Synthesis and properties of reactive oligoketones

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Abstract. Oligoketones based on 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 4,4'-dichlorodiphenyl ketone were synthesized by the method of high-temperature polycondensation under the reaction of nucleophilic substitution; 1,1-dichloro-2,2-di (3,5-dibromo-4-hydroxyphenyl) ethylene and 4,4'-dichlorodiphenyl ketone of varying degrees of polycondensation. Oligoketones have been obtained containing reactive end phenolate groups, which readily enter into polycondensation reactions to form various copolymers. The composition and structure, as well as the conditions for the synthesis of these oligoketones were investigated. The formation of oligomers of a given structure has been confirmed by IR spectroscopy, elemental analysis, and X-ray structural analysis.

1. Introduction

To combine the positive qualities of various classes of polymers in one material, the synthesis of co- and block copolymers containing units of various classes of polymers in their chain has been widely used recently. Depending on the chemical nature of the blocks, their length, the order of alternation, and their ability to crystallize, it is possible to obtain polymers with structure and properties that are significantly different from those of the initial components. There are huge opportunities here, which have recently been widely implemented [1-6].

There are conflicting data in the literature concerning the mechanism of nonequilibrium polycondensation in the synthesis of polyethers in dimethyl sulfoxide (DMSO), in particular, polyether ketones and polyethersulfones. Some authors [7] argue that the reactivity of both functional groups of the dihalogenated derivative is the same and the chemical structure of the diphenoxide anion of bisphenol plays a decisive role, others [8] indicate the difference in the functional groups of the dihalogenated derivative.

The effect of the chemical structure of bisphenols (diphenoxides) on their reactivity in the synthesis of aromatic polyethers is shown in scientific works [9-13]. It was found that the reactivity of bisphenols changes inversely proportional to their acidity or in direct proportion to their basicity and nucleophilicity. Bisphenols with electron-withdrawing groups between oxyphenyl rings interact with 4,4'-dichlorodiphenyl ketone, 4,4'-dichlorodiphenylsulfone more slowly than bisphenols with electron-donor substituents [14-15].

Without denying these facts, it should be noted that these processes must be considered in aggregate, i.e. along with the physicochemical properties of the starting monomers, it is necessary to clearly stipulate the thermodynamic and kinetic conditions of synthesis.

2. Experimental

Let us consider the procedure for the synthesis of oligomers using the example of obtaining an oligoketone based on 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene with n = 1. Into a 150 ml three-necked flask equipped with a stirrer, reflux condenser with a Dean-Stark trap, With a gas bubbler and a thermometer, 2.8114 g (0.01 mol) of 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene, 10 ml of dimethyl sulfoxide and 40 ml of toluene are introduced. With stirring, nitrogen is passed through and the temperature is raised to 70°C. After complete dissolution of 1,1-dichloro-2,2-di (4-hydroxyphenyl)
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ethylen, 1.97 ml of 10.16 N (0.02 mol) sodium hydroxide solution are added. The temperature is raised to 140 °C and the azeotropic toluene-water mixture is distilled off until the water is completely removed. The reaction mass is cooled to 40-50°C and 1.2556 g (0.005 mol) of 4,4′-dichlorodiphenyl ketone is added. The reaction is carried out at 150 °C for 2 hours. The resulting mass is diluted with 10 ml of DMSO and precipitated into acidified distilled water. The form precipitate is filtered off and washed with distilled water until the filtrate reacts negatively to chlorine ions. The resulting oligoether ketone is dried at 50°C for 24 hours, then at 80°C under vacuum, also for 24 hours. The yield of a light-yellow product is 95-97%; softening temperature 77-80°C; the content of the basic substance is not less than 99.9%; sodium chloride is allowed as an impurity in an amount of not more than 0.05-0.1%.

Oligomers with other degrees of condensation were obtained in a similar way, by changing the molar ratios of the starting monomers.

1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 1,1-dichloro-2,2-di (3,5-dibromo-4-hydroxyphenyl) ethylene were purified by recrystallization from aqueous alcohol (water: alcohol = 5:2). After recrystallization, they had melting points equal to 213 and 150°C, respectively.

IR spectral studies were carried out on a Perkin Elmer SPECTRUM TWO IR spectrometer using powdered samples in the range from 4000 to 450 cm–1. Instrument operation mode: resolution - 4 cm–1, number of scans - 10, signal-to-noise ratio> 1300. Before measurements, the samples were pressed into a tablet, the matrix of which was potassium bromide dried at 200 °C (2 mg of the sample and 298 mg KBr).

The study of the crystallinity of polymers was carried out on a DRON-6.0 X-ray diffractometer on copper K - radiation with a wavelength of 1.54051 Å. The survey was carried out in the range of angles q - 7-45 with a given step of 1 per minute with an accuracy of measuring diffraction angles of 0.030 degrees.

3. Results and discussions

The aim of this work was to obtain oligomers with terminal functional groups capable of further entering with a polycondensation reaction with various dihalogen-containing compounds. Optimal conditions for the synthesis of oligomers by a number of factors: the chemical nature of functional groups, the chemical solvent of nucleophilic and electrophilic reagents, the nature of the solvent, the concentration and reaction of the reacting substances, the nature of side factors and temperature. These factors are well studied and devices for such widely used bisphenols as 4,4′-dioxyphephenylpropane and 3,3-di(4-hydroxyphenyl)phthalide. However, oligomers based on 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene (S-2) and 1,1-dichloro-2,2-di (3,5-dibromo-4-hydroxyphenyl) ethylene (TBS-2) first it is necessary to dwell on some issues of data optimization. Let's make a reservation right away that the ratio of the reactants (bisphenol and halogen derivative) was taken based on the theoretically calculated amount, depending on the specified degree of condensation. In all cases, the amount of bisphenol is 1 mol higher than the amount of the corresponding halogen production, which is explained in advance - the preparation of oligomers with reactive terminal hydroxide (phenoxide) groups.

Using various ratios of recent advances to obtain oligomers of various degrees of condensation. When the above oligomers are obtained by the reaction of the nucleophilic process, it is a prerequisite for the process to be carried out by the chemical transformation of –OH groups of bisphenols into diphenolate groups under the action of various bases.

Taking into account the general laws governing the synthesis of oligoesters and the optimal conditions found for each pair of bisphenol and dihalide, oligomers based on 4,4′-dioxyphephenylpropane and 4,4′-dichlorodiphenyl ketone (OK-D) were synthesized; 3,3-di (4-hydroxyphenyl) phthalide and 4,4′-dichlorodiphenyl ketone (OC-F); 1,1-dichloro-2,2-di (4-hydroxyphenyl) ethylene and 4,4′-dichlorodiphenyl ketone (OC-S-2); 1,1-dichloro-2,2-di (3,5-dibromo-4-hydroxyphenyl) ethylene and 4,4′-dichlorodiphenyl ketone (OS-TBS-2).

In general, the indicated oligomers can be represented as follows. At the first stage, from the corresponding bisphenol and NaOH in bisenium, 2 moles of alkali per 1 mole of bisphenol, we obtain
the disodium salt. Toluene was used as an entrainer. Further, by the method of the methodology for the reaction between the diphenolate and the highly dihalide: DMSO [16] in an atmosphere of an inert gas (nitrogen) in an aprotic dipolar solvent:

\[
\text{ONa} \quad \text{NaOH} \quad \text{n NaOH} \quad \text{n NaO} \quad \text{R} \quad \text{R} \quad \text{NaO} \quad \text{ONa}
\]

\[
\text{DMSO(n} \quad \text{1)} \quad \text{n Hal} \quad \text{R} \quad \text{R} \quad \text{Hal}
\]

\[
\text{H} \quad \text{O} \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{OH}
\]

where: \( R = \quad \text{CH}_3 \quad \text{C} \quad \text{C} \quad \text{R} = \quad \text{C} \quad \text{R} \quad \text{C} \quad \text{Cl}_2 \quad \text{X} = \text{H, Br} \)

The structural formulas and conventions of the oligoethers are presented in Table 1.

The average degree of condensation of \( n \) oligomers was used according to the equations:

\[
n = \frac{1}{q} \quad \text{and} \quad q = \frac{N_1}{N_2} - 1
\]

where \( N_1 \) is the number of moles of bisphenol; \( N_2 \) is the number of moles of dihalide; \( q \) - excess of bisphenol.

Moreover, compounds with a degree of condensation \( n = 1 \) can be considered as promising new monomers for polycondensation in the preparation of polyarylates, polycarbonates, polyether ketones, polyethersulfones and a number of other polymers.

The optimal concentration of the starting substances in the solution during the synthesis of oligomers is 1–2 mol/L based on the starting bisphenol. The optimum concentration depends on the chemical structure of the oligomers and the specified degree of polycondensation. In this case, the solubility is largely determined by the starting materials in DMSO. A decrease in the concentration in solution leads to an increase in the reaction time. Excessive completion of the stage can be accompanied by the precipitation of bisphenolate at the initial stage of the synthesis (prevents the complete removal of water from the reaction medium) and hinders its re-dissolution in DMSO, and also prevents mixing of the mass (diffusion inhibition).
Table 1. The structural formulas and conventions of the oligoethers

| Structural formulas | Conventions |
|---------------------|-------------|
| ![Structural Formula](image) | OK-nD |
| ![Structural Formula](image) | OK-nF |
| ![Structural Formula](image) | OK-nS-2 |
| ![Structural Formula](image) | OK-nTBS-2 |

where n is the degree of polycondensation of oligomers.

It should be noted that common to all these processes is their almost non-equilibrium nature and high yield of the target product (95% or more).

The structure of the obtained oligomers was also confirmed by the results of the analysis of the content of hydroxyl groups (Table 2), IR spectroscopy, and X-ray structural analysis was carried out. The table also shows the calculation conditions, the calculated values of the molecular weight of the oligomers and the corresponding softening temperatures.

Table 2. Some properties of oligoethers

| Oligomers | n | Synthesis conditions | T softening, °C | Estimated MM | Content of OH groups, % | Calculated | Found |
|-----------|---|----------------------|----------------|-------------|------------------------|------------|-------|
| OK–1S–2   | 1 |                      | 77-80          | 740         | 4,59                   | 4,55       |       |
| OK–5S–2   | 5 | Temperature = 150-160°C | 85-87          | 2577        | 1,32                   | 1,31       |       |
| OK–10S–2  | 10 |                      | 90-92          | 4874        | 0,70                   | 0,69       |       |
| OK–20S–2  | 20 | Time -2 -3 h | 94-96          | 9467        | 0,36                   | 0,37       |       |
| OK–1TBS–2 | 1 |                      | 114-116        | 1371        | 2,48                   | 2,48       |       |
| OK–5TBS–2 | 5 | Temperature = 150-155°C | 112-114        | 4471        | 0,76                   | 0,77       |       |
| OK–10TBS–2 | 10 |                      | 100-102        | 8345        | 0,41                   | 0,40       |       |
| OK–20TBS–2 | 20 | Time -4 -6 h | 87-90          | 16094       | 0,21                   | 0,22       |       |

X-ray structural analysis performed on powder samples showed that all synthesized oligomers are amorphous (Fig. 1). Diffraction patterns for other oligomers are similar.

For the corresponding oligomers, the IR spectra show groups corresponding to: ether bonds in the region of 1135 cm⁻¹; the isopropylidene group in the diana residue is 2960-2980 cm⁻¹; hydroxyl groups 3300-3600 cm⁻¹; carbonyl group between aromatic rings 1600-1675 cm⁻¹; lactone group in the range of 1710-
1760 cm\(^{-1}\), 2960-2980 cm\(^{-1}\); 1150-1170, 1250 and 1300 cm\(^{-1}\); group \(\text{Ar}_2 - \text{C} = \text{CCl}_2\) in the region of 980 cm\(^{-1}\), group \(\text{C–Br}\) in the region 600–500 cm\(^{-1}\).

**Figure 1.** Diffraction pattern of oligoketone based

The reactivity of the obtained oligomers was also proved by the fact that they were obtained on their basis and phthalic acid molecular polyaric acid dichlorides. Polyarylates were obtained by the method of acceptor-catalytic polycondensation in 1,2-dichloroethane medium according to the following scheme:

![Chemical Structure](image)

It has been shown that using the synthesized oligoketones it is possible to obtain high molecular weight polyesterrylates with a reduced viscosity of 0.5 to 1.2 dl / g. These polymers are readily soluble in chlorinated solvents such as chloroform, methylene chloride, 1,2-dichloroethane.

**Conclusion**

Thus, oligoketones of various structures and compositions were synthesized by the method of high-temperature polycondensation by the mechanism of nucleophilic synthesis. These oligoketones contain active terminal phenolic groups and easily enter into a low-temperature polycondensation reaction in solution with acid dichlorohydrides. Copolymers, other arylate, carbonate, sulfonic and other groups can be obtained by means of end groups based on these oligoketones. The use of oligomers with a given degree of polycondensation makes it possible to obtain aromatic polyesters with controlled molecular
weight and, therefore, with the desired melt viscosity. The latter plays an important role in the processing and creation of composites based on polymers. The results obtained allow the synthesized oligomers to be recommended as reactive compounds for the synthesis of various copolyesters and copolyethers.

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