

Synthesis and Properties of Peroxy Oligomers Obtained by Telomerization Effects of the Presence of Bases

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Abstract

New bifunctional oligomers bearing peroxy groups have been synthesized by telomerization in one step reaction. For obtaining oligoperoxides (PO) by telomerization method, epoxide compounds will react with substances containing labile hydrogen atom. Using the principle of stoichiometric imbalance between diepoxy compounds and substances with mobile hydrogen atoms and employing a functional peroxide as telogen, the synthesis of PO was studied. 2,2-Di[4-(2,3-epoxy-1-propoxy)phenyl]-propane (diglycidyl ether of diphenylol propane - DGEDPP), 1,2-Di(2,3-epoxy-1-propoxy) ethane (diglycidyl ether of ethylene glycol - DGEEG) and 1,2-Epoxy-3-tert-butylperoxypropane (EP) have been synthesized by methods reported in the literature. Chemical structures have been confirmed by NMR and FTIR, number-average molecular weights M_n of PO_s by cryoscopy, active oxygen content [O]_{act} for PO_s was determined by iodometry and epoxy number (*e.n.*) for PO_s was measured via direct titration of PO samples. A 50% solution of potassium or sodium isopropylates in 2-propanol is used to catalyze the telomerisation. Different parameters such as ratio of components, temperature, reaction time have been optimized in vu to get well defined peroxy oligomers.

The presence of peroxy groups in synthesized PO_s allows us to employ these compounds as curing agents for polymers containing unsaturated double bonds and may be used to improve performance of unsaturated polyester GFR systems.

Introduction

As it was reported earlier [1-7], chemical modification of epoxy resins with alkyl- and aralkylhydroperoxides is a method for obtaining oligomers with peroxy groups (PO). The formation of PO proceeds by epoxide ring opening followed by a hydroperoxide addition. Inorganic bases [1] and Lewis acids [4] may be catalysts for the above mentioned reaction. The presence of labile -O-O- bonds in a structure of such oligomers permits us to employ them as active additives for composites [5]. Formation of cured products in the presence of PO is achieved by decomposition of the -O-O- bonds at 383-413 K.

Existing methods of synthesis of PO are not sufficiently effective due to complicated technology.

The objective of this investigation was to undertake the possibility of obtaining such compounds by a

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one step method. A method of telomerization was employed with the purpose of obtaining functional oligomers by simple technology [6].

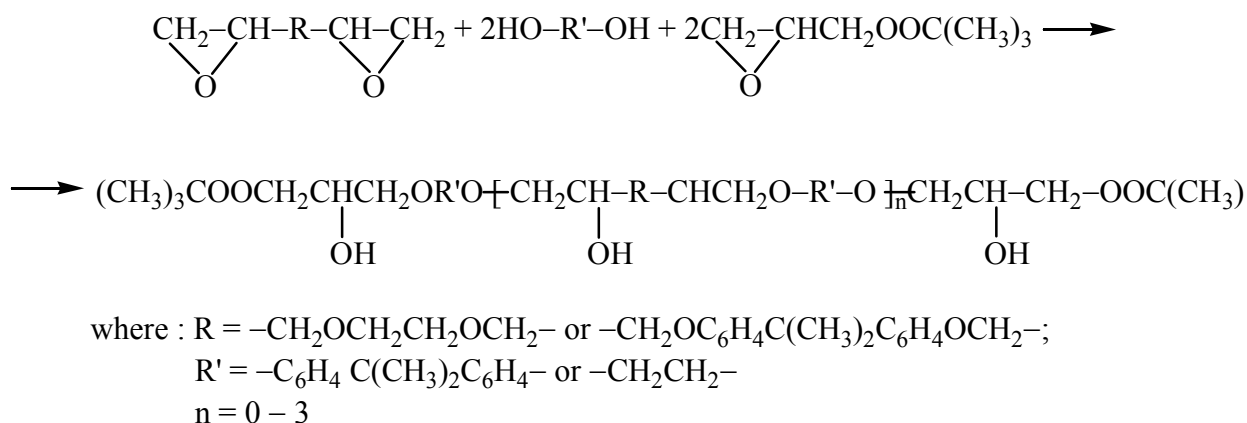
The essential principle of obtaining PO by telomerization method is the reaction of epoxide compounds with substances containing labile hydrogen atom [7]. Using the principle of stoichiometric imbalance between diepoxy compounds and substances with mobile hydrogen atoms and employing a functional peroxide as telogen the synthesis of PO was studied, according to the reaction which shown in Scheme 1.

Inorganic bases were catalysts for this reaction.

Experimental

Starting Reagents and their Purification

4,4'-Dihydroxy-2,2-diphenylolpropane (DPP) was recrystallized from toluene. Experimental melt-



Scheme 1

ing point (m.p.) obtained was 429 K (lit. m.p. 429–430 K [8]).

Ethylene glycol (EG) was distilled under vacuum. The main fraction was dried with sodium sulphate and redistilled. Physico-chemical constants were in conformity with literature data [8].

2,2-Di[4-(2,3-epoxy-1-propoxy)phenyl]-propane (diglycidyl ether of diphenylol propane) (DGEDPP) was obtained by a method reported in the literature [7]. The product as obtained has the following characteristics: n_D^{25} 1.5690 (lit.: n_D^{25} 1.5690 [7]), epoxide number (*e.n.*) 25.30% (theoretical *e.n.* 25.29%) after distillation at 433 K/1 Pa.

1,2-Di(2,3-epoxy-1-propoxy) ethane (diglycidyl ether of ethylene glycol) (DGEEG) was synthesized by the reported method [9]. The characteristics of products were in accordance with literature data [9]: n_D^{30} 1.4498, *e.n.* 49.40%, b.p. 401 K/13.3 hPa.

1,2-Epoxy-3-tert-butylperoxypropane (EP) was synthesized by the reported method [10]. Following properties were measured after distillation at 214 K/1–2 hPa: n_D^{20} 1.4180 (lit. n_D^{20} 1.4180 [10]), *e.n.* 29.40% (theoretical *e.n.* 29.45%).

Solvents (2-propanol, benzene) were purified by the method in literature [11] and their characteristics were in agreement with literature data.

Potassium and sodium isopropylates were prepared by the method reported in literature [8].

Analytical Methods

The number-average molecular weights M_n of PO_s have been determined by cryoscopic method in dioxane. The active oxygen content $[\text{O}]_{\text{act}}$ for PO_s was determined by iodometry. Epoxy number (*e.n.*) for PO_s was measured via direct titration of PO samples with 0.1 N solution of HBr in glacial acetic acid. More

specifically the *e.n.* was calculated as:

$$e.n. = \frac{0.43 \cdot KV}{m} \quad (1)$$

where: *K* – correction coefficient for 0.1 N solution of HBr in glacial acetic acid; *V* – volume of 0.1 N solution of HBr in glacial acetic acid, ml; *m* – mass of the sample of PO , g.

Spectral Methods

Infrared spectra (IR) were obtained using a wave dispersive Perkin – Elmer apparatus with the relevant absorption range in the 4000–400 cm^{-1} region.

Proton magnetic resonances $^1\text{H-NMR}$ were recorded on the BS-487 c spectrometer of Tesla, Brno, Czech Republic, at the frequency $\nu = 80$ MHz in deuterioacetone. Hexamethyldisiloxane was used as internal standard. The chemical displacement of groups signals were determined by evaluating positions of centres of symmetry of these signals.

Determination of Reaction Kinetics

A solution of DPP or EG in 2-propanol was stirred mechanically in a three – neck flask fitted with a thermometer and a dropping funnel. 50% aqueous solution of potassium or sodium hydroxide was added to the mixture at 313–333 K (in case of potassium or sodium isopropylates, a 50% solution was made in 2-propanol). Mixture of DGEDPP or DGEEG and EP was added dropwise. Soon after the completion of this process, the reaction mixture was stirred for 1–7 hours or more. Subsequently the reaction mixture was cooled down to room temperature, mixed with benzene and neutralised with 30% solution of acetic acid. The organic layer was washed with water, the volatile products removed at 323–328 K/1–3 hPa. PO_s

were characterised with respect to the peroxide and epoxide content, molecular weight as well as functionality.

Functionality (f) of obtained PO_s was calculated using the equation:

$$f = \frac{M}{M_{\text{eqv}}} \quad (2)$$

where equivalent molecular weight M_{eqv} was calculated as follows:

$$M_{\text{eqv}} = M_{\text{fg}} \cdot 100 / C_{\text{fg}} \quad (3)$$

where: M and M_{fg} are the molecular weight of PO and functional group ($-\text{O}-\text{O}-$) respectively, C_{fg} – concentration (% by mass) of functional group in PO.

Synthesis of Peroxy Oligomers

Peroxy oligomers (PO_s) marked as PO – I, PO – II and PO – III were obtained as follows:

In a 3 necked flask equipped with mechanical stirrer, thermometer and dropping funnel were dissolved 0.025 moles of DPP or EG in 15 ml of 2-propanol. Then a solution of 1.0 g of 50% aqueous potassium

hydroxide and a mixture comprising 0.0125 moles DGEEG or DGEDPP and 0.03125 moles of EP was added at 323 K. The reaction mixture was stirred for 5 hr and allowed to cool to room temperature, mixed with benzene and neutralized with 30% aqueous solution of acetic acid. Organic layer was washed with water and volatile products were removed at 323–328 K/1–2 hPa to a constant mass. Characteristics of PO_s are given in Table 1.

Reaction Kinetics

Effect of Catalyst

Potassium and sodium hydroperoxides, as well as their isopropylates in amount of 14–56% by mole to EP content in a reaction mixture were studied as catalysts for the reaction introduced on the Scheme 1.

The influence nature and quantity of catalyst used for the process of PO_s formation are given in Table 2.

It is evident from Table 2 that potassium hydroxide at 28% by mole to EP shows the highest catalytical activity. Further increase of potassium hydroxide content in the reaction mixture from 28 to 56% by mole has practically no effect in increasing the active oxy-

Table 1
Characteristics of Peroxy Oligomers

PO	Epoxy Compound	Monomer	Mn	Active Oxygen Content, ($[\text{O}]_{\text{act}}$) %	Functionality, (f)
PO – I	DGEEG	DPP	800	1.1	0.55
PO – II	DGEDPP	DPP	970	2.4	1.45
PO – III	DGEDPP	EG	640	1.2	0.48

Table 2
Influence of Nature and Quantity of Catalyst on Functional Groups Content

Catalyst	Quantity of the Catalyst, % by mole	Content, %		Note
		$[\text{O}]_{\text{act}}$	<i>e.n.</i>	
KOH	14	0.885	5.0	
KOH	28	1.00	1.75	
KOH	42	1.05	absent	The reaction mass gets darker
KOH	56	1.00	absent	The reaction mass gets darker
NaOH	28	0.80	5.50	
$\text{K}_{\text{iso}} - \text{Pr}$	28	0.95	1.90	
$\text{Na}_{\text{iso}} - \text{Pr}$	28	0.77	6.20	

Note: Temperature of a reaction 313 K. Duration of the process 4 hours. Molar ratio DPP:DGEEG:EP = 2:1:2.5

gen content. However, this increases the rate of formation of side products, as evidenced by the growing darkness of the reaction medium and the formation of resinous products. It may be explained by the decomposition in the presence of base of starting reagents as well as the formed peroxide compounds. Similar results were obtained when potassium isopropylate ($K_{iso} - P_r$) was used. However, KOH compared with $K_{iso} - P_r$ is a more accessible reagent.

Influence of Correlation between Starting Reagents

It is obvious from Fig. 1 that the highest functionality considering the content of peroxy groups in PO_s is achieved when the molar ratio DPP:DGEEG:EP = 2:1:2.5. Further increase of telogen content in a reaction mixture leads to a decrease of functionality in spite of increase in the active oxygen content.

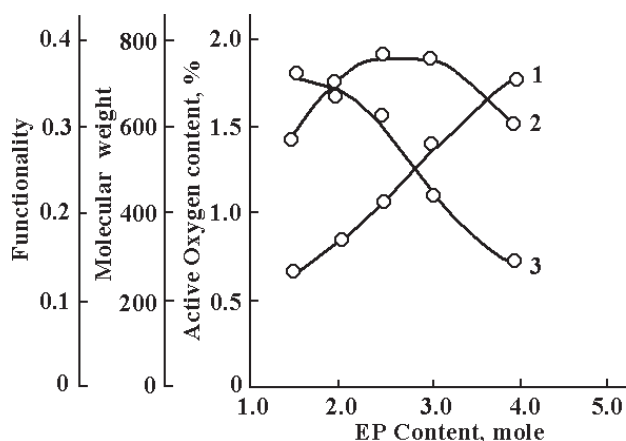


Fig. 1. Dependence of active oxygen content (1), molecular weight (2) and functionality of oligomer (3) vs EP content in starting mixture.

Influence of Temperature and the Reaction Time

The effect of temperature and the reaction time upon characteristics of PO_s (Fig. 2 and Table 3) was studied. The most interesting temperature for the process is found to be 323 K. Under this condition the epoxide groups are completely exhausted and the highest content of active oxygen in oligomers is achieved. By increasing the temperature up to 333 K, there occurs a sharp increases in the peroxide groups content and the decrease of the epoxide groups content in oligomers. However, under this condition the formation of side products was observed by the grow-

ing darkness in the reaction medium. More precisely, when temperature is increased up to 333 K, the rates of both the main and side reactions also increase.

It is evident from Fig. 2 that peroxide groups content in PO_s goes through the maximum. If this data are compared with the results given in Table 3, it is obvious that the increasing durability of the reaction results in the increase of the common content of $-O-O-$ bonds in PO_s . The increase of functionality of oligomers confirms this statement (Table 3).

Synthesis of PO_s by Telomerization

Starting Material and Reaction Conditions

The results reported in the preceding sections

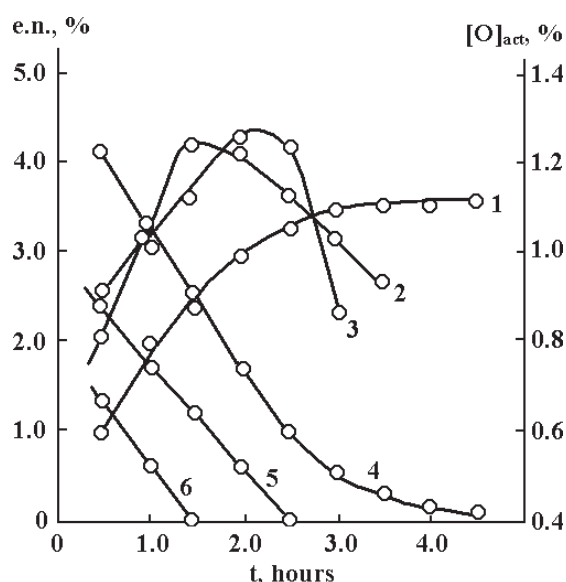


Fig. 2. Dependence of active oxygen (1, 2, 3) and epoxy groups content (4, 5, 6) in oligomer vs. duration of the reaction at 313 (1, 4), 323 (2, 5) and 333 K (3, 6)

Table 3
Characteristics of PO_s

Duration of the Reaction	Mn	Active Oxygen Content, ($[O]_{act}$) %	Functionality, (f)
1	380	0.81	0.119
2	490	1.05	0.32
3	550	1.25	0.43
4	640	1.25	0.50
5	800	1.10	0.55
6	940	1.03	0.60

Note: Temperature of the reaction – 313 K, duration – 4 hours, the catalyst quantity – 28% by mole to EP content.

made it possible for the development of a successful procedure for the synthesis of peroxy oligomers by telomerization. DGEDPP and DGEEG were employed as diepoxy compounds, DPP and EG as monomers with active hydrogen atoms. Molar ratio of diglycidyl ether:monomer:EP was 1:2:2.5. Potassium hydroxide was 28% by moles to content of EP in the reaction mixture. Temperature of the process was 323 K and the reaction period was 5 hours. All the peroxides were viscous light yellow products, stable at room temperature and soluble in organic solvents.

Spectral Characteristics of PO_s

Spectroscopic measurements were performed as described in subsection *Spectral Methods*.

Synthesized oligomers PO – I, PO – II, PO – III do not contain epoxy groups. IR spectra show no absorption at 910 cm⁻¹ related to valence vibration of epoxy groups. Similarly, ¹H – NMR spectra have no proton signals in 2.3 – 3.1 ppm which indicates the absence of epoxy groups.

At the same time, IR spectra exhibit weak bands of absorption at 865 cm⁻¹ which may be related to covalent vibration of –O–O– bonds, as well as doublet at 1380 and 1360 cm⁻¹, ascribed to (CH₃)₃C – group. This shows the presence of peroxide groups in PO_s molecules.

Peroxide groups in oligomers are also recognized in the ¹H – NMR spectra by proton resonances of (CH₃)₃C – groups introduced into the structure of oligomers by telogen. The presence of hydroxy groups, formed by epoxide ring opening was discovered both by the presence of wide absorption band in 3350–3400 cm⁻¹ region and proton resonance at 4.88–5.55 ppm, able to be displaced into strong field due to heating up to 313 K.

Proton signals in 3.52–3.88 ppm region and stretching vibration near 1100 cm⁻¹ indicates the presence of ether bonds in the structure of PO.

Network Formation

The presence of peroxy groups in synthesized PO_s allows us to employ these compounds as curing agents for polymers containing unsaturated double bonds.

The rate of formation of three-dimensional networks depends significantly upon the temperature. The process proceeds quite slowly at 383 K, but at a reasonable rates at 403 K, depending again on the initial PO concentration. Materials with high content

of insoluble products can be obtained at 423 K. The content of synthesized PO in polymeric mixture is 25–30% by mass.

Conclusion

New types of peroxy oligomers containing epoxy structure in the backbone have been studied. They represent a new class of additives to improve mechanical properties of classical matrices of composites [12] such as unsaturated polyester/glass fibers GFR types.

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