical structure of the synthesized samples[4]. Thus, poly(p-oxybenzoate) exhibits among other samples the highest resistance to elevated temperatures. However, the intractability of C-1 causes certain difficulties in processing this polymer. Thermotropic oligoesters C-2 and C-3 are processed in LC state at 140-170 °C and 140-250 °C, respectively. Moreover, since their macromolecules contain reactive terminal groups, the processing at elevated temperatures will be accompanied by further chain growth. From the thermal studies, it can be concluded that the higher content of aromatic units in macromolecules enhances the thermal stability of polymeric material.

**References**

[1] Thakur V K, Kessler M R 2016 Liquid Crystalline Polymers (Cham: Springer)
[2] Deberdeev T R, Akhmetshina A I, Karimova L K, Ignat’eva E K, Deberdeev R Ya and Berlin A A 2020 *Polym. Sci. Ser. C* 62 145
[3] Akhmetshina A I, Ignat’eva E K, Deberdeev T R, Karimova L K, Yuminova Yu N, Berlin A A and Deberdeev R Ya 2019 *Polym. Sci. Ser. D* 12 427
[4] Kricheldorf H R and Schwarz G 1990 *Polymer* 31 481
[5] Kim J Y 2009 *Materials* 2 1955.