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SYNTHESIS AND PROPERTIES OF OLIGOMERS WITH HYDROXY END-GROUPS

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Abstract. Methods of oligomers (polymers) with hydroxy end-groups obtaining are examined. The synthesis of hydroxy-containing oligomers based on epoxy resins is of special attention. The molecules of mentioned oligomers apart from free primary and secondary hydroxy groups contain epoxy, peroxy, carboxy or acrylic groups.

Keywords: oligomer, hydroxy end-groups, synthesis, functional groups, epoxy resin.

1. Introduction

Oligomers (polymers) with functional groups are widely used for the production of protective coatings, compounds, glues, *etc*. [1]. On the one hand the presence of functional group allows to control operating properties and on the other hand – to develop the products of complicated configuration without significant shrinkage using casting. At the same time the presence of reactive group in the oligomer (polymer) structure allows to combine different by nature polymers in the same structure.

Among all known polymers with functional groups the products with hydroxy groups are of special interest [1-4]. The presence of hydroxy group allows to create a series of polyurethane materials [1-10], converting –OH groups into isocyanate [11-13], chloranhydride [14], epoxy [15], amine [16] groups.

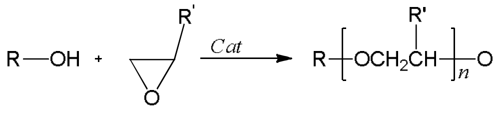
The literature data [17, 18] show that oligomer-type compounds with hydroxy end-groups are mainly synthesized as a raw material for the production of polyurethanes. Apart from these compounds there are oligomers (polymers) with hydroxy groups in the side chains. Such oligomers are obtained *via* epoxy resins modification by various compounds, namely alcohols, phenols, acids, their anhydrides, *etc*. [19-26]. The resulting secondary hydroxy groups are less reactive compared to the primary groups situated at the macromolecule ends. This fact makes difficulties for modified epoxy resins usage in the formation of cross-linked structures with some compounds, isocyanates in particular.

Below we examine the main methods of oligomers (polymers) with hydroxy end-groups obtaining. The introduction of definite fragments into the epoxy resin allowing to obtain the compounds with hydroxy end-groups is discussed in the separate subsection.

2. Synthesis of Oligomers (Polymers) with Hydroxy End-Groups

2.1. Synthesis *via* Ionic Polymerization of Epoxides

The synthesis of oligomers with hydroxy end-groups *via* polymerization of alkylene oxides which is initiated by the compounds with hydroxy group may be described as follows [27-29]:



$$R{-}OH + \underset{O}{\triangle}{-}R' \xrightarrow{Cat} R{+}OCH_2\overset{R'}{\overset{|}{C}}H{+}_{n}O \qquad (1)$$

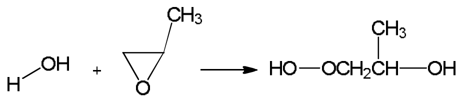
where R and R' – alkyl fragments.

As the catalyst of the reaction (1) following compounds are used: anionic catalysts NaOH, KOH, CsOH, $Sr(OH)_2$, $Ba(OH)_2$, calcium naphthenates [30-34]; cationic catalysts: BF_3, PF_5, SbF_5, HPF_6, $HSbF_6$, CF_3SO_3H,

$Al(CF_3SO_3)_3$, *etc.* [35-37]; coordination catalysts: $Al(OR)_3$, $Zn(OR)_2$, $Ti(OR)_4$, $Zn_3[Co(CN)_6]_3$ [38-43].

To synthesize polyetherpolyols with great molecular mass the catalysts mostly used in the industry are potassium hydroxide [44-46] and so called DMC-catalysts (Double Metal Cyanide Catalysts) based on non-stoichiometric complexes – $Zn_3[Co(CN)_6]_3 \cdot ZnCl_2 \cdot y\text{Ligand} \cdot zH_2O$ [47-49]. Dimethyl ethers of ethylene glycol and diethylene glycol, 1,4-dioxane, dimethylsulfoxide and *N*-methylpyrrolidone are used as ligands. DMC-catalysts are more expensive compared to KOH but they are much more effective [50-53].

Gagnon and Bailey [54, 55] show that polyetherdiols are obtained using water as an initiator of propylene oxide polymerization. During the process 1,2-propylene glycol is formed which is further an initiator of polymerization.



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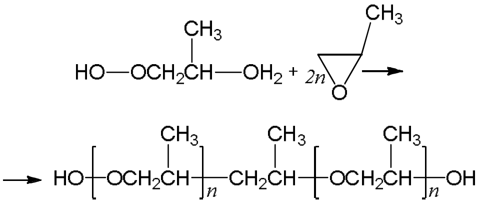
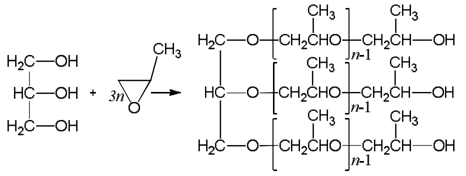
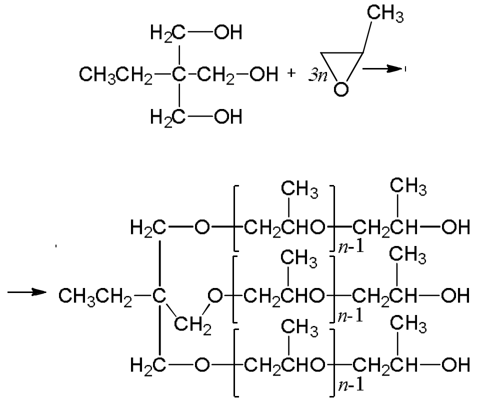


(3)

When using glycerin (propanetriol) or trimethylolpropane as initiators, then polyether triols are formed [56, 57]:



(4)



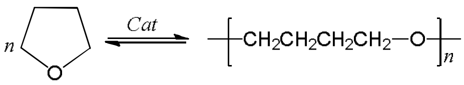
(5)

When using compounds with greater number of functional groups – (tetra- or pentaols) the corresponding polyethers with hydroxy end-groups are formed.

The products obtained according to Eqs. (1)-(5) are characterized by molecular weight of 2000–6500 g/mol and functionality of 2-3 hydroxy groups per molecule. Such compounds are used to produce elastic polyurethanes [2-4].

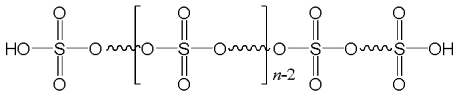
2.2. Synthesis Based on Tetrahydrofurane

Oligomers with hydroxy end-groups are also obtained *via* cationic polymerization of tetrahydrofurane [58, 59].



(6)

Louis and Bronsted-Louri acids are the catalysts of Eq. (6). For example, at 263–308 K using fluosulfonic acid ($HFSO_3$) as a catalyst one can obtain polytetrahydrofurane with small molecular weight [60]. Its formula is given below:



$$HO-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O\sim\sim\left[O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O\sim\sim\right]_{n-2}O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O\sim\sim\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-OH \quad (7)$$

G. Heinsohn *et al.* [61] show the formation of compound (8) using acetanhydride and $HSbF_6$. If this compound undergoes hydrolysis (alcoholysis) in the presence of $Ba(OH)_2$ catalyst then α,ω-hydroxy-telechelatic polytetrahydrofurane is formed (Eq. (9)).

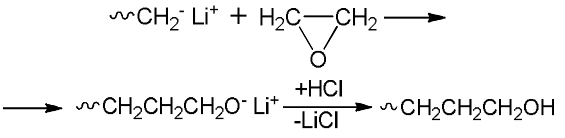
$$CH_3CO\left[CH_2CH_2CH_2CH_2O\right]_{n+1}CH_2CH_2CH_2CH_2-OCOCH_3 \quad (8)$$

$$HO\left[CH_2CH_2CH_2CH_2O\right]_{n+1}CH_2CH_2CH_2CH_2-OH \quad (9)$$

So, depending on type of initiator and catalyst polytetrafurane with different structures and molecular weight may be obtained. Corresponding oligomers are characterized by molecular weight of 600–2500 g/mol and functionality of 2 hydroxy groups per molecule. Such compounds are used to produce elastic polyurethanes [4].

2.3. Synthesis Based on Vinyl and Diene Monomers

To synthesize oligomers with hydroxy end-groups an anionic oligomerization of vinyl and diene monomers under the action of alkali metals and their alkyl derivatives is also used [62]. The synthesis is carried out in the presence of aliphatic or aromatic solvent at 263–273 K. Metalorganic oligomer, obtained at the first stage, reacts with alkylene oxide or oxygen (Eq. (10)). To extract hydroxy-containing oligomer the synthesized alcoholate is acidulated:



(10)

When using polar solvents at the first stage of the process one can obtain oligomer with 1-2 links, using non-polar solvents – 1-4 links. It should be also noted that the mentioned process is characterized by low reaction rates and thus it is impossible to obtain compounds with necessary molecular weight. To avoid this disadvantage trialkyl ammonium may be used as a regulator. It allows to obtain low-molecular oligoisoprene with complex organometallic end-groups. When substituting these groups for hydroxy ones, the compounds with molecular weight of 1000–3000 g/mol are obtained.

2.4. Synthesis with Radical Initiators of Peroxy or Azodinitrile Types

Reactive hydroxy-containing oligomers are also obtained *via* chain oligomerization in the presence of functional radical initiators of peroxy or azodinitrile type. The advantage of this method is a possibility of oligomers synthesis by only one stage, because initiators contain functional groups [63, 64]:

$$\begin{aligned} &XR\text{-}RX \longrightarrow 2XR^* \\ &XR^* + nM \longrightarrow X(M)n^* \\ &X(M)n^* + {}^*(M)nX \longrightarrow X\text{-}(M)2n\text{-}X \end{aligned} \qquad (11)$$

where R – alkyl fragment, X – functional group.

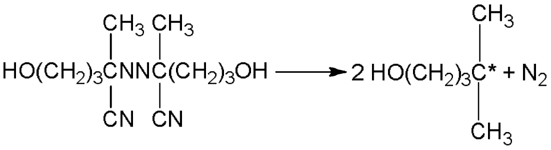
To provide oligomers bifunctionality the initiator should contain functional groups and have bis-structure; during polymerization the chain should be broken *via* recombination, not disproportionation [63]. Sparov and Hope [65, 66] proposed the oligomers synthesis using hydrogen peroxide as an initiator. Necessary for polymerization radicals are formed by redox reaction proceeding in aqueous medium between hydrogen peroxide and Fe(II) salts (Fenton process):

$$H_2O_2 + Fe^{2+} \longrightarrow HO^* + HO^- + Fe^{2+} \qquad (12)$$

The formed radicals initiate polymerization of unsaturated monomers followed by obtaining of oligomers with hydroxy end-groups.

Many works describe synthesis of hydroxy-containing oligomers *via* thermal polymerization using hydrogen peroxide [67-69]. The synthesis is carried out in autoclave in the medium of lower alcohols within the range of 353–373 K for 10–14 h. The molecular weight of resulting products is 600–6000 g/mol.

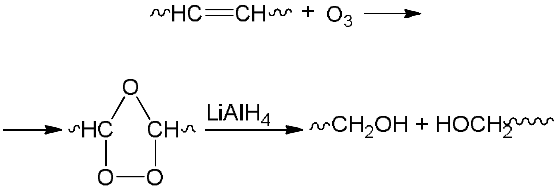
W. Heitz and R. Shliakhter [70, 71] proposed to synthesize α,ω-hydroxyoligotriols using 4,4'-azo-bis(4-cyanpentanol) as an initiator. Its thermal decomposition is described by Eq. (13):



$$HO(CH_2)_3C(CH_3)(CN)N{=}NC(CH_3)(CN)(CH_2)_3OH \longrightarrow 2\,HO(CH_2)_3C^*(CH_3)_2 + N_2 \qquad (13)$$

The radicals initiate monomer polymerization resulting in the formation of oligomers with end groups which are initiator fragments. The synthesis is carried out at 333 K in acetone medium [72]. The peculiarity of azodinitrile initiators is that they don't participate in chain transfer to monomer and solvent and they are insensitive to induction decomposition that allows to obtain oligomers with high degree of bifunctionality under mild conditions [73].

I. Zaripov *et al.* [74] proposed to synthesize oligomers of the mentioned type by ozonolitic destruction of rubbers:



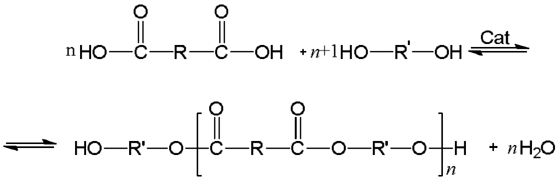
(14)

However, to obtain molecular-homogeneous oligomers the primary oligomers must meet the following requirements: short bonds must be uniformly distributed in the macromolecule and unsaturated bonds must be in the main chain, not in the side ones.

These oligomers are used for the production of polyurethanes [3, 4, 75].

2.5. Synthesis *via* Polycondensation of Dibasic Acids with Glycols

The reaction proceeds according to Eq. (15):



$$n\,HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH + n{+}1\,HO-R'-OH \xrightleftharpoons{Cat} HO-R'-O-\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O\right]_n-H + n\,H_2O \quad (15)$$

where R and R' – alkyl fragments.

The synthesis is carried out at 423–473 K in the medium of organic solvent. The molecular weight of the synthesized oligomers may be controlled by molar ratio between the initial reagents [74]. Dibasic acids may react with glycols without a catalyst (autocatalysis by carboxy groups of the acid) but in order to accelerate the reaction and to reduce the final acidity the process is catalyzed by *p*-toluenesulfonic acid, tetrabutyl titanate, zinc acetate, *etc*. [77, 78].

In the industry polyesterglycols are obtained by the reaction between adipic acid and ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,4-butandiol, neopentyl glycol and 1,6-hexanediol [79-81]. I. Metliakova *et al*. [82] propose to obtain oligoesters with hydroxy end-groupos *via* condensation of adipic acid with triethanolamine. It should be noted that the rate of the reaction with triethanolamine is higher than that with glycols.

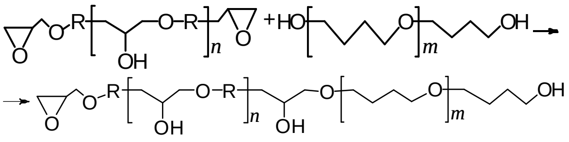
D. Filipchenko *et al*. [83] synthesized unsaturated hydroxy-containing oligoesters *via* condensation of maleic and phthalic anhydride with 1,2-epoxy-3-chloropropane in the presence of Louis acids. The resulting products have molecular weight of 1000–14000 g/mol and different length of glycol fragment. The authors notice that resulting products are characterized by high fire-resistance and chemical stability; they may be used as components of protective coatings.

3. Synthesis of Reactive Oligomers with Hydroxy Groups Based on Epoxy Resins

In comparison with other functional compounds the epoxy oligomers have unstable trinomial cycles capable to react under definite conditions with compounds containing a mobile hydrogen atom in their structure. This allows to synthesize oligomer products with hydroxy groups. Below we examine possible synthesis of oligomers which contain simultaneously free primary hydroxy group and other functional groups such as epoxy, peroxy, carboxy and acrylic ones.

3.1. Synthesis of Oligomers with Hydroxy and Epoxy Groups

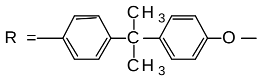
ED-24 and ED-20 epoxy resins are used as initial reagents to synthesize oligomers with hydroxy and epoxy groups. 1,4-Butandiol (BD) and PolyTHF 2000 (PHTF) have hydrogen mobile atom and are used as modifiers. The synthesis is carried out according to Eq. (16):



(16)

Oligomer I-IV

where n = 2, m = 0 (Oligomer II); n = 2, m = 26–28 (Oligomer IV); n = 0, m = 0 (Oligomer I); n = 0, m = 26–28 (Oligomer III);



Isopropyl alcohol and toluene are reaction media [84]. Taking into account the precipitation of the resulting products from the reaction mass while using toluene, it is proposed to use isopropyl alcohol as a solvent.

Quaternary ammonium salts and potassium hydroxide were studied as the reaction catalysts [84, 85]. It is shown that at 353 K for 1.5 h benzyl tetraethylammonium chloride (BTEACh) in amount of 30 mol % per 1 g-eq. epoxy groups changes the concentration of epoxy groups. At the same time KOH (30 mol % per 1 g-eq. epoxy groups) initiates the reaction (16) but the proceeding of side reactions is also observed. The decrease in KOH amount decreases the number of side reactions and the reaction rate between ED-20 and BD. The increase in reaction rate and decrease in number of side reactions may be achieved using BTEACh+KOH catalytic system with stoichiometric ratio (5:5 mol % per 1 g-eq. epoxy groups). The authors [85, 86] assert that actual catalyst of the reaction (16) is quaternary ammonium hydroxide formed due to the reaction between BTEACh and KOH.

The characteristics of the synthesized oligomers are given in Table 1.

High-performance liquid chromatography with mass spectrometry detection (HPLC-MS) [87] was used to investigate the composition of the synthesized oligomers taking Oligomer I as an example. It was found that the content of oligomer with primary hydroxy and epoxy groups is above 80 %. The presence of mentioned groups was confirmed by ^{13}C NMR spectroscopy (signals at 62.44–62.47 ppm for hydroxy groups and 50.12–50.13 ppm for epoxy groups).

Table 1

Characteristics of the synthesized oligomers

Initial resin	Compound with hydroxy groups	Oligomer characteristics				
		Oligomer symbol	M_n, g/mol	Epoxy groups concentration, %	Hydroxyl number, mgKOH/g	Yield, %
ED-24	BD	I	420	11.2	277	98.4
ED-20	PHTF	II	460	8.6	365	97.7
ED-24	BD	III	2280	3.3	53	97.5
ED-20	PHTF	IV	2330	1.9	72	96.8

Table 2

Characteristics of the synthesized oligomers

Initial compound	Compound with hydroxy groups	Oligomer characteristics				
		Oligomer symbol	M_n, g/mol	[O$_{act}$], %	Hydroxyl number, mgKOH/g	Yield, %
PO	BD	V	490	1.9	189	92.2
PO	PHTF	VI	2370	1.1	82	94.1

Table 3

Characteristic of the synthesized oligomer

M_n, g/mol	Acid number, mgKOH/g	Hydroxyl number, mgKOH/g	Yield, %
560	9	373	96.8

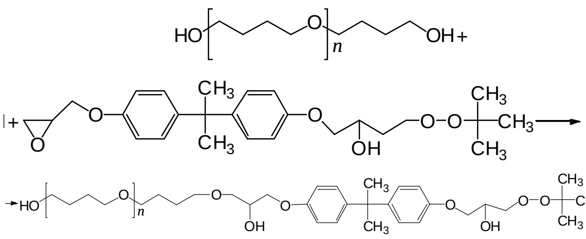
Table 4

Characteristics of the synthesized oligomers

Initial compound	Compound with hydroxy groups	Oligomer characteristics				
		Oligomer symbol	M_n, g/mol	Bromine number, gBr$_2$/100g	Hydroxyl number, mgKOH/g	Yield, %
Acrylic acid	Oligomer-I	VIII	490	16.1	351	98.1
Acrylic acid	Oligomer-III	IX	2350	12.4	84	98.3

3.2. Synthesis of Oligomers with Hydroxy and Peroxy Groups

Oligomers with hydroxy and peroxy groups are synthesized according to Eq. (17):



(17)

Oligomers V, VI

where n = 0 (Oligomer V);
n = 26–28 (Oligomer VI).

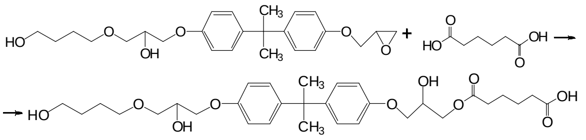
The initial compound for the synthesis was oligomer with free epoxy and peroxy group (PO) synthesized in accordance with the procedure described in [88, 89]. 1,4-Butandiol (BD) and PolyTHF 2000 (PHTF) are the modifiers. The ratio between PO and modifier is 1:1. The system BTEACh+KOH is the catalyst (30:30 mol % per 1 g-eq. epoxy groups). The reaction temperature is 323 K, reaction time is 25 h.

The characteristics of the synthesized oligomers are given in Table 2.

The presence of hydroxy and peroxy groups was confirmed by ^{13}C NMR spectroscopy (signals at 62.72–63.541 ppm and 29.71–30.99 ppm, respectively).

3.3. Synthesis of Oligomers with Hydroxy and Carboxy Groups

For the synthesis of oligomer with carboxy groups we used previously synthesized Oligomer-I [90] and adipic acid. Oligomer VII was synthesized according to Eq. (18):



(18)

Oligomer VII

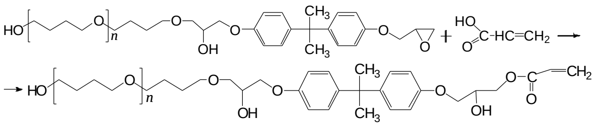
The catalyst of the reaction (18) is BTEACh in amount of 30 mol % per 1 g-eq. epoxy group. The reaction temperature is 353 K, reaction time is 3 h. Reagents ratio is 1:1. The characteristic of Oligomer VII is given in Table 3.

The presence of hydroxy and carboxy groups was confirmed by ^{13}C NMR spectroscopy (signals at 62.37 ppm and 177.08 ppm, respectively).

The simultaneous presence of carboxy and hydroxy groups in the oligomers structure extends the potential of these compounds to obtain different polymer materials. Such materials are characterized by high adhesion and elasticity.

3.4. Synthesis of Oligomers with Hydroxy Group and Acrylic Fragment

To synthesize oligomers with hydroxy group and acrylic fragments previously synthesized Oligomer I and III were used. Acrylic acid was used as a modifier [91]. The synthesis was carried out according to Eq. (19):



(19)

Oligomers VIII, IX

where n = 0 (Oligomer VIII)
n = 26–28 (Oligomer IX)

The synthesis conditions are: temperature 373 K; process time 7 h; catalyst – triethylamine in amount of 1 wt %. The characteristics of Oligomer VIII and IX are given in Table 4.

The presence of primary hydroxy groups and acrylic fragment was confirmed by ^{13}C NMR spectroscopy (signals at 62.77–62.79 ppm and 113.64–113.71 ppm, respectively).

Epoxy resins modified by alcohols may be used for the production of lacquer and protective coatings, as a glue composition and filler in rubbers, and as a component of bitumen-polymeric blends [84-91].

4. Conclusions

The main synthesis methods to obtain oliogmers (polymers) with hydroxy end-groups have been reviewed. The advanced synthesis based on epoxy compounds was discussed as well. The simultaneous presence of hydroxy end-groups and other functional groups in oligomer molecules is useful to produce polymer materials, polyurethanes in particular, due to reaction of these compounds with isocyanates.

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СИНТЕЗ І ВЛАСТИВОСТІ ОЛІГОМЕРІВ З КІНЦЕВИМИ ГІДРОКСИЛЬНИМИ ГРУПАМИ

Анотація. *Розглянуті методи одержання олігомерів (полімерів) з кінцевими гідроксильними групами. Особлива увага приділена синтезу гідроксилвмісних олігомерів на основі епоксидних смол , які у своїх молекулах крім вільних первинної та вторинної гідроксильних груп, містять іншу функційну групу, зокрема, епоксидну, пероксиду, карбоксильну чи акрилатну.*

Ключові слова*: олігомер, кінцеві гідроксильні групи, синтез, функційні групи, епоксидна смола.*